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Corrosion Engineering, Science and Technology
The International Journal of Corrosion Processes and Corrosion Control

ISSN: 1478-422X (Print) 1743-2782 (Online) Journal homepage: https://www.tandfonline.com/loi/ycst20

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To cite this article: Fábio Vidal, Romeu Vicente, A. C. Bastos, A. M. Ferro Rocha & J. Mendes Silva (2019) Atmospheric corrosion in two different urban environments in Portugal: results of one-year exposure, Corrosion Engineering, Science and Technology, 54:7, 614-626, DOI: 10.1080/1478422X.2019.1646007

To link to this article: https://doi.org/10.1080/1478422X.2019.1646007

CORROSION ENGINEERING, SCIENCE AND TECHNOLOGY
2019, VOL. 54, NO. 7, 614–626
https://doi.org/10.1080/1478422X.2019.1646007

Atmospheric corrosion in two different urban environments in Portugal: results of one-year exposure

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ABSTRACT

An atmospheric corrosion campaign was carried out to update the information on the environmental corrosivity in Portugal, available from earlier MICAT and ICP-Materials projects. This communication summarises the initial atmospheric corrosion of copper, zinc and grey cast iron in the cities of Coimbra and Aveiro. The new data was produced in the scope of the project *TRAPHIC*, which aimed at evaluating the effects of air pollution on materials in the city of Coimbra. Samples of the three metals were exposed in three different locations and the surface modifications were monitored over time together with the local environmental conditions. Chromatic alterations in copper and zinc were analysed and corrosion products were characterised using SEM/EDS. First-year corrosion rates were measured for the three locations to complement the national corrosivity map. Results indicate the reduction of acidic pollution and decreasing of corrosion rates over the past 30 years in Portugal.

ARTICLE HISTORY
Received 13 May 2019
Accepted 16 July 2019

KEYWORDS
Atmospheric corrosivity; corrosion; copper; grey cast iron; zinc

Introduction

Atmospheric corrosion, by its omnipresence, is responsible for a great part of the corrosion costs worldwide [1] which are estimated to be between 2 and 5% of the Gross Domestic Product in each country every year [2]. Given the high impact of corrosion, maps of atmospheric corrosivity were produced in many countries to predict the durability of materials in different locations in order to reduce costs and extend the service life of structures and equipment.

Portugal joined the list of countries with information about its environmental corrosivity in the 1990s after the edition of the Portuguese National Map of Atmospheric Corrosion (MNCA – *Mapa Nacional de Corrosão Atmosférica*) [3], produced in the frame of the MICAT project (Ibero-American Map of Atmospheric Corrosiveness) which analysed the corrosion of mild steel, zinc, copper and aluminium in 14 countries from 1988 to 1994 [4,5]. The MNCA network of test sites comprised 19 locations across the country, including 2 sites in the island of São Miguel (Azores) and the 3 sites from the MICAT network – Leixões, Sines and Pêgo. Samples of carbon steel, zinc, copper and aluminium were exposed between 1989 and 1993 and 3 environmental parameters were monitored: time of wetness (TOW), sulphur dioxide (SO_2) and chloride (Cl^-) deposition rate. At that time, the ICP-Materials international network [6,7] included a test site in Portugal on the rooftop of the *Jerónimos* Monastery in Lisbon, exposing standard metals for 8 years (1987–95). These projects were developed in a period where the acidic effects of SO_2 were prevalent, a scenario that no longer exists in most urban areas. In fact, Tidblad has predicted that future corrosion will be dominated by chloride attack near the coastline, while acidic pollution will be of less concern, resulting in a low to medium corrosivity in inland [8].

Along with the protection of metallic infrastructures, particularly in coastal and near-coastal locations [9,10], another problem is the vulnerability of metal and stone elements in built heritage [11]. Di Turo et al. [12] performed a European risk assessment for pollution impacts on cultural heritage materials and verified a pollution abatement since 1980 that led to a significant reduction of the recession levels on limestone, but with a lesser impact on copper and bronze corrosion rates.

This concern with the preservation of cultural heritage has led to the development of the TRAPHIC project [13], with the goal of evaluating the effect of pollution in the city of Coimbra, home to several UNESCO World Heritage sites. Two test sites were installed in Coimbra, one in the *Fernão de Magalhães* Avenue, a place with an elevated traffic density, and the other inside the Geophysics Institute of the University of Coimbra, within the urban perimeter. A third test site was installed in the city of Aveiro, inside the University meteorological station, located 50 m from a shallow area of the Ria de Aveiro, an extensive salt-water estuary connecting the Atlantic Ocean and the *Vouga* River. Attention was given to the changes in appearance of the different materials upon atmospheric exposure which is of key importance in architecture. Additionally, corrosion rates of copper, zinc and grey cast iron were obtained for the first year of exposure. While copper and zinc are metals commonly used in atmospheric corrosion studies, corrosion information on grey cast iron is relatively scarce compared to other structural steels. Grey cast iron is the most widely used of all cast irons, extensively applied in the past in water supply pipelines, but also in large

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infrastructures such as bridge piers due to its higher corrosion resistance [14].

The results herein complement and add new information to the atmospheric corrosion studies developed in the past in Portuguese territory, by performing tests in two major cities which were not previously included in the network of test sites: Coimbra and Aveiro. Figure 1 shows the national test sites for the MNCA, MICAT, ICP-Materials and TRAPHIC projects. It also shows the location of the buildings and monuments in Coimbra classified as World Heritage. In Aveiro, along with the proximity to the Ocean (around 8 km) and the presence of the estuary, the city is surrounded by relevant industrial activity, including the Cacia Industrial Complex (dedicated to the production of paper pulp) located 8 km northeast from the city and a source of sulphur-containing emissions, with a reported emission of 668 tonnes of SO_2 in 2017 [15].

Materials and methods

Metals

Three common metals used in architectural applications were tested: commercial electrolytic copper plate (99.90% Cu with 0.02% P and traces of O and Ag), commercial zinc sheet (pure zinc with small additions of Cu, Ti and Al to improve mechanical properties) and grey cast iron produced in a local company (3% C, 1.5% Si, Mn < 0.1%, $P < 0.6\%$, S < 0.1%, Fe balance). The lamellar microstructure of the carbon flakes on grey cast iron is shown in Figure 2. All samples were 10×15 cm^2 in size and the thickness was 0.7 mm for copper and zinc, and 3–5 mm for grey cast iron.

Exposure sites

Metal samples (12 replicas of each metal) were placed in a 45° angle, in unsheltered racks facing south, following the recommendations of standard ISO 8565 [17]. The racks were installed in Coimbra, one on a rooftop in the Fernão de Magalhães Avenue, another inside the Geophysics Institute, and a third in Aveiro, inside University Campus (Figure 3), as described in [18].

Methods

The samples were exposed from August 2017 to August 2018. At months 3, 8 and 13, three samples of each metal were removed for surface analysis and measurement of corrosion rates. Lightness and chromatic alterations in

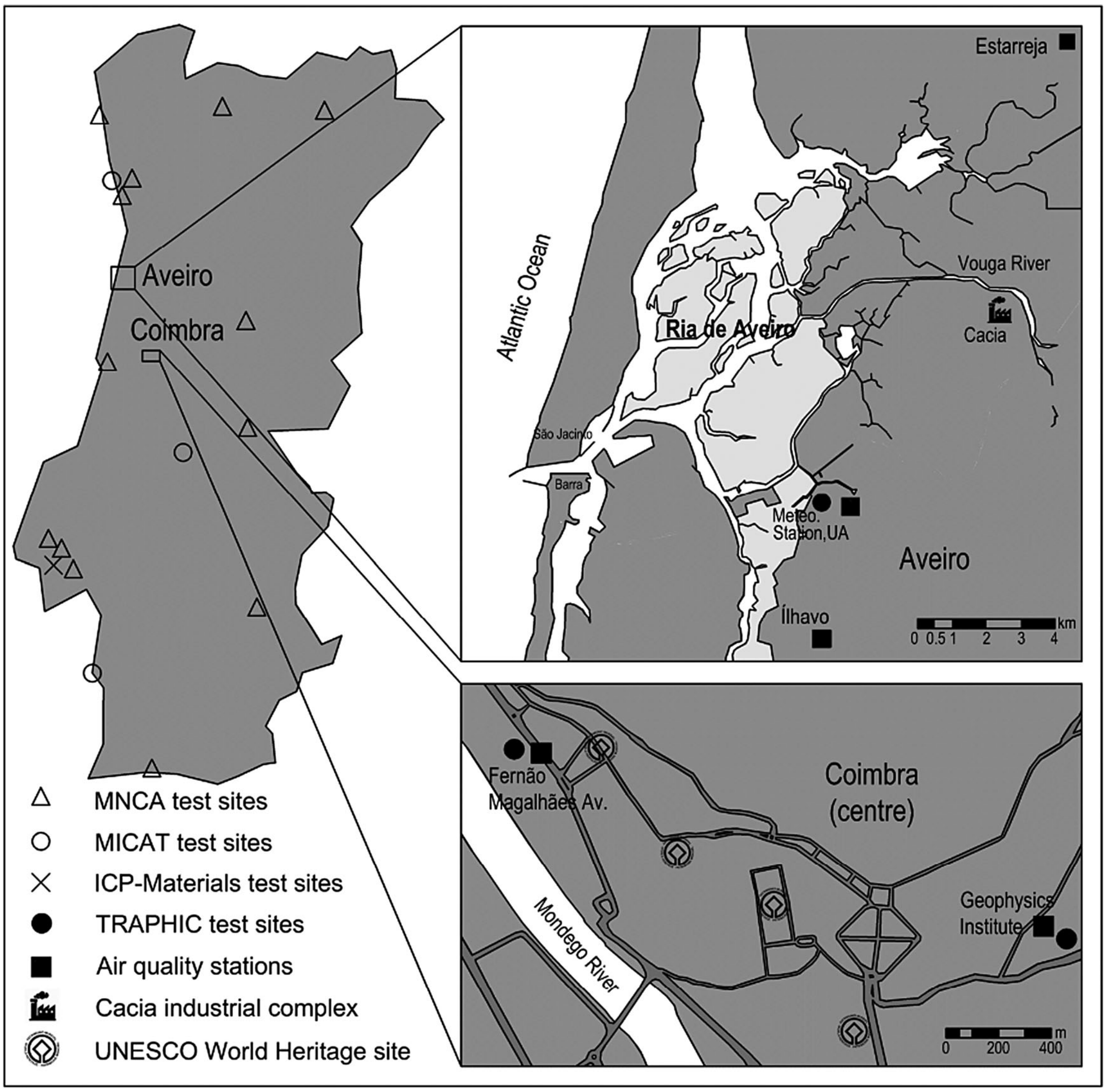

Figure 1. Portuguese past and present corrosivity test site network: MNCA, MICAT, ICP-Materials and current TRAPHIC sites in Coimbra's city centre and in Aveiro region, including the extension of the Ria de Aveiro estuary (partly adapted from [16]).

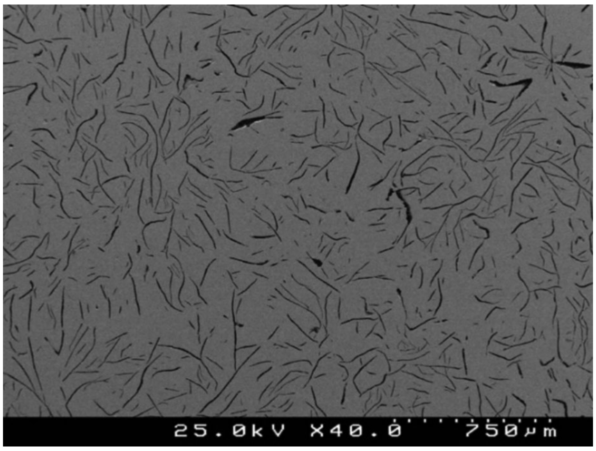

Figure 2. Micrograph of the grey cast iron used in this work.

Figure 3. Exposure site in the University of Aveiro's meteorological station.

the CIElab colour space were measured on copper and zinc using a *Konica Minolta CM-700d* spectrophotometer. The corrosion products were analysed at the end of exposure by Scanning Electron Microscopy (Hitachi S-4100 microscope) coupled with Energy-dispersive X-ray spectroscopy (Rontec spectrometer). Corrosion rates were determined by mass loss, according to ISO 9226 [19]. The removal of corrosion products on zinc followed ISO 9226 and used a solution of 25% glycine in distilled water (saturated solution). The removal of corrosion products from copper and cast iron followed ISO 8407 [20] and used a solution of hydrochloric acid in water (1:1, vol vol^{-1}). For cast iron, the solution contained 3.5 g L^{-1} of hexamethylenetetramine, a corrosion inhibitor. In all cases, the removal of corrosion products was performed at room temperature. Pollutant data was collected from national online databases and due to Aveiro's proximity to the ocean and to the salty Ria de Aveiro, a wet candle was installed near the exposure rack (seen on the left of Figure 3) following the ASTM Standard G140-02 [21]. The chloride deposition information was compared to local wind and precipitation regimes. The city of Coimbra is located approximately 40 km from the coast, therefore the significance of chloride-induced corrosion was considered negligible [22].

Results

Environmental parameters

Meteorological data and TOW

Weather data during the exposure period in the various locations were obtained from the meteorological stations located in the Geophysics Institute, in Coimbra, and in the University of Aveiro. Temperature (T), relative humidity (RH) and accumulated precipitation (P) data are shown in Tables 1 and 2.

Weather conditions indicate that Coimbra registers higher temperatures compared to Aveiro, particularly during the summer, while Aveiro registers higher RH in the same period. Annual precipitation can be considered similar, but rainwater is more acidic in Aveiro (4.48–6.88 [24]) compared to the average rainwater pH in Coimbra (around 6.85 [25]), according to samples collected between 2008 and 2014.

From an atmospheric corrosion perspective, TOW is more important than precipitation, as it describes the amount of time the metal remains wet, creating an electrolyte layer to sustain corrosion. According to ISO 9223 [26], TOW can be determined by coupling temperature and RH conditions, assuming that corrosion will occur during the hours in which temperatures are above 0°C and RH above 80%. This definition has been mentioned to lack an upper temperature threshold [27] and disregards the importance of hygroscopic deposits on the metal surface [28]. The TOW in the exposure sites during the test period was calculated according to ISO 9223 and is given in Table 3. For the Fernão de Magalhães measurements, a temperature and humidity sensor was installed on the rooftop.

The three test sites fall in level τ_4 of TOW according to ISO 9223, which is typical of most outdoor environments, except in dry or cold climates. Aveiro shows the highest value of TOW, mainly due to a more humid summer, with the temperature and humidity criteria being met in 58% of the registrations. In this city, the TOW is significantly higher during the spring and summer (69% of the hours compared to 47% in the autumn and winter). In Coimbra, both testing sites have similar TOW, which occurs in 48% of the time, with no significant variation between the warm and cold seasons (47% and 49%, respectively). The higher value in the Geophysics Institute can be attributed to a slightly higher humidity due to the proximity to vegetation and to the nearly 1°C higher average temperature on the rooftop location of the Fernão de Magalhães Avenue.

It is worth mentioning that a RH above 80% never occurred at temperatures below 0°C nor above 25°C (upper limit suggested in [27] for tropical climates), which means that TOW in the three sites during the testing time was temperature-independent, i.e. regulated solely by the number of hours RH was above 80%. The establishment of an upper limit for temperature therefore presents little impact in the Portuguese climate. It would take a 19.6°C limit to reduce TOW by 5% in Coimbra (a temperature that is most likely

Table 1. Meteorological data (monthly averages) in Coimbra during the exposure period (2017–18).

	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	Mai	Jun	Jul	Aug	Mean
T (°C)	21.8	18.9	19.7	14.2	10.3	10.3	9.7	10.8	13.5	16.2	18.3	20.3	23.2	15.9
RH^{a} (%)	67	72	61	68	77	82	73	82	79	72	79	78	68	74
P (mm)	25.4	5.3	26.8	41.8	138.7	82.3	18.1	281.8	170.7	55.6	112.5	21.7	1.0	981.7^{b}

[a] Missing data retrieved from [23].
[b] Total accumulated precipitation.

Table 2. Meteorological data (monthly averages) in Aveiro during the exposure period (2017–18).

	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	Mai	Jun	Jul	Aug	Mean
T (°C)	19.2	17.1	17.6	13.1	11.0	10.6	10.8	12.3	13.9	16.1	18.3	20.5	20.7	15.5
RH (%)	84	82	70	73	75	80	73	82	84	82	88	86	84	81
P (mm)	4.2	6.2	34.0	49.8	104.5	113.8	86.8	176.0	160.0	23.8	54.8	2.6	0.0	816.5[a]

[a]Total accumulated precipitation.

Table 3. TOW according to ISO 9223 [26] in the exposure sites.

Test site	TOW (h y^{-1})	TOW level according to ISO 9223
Coimbra (Geophysics)	3613	τ_4
Coimbra (Fernão de Magalhães Av.)	3596	τ_4
Univ. Aveiro	4728	τ_4

Table 4. Estimation of the average SO_2 concentrations for the TRAPHIC test sites during the period of exposure.

Test site	Average SO_2 concentration (µg m^{-3})
Geophysics Institute, Coimbra	0.30
Fernão de Magalhães Avenue, Coimbra	0.40
University of Aveiro	2.00

insufficient to enhance evaporation), while the limit in Aveiro would be of 21.1°C.

SO_2 concentrations

Many atmospheric corrosion studies have focused on the acidic effects of sulphur dioxide, the dominant corrosive species, especially during the 1980s and 1990s due to uncontrolled industrial and traffic-related emissions. This SO_2-dominating situation is no longer verified in European cities without a strong industrial influence. The atmospheric concentration of SO_2 is nowadays of lesser concern and, as a consequence, the number of SO_2 monitoring stations has been reduced. Following this trend, the number of stations in the Portuguese national air quality network that monitor SO_2 decreased from 63 in 2010 to 26 in 2017. The average SO_2 concentration in 2017 lied between 0.23 and 14.49 µg m^{-3} [29], with an hourly maximum of 532 µg m^{-3}, well below the admissible European limits: daily average values must not exceed 125 µg m^{-3} more than 3 times a year (occurred once), while hourly concentrations must not exceed 350 µg m^{-3} more than 24 times a year (occurred 5 times) [30]. These values can be compared with the concentrations reached in the 1990s (the oldest available information is from 1995) with an average hourly value varying between 4.33 and 21.56 µg m^{-3} and a national hourly maximum of 956 µg m^{-3} [29], revealing the improvements in air quality in Portugal.

Regarding the TRAPHIC test sites, the Portuguese Environmental Agency (APA) has published the total pollutant emissions per county in 2015 [31]. Analysing the SO_2 data, the county of Aveiro was ranked the 7th highest SO_2 emitter in continental Portugal with total emission of 1437 tonnes, while Coimbra was the 14th, emitting 516 tonnes of SO_2. The industrial emissions in Aveiro totalised 1352 tonnes, with those from the Cacia Industrial Complex representing around half of that value. Presently, SO_2 is not monitored in Coimbra and Aveiro (centre). Therefore, the SO_2 concentrations in the three test sites were estimated from the last known values and nearby stations/measurements (Table 4).

In the Geophysics Institute, an hourly average of 0.88 µg m^{-3} and an hourly maximum of 18 µg m^{-3} were registered in 2014–15. Concentrations dropped to an average 0.27 µg m^{-3} and hourly maximum of 12 µg m^{-3} according to nearby measurements performed in 2017 in the scope of the TRAPHIC framework, therefore, present values were estimated at around 0.30 µg m^{-3}. Records from the Fernão de Magalhães Avenue are older, however were 35% higher than those in the Geophysics Institute when measurements were available in both locations, therefore present values were estimated at around 0.40 µg m^{-3}. Concerning Aveiro, data is available in the nearby stations of Ílhavo (5 km south) and Estarreja (14 km northeast). While Ílhavo has no industrial activity, Estarreja is closer to the Cacia Industrial Complex and significantly contributes to Aveiro's annual industrial emissions, therefore better representing the expected air quality levels. The average SO_2 concentration in Estarreja during the months of exposure was 1.96 µg m^{-3} and maximum 218 µg m^{-3} [29], therefore the annual average in the centre of Aveiro was estimated to be around 2.00 µg m^{-3}.

Chloride deposition

Measurements performed for one year with the wet candle are listed in Table 5. The average chloride deposition rate was 29.7 mg.m^{-2}.d^{-1}, corresponding to a S_1 airborne salinity level according to ISO standard 9223, and indicating a moderate aggressiveness [26]. The moderate deposition is consistent with the distance to the coastline of around 7.6 km.

The influence of wind regimes on chloride deposition has been studied [32–36], mainly to justify the fluctuations in chloride deposition. Key parameters found in the literature are the distance to ocean and wind intensity, direction and persistence. In addition, a wind velocity of 3 m s^{-1}, was identified as a critical threshold for the increase of chloride deposition [33–35].

Analysing the weather information retrieved from the University of Aveiro's meteorological station, it was verified that the chloride deposition depends on three main factors: (i) velocity of western winds (west (W), northwest (NW) or southwest (SW), i.e. winds coming from the sea transporting salt spray); (ii) the linear distance to shoreline for each wind direction; and (iii) the accumulated precipitation as an enhancing factor. The wind velocity alone, i.e. the maximum daily average western winds (W_{max}), correlated well with the chloride deposition, however the correlation improved when an optimal wind velocity (denominated as effective wind velocity, W_{eff}) was used, which is the wind velocity corresponding to the highest ratio between velocity and distance to shoreline (Figure 4).

Finally, the values of chloride deposition were better explained when precipitation was included as an enhancing factor. During precipitation, the wet candle remains saturated for longer periods, which facilitates the deposition of chlorides. The influence of precipitation was divided into 4 categories: (i) below 10 mm, during which chloride deposition was very low, even with strong western winds; (ii) between

Table 5. Chloride deposition rate in Aveiro.

Wet candle	Exposure period	Days	Chloride deposition rate (mg.m^{-2}.d^{-1})	Annual average (mg.m^{-2}.d^{-1})	ISO 9223 airborne salinity level
1	13/10/2017–13/11/2017	31	18.7	29.7	S_1
2	13/11/2017–14/12/2017	31	53.3		
3	14/12/2017–16/01/2018	33	33.5		
4	16/01/2018–16/02/2018	31	20.2		
5	16/02/2018–16/03/2018	28	77.4		
6	19/03/2018–23/04/2018	35	56.2		
7	23/04/2018–23/05/2018	30	18.3		
8	23/05/2018–25/06/2018	33	12.7		
9	25/06/2018–30/07/2018	35	10.0		
10	30/07/2018–30/08/2018	31	12.9		
11	30/08/2018–01/10/2018	32	4.8		
12	01/10/2018–02/11/2018	32	38.2		

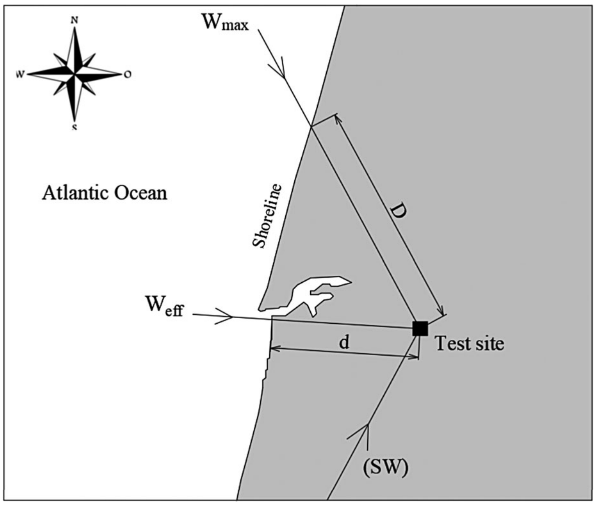

Figure 4. Schematic representation of the definition of effective wind (according to distance to shore) as a main factor.

10 and 25 mm, still disfavouring chloride deposition; (iii) between 50 and 100 mm, in which an increase in chloride deposition was observed; and (iv) above 100 mm, corresponding to rainy months, with significant chloride deposition. The factors above are organised in Table 6 for decreasing chloride deposition.

The chloride deposition followed the trend of W_{eff} adjusted with the accumulated precipitation in all cases except for candle 8. Figure 5 shows how chloride deposition decreases as effective wind velocity also decreases, except when precipitation is considerably low, disfavouring deposition even with higher wind velocities. The combination of both factors during the rainy months (February to April) led to the highest chloride deposition in the period of candles 5 and 6, while the absence or low precipitation registered during the periods of candles 7, 9, 10 and 11 significantly led to low deposition levels, despite high wind velocities.

Table 6. Chloride deposition of each wet candle and main weather variables influencing deposition rates.

Chloride deposition rate (mg.m^{-2}.d^{-1})	Wet candle number	Distance to shore (km)	Effective wind velocity (m s^{-1})	Accumulated precipitation (mm)
77.4	5	9.9	11.3	176.0
56.2	6	9.0	10.1	178.6
53.3	2	13.4	8.6	67.0
38.2	12	10.4	7.0	81.8
33.5	3	7.6	5.8	151.3
20.2	4	8.2	4.0	61.4
18.7	1	10.5	4.1	53.8
18.3	7	7.6	4.8	21.0
12.9	10	13.0	7.3	0.0
12.7	8	7.6	5.4	70.8
10.0	9	10.5	5.0	6.6
4.8	11	13.1	4.1	0.8

Other pollutants

In addition to chloride and sulphur dioxide, other species can also play an important role in atmospheric corrosion like, for example, nitrogen dioxide (NO_2), ozone (O_3), and hygroscopic particulate matter. Data on these pollutants in Aveiro and Coimbra are presented in Table 7. Information on O_3 was only available in the Geophysics Institute, presenting an elevated annual concentration (hourly maximum of 160 µg m^{-3}).

Considering the established decreases in SO_2 concentrations, recent studies have also focused on the acidic effects of nitric acid (HNO_3), a pollutant that has not shown signs of decreasing in recent years. Studies have shown corrosion rates and deposition velocities of HNO_3 on copper, zinc and steel far higher than the combination of SO_2 with the stated oxidisers (NO_2 and O_3) [37]. This pollutant is not generally measured but can be empirically estimated based on NO_2 and O_3 concentrations according to the CLRTAP (Convention of Long-Range Transboundary Air Pollution [38]). In the Geophysics Institute, it results in an annual concentration of HNO_3 of 1 µg m^{-3}, similar to the concentration actually measured in Lisbon [39].

Metals corrosion

Appearance of the samples surface

The physical appearance of bare metals when exposed to the environment is a very relevant topic in civil engineering and architecture. Metals age differently depending on the exposure conditions, and the corrosion products formed at the surface lead to loss of reflectance and chromatic alterations. This is easily observed in Figure 6 with specimens of zinc, copper and grey cast iron before and after 1 year of natural exposure in Aveiro and in Coimbra. All samples presented obvious signs of corrosion, without substantial differences between sites for zinc and cast iron. In the case of copper, however, the colour varied from a dull brown colour in Coimbra to a reddish coloration in Aveiro after exposure.

The lightness and chromatic alterations in copper and zinc after 3 and 13 months of exposure are presented in Figure 7 in the CIElab colour space. The lightness (L*) varies from 100 (white) to 0 (black). Copper suffered a reduction of 40% in the first 3 months and 44% after 13 months. On zinc the reduction was of 25% in the first 3 months with no further change until month 13.

The colour coordinates are ±a*, ranging from green to red, and ±b* ranging from blue to yellow. Not much changes

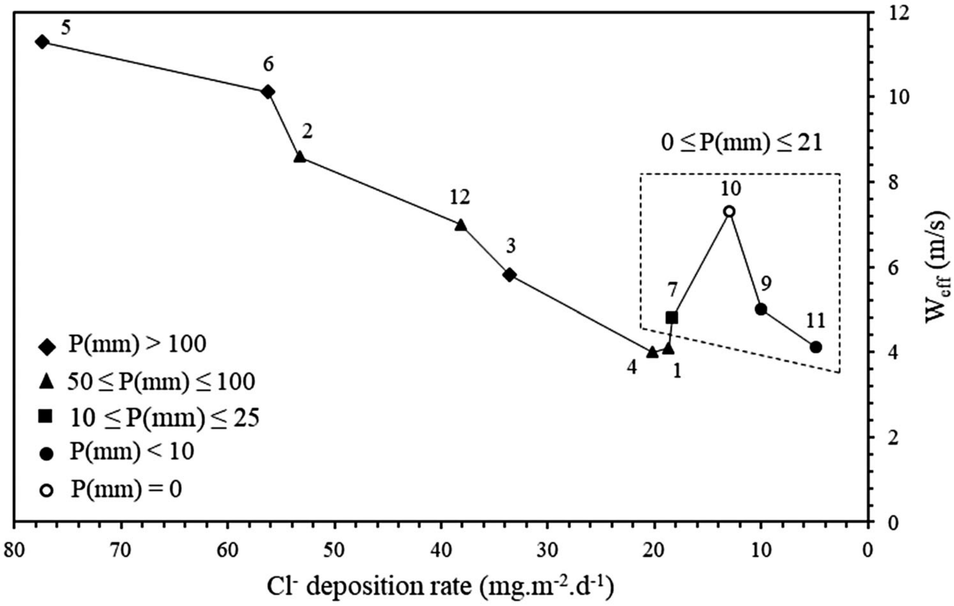

Figure 5. Chloride deposition relationship with effective wind velocity and precipitation.

Table 7. Pollutant data (annual averages) extracted from air quality stations in the centre of Coimbra and Aveiro (2017–18) [29].

Air quality station	NO_2 ($\mu g\ m^{-3}$)	PM_{10}^{a} ($\mu g\ m^{-3}$)	O_3 ($\mu g\ m^{-3}$)
Coimbra (Geophysics Institute)	16.5	17.0	51.1
Coimbra (Fernão de Magalhães Av.)	26.3	25.2	-
Aveiro	24.7	21.7	-

[a] Particulate matter of 10 µm or less in diameter.

occurred on zinc during the first year of exposure, with the b* coordinate practically unaltered and a slight increase in the a* coordinate. On copper the changes were more pronounced, confirming the differences already visible to the naked eye in the samples from Aveiro and Coimbra. After 3 months of exposure, the a* coordinate (red) in Aveiro was significantly higher than the registered in Coimbra, although the difference declined with time. For longer exposures, the coordinates will most likely enter the – a* quadrant as the samples will begin to acquire a greenish coloration due to the formation of chloride compounds such as atacamite or paratacamite, and/or the -b* quadrant if the influence of sulphur is dominant, leading to the formation of light-blue sulphur compounds such as posnjakite or langite [40].

Characterisation of corrosion products

SEM/EDS were used to characterise the corrosion products. Figure 8 shows general microscopic views of zinc and grey cast iron after one year of direct exposure to the environment in Aveiro and Coimbra. In all samples analysed by EDS, only oxygen and the main metal were measured. In grey cast iron a small amount of silicon was also detected (up to 4%). The oxygen content may provide a rough estimation of the amount of corrosion products. On zinc, samples from Aveiro contained 20% of oxygen, compared to 16% in the Geophysics Institute and 13% in the Fernão de Magalhães Avenue. In cast iron samples the amount was 26–27% in all samples and in copper all samples showed 11–12%.

Curiously, no chloride or sulphur was found in spectra acquired on large areas of the samples to obtain a general overview of the surface composition. The absence of these elements in the EDS analysis can be attributed to: (i) the short exposure duration, since the most common and stable corrosion products only form after years of exposure; and (ii) the unsheltered exposure conditions, favouring wash-off of reactants and corrosion products.

Indeed, it has been reported that in unsheltered zinc exposed to rural or urban atmospheres, the sulphur-

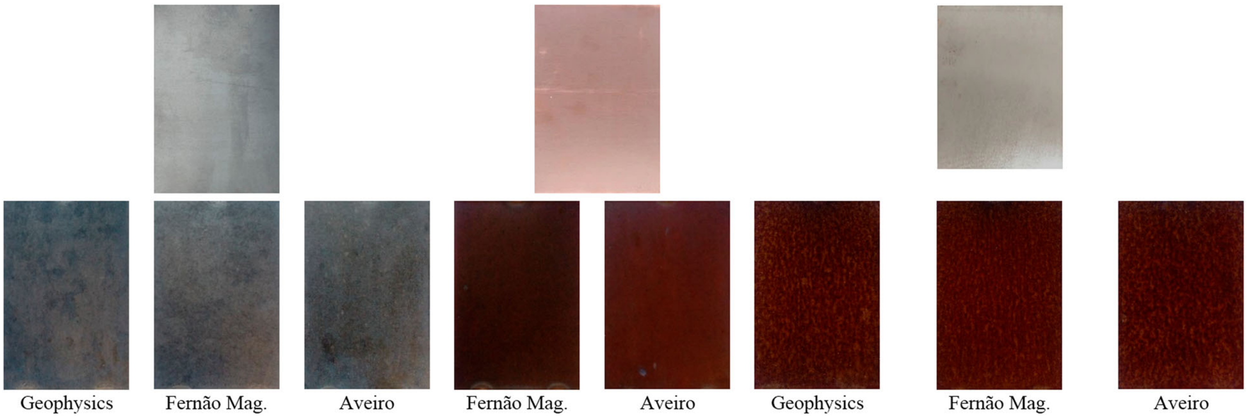

Figure 6. Photographic registration of the unexposed (top) and exposed after 1-year (bottom) samples of zinc (left), copper (centre) and grey cast iron (right). Size of plates is 10 × 15 cm^2.

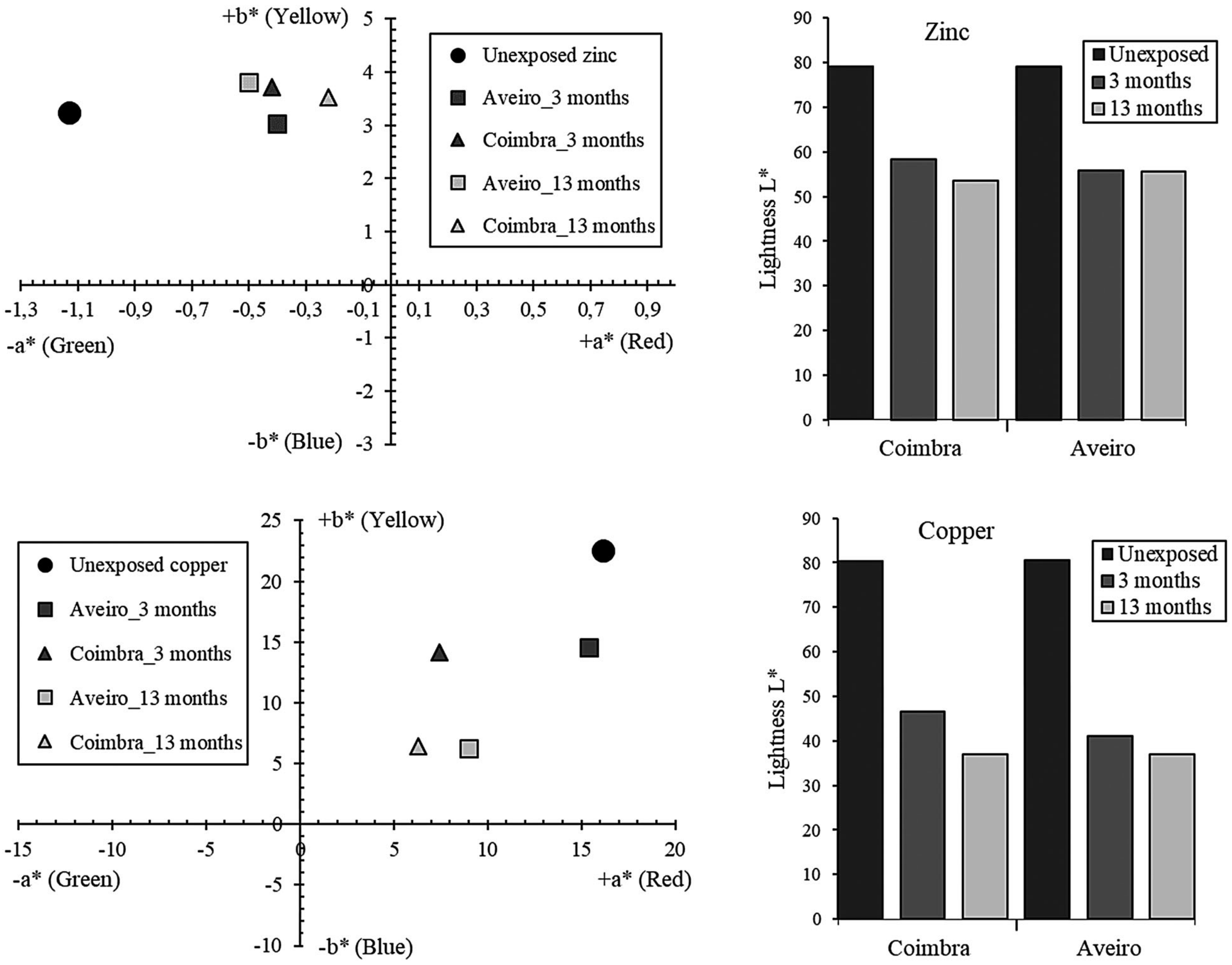

Figure 7. Spectrophotometry results indicating lightness and chromatic changes in copper and zinc.

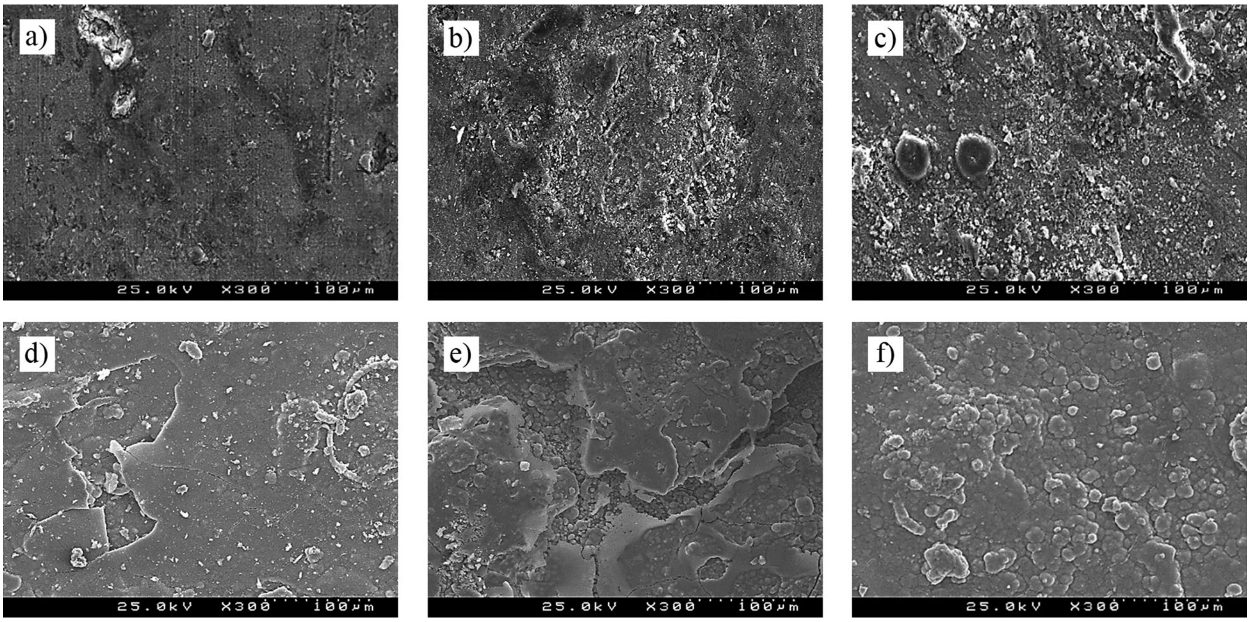

Figure 8. SEM images of zinc (a–c) and cast iron (d–f) surfaces after 1-year exposure in: Fernão de Magalhães Avenue, Coimbra (a,d); Geophysics Institute, Coimbra (b, e); University of Aveiro (c,f).

containing compounds are frequently dissolved and removed from the surface by precipitation events which delay the final phase of the corrosion products sequence (comprising mainly zinc hydroxysulphate, formed after only a few days in sheltered conditions) well beyond the first year of exposure [40]. The final phase might not even include sulphur, as reported in reference [41], where zinc hydroxycarbonate was found to be the final corrosion product of unsheltered zinc exposed in a rural area. Similarly, in marine environments, sheltered samples exhibit chloride-containing products after a few months of exposure [42], while in unsheltered samples, even if evidencing the presence of simonkolleite or zinc oxychloride, the chloride compounds are never very abundant, as they are washed away by rainfall [40].

On copper, the scenario is similar. An intermediate phase of copper corrosion products may include large amounts of cuprite (the initial copper oxide), posnjakite and langite (sulphate compounds) and atacamite (chloride compound). However, studies have reported no or small amounts of sulphate and chloride compounds after 1 year of exposure in unsheltered conditions, which remain small even after several years, compared to sheltered exposure [43].

Sulphur and chlorine where not detected on EDS analyses of wide areas of the samples, but on specific points it was possible to detect these elements in amounts ranging between 1 and 7%. After one year of exposure the amount of chlorine in samples from Aveiro and Coimbra was similar, which might be explained by the wash-off of the samples. Sulphur was detected only in samples from Aveiro, expressing the higher concentration of SO_2 due to the nearby Cacia Industrial Complex.

Figure 9 shows SEM images of localised points on copper where sulphur and chlorine have been detected. Micrographs (a) and (b) present crystal-shaped corrosion products that resemble the schematic representation of brochantite crystals given in reference [44]. However, the quantity of sulphur is very small (2–3%) and these crystals may be an early stage of posnjakite or brochantite formation, that precipitate over a cuprite layer [44,45], resulting in small blue spots, that may ultimately cover most of the surface after a few years. These crystals were observed only in Aveiro's samples. Micrographs (c) and (d) depict an area with low adherent corrosion products leading to flacking [46], where chlorine containing products accumulate.

Corrosion rates

Figure 10 shows the variation of corrosion rates of the three metals in the first year of exposure, expressed as thickness reduction per year ($\mu m\ y^{-1}$), according to ISO 9226 [19]. After one year of exposure, the corrosion rates were 0.6–1 $\mu m\ y^{-1}$ for zinc, 0.8–1.6 $\mu m\ y^{-1}$ for copper and 13–17 $\mu m\ y^{-1}$ for grey cast iron. Aveiro presented the highest corrosion rates, followed by the Geophysics Institute in Coimbra and then the Fernão de Magalhães Avenue, also in Coimbra. The rates follow the aggressiveness expected for each site taking into consideration the existing levels of SO_2, Cl^- and TOW. This last parameter was the most determinant for the corrosivity of the test sites. In Coimbra, the two sites are less than 2 km apart and, in spite of the pollution levels being larger in the Fernão de Magalhães Avenue, the highest corrosion rates were measured in the Geophysics Institute, where TOW is higher, most likely due to proximity to vegetation.

Figure 10 also shows that corrosion rates decrease with time of exposure. The accumulation of corrosion products at the surface hampers the ingress of reactants (e.g. water and oxygen) and increases the resistance of the electric path between anodes and cathodes of the corrosion cell. The corrosion rates continue decreasing after the first year and the stabilisation of the layer of corrosion products can take several years, as for copper [44] and weathering steels [47], for example.

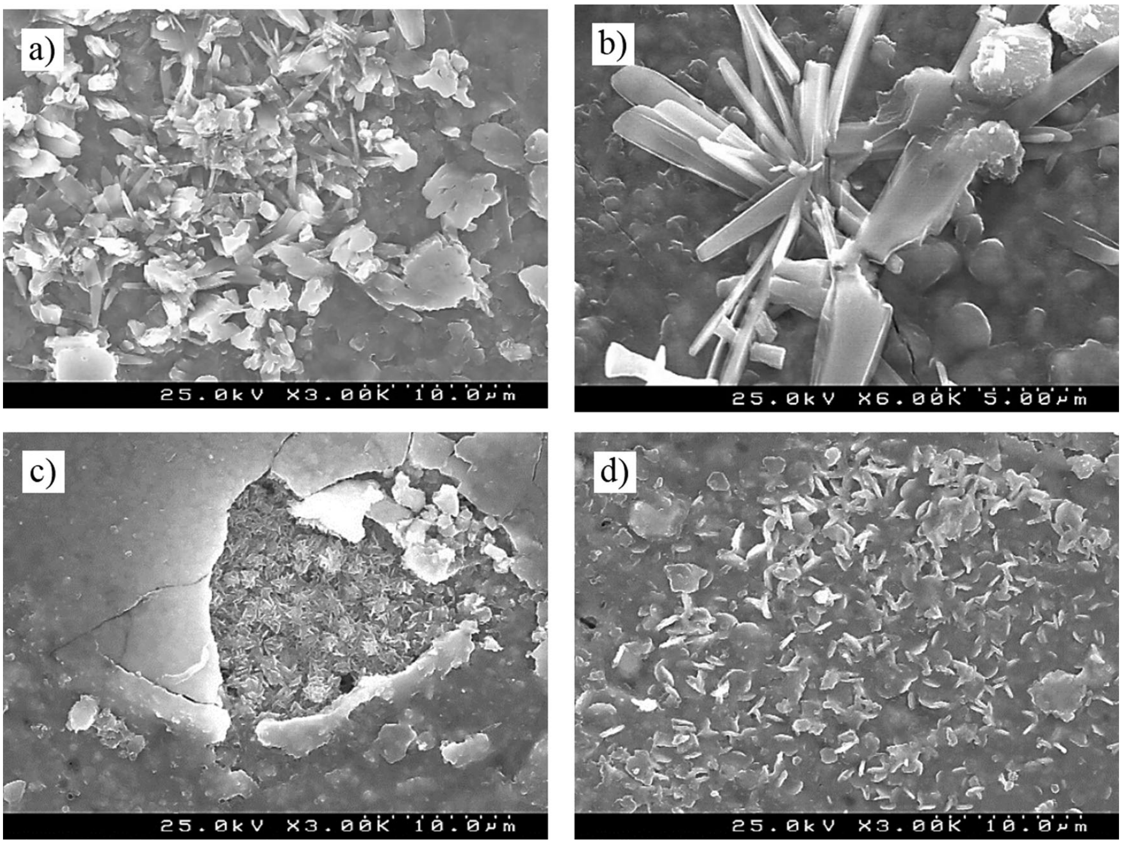

Figure 9. SEM images of copper samples with higher traces of sulphur (a,b) and chlorine (c,d) in total composition.

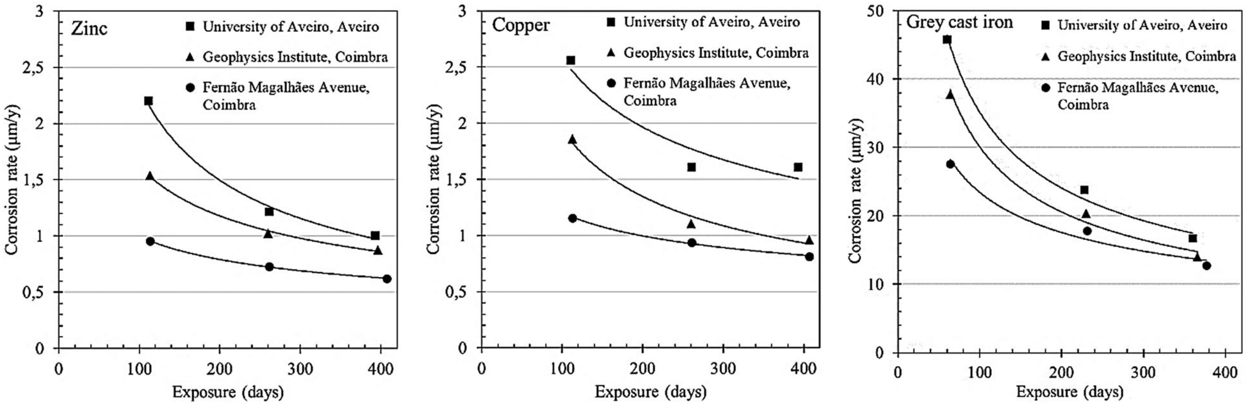

Figure 10. Evolution of the corrosion rates of zinc, copper and grey cast iron during 1 year of exposure in Coimbra and Aveiro.

Discussion

Changes in corrosivity in 30 years

The corrosion rates obtained in this work can be compared with the corrosion rates obtained in 1990–91 during the first-year of exposure in the sites for the MNCA atlas. Figure 11 shows the rates in the 17 MNCA continental test sites, randomly numbered, and the TRAPHIC test sites numbered as 18 (Geophysics Institute), 19 (Fernão de Magalhães Avenue) and 20 (University of Aveiro). The difference in magnitudes is clear, with the present rates being significantly below the average MNCA rates.

In Aveiro, the most aggressive of the three sites, the corrosion rates of zinc and copper are around 60% lower and cast iron is 86% lower than the average corrosion rates measured in 1990–91. This occurs even though the TOW and chloride deposition in Aveiro are, respectively, 88% and 53% higher than the values registered on the MNCA sites in 1990–91. The difference seems to be the concentration of SO_2, which is now much smaller, and is a clear indication that this was a highly influential variable in controlling the corrosion rates in the past.

Dependence of environmental parameters

During the 1990s, international corrosion campaigns have related corrosion rates with environmental data through the statistical development of dose–response functions. While the ICP-Materials programme excludes sites with the relevant influence of chloride, relating corrosion rates with other air pollutants and meteorological data, the MICAT and MNCA atlas focused mainly on chloride, SO_2 and TOW [5]. MNCA data on the three dominant parameters along with corrosion rates for the first year of exposure (1990–91) are presented in Figure 12, in order to determine the parameters dependence. Analysing the figure, the corrosion rates of copper do not seem to relate well with any of the environmental parameters. In the case of zinc, corrosion rates seem to relate well to variations in SO_2 deposition, while for carbon steel, the variation in corrosion rates seems to relate with chloride and SO_2 deposition. No clear relation with TOW can be seen.

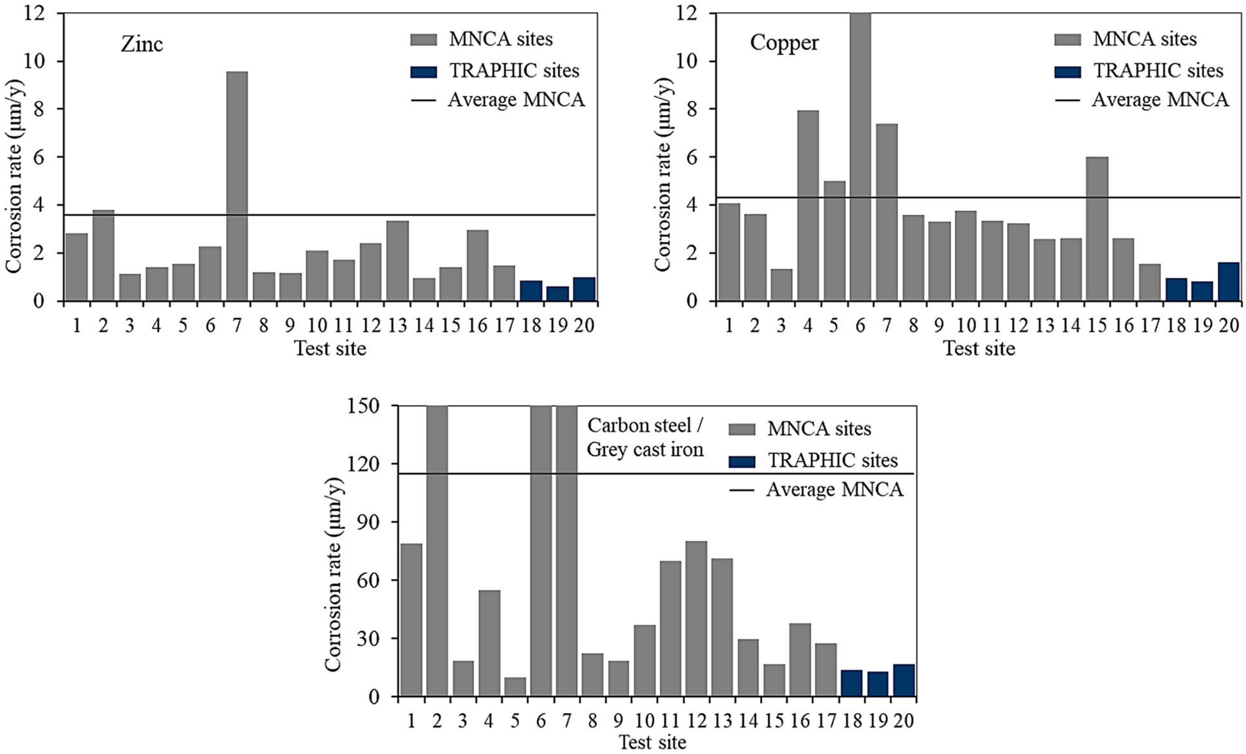

Figure 11. Corrosion rates in 1990–91 (MNCA [3]) and in 2017–18 (TRAPHIC test sites).

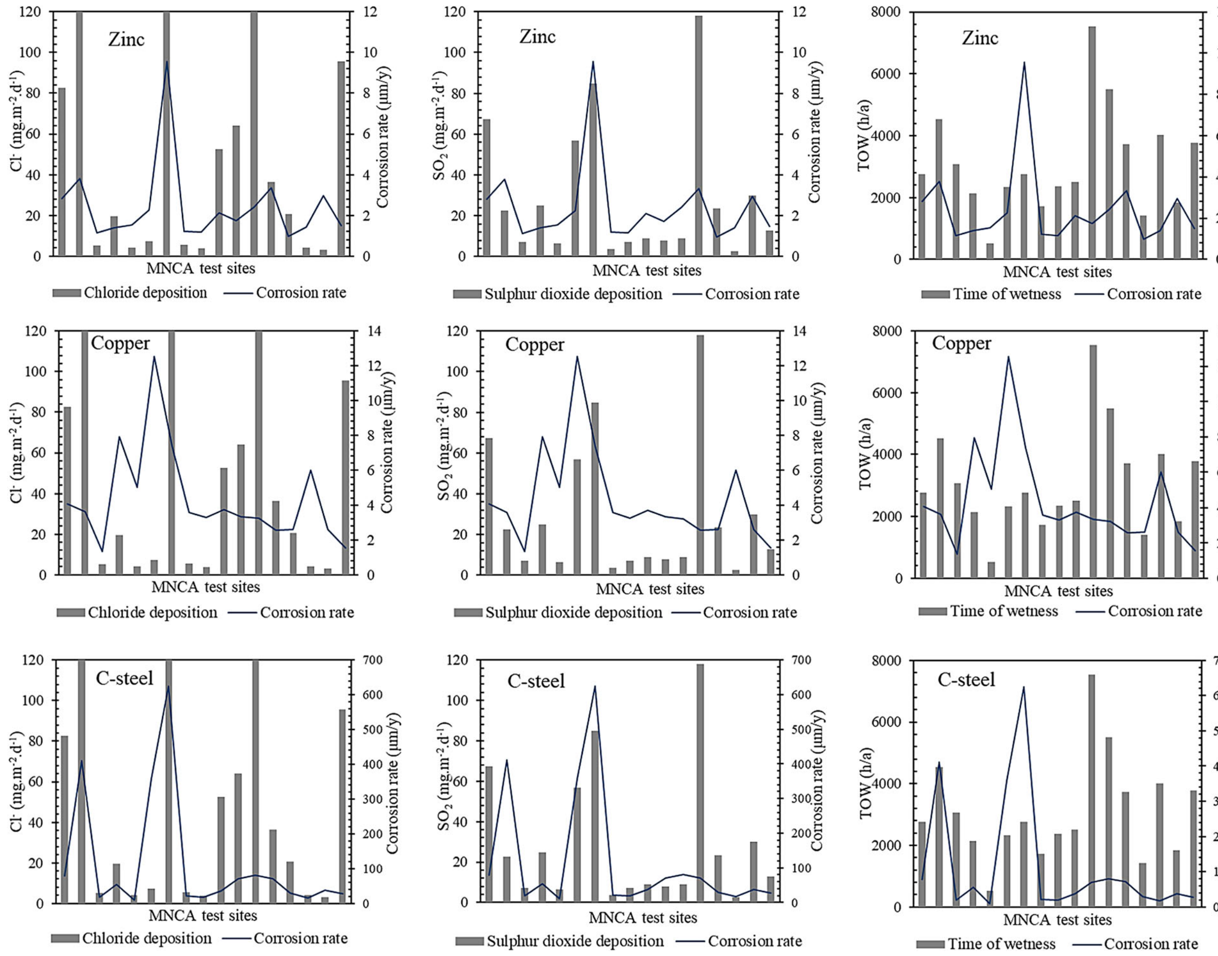

Figure 12. Environmental variables and corrosion rates measured in the MNCA in 1990–91 for zinc, copper and carbon steel [3]. The upper limits (*y*-axis) for Cl⁻ were limited in 3 stations (reaching as high as 780 mg.m^{-2}.d^{-1}) for the sake of better visualisation.

To confirm these dependences, multiple linear regression analysis was performed with the first year MNCA published data [3], considering the 3 dominant environmental variables. The statistical analysis is based on 17 available observations (17 test sites nationwide), however, this approach allows the confirmation of the variables' dependence, as well as determine if the TRAPHIC experimental data fits the regression procedure. The corrosion data for zinc revealed the highest correlation to the variables ($R = 0.97$), confirming no statistical significance for TOW, while SO_2 is the most influential. In the case of carbon steel, the corrosion data revealed a good fit ($R = 0.82$), although little variance was attributed to the chosen variables, where only chloride deposition showed statistical significance. The multiple regression for the copper data confirmed no correlation ($R = 0.34$). Since zinc presented higher correlation, a comparison to experimental data from the TRAPHIC project was performed for this metal (the other two show too scattered results). The graphical representation of the regression study is shown in Figure 13, illustrating measured vs predicted corrosion rates using the multiple linear regression expression, with a 20% margin for relative error. Zinc corrosion rates for the three TRAPHIC test sites were then calculated using the regression expression and plotted against the measured rates as an '*x*'.

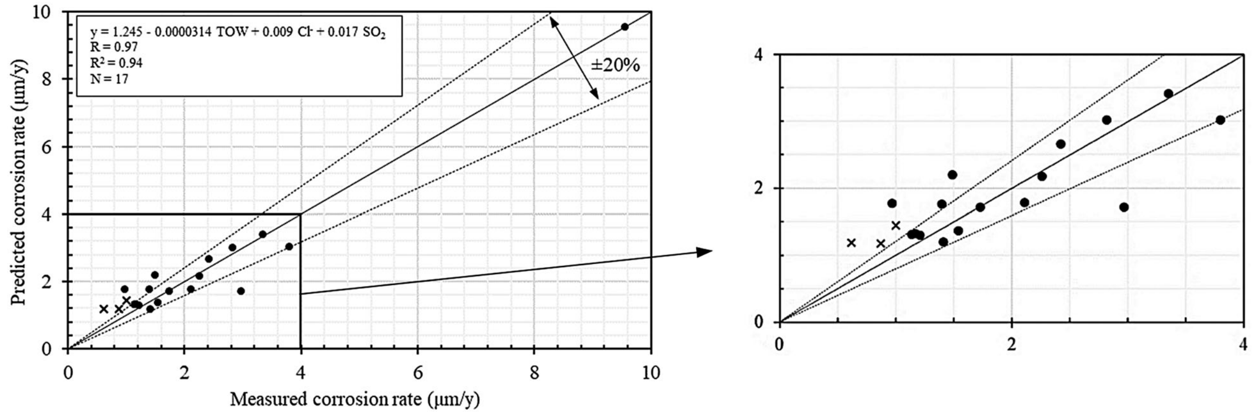

Figure 13. Measured *vs* predicted zinc corrosion rates using the multiple regression expression obtained from MNCA 1990–91 data [3]. TRAPHIC results from 2017 to 2018 are marked as '*x*'.

Table 8. Atmospheric corrosivity of test sites according to ISO 9223 [26].

Test site	Zinc	Copper	Grey cast iron
Geophysics Institute, Coimbra	C3	C3	C2
Fernão de Magalhães Av., Coimbra	C2	C3	C2
University of Aveiro	C3	C4	C2

Corrosion rates for zinc obtained in the scope of the TRAPHIC project do not fit the regression developed with MNCA data, presenting deviations of 36% in the Geophysics Institute, 45% in Aveiro and 92% in the Fernão de Magalhães Avenue. Most of the error is associated to the fact that corrosion rates estimated within TRAPHIC are significantly lower than in the MNCA, below the intercept constant ($\beta_0 = 1.245$), rendering the predicted rates higher than those measured. Nevertheless, the highest weight given to SO_2 and the absence of significance to the TOW variable also helps explain the significant deviation associated to the Fernão de Magalhães Avenue, since the regression predicts that corrosion in this site should be higher than in the Geophysics Institute, which it did not. This combination of results leads to the conclusion that environmental characteristics have changed the rate of corrosion in the past decades, since in the 1980s and 1990s corrosivity was mostly influenced by elevated levels of SO_2 (and chlorides in near-coastal locations), masking the influence of TOW in the MNCA sites.

Mapping corrosivity according to ISO 9223

The corrosivity of the three TRAPHIC test sites is given in Table 8. The least aggressive site was the Fernão de Magalhães Avenue in Coimbra, with a corrosivity level varying between C2 and C3 depending on the metal, followed by the Geophysics Institute, and finally Aveiro with a C3 level for zinc, C4 for copper and C2 for grey cast iron. Note that the international standard refers to carbon steel, not grey cast iron. The corrosion rate of grey cast iron is lower than mild steel because of the higher amounts of silicon and carbon.

Melchers [14] has found that the long-term rates of corrosion of cast irons exposed to marine and inland atmospheres are significantly lower than of mild and low alloy steels. This was considered to be the result of the graphitised layer holding protective corrosion products more effectively and thus providing a more effective diffusion barrier than in the case of mild steel.

Figure 14 summarises the information about the atmospheric corrosivity in Portugal for zinc, copper and carbon steel based on the MNCA atlas (1990–93) [3], the data from the ICP-Materials programme (1987–88) [48,49], and the new additions from the TRAPHIC project (2017–18).

An attempt to update the corrosivity maps to the present day is presented in Figure 15, using simple interpolation from Figure 14 and the most recent data on SO_2 emissions across the country [31]. It is admitted that chloride concentrations have not changed significantly since 1980–90. In the past 30 years, it is believed that the corrosivity has decreased by one order of magnitude (or corrosivity category) due to overall reduction of SO_2 emissions. Figure 15 suggests that the corrosivity should remain high near the coastline due to chloride contamination and higher TOW, and in a few industrial areas with SO_2 pollution. This scenario appears to meet Tidblad predictions [8] for the corrosion of carbon steel and zinc in 2070, where most of the Portuguese territory would exhibit a C2 category, except near the coast where they may vary between C3 and C5. Inland, where chloride contamination is negligible, corrosivity will mainly depend on local conditions (pollution) and TOW.

Conclusions

This work analysed the corrosion of copper, zinc and grey cast iron during the first year of atmospheric exposure in the Portuguese cities of Aveiro and Coimbra. The corrosion rates after 1 year of exposure were 0.6–1 μm y^{-1} for zinc, 0.8–1.6 μm y^{-1} for copper and 13–17 μm y^{-1} for grey cast iron, which correspond to atmospheric corrosivities of

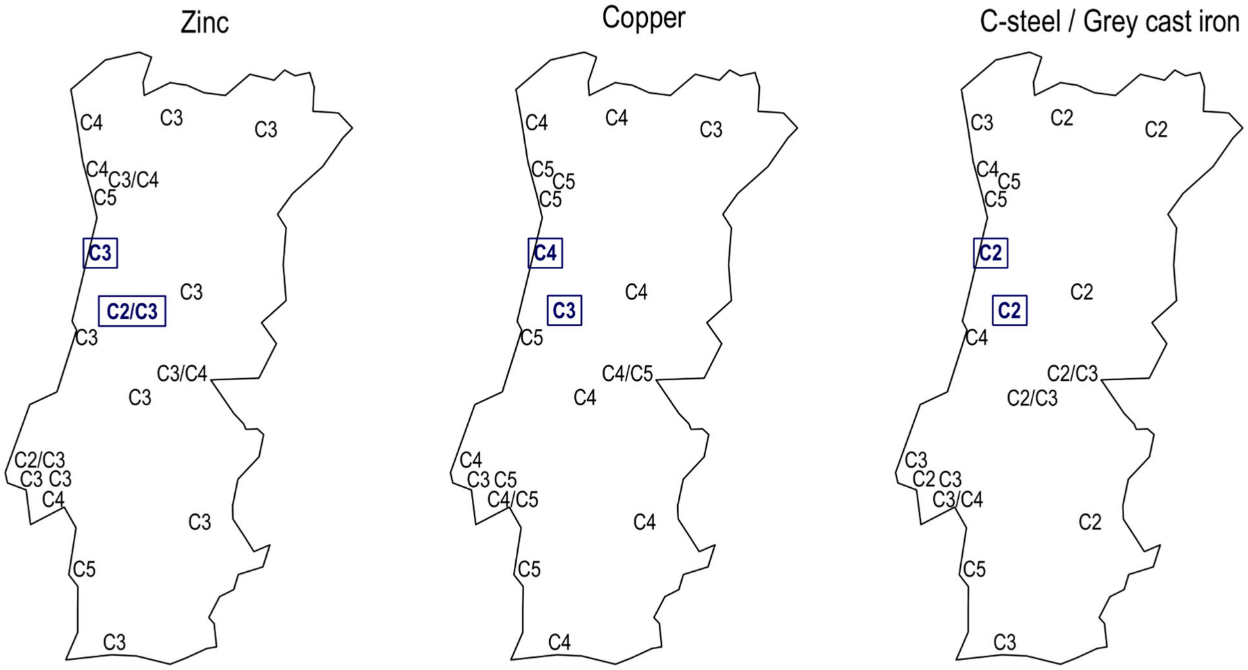

Figure 14. Atmospheric corrosivity in Portugal according to the Portuguese National Atlas (MNCA, 1990–93 [3]), complemented with ICP-Materials data for Lisbon (1987–88 [48,49]) and the new TRAPHIC results for Coimbra and Aveiro (2017–18) in boxes.

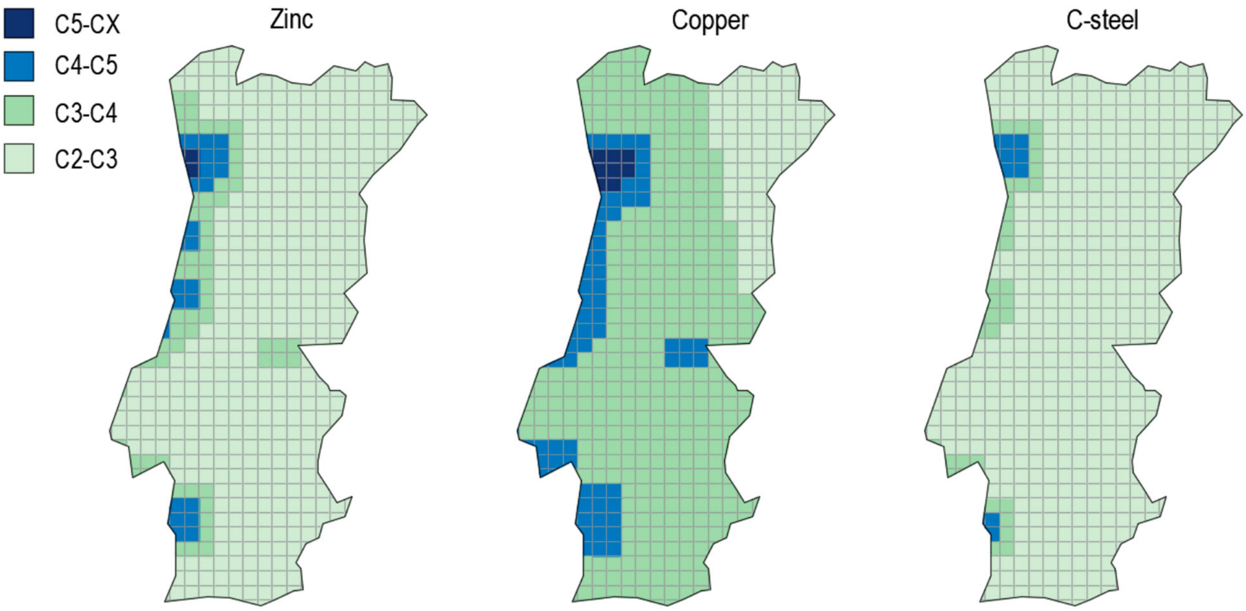

Figure 15. Prediction of the atmospheric corrosivity in Portugal at present date.

C2/C3 for zinc, C3/C4 for copper and C2 for grey cast iron. Compared to corrosion rates measured in the 1980s and 1990s, the present values show a significant decrease that has been attributed to the decrease in SO_2 concentrations in today's atmosphere.

It is predicted that the corrosivity in most of the Portuguese territory will depend mainly on the TOW, except very close to the ocean where the chloride concentration will play a crucial role. Some results also suggested that the definition of TOW in ISO 9223 may require a revision in order to better address the influence of temperature and, more importantly, the effect of depositing hygroscopic particles.

Acknowledgements

The authors would like to thank Professor Lídia Gil Catarino of the University of Coimbra for the guidance and support given regarding the use and interpretation of the spectrophotometric results. The authors would also like to thank Professor José M. Castanheira of the University of Aveiro for authorising the use of space for the rack and for providing data on meteorological variables observed in the meteorological station of the University of Aveiro. Finally, the authors would like to thank the Geophysics Institute of Coimbra for providing the space to perform this work, specifically Eng. Paulo Ribeiro for the support given to this project and for providing the required data from the Geophysics Institute's meteorological station.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Fundação para a Ciência e aTecnologia (FCT) in the framework of the research project 'TRAPHIC – Traffic-related air pollution impacts on historic city centres: an integrated approach', reference P2020-PTDC/ECM-URB/3329/2014.

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