Authors' response to Referees' comments

Dear Editor,

We thank both you and the referees for the fruitful reviews on our manuscript and their support to our findings (acp-2016-196).

As you will see, we have taken into account all comments, suggestions etc made by the referees and revised our manuscript, accordingly.

Please find below a point-by-point response to the referees' comments along with our actions. The marked-up version of our manuscript (using track changes) follows this letter.

Thanking you once more

Yours sincerely

Prof. Costas Varotsos

Point-by-point response to Referees' comments:

Referee #1:

Referee comment

"This paper presents and discusses corrosion/soiling experimental results of different materials (carbon and weathering steel, copper, zinc, limestone, modern glass) due to air pollution, together with climatic parameters, obtained during different one year exposure periods performed at Athens, Greece, since 2003. The authors also present/compare their results with corrosion/soiling estimations obtained using Dose Response Functions (DRFs for multi-pollutant situation) already presented in the literature and propose new DRFs targeted to Athens, Greece. The paper addresses relevant scientific questions within the scope of Atmospheric Chemistry and Physics journal. The overall presentation is also well structured and clear, and the conclusions are substantial. This manuscript is interesting because it presents new DRFs for different materials based on the new atmospheric multi-pollutant situation and climatic parameters at Athens, Greece. Therefore, I recommend publication of this paper after a few minor comments have been addressed. I would also like to notice that authors have taken into account all the comments made in my previous report."

Response

No comment

Referee comment

"Page 1, line 13: Use capital for the initial letters of the words "dose response functions"."

Response

We made the proposed change in the revised manuscript.

Referee comment
“Page 1, line 14: “Dose” instead of “dose”, “Response instead of “response”.”

Response
We made the proposed change in the revised manuscript.

Referee comment
“Page 1, line 15: “Function” instead of “function”.”

Response
We made the proposed change in the revised manuscript.

Referee comment
“Page 2, line 5: As before, use capital for the initial letters of the words “dose response functions”.”

Response
We made the proposed change in the revised manuscript.

Referee comment
“Page 2, line 26: Here it is referred that “sheltered samples” are exposed in the box under the rack while in same page, line 29 is referred that only modern glass sample is exposed there. Please clarify.”

Response
In the revised manuscript we changed “sheltered samples” to “sheltered sample”.

Referee comment
“Page 3, line 16: “… structural metals/alloys” instead of “… structural metals”.”

Response
We made the proposed change in the revised manuscript.

Referee comment
“Page 3, line 20: “… structural metal/alloy” instead of “… structural metal”.”

Response
We made the proposed change in the revised manuscript.

Referee comment
"I would suggest authors to unify figures where applicable, for example figs. 2 and 3, figs. 4 and 5, figs. 6 and 7, figs. 9 and 10."

Response
In the revised manuscript we unified the proposed figures according to Referee's instructions and we also changed figures numbering, in captions and in text, accordingly.

Referee comment
"Page 4, line 6: "… sensitive alloys" instead of "sensitive metals"."
Response
We made the proposed change in the revised manuscript.

Referee comment
"Page 5, line 7: Be consistent with the "Dose Response Function" term."

Response
We made the proposed change in the revised manuscript.

Referee comment
"In each given equation, with a few exceptions (Eq. 4, 6, 10), there is a constant factor, meaning that even in case all other factors were 0 there will be corrosion on materials. Could you please give an explanation about this?"

Response
In the given equations the constants denote materials' corrosion due to other factors which are not included in the presented equations. Such two factors are, for example, sunlight and wind.

Referee comment
"Page 6, lines 31-33: Give the meaning of these terms in the same way as for the case of HNO_3 in Page 7, line 1. Erase the terms "annual average"."

Response
We made the proposed change in the revised manuscript.

Referee comment
"Page 6, line 34: Erase the term "annual average"."

Response
The term "annual average" was deleted from the manuscript.

Referee comment
“Page 7, line 15: “DRF (Eq. 3) estimations” instead of “DRFs estimations”.”

Response
We made the proposed change in the revised manuscript.

Referee comment
Page 7, lines 18-23: Specify which equation (equation number) is considered for each material.

Response
We added equations numbers in the revised manuscript.

Referee #3:

Referee comment
“The manuscript presents corrosion and soiling results of materials exposed under real environmental conditions as well as corrosion and soling estimations obtained using dose response functions. Among the materials studied are copper, carbon steel, weathering steel, zinc, modern glass and limestone. The experimental campaign covers the period from 2003 to 2012. An important contribution of this work is the development of new dose response functions for the particular case of Athens, Greece based on the current pollutant situation. Such kind of information is not available in the literature.

I believe that the paper is consistent with the fields of Atmospheric Chemistry and Physics journal. The paper is well structured and follows journal instructions. I recommend the publication of the paper after the proposed minor changes have been made.”

Response
No comment

Referee comment
“The parameter “H” of the equations 6 and 10 are not defined. Add its definition in the given list.”

Response
We added parameter “H” definition in the given list.

Referee comment
“In the title of Eq. 4 are given the chemical characteristics of the weathering steel. This information should be erased from this point and added in text where weathering steel is referred. Same info for the rest metal/alloys should be added.”

Response
Information about weathering steel was erased from Eq. 4 and was added in page 2, line 35. Same information about the rest metal/alloys were also added in page 2, lines 34-37.

Referee comment
“Different figures concerning the same material, like for examples 2 and 3 but also others, could be presented as one figure defined (a) and (b).”

Response
In the revised manuscript we unified the proposed figures according to Referee’s instructions. We also changed figures numbering, in captions and in text, accordingly.

Referee comment
“In fig. 16, I would suggest the authors to change the order of the materials in axis x. It would be more useful for the reader the results of each material to be placed side by side in chronological order.”

Response
We revised fig. 16 according to Referee’s instructions.

Referee comment
“In the legends of figures 11-15 add the equations numbers of DRFs.”

Response
We revised fig. 11-15 legends, adding equations numbers, according to Referee’s instructions.

Referee comment
“Page 22, caption: “by ICP DRF” instead of “by DRFs”.”

Response
We made the proposed change in the revised manuscript.

Referee comment
Page 25, caption: “surface recession” instead of “recession”

Response
We made the proposed change in the revised manuscript.

Authors’ changes in manuscript

We added a few lines about the interaction of air pollutants with aerosols and made small editing corrections for reader’s convenience.

Impacts of air pollution and climate on materials in Athens, Greece

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Abstract. For more than 10 years now the National and Kapodistrian University of Athens,, Greece, contributes to the UN/ECE ICP Materials programme for monitoring of the corrosion/soiling levels of different kind of materials due to environmental air-quality parameters. In this paper we present the results obtained from the analysis of such observational data that were collected in Athens during the period 2003-2012. According to these results the corrosion/soiling of the particular exposed materials tend to decrease over the years, except for the case of copper. Based on this long experimental database applicable to multi-pollutant situation of the Athens basin we present ~~dose~~ Dose ~~response~~ Response ~~functions~~ Functions (DRFs) considering, that "~~*dose*~~*Dose*" stands for the air pollutant concentration, "~~*response*~~*Response*" for the material mass loss (normally per annum) and the "~~*function*~~*Function*" the relationship derived by the best statistical fit to the data.

1 Introduction

Climatic parameters and air pollutants are of major importance for the deterioration of many materials used in buildings and cultural monuments (Ferm et al., 2005, 2006; Varotsos et al., 2009; Tzanis et al., 2009a, 2011; Tidblad et al., 2012). These pollutants are mainly emitted by industrial and agricultural activities, as well as by the transport sector, and beyond their effects on human health and ecosystems, they also contribute to the deterioration of cultural monuments both on the local scale and over long distances (Köhler et al., 2001; Ondov et al., 2006; Ebel et al., 2007; Tzanis et al., 2009b; Jacovides et al., 1994; Efstathiou et al., 2005; Varotsos et al., 1994, 2011, 2014; Reid et al., 1998; Chattopadhyay et al., 2012; Krapivin and Shutko, 2012; Merlaud et al., 2012; Cracknell and Varotsos, 1994, 1995; Xue et al., 2014; Monks et al., 2015). The world's cultural heritage is very diverse and costly to maintain. Repairing costs for deterioration of various materials due to air pollution, together with climatic parameters, are huge (Doytchinov et al., 2011), while the damage to cultural objects endangers seriously the cultural heritage.

Effective policy making requires an adequate scientific basis to assess the effects of pollution and climate change on materials. In this context, the United Nations Economic Commission for Europe (UNECE) adopted the Convention on Long-range Transboundary Air Pollution (CLRTAP) to address the problems of air pollution. In the framework of the UNECE/CLRTAP the International Co-operative Programme on Effects on Materials including Historic and Cultural Monuments (ICP Materials) was launched, in order to provide, among others, a scientific basis for the study of important materials' degradation due to atmospheric pollution and climate parameters. The Athens, Greece with significant cultural heritage monuments (UNESCO Cultural Heritage site: Acropolis, Parthenon) has been involved in ICP Materials since 2002 as a targeted field exposure test site, participating also in the EU project MULTI-ASSESS (Model for multi pollutant impact and assessment of threshold levels for cultural heritage: http://www.corr-institute.se/multi-assess/web/page.aspx).

An important contribution to this effort is the development of ~~dose-~~Dose ~~response-~~Response ~~functions~~ Functions (DRFs) for particular materials. DRFs are relationships between the corrosion or soiling rates and the levels or loads of pollutants in combination with climatic parameters. The corrosion is mainly caused by chemical reactions on the material surface involving air pollutants (e.g., SO_2, NO_x and O_3), while soiling is principally depicted as loss of reflectance (Watt et al., 2008). Concerning the latter, the incorporation of PM_{10} concentration in the above mentioned relationship allows for the generation of empirical D~~d~~ose– ~~r~~Response F~~f~~unctions for soiling (Brimblecombe and Grossi, 2005). The interaction of aerosols and air-pollutants is complex (e.g. confined not only to the aerosol surface but at least several hundred Angstroms deep) and must be taken into account from the boundary layer up to the stratosphere. In this connection, the uptake (e.g. via diffusion) of the gaseous pollutants on the solid aerosols, can be influenced by the point defects existing in the crystals of the solid aerosols (Varotsos and Zellner 2010; Lazaridou et al. 1985; Reid et al. 1998; Londos et al., 1996; Sarlis et al., 1997; Varotsos and Cracknell, 1994).

The DRFs are used for the assessment of pollution tolerable levels and to recommend target levels to be implemented in the future development of measures on urban air quality in order to minimise the pollution effects on historic and cultural objects. In addition, they can be used in sites where there are no experimental results in order to make estimations of corrosion/soiling rates. According to previous studies implemented in Athens, carbon steel has been proven that is the material which suffers more from corrosion than the others exposed metals/alloys. On the contrary, copper is the most durable (Tzanis et al., 2011). Another study has revealed that the greatest part of the deposited particle mass is not water soluble, while in the water soluble part of it there is an unbalance between the cations and anions with the cations to surpass anions (Tzanis et al., 2009a).

In this study we present the most recent results from the UNECE/ICP Materials trend exposure programme 2011-2012 obtained in Athens, Greece test site, along with the corresponding measurements from previous exposure periods for comparison reasons. We also demonstrate the comparison between experimental results and theoretical corrosion/soiling estimations by employing the newly developed DRFs for the campaigns conducted in Athens, Greece.

2 Experimental

For the purpose of MULTI-ASSESS and UNECE ICP Materials trend exposure programmes, a station is installed in central Athens, Greece (37°59´57´´ N, 23°43´59´´ E), since 2003. The main rack - field exposure site with exposure samples and the carousel on rack along with sheltered sample~~s~~ enclosed in a box under the rack, for the last exposure period, are shown in Fig. 1. Specimens of the materials carbon steel (C < 0.2 %, P < 0.07 %, Cr < 0.07 % according to CSN 11373) (6 samples), 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%) (9 samples), zinc (99.99%) (6 samples), copper (99%, DIN 1787) (3 samples), aluminium (>99.5%) (3 samples), limestone (6 samples), and modern glass (1 sample) were installed on the main rack. The vast majority of the specimens were exposed in unsheltered positions, while the modern glass in sheltered position inside the aluminium box with open bottom. The exposure time for modern glass and copper as well as for three samples of carbon steel, weathering steel, zinc and limestone was one year, while the rest samples are scheduled to be withdrawn in a later time. The withdrawn specimens were sent to the responsible subcentres in Europe (see Table 1) for further analysis and evaluation of soiling or corrosion attack.

In particular, for the determination of multi-pollutant effects on materials, chemical analysis of the specimens was conducted and basic parameters as the weight change, mass loss, surface recession, haze, the total deposited mass of particles per surface unit of glass (TP/S) were calculated. For comparison reasons, as also indicated in Introduction, the corrosion and soiling values for the exposure period 2011-2012 was complemented with the available data collected previously (2003-2004, 2005-2006 and 2008-2009) in the frame of MULTI-ASSESS and UNECE ICP Materials programmes, in which the Athens station has been involved.

In addition, the diffusive passive samplers for the surface air-pollutants (SO_2, HNO_3, HCOOH, CH_3COOH, HCl and HF) measurements and the passive particle collector (aerosols) that were used (shown also in Fig. 1), were prepared at Swedish Environmental Research Institute (IVL). The samplers were mounted under a metal disc ca 2m above the ground in order to protect them from rain and direct sunshine and after the exposure, they were returned to IVL for analysis. The main aim of these measurements was to correlate the pollutants concentrations with the degradation rate of the exposed material specimens.

3 Results and discussion

As mentioned before, in order to study the corrosion of structural metals/alloys (copper, zinc, carbon and weathering steel), the parameters weight change and mass loss were evaluated. Figures 2-~~7~~ 4 present the weight change and mass loss values obtained after the analysis of the exposed specimens. In these figures the experimental results of previous expositions are also presented. It should be mentioned that the presented values are the mean values obtained for the three specimens of each structural metal/alloy exposed during the aforementioned exposure periods.

The parameter “weight change” describes the difference in specimen’s mass after the exposure minus its initial mass. If the specimen was exposed under sheltered conditions this parameter is expected to be positive due to uptake processes (e.g. deposition) and the lack of any mass loss mechanism. In the case of unsheltered exposition, weight change can be positive or negative depending on the balance among uptake and loss mechanisms. According to the results obtained for the case of copper (Fig. 2a), mean weight change of samples exposed during 2011-2012 period is almost 1.5 times greater than that of the samples exposed during 2003-2004 (Tidblad et al., 2013).

The parameter “mass loss” expresses the difference in specimen’s initial mass minus the specimen’s mass after removing its corroded part. It should be mentioned here that both the weight change and mass loss parameters are affected by the run-off and the chemical composition of the corrosion layer (Horalek et al., 2005). The experimental results of the mass loss, for copper, zinc and carbon steel, are presented in Figs. ~~3~~2b, ~~5~~ 3b and ~~7~~4b, respectively. According to these results, mass loss of copper is shown to have increased since 2003-2004; however, this increase has been minimal (1.075 times greater). On the contrary, mass loss of zinc and carbon steel samples decreases continuously after the period 2005-2006. The greatest values of mass loss for both materials were recorded for the case of Athens, Greece, during that period. Last results denote reduce of zinc mass loss of about 36% and reduce of carbon steel mass loss of about 55% since that period. The corrosion rates of carbon steel are shown to have decreased significantly during 2011-2012, possibly due to the reduced levels of SO_2 and PM_{10} which have been measured. In addition, first results show that pollution has a significant effect on corrosion rate of weathering steel. Mean mass loss of weathering steel samples during 2011-2012 exposition was evaluated to 82.8 g m^{-2} (Tidblad et al., 2013). The carbon and weathering steel arises to be the most sensitive ~~metals~~alloys, among the exposed ones, to the mass loss, while copper is the most durable. That means that steel is the most sensitive material to the corrosion while copper suffered less by atmospheric corrosion. Considering climate change future projections it is expected an increase in temperature, relative humidity and precipitation (IPCC, 2013) factors which favour corrosion rate. However, corrosion rate is also affected by pollutants levels which generally are decreasing. So the question “how much climate change affects materials corrosion?” needs very careful approach.

In the case of zinc samples, chemical analyses were performed to water solutions of the corrosion products. These solutions were analysed for inorganic acids, formate and acetate. The aim was the identification of corrosive media which affected metal surface. The results can not be used for quantitative analysis but they are useful for qualitative conclusions about the substances which mainly corroded zinc samples (Tidblad et al., 2013). The analysis showed that chloride ions, water-soluble sulphate and nitrates are involved in the corrosion processes of the exposed zinc samples in Athens. No traces of formate and acetate were found.

For the evaluation of corrosion of limestone specimens exposed in unsheltered positions, surface recession, was calculated. This parameter is defined by the formula $R = \frac{W_1 - W_0}{A \cdot \rho}$, where W_0 is sample’s weight before the exposure, W_1 is sample’s weight after the exposure, A is the total surface area of sample and ρ is the density of the limestone. The results of surface recession for the limestone specimens exposed, under unsheltered conditions, for one year are presented in Fig. ~~8~~ 5 along with the same results obtained during previous exposure periods. Generally, the recession of limestone has decreased slightly after the period 2005-2006 due possible to the reduced pollution levels. It is also obvious from this figure that recession during last exposure period (2011-2012) is slightly higher than the previous one, perhaps due to a small increase in NO_2 concentration during this period.

Another material studied during this exposure period was modern glass. This one is not part of historic and cultural monuments but it is a material which is used widely in synchronous art as well as in other kind of modern constructions. In addition to that, modern glass is also an ideal material for soiling studies because it is transparent, flat, non-porous and chemically inert. Due to these properties modern glass does not affect particles deposition and accumulation (Lombardo et al., 2010).

In order to evaluate soiling two parameters are investigated; the total deposited mass of particles per surface unit of glass (TP/S) in μg cm^{-2} and haze defined as the ratio, expressed in percentage, of the diffuse to direct transmitted light. Modern glass samples were exposed under sheltered conditions during all exposure periods.

The obtained results for TP/S and haze are presented in Figs. ~~9~~ 6a and ~~10~~6b, respectively. Regarding TP/S it shows a clear decreasing trend through the exposure periods. Maximum value was recorded during 2003-2004 and it is proven to be about 4 times greater than the next periods. Minimum value was recorded during 2011-2012 exposure period. The range of haze is similar for the exposure periods 2005-2006, 2008-2009 and 2011-2012 while the minimum value is presented for 2011-2012 and the maximum for 2003-2004.

The corrosion or soiling values presented above and environmental parameters mentioned in section 2, along with data from previous experimental campaigns, were analysed in order to develop the ~~dose~~Dose -~~r~~Response ~~functions~~ Functions for corrosion and soiling for materials under study. The results for DRFs (for multi pollutant situation except for the case of weathering steel) based on data from all the ICP Materials test sites are presented below in Eqs. (1-6) (Kucera et al., 2005, 2007; Watt et al., 2008; Verney-Carron and Lombardo, 2013) along with correlation coefficients R^2, Root Mean Square Deviations (RMSD) and Normalized Root Mean Square Deviations (NRMSD) between observed and predicted values for Athens, Greece. In addition to these, we present newly developed DRFs, Eqs. (7-10), along with the correlation coefficients R^2, RMSD and NRMSD between observed and new predicted values for carbon steel, zinc, limestone and modern glass for the case of Athens, Greece. The obtained values of these statistical parameters are given in Table 2. For copper and weathering steel the available data were not adequate for developing new DRFs. All the presented below DRFs (Eqs 1, 2, 3, 4, 5, 7, 8, 9) are valid for one year exposure except for modern glass (Eqs. 6, 10) where t denotes the exposure duration in days. These DRFs are based on parameters already defined by UNECE/ICP Materials group and were obtained implementing nonlinear regression analysis for carbon steel, zinc and limestone and multiple linear regression for the modern glass case. In the given equations the constants denote materials' corrosion due to other factors which are not included in the presented equations. Such two factors are, for example, sunlight and wind. It should be noted that the time factor in the new DRF for modern glass (Eq. 10) remained the same as in Eq. (6) (see Lombardo et al., 2010).

Carbon steel

$ML = 51 + 1.39[SO_2]^{0.6}Rh_{60}e^{f(T)} + 1.29Rain[H^+] + 0.593PM_{10}$ (Eq. 1)

$f(T) = 0.15(T-10)$ when $T<10°C$ (Eq. 1.1), otherwise $f(T) = -0.054(T-10)$ (Eq. 1.2)

Zinc

$ML = 3.5 + 0.471[SO_2]^{0.22}e^{0.018Rh+f(T)} + 0.041Rain[H^+] + 1.37[HNO_3]$ (Eq.2)

$f(T) = 0.062(T-10)$ when $T<10°C$ (Eq. 2.1), otherwise $f(T) = -0.021(T-10)$ (Eq. 2.2)

Limestone

$R = 4.0 + 0.0059[SO_2]Rh_{60} + 0.054Rain[H^+] + 0.078[HNO_3]Rh_{60} + 0.0258PM_{10}$ (Eq. 3)

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%)~~

$ML = 34[SO_2]^{0.13}e^{0.020Rh + f(T)}$ (Eq. 4)

$f(T) = 0.059(T-10)$ when $T\leq10°C$ (Eq. 4.1), otherwise $-0.036(T-10)$ (Eq. 4.2)

Copper

$ML = 4.21 + 0.00201[SO_2]^{0.4}[O_3]Rh_{60}e^{f(T)} + 0.0878Rain[H^+]$ (Eq. 5)

$f(T) = 0.083(T-10)$ when $T\leq10°C$ (Eq. 5.1), otherwise $-0.032(T-10)$ (Eq. 5.2)

Modern glass

$H = (0.2215\ [SO_2] + 0.1367\ [NO_2] + 0.1092\ PM_{10}) / (1 + (382/t)^{1.86})$ (Eq. 6)

Carbon steel for Athens

$ML = 10 + 0.012[SO_2]^{2.152}Rh_{60}e^{f(T)} + 1.29Rain[H^+] + 1.263PM_{10}$ (Eq. 7)

$f(T) = 0.15(T-10)$ when $T<10°C$ (Eq. 7.1), otherwise $f(T) = -0.\ 054(T-10)$ (Eq. 7.2)

Zinc for Athens

$ML = 3.5 + 0.004[SO_2]^{0.408}e^{0.082Rh+f(T)} + 0.041Rain[H^+] + 0.138[HNO_3]$ (Eq. 8)

$f(T) = 0.062(T-10)$ when $T<10°C$ (Eq. 8.1), otherwise $f(T) = -0.021(T-10)$ (Eq. 8.2)

Limestone for Athens

$R = 4.0+ 0.002[SO_2]Rh_{60} + 0.054Rain[H^+] + 0.05[HNO_3]Rh_{60} + 0.106PM_{10}$ (Eq. 9)

Modern glass for Athens

$H = (0.204\ [SO_2] + 0.016\ [NO_2] + 0.319\ PM_{10}) / (1+(382/t)^{1.86})$ (Eq. 10)

where

ML = mass loss by corrosion attack, g m^{-2}

R = surface recession, µm (absolute values)

H = haze (%)

t = exposure time, days

Rh = relative humidity, % - annual average

Rh_{60} = Rh – 60 when Rh > 60, 0 otherwise

T = temperature, °C - annual average

$[SO_2]$ = annual average concentration, µg m^{-3}~~concentration, µg m^{-3} – annual average~~

$[O_3]$ = annual average concentration, µg m^{-3}~~concentration, µg m^{-3} – annual average~~

$[NO_2]$ = annual average concentration, µg m^{-3}~~concentration, µg m^{-3} – annual average~~

Rain = amount of precipitation, mm $year^{-1}$ ~~– annual average~~

$[HNO_3]$ = annual average concentration, µg m^{-3}

PM_{10} = annual average concentration, µg m^{-3}

$[H^+]$ = concentration, mg l^{-1} - annual average. The unit for $[H^+]$ is not the normal one (mol l^{-1}) used for this denomination and the relation between pH and $[H^+]$ is therefore here $[H^+] = 1007{,}97\ 10^{-pH} \approx 10^{3-pH}$.

In the Figs. ~~11~~7-~~15-~~11 we present the above DRFs' (for all the ICP Materials test sites ("ICP DRF") and for Athens ("Athens DRF")) results along with the experimental values ("Observed") obtained at Athens, Greece. For the case of weathering steel, the estimated mass loss is 100.6 g m^{-2} while as mentioned before the observed value is 82.8 g m^{-2}. A general remark for the case of Athens is that the ICP DRFs results for the case of metals/alloys overestimate the corrosion levels while for limestone and modern glass they underestimate corrosion/soiling levels for all the exposure periods. Specifically, in case of copper the overestimation is almost 17% for 2003-2004 period and almost 9% for the 2011-2012 period. In case of zinc the overestimated mass loss ranges from 8 to 47% for all exposure periods. Carbon steel mass loss is greater than the observed by 3 to 35% through all exposure periods, while the weathering steel's mass loss is estimated almost 22% greater than the observed one.

Limestone results reveal that DRF (Eq. 3)~~s~~ estimations underestimate corrosion levels by 29 to 47%. In case of modern glass the observed haze is 4 to 34% greater than the estimated values for all the exposure periods except for the case of 2005-2006 where an overestimation of about 6% is noticed.

DRFs for Athens case present improved estimations. In particular, in case of zinc new DRF (Eq. 8) estimations underestimate mass loss by about 0% to 3% except for the case of 2008-2009 exposure period where an overestimation of 3% is noticed. In case of carbon steel new estimations (Eq. 7) underestimate mass loss by about 1% for all exposure periods except for last one where an overestimation of 3% is noticed. New DRF (Eq. 9) estimations for limestone recession are between -14% (underestimation) to 10% (overestimation), while the estimated from Athens DRF (Eq. 10) modern glass haze differs from the observed values from -24 to 21%. This range of differences may indicate that for the Athens, Greece case the parameters used in DRF for the modern glass are not sufficient and more experimental data are needed in order to specify the factors which affect haze. In Fig. ~~16~~ 12 are presented the percentage contribution of each Athens DRF factor to the total corrosion/soiling of each material for all exposure periods.

4 Conclusions

According to the above mentioned results, all the exposed materials, except for copper, present reduced corrosion/soiling levels through the years. In case of copper, it presents almost 7% greater mass loss during the last exposure period than during 2003-2004. According to DRFs O_3 is a parameter which affects copper mass loss, while it does not affect the rest materials. So a possible explanation to this could be the increased level of O_3 during 2011-2012 (23.7 μg m^{-3}) compared to 2003-2004 (19.7 μg m^{-3}). New developed DRFs for the particular case of Athens, Greece improve the obtained estimations for corrosion and soiling of the materials under study. However, these DRFs will be re-evaluated when new data from the 2014-2015 exposure period are available.

Acknowledgements

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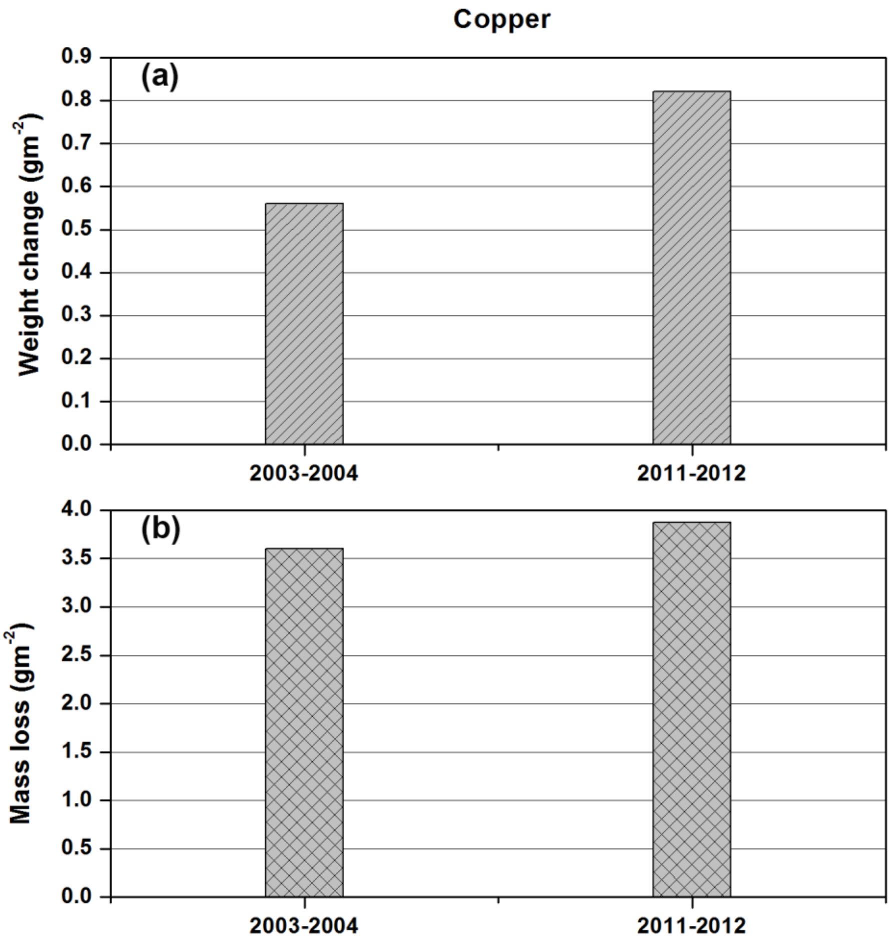
Table 1: Responsible subcentres for the evaluation of corrosion or soiling of the exposed materials for the period 2011-2012.

Material	**Responsible subcentre**
Carbon steel	SVUOM, Czech Republic
Weathering steel	CENIM/CSIC, Spain
Zinc	EMPA, Switzerland
Copper	KIMAB, Sweden
Limestone	BRE, Watford, UK
Modern glass	Univeristy Paris XII, LISA, France

Table 2: Correlation coefficients R^2, Root Mean Square Deviations (RMSD) and Normalized Root Mean Square Deviations (NRMSD) between observed and predicted values for Athens, Greece. The abbreviation "nss" declares not statistically significant value at 95% confidence interval while "ss" statistically significant value at 95% confidence interval.

Dose Response Function		R^2	RMSD	NRMSD (%)
Carbon steel	(Eq.1)	0.972 (ss)	12.57	19
Carbon steel for Athens	(Eq.7)	0.999 (ss)	1.07	2
Zinc	(Eq.2)	0.581 (nss)	2.01	80
Zinc for Athens	(Eq.8)	0.995 (ss)	0.096	4
Limestone	(Eq.3)	0.556 (nss)	3.79	230
Limestone for Athens	(Eq.9)	0.653 (ss)	0.796	48
Modern glass	(Eq.6)	0.797 (nss)	2.24	48
Modern glass for Athens	(Eq.10)	0.809 (ss)	1.5	32

Figure 1: The exposure site in the Athens centre (Greece). The top panel shows the carousel (on the right) and the main rack (on the left) with the material specimens, which was installed in Athens and consisted of an inclined plane and an aluminium box with open bottom (middle panel). The middle panel shows aluminium box (on the left) and the glass specimens in the aluminium box (on the right). The bottom panel shows the diffusive passive samplers for the surface air-pollutants measurements and the passive particle collector under the rain shield.



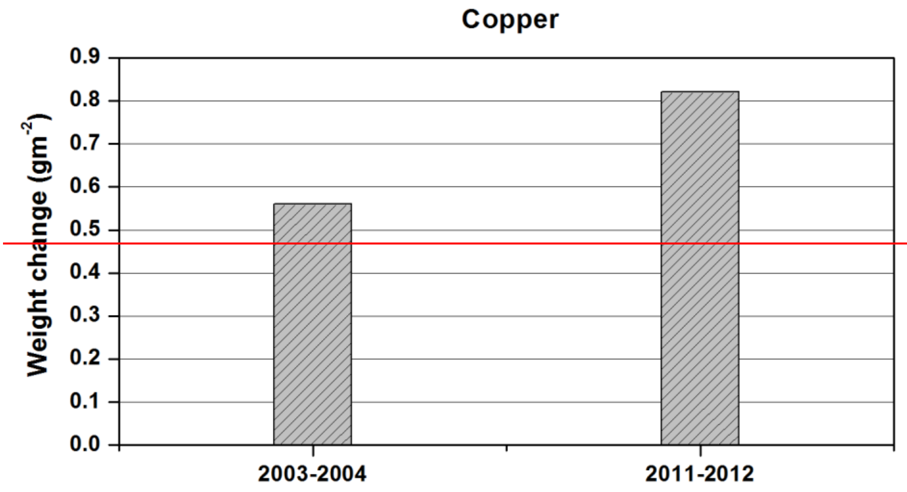
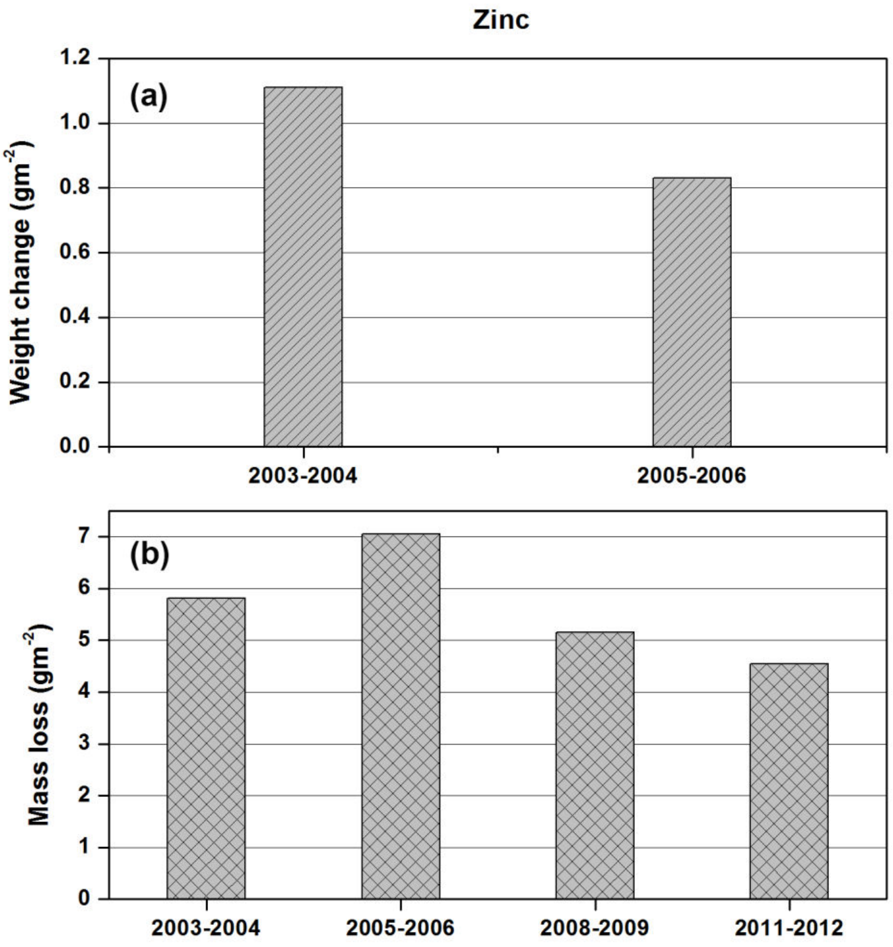


Figure 2: (a) Mean weight change and (b) mean mass loss of copper samples exposed during the periods 2003-2004 and 2011-2012.



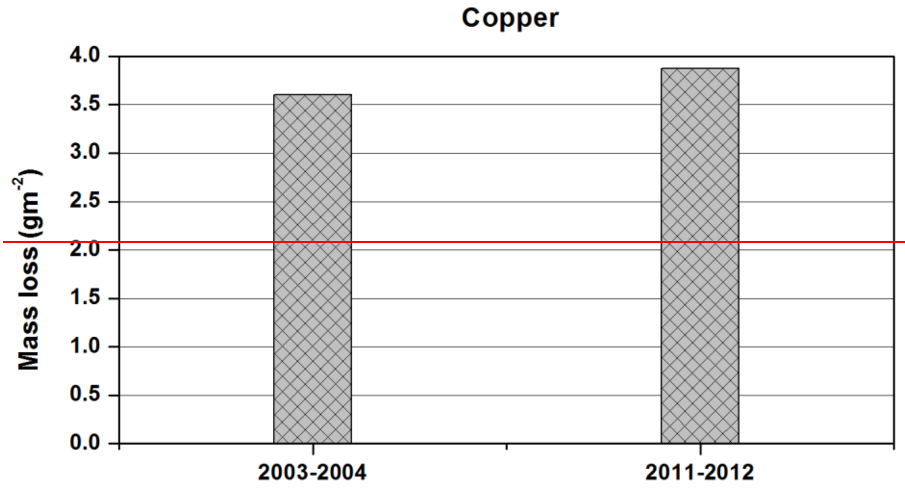


Figure 3: (a) Mean weight change of zinc samples exposed during the periods 2003-2004 and 2005-2006. and (b) mean mass loss of zinc samples exposed during the periods 2003-2004, 2005-2006, 2008-2009 and 2011-2012.~~Mean mass loss of copper samples exposed during the periods 2003-2004 and 2011-2012.~~

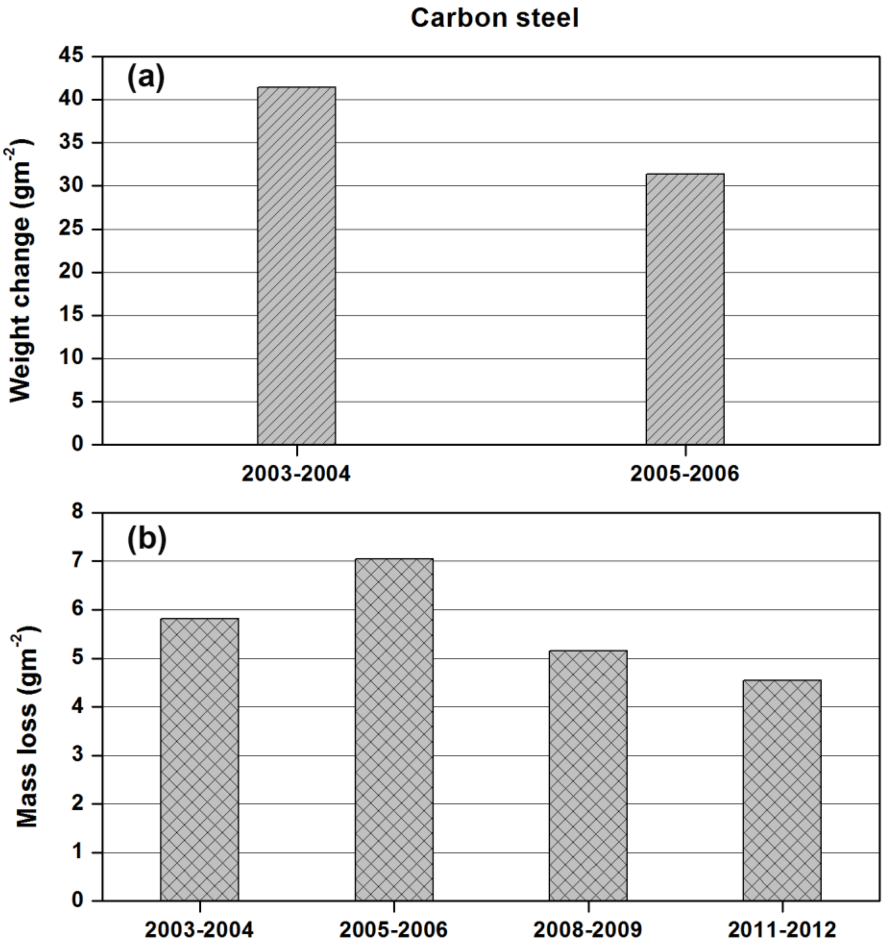
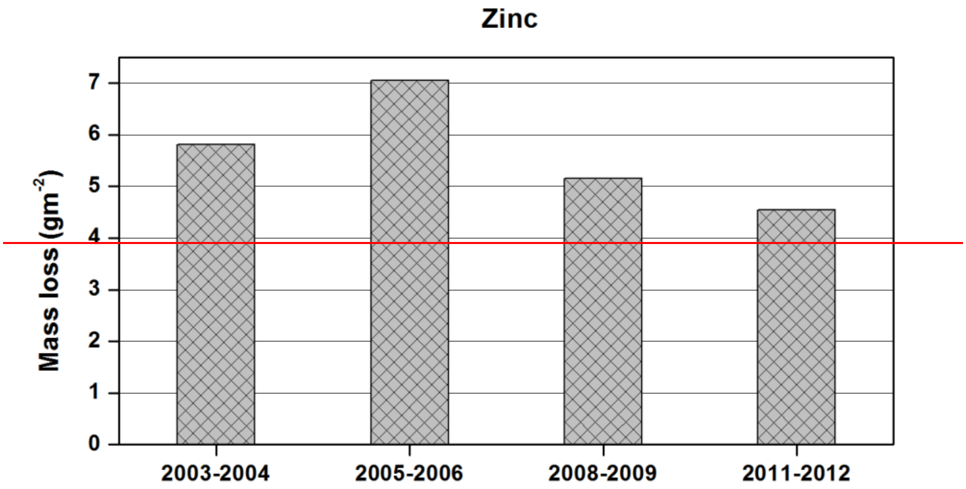
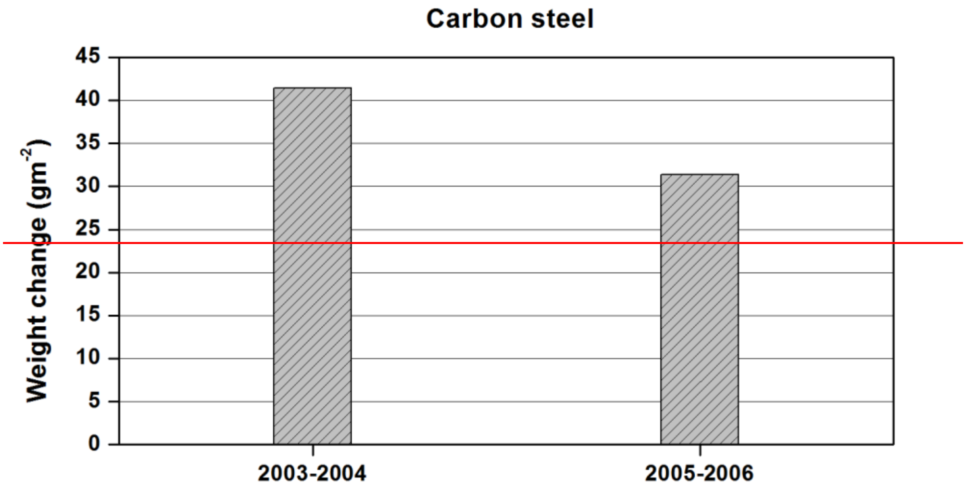


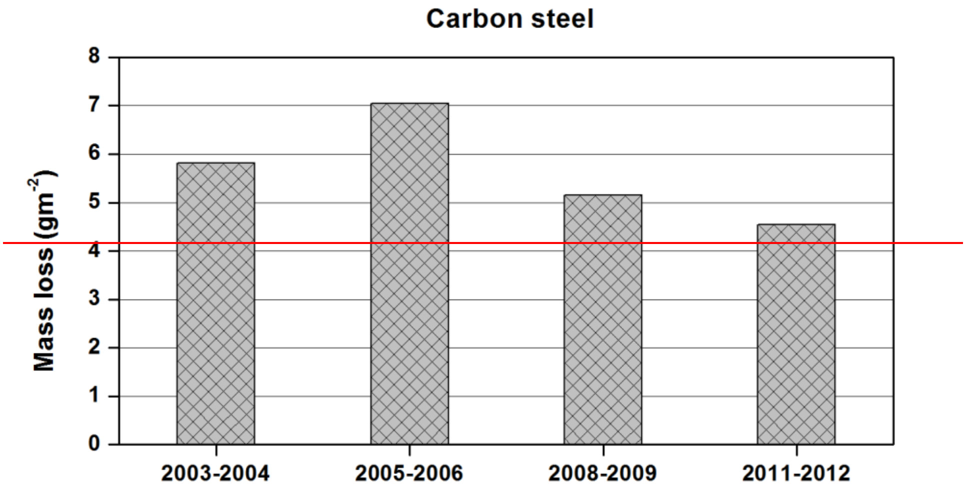
Figure 4: (a) Mean weight change of carbon steel samples exposed during the periods 2003-2004 and 2005-2006 and (b) mean mass loss of carbon steel samples exposed during the periods 2003-2004, 2005-2006, 2008-2009 and 2011-2012.~~Mean weight change of zinc samples exposed during the periods 2003-2004 and 2005-2006.~~



~~**Figure 5: Mean mass loss of zinc samples exposed during the periods 2003-2004, 2005-2006, 2008-2009 and 2011-2012.**~~



~~**Figure 6: Mean weight change of carbon steel samples exposed during the periods 2003-2004 and 2005-2006.**~~



~~**Figure 7: Mean mass loss of carbon steel samples exposed during the periods 2003-2004, 2005-2006, 2008-2009 and 2011-2012.**~~

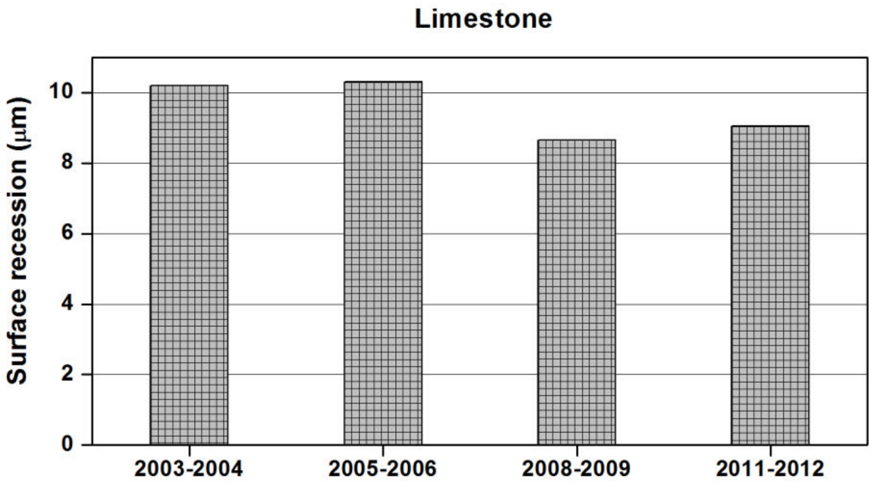
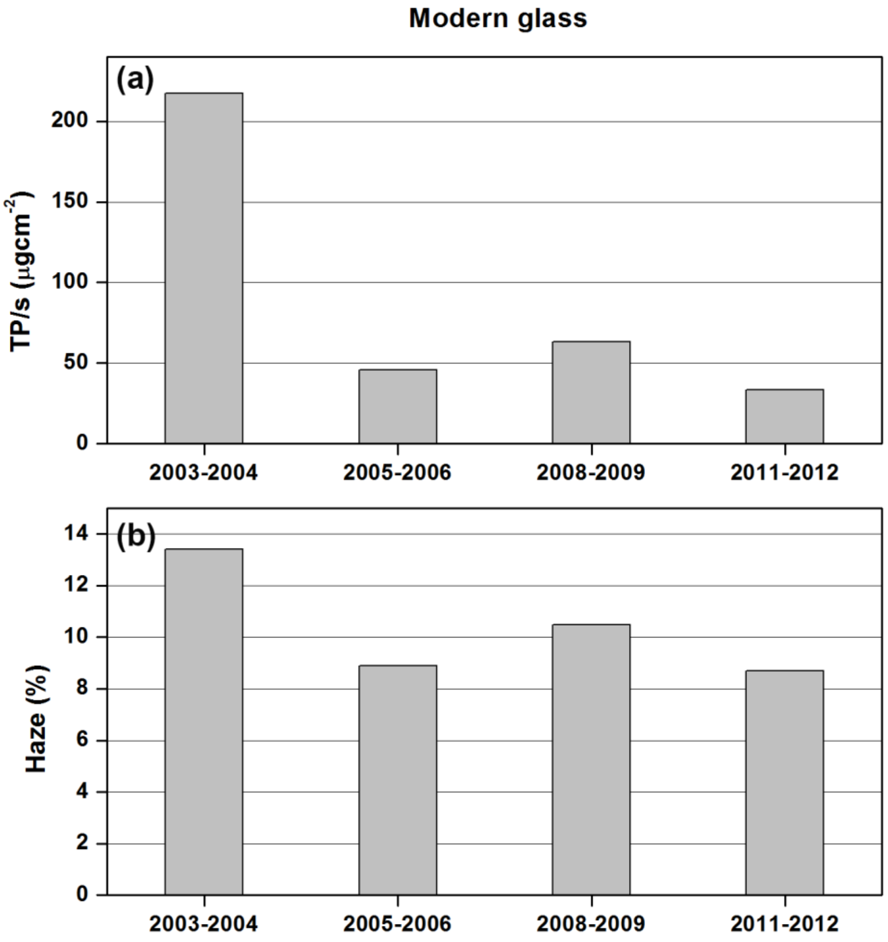


Figure 5~~8~~: Surface recession of limestone exposed in unsheltered positions for the periods 2003-2004, 2005-2006, 2008-2009 and 2011-2012.



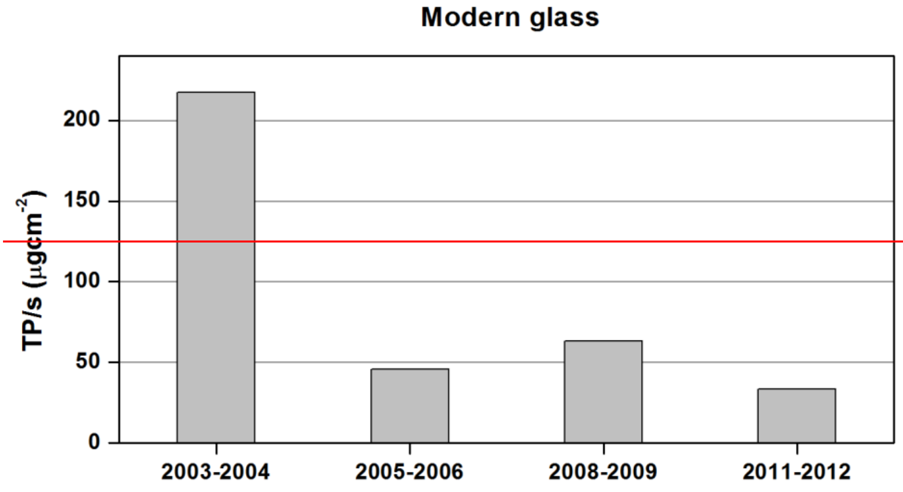
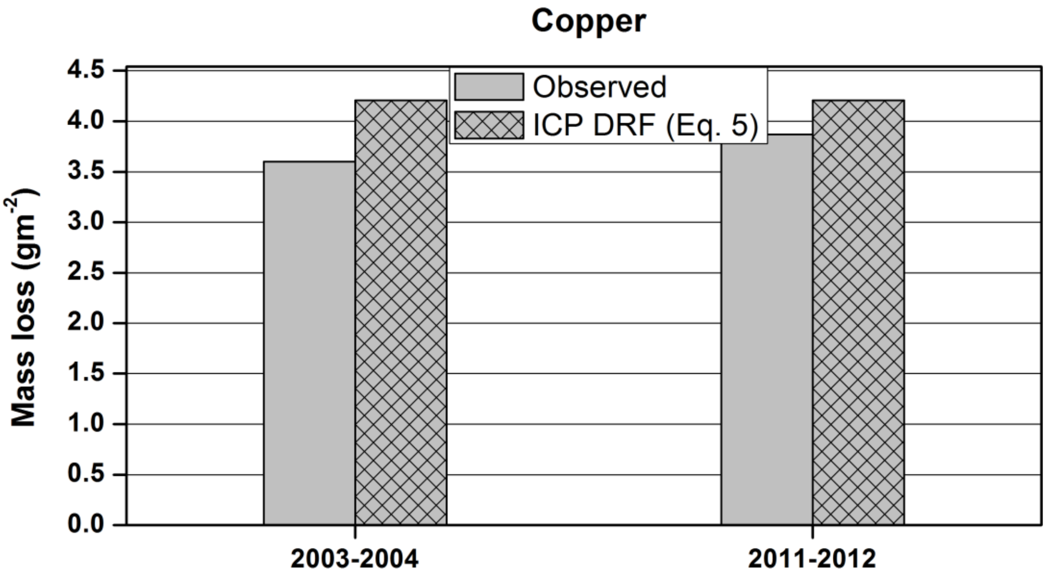


Figure 6~~9~~: (a) TP/S (μg cm^{-2}) and (b) Haze (%) for modern glass exposed for the periods 2003-2004, 2005-2006, 2008-2009 and 2011-2012.

~~**Figure 10: Haze (%) for modern glass exposed for the periods 2003-2004, 2005-2006, 2008-2009 and 2011-2012.**~~



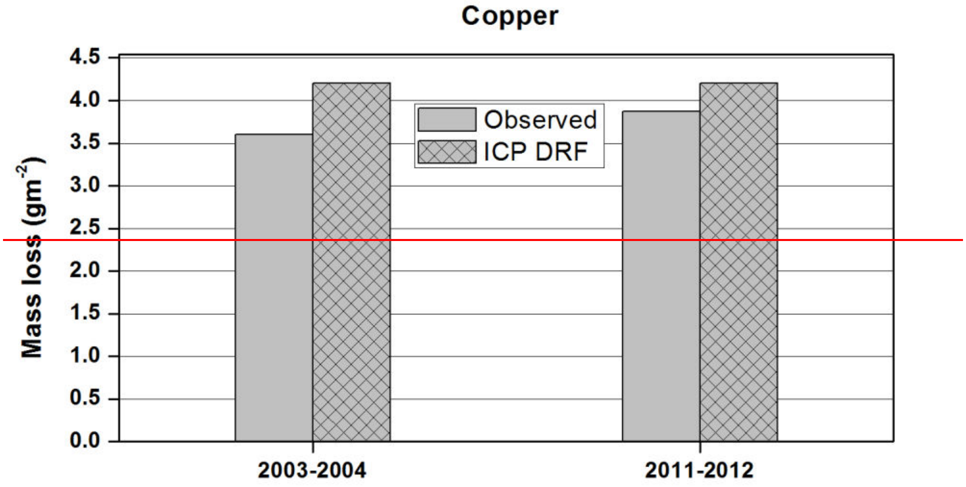
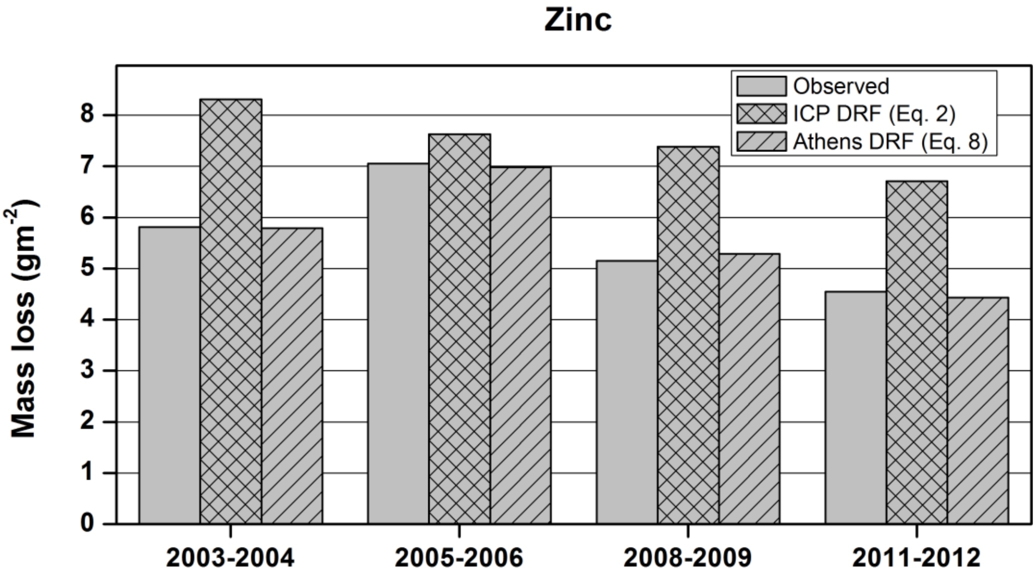


Figure 7~~11~~: Experimental obtained mass loss values at Athens, Greece for the case of copper along with the predicted ones by ICP DRF~~s~~.



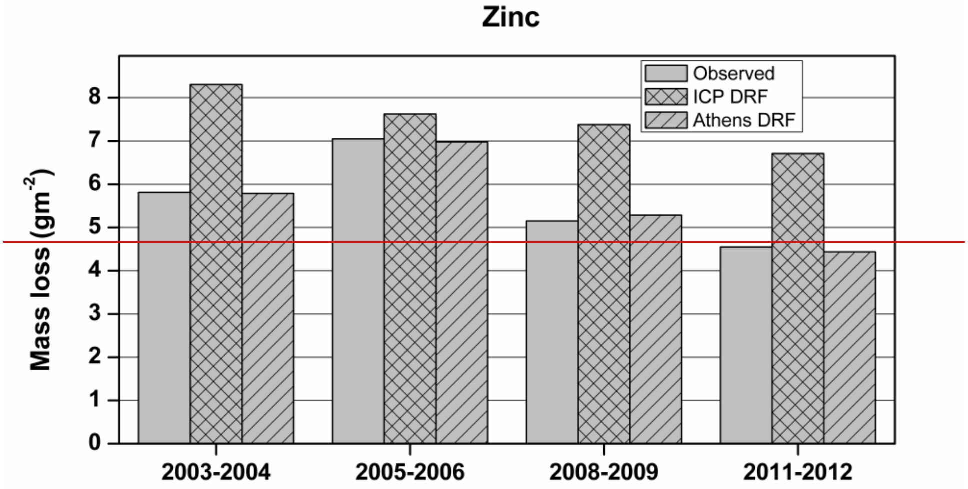
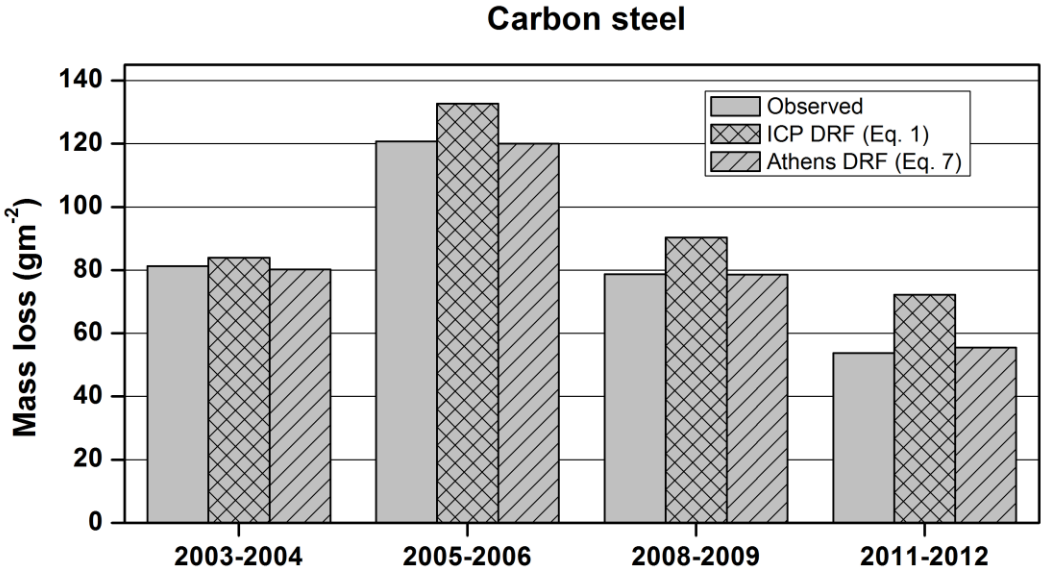


Figure 8~~12~~: Experimental obtained mass loss values at Athens, Greece for the case of zinc along with the predicted ones by DRFs.



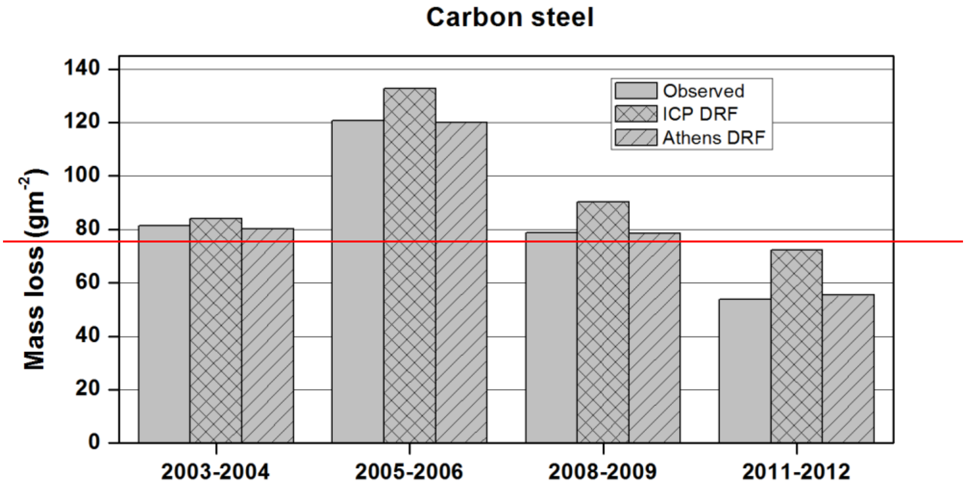
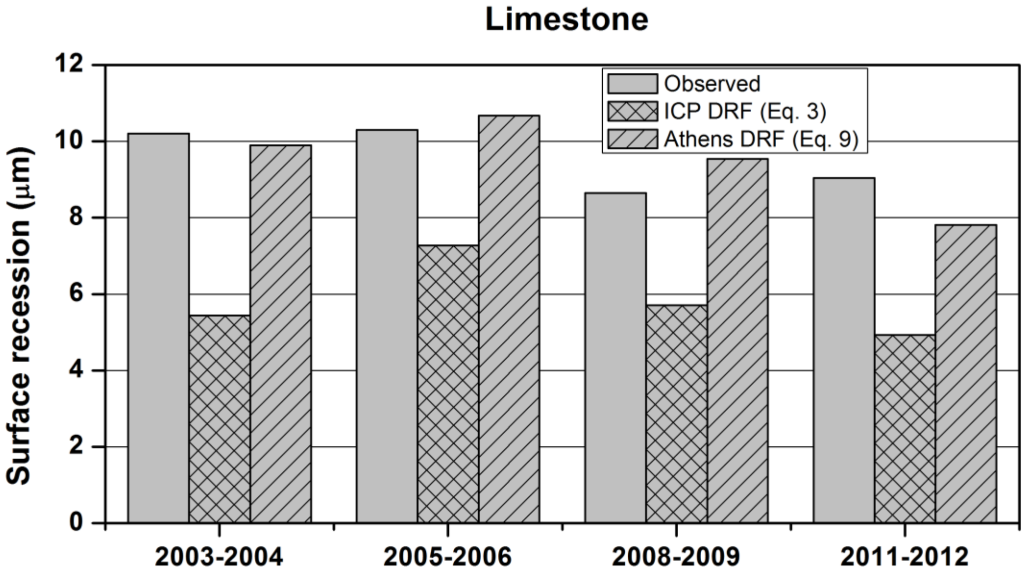


Figure 9~~13~~: Experimental obtained mass loss values at Athens, Greece for the case of carbon steel along with the predicted ones by DRFs.



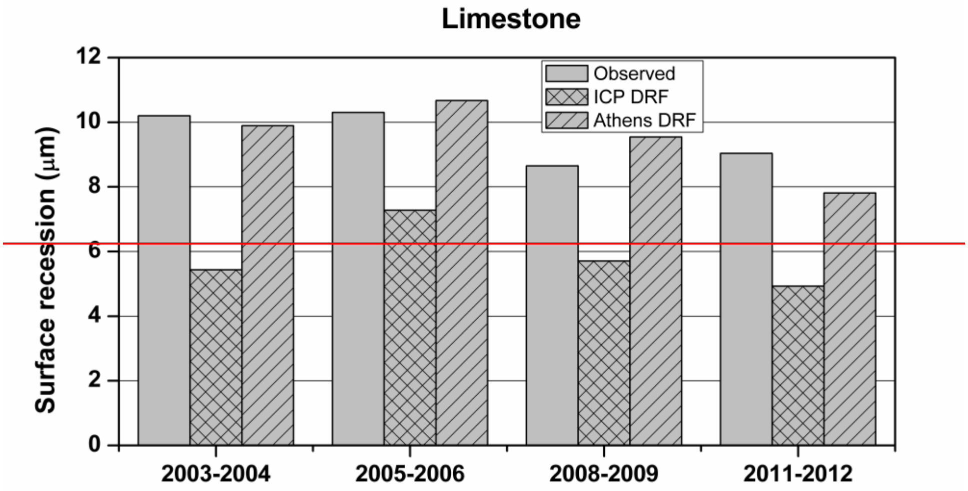
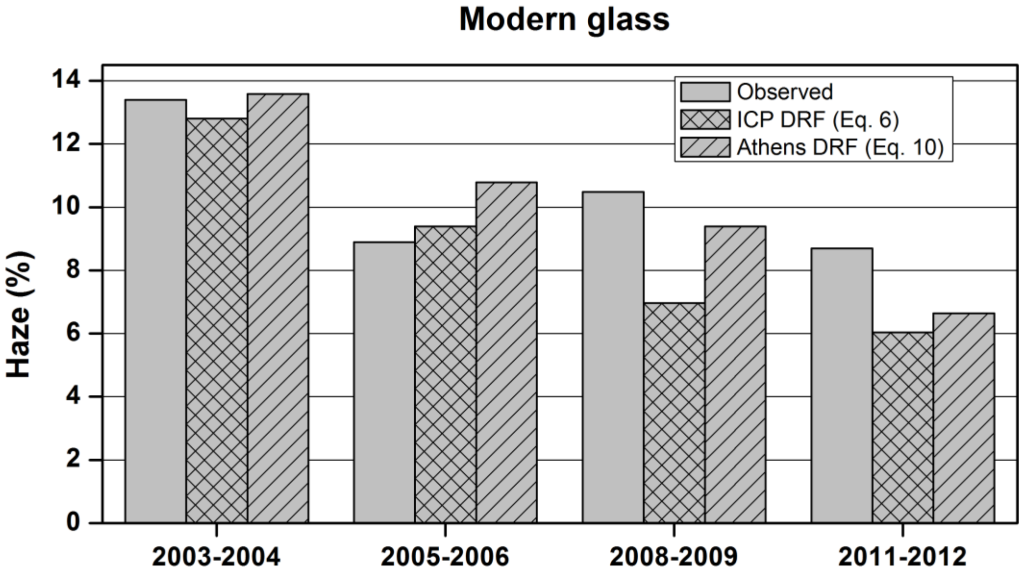


Figure 104: Experimental obtained surface recession values at Athens, Greece for the case of limestone along with the predicted ones by DRFs.



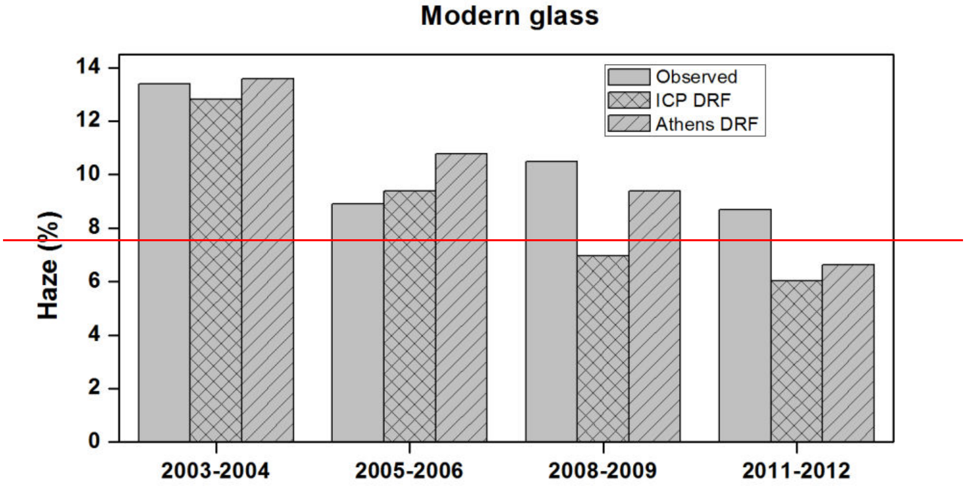


Figure 1~~5~~1: Experimental obtained haze values at Athens, Greece for the case of modern glass along with the predicted ones by DRFs.

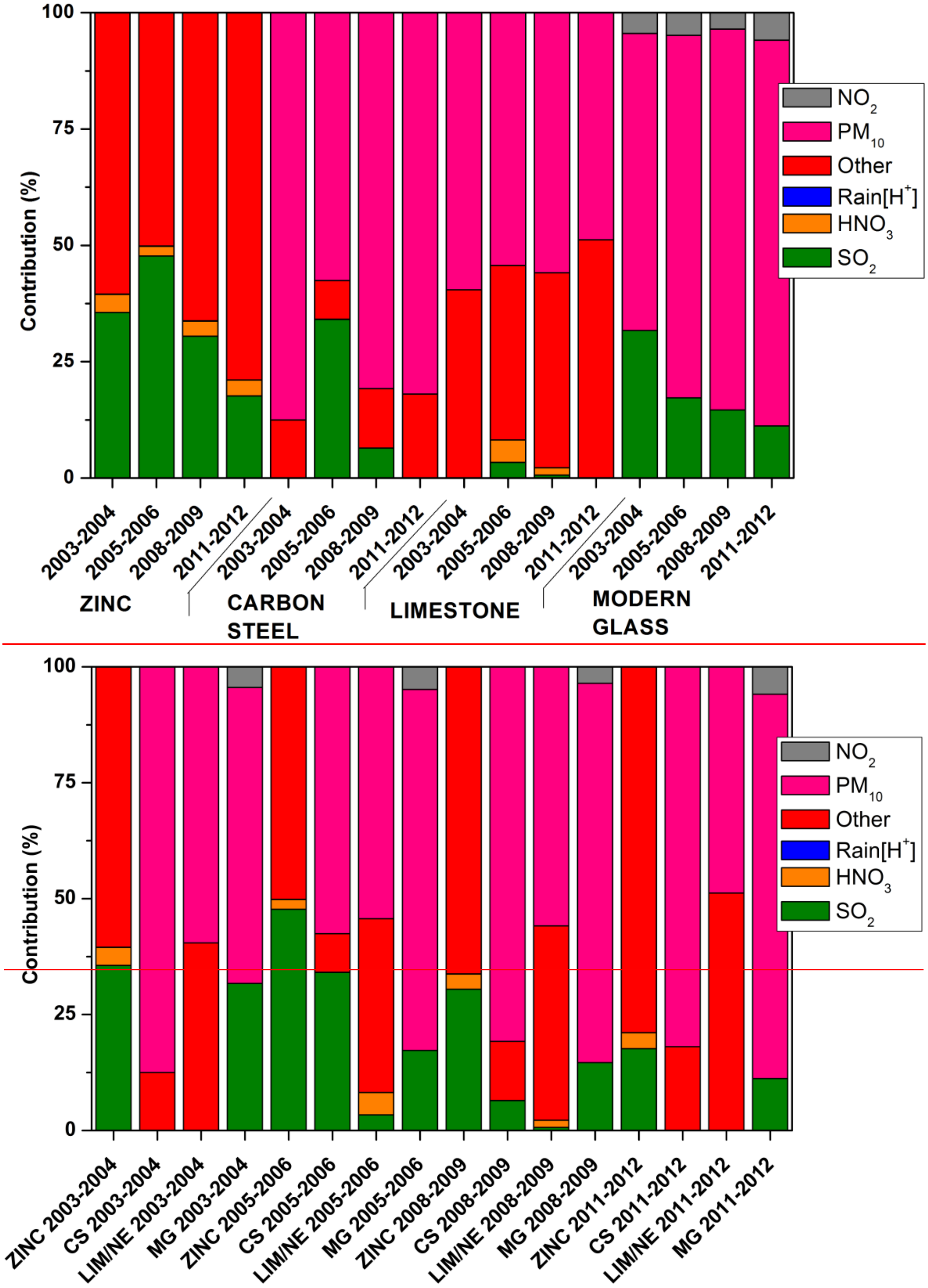


Figure 12~~6~~: The percentage contribution of each Athens DRF factor to the total corrosion/soiling of each material for all exposure periods. ~~**“CS” stands for Carbon Steel, “LIM/NE” stands for Limestone and “MG” stands for Modern Glass.**~~