ORIGINAL RESEARCH PAPER

Estimation and mapping of the contribution of nitric acid to atmospheric corrosion of zinc

J.O. Castillo-Miranda1,*, F.J. Rodríguez-Gómez1, J. Genescá-Llongueras2, L.G. Ruiz-Suárez3, J.A. García-Reynoso3

1Departamento de Ingeniería Metalúrgica, Facultad de Química, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, C.P. 04510, Ciudad de México, México
2Polo Universitario de Tecnología Avanzada, Universidad Nacional Autónoma de México, Vía de la Innovación 410 PIIT Autopista Monterrey-Aeropuerto Km. 10 C.P. 66629, Apodaca, Nuevo León, México
3Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Circuito de la Investigación Científica, Ciudad Universitaria, C.P. 04510, Ciudad de México, México

BACKGROUND AND OBJECTIVES: Atmospheric zinc corrosion in the Mexico City Metropolitan area has long been attributed mainly to the effect of pollutants such as sulfur dioxide. There are changes in the urban atmosphere’s chemical composition due to the implementation of air quality policies focused on reducing the emission of sulfur dioxide and other pollutants. This study’s objectives were to estimate and map the contribution of nitric acid on zinc’s atmospheric corrosion process.

METHODS: The impact of nitric acid on zinc is feasible to estimate using a function for a multi-pollutant situation. This function contemplates the sum of two contributions: one of nitric acid and another that includes sulfuric acid and climatic parameters. The multi-pollutant function is suitable to apply in areas without the strong influence of chlorides and tropical and subtropical climates, comparable to the Mexico City Metropolitan area.

FINDINGS: The results showed that spatial and temporal estimation of corrosion rates in grams per square meter of zinc was made for 2015-2019, using data modeling in a geographic information system. The maps of corrosion rates allowed us to visualize that, in general, the “southwest” zone has the most significant effects and that the lowest corrosion rates were presented in 2019 as an outcome of the implementation of air quality programs. Furthermore, a contribution of nitric acid up to 32% to the zinc corrosion rate was estimated.

CONCLUSION: The construction of corrosion rate maps provides a spatial and temporal estimate that allows visualizing areas where zinc materials are at risk corrosion due to the dispersion of atmospheric pollutants and climatic parameters. Likewise, it can represent a decision-making tool for the implementation of atmospheric corrosion studies of materials.

ARTICLE INFO

Article History:
Received 04 January 2021
Revised 09 April 2021
Accepted 24 April 2021

Keywords:
Air pollution
Damage to materials
Geographic information systems (GIS)
Multi-pollutant function
Urban atmosphere

ABSTRACT

BACKGROUND AND OBJECTIVES: Atmospheric zinc corrosion in the Mexico City Metropolitan area has long been attributed mainly to the effect of pollutants such as sulfur dioxide. There are changes in the urban atmosphere’s chemical composition due to the implementation of air quality policies focused on reducing the emission of sulfur dioxide and other pollutants. This study’s objectives were to estimate and map the contribution of nitric acid on zinc’s atmospheric corrosion process.

METHODS: The impact of nitric acid on zinc is feasible to estimate using a function for a multi-pollutant situation. This function contemplates the sum of two contributions: one of nitric acid and another that includes sulfuric acid and climatic parameters. The multi-pollutant function is suitable to apply in areas without the strong influence of chlorides and tropical and subtropical climates, comparable to the Mexico City Metropolitan area.

FINDINGS: The results showed that spatial and temporal estimation of corrosion rates in grams per square meter of zinc was made for 2015-2019, using data modeling in a geographic information system. The maps of corrosion rates allowed us to visualize that, in general, the “southwest” zone has the most significant effects and that the lowest corrosion rates were presented in 2019 as an outcome of the implementation of air quality programs. Furthermore, a contribution of nitric acid up to 32% to the zinc corrosion rate was estimated.

CONCLUSION: The construction of corrosion rate maps provides a spatial and temporal estimate that allows visualizing areas where zinc materials are at risk corrosion due to the dispersion of atmospheric pollutants and climatic parameters. Likewise, it can represent a decision-making tool for the implementation of atmospheric corrosion studies of materials.
INTRODUCTION

The atmospheric corrosion process of hot-dip zinc-coated steel occurs in environments influenced by industrial activities with emissions of sulfur dioxide (SO\textsubscript{2}), nitrogen oxides (NO\textsubscript{x}), and hydrogen sulfide (H\textsubscript{2}S). In marine environments, the reaction occurs with chlorides, together with carbon dioxide (CO\textsubscript{2}) and water (H\textsubscript{2}O) (Friel, 1986). The hydrogen potential (pH) of the aqueous surface film depends on the atmospheric concentration of SO\textsubscript{2} and NO\textsubscript{x}, essential for the corrosion process because it controls the dissolution of the passive oxyhydroxide surface (Graedel, 1989; Graedel and Frankenthal, 1990). Corrosive atmospheric trace substances, such as SO\textsubscript{2}, nitrogen dioxide (NO\textsubscript{x}), and hydrogen chloride (HCl), accelerate metallic corrosion by acidifying the surface electrolyte and accelerate metal corrosion (Johansson, 1990). Knotková and Bartoň (1992) analyzed the contribution of acid deposition as a heterogeneous dynamic system of atmospheric corrosion metals. Kucera and Fitz (1995) considered that an acid effect in the atmosphere due to a multi-pollutant situation was the cause of the damage to materials. The deterioration of various materials, to some extent, is caused by acid gases such as SO\textsubscript{2}, nitric acid (HNO\textsubscript{3}), and HCl (Ferm et al., 2005). Current studies indicate that the corrosion effect of HNO\textsubscript{3} exceeds SO\textsubscript{2}, with a factor between 2 and 20 depending on the exposed material (Tidblad et al., 2009). Atmospheric corrosion metals have long been attributed to SO\textsubscript{2} and chlorides (Cl\textsuperscript{-}), which has been demonstrated in laboratory weathering exposures and proven in field exposures. So, the promulgation of environmental protection laws in industrialized countries, in addition to the efforts inside the limits of the Convention of the United Nations Economic Commissions for Europe (UN ECE) on Long-range Transboundary Air Pollution (CLRTAP), led to a notable decrease in SO\textsubscript{2} levels. However, the concentration levels of other air pollutants, such as NO\textsubscript{x} and ozone (O\textsubscript{3}), remained or even increased slightly. Therefore, the effect of SO\textsubscript{2} needs to be considered in a multi-pollutant situation with other polluting gases such as NO\textsubscript{x} and O\textsubscript{3}, including particles (Oesch and Faller, 1997; Tidblad et al., 2002a). The levels of environmental concentration for HNO\textsubscript{3} are lower concerning SO\textsubscript{2}; however, depending on the aggressiveness, HNO\textsubscript{3} can be compared to SO\textsubscript{2} in a multi-pollutant situation (Tidblad et al., 2009).

Atmospheric sulfur levels have been better controlled, and there has been a considerable reduction in SO\textsubscript{2} emissions, while the concentration of NO\textsubscript{x} and HNO\textsubscript{3} has increased due to emissions from automobile traffic (Graedel and Frankental, 1990; Pantani et al., 1998). HNO\textsubscript{3} has higher concentrations in urban areas than in rural areas, but they are lower than NO\textsubscript{2} in urban areas (Ferm et al., 2005). The current study’s main objective is to estimate nitric acid’s spatial and temporal contribution to zinc’s atmospheric corrosion in the Mexico City Metropolitan Area (MCMA) for 2015-2019. Maps of corrosion rates in grams per square meter (g/m\textsuperscript{2}) were constructed to achieve this objective. Also, the maps provide a spatial estimate of the corrosion risk of zinc materials when exposed to a polluted atmosphere. This study was carried out in the Mexico City Metropolitan Area in 2020.

The behavior of HNO\textsubscript{3} in the atmosphere of the Mexico City Metropolitan area

The Mexico City Metropolitan Area (MCMA) is located between north 19° 03’ to 19° 54’ latitude and 98° 38’ to 99° 31’ west longitude. It is part of an endorheic basin, with an average altitude of 2,240 meters above sea level. It is in the “East” area of the region known as the Transverse Neovolcanic System. The latitude of the MCMA can accelerate the photochemical reactions of pollutants in the atmosphere due to intense solar radiation. Likewise, there are anticyclonic systems in the area that keep the sky clear and increase the photochemical capacity of the atmosphere (SMA, 2008). MCMA is one of the largest megacities worldwide, as it has a population of more than 21 million people (UN, 2016). MCMA lies in central Mexico, at a tropical latitude where the climate is semi-dry temperate tropical in the northeast region; in the center, the temperate subhumid predominates, and in the upper, semi-cold subhumid type regions. Generally, the main entry of wind is located in the north, although there may be wind flow from south to north (Jáuregui, 2000; INEGI, 2007). The rainy season with high relative humidity occurs from May to October (Jáuregui and Romales, 1996), causing the levels of some pollutants to drop due to atmospheric instability. The upper levels of precipitation are registered in the mountainous areas and the lowest mainly in the northeast (INEGI, 2007). A study of the chemical composition of rain samples in Mexico City through multiple regression
analysis for the period 1994-2000 showed that the contribution of Cl⁻ (chloride-based sea salt) with sodium ion (Na⁺) and potassium ion (K⁺) was 2.2 percentage (%) at the prediction of the hydrogen ion (H⁺) concentration. It allows us to assume that the chlorides found in rainwater come from sources other than sea salt. Likewise, Mexico City is placed at more than 300 kilometres (km) from the nearest shore, surrounded by high mountains. The Sierra Madre Oriental, with mountains above 4000 meters above sea level, is located near the Gulf of Mexico coast, where heavy rains are produced that intervene in further eliminating sea salt aerosols (Báez et al., 2006). A study of the humid atmospheric deposition in the 2013-2016 period in the MCMA indicated that the calcium Ca²⁺ and Cl⁻ ions represented total annual deposits of 8% to 9% and 3% to 8% (Avila, 2018). The presence of chlorides could be attributed to emissions of approximately 30,000 small, medium, and heavy industries located in the northern part of the MCMA and the residential use of hypochlorite. There are hypochlorite production, ferrous and non-ferrous foundries, glass producers, motor vehicle manufacturers (a foundry), automobile assembly, plant factories, lime, brick, ceramics, cement, and tires (García et al., 2009). The altitude of the MCMA leads to a lower oxygen content of the air, approximately 23% lower than at sea level. It causes the combustion processes to operate poorly and diffuse a greater quantity of pollutants into the atmosphere, together with the surrounding mountain chain, which favors its stagnation (Molina and Molina, 2002). In 2016, Mexico City registered 2.3 million vehicles; the most abundant are those for private use, such as cars, Sport Utility Vehicle (SUVs), and motorcycles, which account for 83% of the total fleet. Total emissions of nitrogen oxides from this vehicle fleet represented a total of 60,907 Megagrams per year (Mg/y), with private cars and trucks being the main generators with an amount of 52,437 [Mg/y], which represents 86% of the total (SEDEMA, 2018a). The concentrations of SO₂ and NO₂ in the ambient air remained during 2017 below the limit concentrations required by the Official Mexican Environmental Health Standards. The Tula-Tepeji corridor remains the most important source of sulfur dioxide for Mexico City. An analysis of the trend indicated that since 2000, SO₂ concentrations maintained a downward trend, while nitrogen oxides did not show a significant trend. NO₂ contributes about 60% of the total concentration of nitrogen oxides. Also, acid rain samples were recorded in the rainy season at places south and east of Mexico City (SEDEMA, 2018b). Studies on the monitoring of the atmospheric concentration of HNO₃ in the MCMA and its spatial distribution are scarce. HNO₃ shows a behavior similar to ozone, reaching a maximum level during the day and a low level at night. Also, it tends to increase its concentration from north-northeast to south-southwest (Moya et al., 2004; Zheng et al., 2008; Wood et al., 2009; Cuevas, 2014). A map of the annual average concentration of HNO₃ micrograms per cubic meter (µg/m³) for the year 2007 shows that the highest concentration levels are located in the northwest area of the MCMA (Castillo-Miranda et al., 2017). The climatic conditions in the MCMA area are as follows: In 2015, average temperature 16.4 °C. April hottest 18.7 °C. Relative humidity (RH) average 62%, atypical rain during march and April (35 and 17 mm). Average precipitation 672 millimeters (mm). Barometric pressure average 584 millimeters of mercury (mmHg) (581-588 interval). Average wind speed 2.0 meters per second (m/s), highest values during October 2.3 m/s (SEDEMA, 2016). In 2016, average temperature 16.2 °C. May hottest 19.5 °C. RH 57% average. Average precipitation 965 mm. Barometric pressure average 585 mmHg (575 - 591 interval). Average wind speed 2.1 m/s (SEDEMA, 2017). In 2017, average temperature 16.8 °C. May hottest 19.7 °C. RH 54% average. Average precipitation 965 mm. Barometric pressure average 585 mmHg (580 - 591 interval). Average wind speed 2.1 m/s (SEDEMA, 2018c). In 2018, average temperature 16.7 °C, May hottest 19.4 °C. RH 57.1% average. Average precipitation 786.2 mm. Barometric pressure average 584.9 mmHg (583 - 589 interval). Average wind speed 2.0 m/s (SEDEMA, 2020b). In 2019, average temperature 17.4 °C. RH 53.2%, Average precipitation 565.3 mm. Average wind speed 2.1 m/s (CONAGUA, 2019). For pollutant SO₂ has a reduction between 2015 to 2019 from near 70 parts per billion (ppb) go 47 ppb. In case of the NO₂ from near 130 ppb to 110 ppb (SEDEMA, 2020c).

Effects of nitric acid on zinc corrosion

In the modern urban atmosphere, the concentration levels of SO₂ tend to decrease, increasing the relative importance of other trace gases such as NO₂. The importance of NO₂ lies in being the
precursor of HNO₃ that participates in the materials’ degradation processes (Graedel and Schwartz, 1977; Svensson and Johansson, 1993). HNO₃ is a molecule that quickly adsorbs to surfaces, specifically if there is water on the surface. Due to its high solubility in water, HNO₃ is rapidly deposited on surfaces and in water droplets (Seinfeld and Pandis, 2016; Finlayson-Pitts and Pitts Jr., 2000). It experiences dry and wet deposition rapidly, with deposition rates in the range of 1-5 cm/s (Finlayson-Pitts and Pitts Jr., 2000). The atmospheric removal processes for nitric acid gas are by wet and dry deposition. The estimated half-life for dry and wet nitric acid deposition is 1.5 to 2 days and 2 to 3 days, respectively. There is also an efficient removal of nitric acid during precipitation events (Hamilton and Crabbe, 2009). Laboratory studies (Edney and Stiles, 1986; Svensson and Johansson, 1993) have been conducted on the effect of SO₂, NOx, and oxidants on the early stages of the galvanized steel atmospheric corrosion. This corrosion is due to the dry deposition of SO₂ and HNO₃, and HNO₃ is likewise a source of wet NOₓ (Edney et al., 1986). They also found that the deposition rate was 0.02 centimeter per second (cm/s) for NO₂ and HNO₃ was 2.0 (m/s). The only relevant role of atmospheric nitrogen is likely to serve as an acidifying species in the precipitation and deposited aerosol particles, as shown in Fig. 1.

Nitric acid is the main gaseous component that dissolves in the aqueous surface layer, and nitrates come from both particles and the quantity of precipitation. Trace amounts of nitrates in the zinc corrosion layers were discovered, and it was possibly zinc nitrate (Zn(NO₃)₂) (Graedel, 1989). Friel (1986) obtained nitrate ions in low concentrations from the zinc corrosion layers. Oesch and Faller (1997) reported the formation of basic zinc nitrate Zn₅(NO₃)₂(OH)₈ • 2H₂O, which is formed when zinc is exposed to parts per million (ppm) levels of NO₂. HNO₃ has a very high dry deposition rate (V_d) that is generally independent of relative humidity and is rapidly adsorbed on most surfaces, making it relatively more harmful for dry and hot climates (Kucera, 2003; Tidblad et al., 2012). Deposited nitrate particles are associated with coarse particles. These coarse particles are commonly alkaline and can also contain sodium chloride. This composition makes them a sink for nitric acid. The reaction can be carried out in the atmosphere or deposited particles (Tidblad et al., 2012). Laboratory experiments and data from the literature show that the relatively high (V_d) of HNO₃ has mainly been attributed to the extreme adherence and reactivity of HNO₃ (Samie, 2007b). Also, the solubility of HNO₃ in water, according to Henry's law coefficients (2.1 x 10⁵ mole per liter atmosphere (mol/L atm), is higher than SO₂ and NO₂, which have 1.24 and 0.01 mol/L atm, respectively (Seinfeld and Pandis, 2016; Oesch, 1996). It allows a high solubility of HNO₃ in the electrolytic layer and increases the corrosion rate (Samie et al., 2007b). HNO₃ is soluble in water,
and the concentration in urban environments is relatively low (1-4) µg/m³ compared to SO$_2$ (1-20) µg/m³. Nitrate salts (NO$_3^-$) are formed when metals react with HNO$_3$; however, nitrate salts are soluble in water, and this may be one reason for the rare occurrence of nitrates in layers of corrosion products (Samie et al., 2007a). Pure zinc plates were exposed in the field for a year, within the Model for Multi-pollutant Impact and Assessment of Threshold Levels for Cultural Heritage (MULTI-ASSESS) and Regional Air Pollution in Developing Countries (RAPIDC) programs in Europe, Asia, and Africa. The Fourier transform spectroscopy (FTIR) technique demonstrated the presence of nitrates as corrosion products. Likewise, nitrates with high solubility are found in greater quantity on the plate’s backside since they are less affected by precipitates. Furthermore, essential nitrates (Zn$_3$(NO$_3$)$_2$(OH)$_8$ • 2H$_2$O) are generally more soluble in acidic solutions than in water. Therefore, the pH decreases in the absorption layer when acidic contaminants dissolve. Consequently, the essential nitrates are dissolved and removed from the surface by the presence of rain. Accordingly, the zinc front side corrodes more because it has a less protective layer of basic nitrate (Samie et al., 2007a).

Damage functions

The development of various exposure studies has shown that atmospheric corrosion is a phenomenon that varies considerably in each locality (Guttman and Sereda, 1968). The development and use of a damage function applying the fundamental principles of thermodynamics and kinetics of atmospheric corrosion allow predicting galvanized steel structures corrosion rates due to dry and wet deposition (Spence and Haynie, 1990). The dose-response functions should reflect the physicochemical nature of atmospheric corrosion and each parameter’s contribution to the global effect (Leuenberger-Minger et al., 2002). Since atmospheric corrosion affects all structures exposed to potentially corrosive environments, many countries have established programs dedicated to understanding and monitoring (Roberge et al., 2002). In some cases, atmospheric exposure programs are conducted to assess the corrosivity of specific atmospheres. This type of information can help choose coatings or corrosion protection systems at particular sites (Dean Jr., 2005).

A set of exhibition programs such as International testing program [] (ISOCORRAG), Ibero-American Map of Atmospheric Corrosiveness (MICAT), International Co-operative Programme on Effects on Materials, including Historical and Cultural Monuments (ICP materials), Model for Multi-pollutant Impact, and MULTI-ASSESS and RAPIDC have been developed in the last decades in different parts of the world. The International Testing Program (ISOCORRAG) began in 1987-1989 with International Organization for Standardization/Technical Committees 156 (ISO/TC 156) test methods and procedures to provide environmental and corrosion data. It includes 53 test sites in 14 countries located in Europe, Argentina, Canada, Japan, New Zealand, and the United States (Knotková, 1993). However, the ISOCORRAG and MICAT programs lack data on gases other than SO$_2$ and wet deposition (Tidblad et al., 2009). However, atmospheric corrosivity can be estimated with consistent environmental information to establish damage functions, based on a statistical analysis of the databases’ information (Morcillo et al., 2002). The ICP Materials program had its first stage (1987–1995), where dose-response functions were developed with long-term data on corrosion and contamination to investigate the effect of acid deposition on materials. It includes non-marine sites, lacks data on the dry deposition of chlorides and HNO$_3$ and particles. In this period, SO$_2$ concentrations were still relatively high but decreasing. It led to the need for a new multi-pollutant exposure program (1997–2001). This program aimed to determine both the effect of SO$_2$ and other important air pollutants such as HNO$_3$ and particles. In the 2002-2003 period, the MULTI-ASSESS project included HNO$_3$ and particles as mandatory parameters (Tidblad et al., 2012). Also, RAPIDC project included measurements of HNO$_3$ and particulate matter. Also, the program was set up with 18 sites in the South and Southeast of Asia and South Africa, which have tropical and subtropical climates. Both the MULTI-ASSESS Program and RAPIDC are the most suitable for investigating the effects of multiple pollutants in non-marine environments (Tidblad et al., 2009). After one year (2002-2003), zinc RAPIDC exposure’s corrosion is lower than expected compared to values calculated (Tidblad et al., 2007) using the best available dose-response functions. However, due to the relatively high measured SO$_2$ levels, it was correct to use functions for the dominant SO$_2$ situation developed within the ICP Materials program (Tidblad...
et al., 2001). The International Organization for Standardization (ISO) ISO 9223 standard is intended to evaluate the corrosivity category for metals. This category explicitly describes the corrosiveness of outer atmospheres through the development of dose-response functions. Considering the above, the dose-response function for zinc is supported on data after one year of exposure. It can, therefore, only be used for classification objects (Zn, N=116, R²=0.78), using Eq. 1 (Tidblad et al., 2002b).

\[
C_{Zn} = 0.0053 \text{SO}_2^{0.43} \text{TOW}^{0.53} \exp \{\text{f}_{\text{Zn}}\} + 0.00071 \text{Cl}^{-0.68} \text{TOW}^{0.30} \exp\{0.11T\} \tag{1}
\]

Where;

\( C_{Zn} \) = Corrosion attack after 1 year of exposure in µm of zinc; \( T \)=Temperature in °C; \( \text{TOW} \)=Time of wetness in hour per year (h/y); \( \text{SO}_2 \)= \( \text{SO}_2 \) deposition in milligram per square meter day (mg/m²/day); \( \text{Cl}^- \)= \( \text{Cl}^- \) deposition in mg/m²/day.

**Corrosivity mapping**

Mapping the regional distribution of corrosivity is a method that provides general information on corrosion, rational use, and selection of material protection measures. The mapping must be based on the knowledge of the deterioration and kinetic processes based on external factors, and it generalizes the information supported on local environmental conditions. Likewise, it requires available information on the levels of atmospheric environmental components and converts it into values on the effects of corrosion. The above is achieved using damage equations (dose-response functions) obtained from empirical procedures applied to data processing using GIS technologies (Knotková and Kreislova, 2007). The classification of the different atmospheric basins based on corrosivity serves to select optimal metallic materials and coatings for adequate protection against corrosion in a country (Genescá and Rodriguez, 1992). The atmospheric corrosion maps for metals in Mexico were designed according to the ISO 9223 classification system. They required annual mean corrosion values in test stations, meteorological data, and atmospheric pollution such as \( \text{SO}_2 \) and chloride ions (Cl) (Mariaca et al., 1999). Corrosivity maps were constructed for zinc, copper, and aluminum in the MCMA, by characterizing the atmospheric aggressiveness on these materials based on the ISO 9223 standard. Furthermore, atmospheric aggressiveness does not necessarily correspond to the most polluted areas since it depends on the relative humidity and wetting time (Muñoz and Uruchurtu, 2002).

**MATERIALS AND METHODS**

**Selection of the dose-response function**

The dose-response functions are empirical expressions and then simplifications that indicate the relationship between the rate of corrosion or deterioration and the levels of pollutants combined with climatic parameters (Kucera, 2004). At first, the dose-response functions were more focused on \( \text{SO}_2 \), as the main stimulator of corrosion. These functions were denoted as dose-response functions for the dominant \( \text{SO}_2 \) situation. However, as there have been changes in the atmosphere’s chemical composition, there are higher levels of concentration of nitrogen, ozone, and particles than of \( \text{SO}_2 \). The above made it possible to propose “multi-pollutant” type functions. Multi-pollutant functions are preferable at high levels of particulate and nitrogen pollutants in the air. The above occurs in urban atmospheres dominated by traffic (Kucera, 2005). Other important factors in applying the multi-pollutant dose-response function are chloride concentration \([\text{Cl}^-]\) and Temperature (T).

This function is applicable in geographic areas without the influence of chlorides, have been developed and suggested to be implemented in countries with tropical and subtropical climates, characteristic of the MCMA. Likewise, in these climates, the corrosion rate of zinc in field tests consisting of a rack for placing zinc samples and holding passive samplers for gases is lower compared to the corrosion rates obtained with the best available dose-response functions (Tidblad et al., 2007). Table 1 shows the annual average concentration levels of \( \text{SO}_2 \), \( \text{NO}_2 \), and \( \text{Cl}^- \) and the yearly average temperature obtained from the monitoring stations located in the MCMA in the period 2015-2019 (SEDEMA, 2020a). The concentration levels of \( \text{SO}_2 \) in general, are low and are more noticeable for the year 2019. The concentration levels of \( \text{NO}_2 \) are higher than \( \text{SO}_2 \). The \( \text{Cl}^- \) concentration is less than 5 milligrams per liter (mg/L), and the temperature is greater than 10 °C, which suggests the use of a multi-pollutant dose-response function that includes the effect of \( \text{HNO}_3 \).
Dose-response functions are importantly applied to map areas of increased risk corrosion and to calculate corrosion costs. Furthermore, it is possible to estimate the loss of mass of zinc for a multi-pollutant situation (Kucera et al., 2007). The statistical processing of data from materials exposed in the field generated a dose-response function for the loss of zinc mass after one year of exposure, using Eq. 2 (Kucera, 2005).

\[
ML = 3.53 + 0.471[SO_2]^{0.22}e^{0.018RH+f(T)} + 0.041Rain[H^+] + 1.37[HNO_3] \quad (2)
\]

\[
f(T) = 0.062(T-10) \text{ when } T \leq 10^\circ C,
\]

\[
f(T) = -0.021(T-10) \text{ otherwise}
\]

Where ML is the corrosion rate in g/m², [SO\(_2\)] and [HNO\(_3\)] is the concentration in micrograms per cubic meter (µg/m\(^3\)), RH is the relative humidity in %, Rain is the amount of precipitation in millimeters (mm), [H\(^+\)] is the H\(^+\) concentration of rainfall in mg/L, and T is the temperature in °C. Eq. 2 shows an evident effect of HNO\(_3\) on zinc corrosion and represents the sum of two contributions, one from HNO\(_3\) and the other from corrosion-enhancing factors including SO\(_2\) (Samie et al, 2007a). They also found a relatively good correlation between the extrapolated zinc mass loss, based on laboratory exposures, and the dose-response function based on a statistical analysis of field data. The multi-pollutant function includes nitric acid that any MCMA monitoring station does not measure. Eq. 3 developed within the MULTI-ASSESS project can be used to calculate the annual concentration of HNO\(_3\) when there are no values (Kucera, 2005):

\[
[HNO_3] = 516 \cdot e^{3400/(T+273)} ([NO_2] \cdot [O_3] \cdot RH)^{0.5} \quad (3)
\]

Where [HNO\(_3\)], [NO\(_2\)], and [O\(_3\)] is the concentration in µg/m\(^3\); RH is the relative humidity in %, and T is the temperature in degree Celsius (°C). The oxidation process from NO\(_2\) to HNO\(_3\) described in equations (4-21) contemplates the chemical species of Eq. 3.

The NO\(_2\) molecule absorbs sunlight at wavelengths <430 nm and can break one of the NO bonds and generate the reactive ground-state oxygen atom, O (\(^1\)P), and a NO molecule, using Eq. 4 (Seinfeld, 1980).

\[
NO_2 + hv \rightarrow NO + O(\(^1\)P) \quad (4)
\]

The exceptionally reactive triplet-p oxygen atom formed regularly collides with oxygen molecules to form ozone, using Eq. 5.

\[
O(\(^1\)P) + O + M \rightarrow O_2 + M \quad (5)
\]

Under typical polluted atmosphere conditions, the ozone molecule will often react with NO to regenerate NO\(_2\), using Eq. 6.

\[
O_3 + NO \rightarrow NO_2 + O_2 \quad (6)
\]

Ozone can also photolyze, using Eqs. 7 and 8.

\[
O_3 + h\nu \rightarrow O_2 (1\Delta, 3\Sigma) + O(\(^1\)D, 3P) \quad (7)
\]

\[
O_3 + h\nu \rightarrow O_2 (1\Delta, 3\Sigma) + O(\(^3\)P) \quad (8)
\]

The singlet-D oxygen atom is considerably more reactive than the ground-state triplet-P oxygen atom, using Eq. 9. Apart from deactivation.

\[
O(\(^1\)D) + M \rightarrow O(\(^3\)P) + M \quad (9)
\]

It reacts with water to form the hydroxyl radical, using Eq. 10.

\[
O(\(^1\)D) + H_2O \rightarrow 2OH \quad (10)
\]

Ozone can react with nitrogen dioxide to produce...
symmetrical nitrogen trioxide, using Eq. 11.

\[ \text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2 \]  

(11)

The \text{NO}_3 \text{ species forms dinitrogen pentoxide, by reaction with nitrogen dioxide, using Eq. 12.}

\[ \text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5 \]  

(12)

Dinitrogen pentoxide can rearrange to form \text{NO}_3 and \text{NO}_2 or maybe react with water to form nitric acid, using Eqs. 13 and 14.

\[ \text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2 \]  

(13)

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HONO}_2 \]  

(14)

The subsequent reaction can take place between oxygen atoms and \text{NO}_2 using Eq. 15.

\[ \text{NO}_2 + \text{O}^{(3P)} \rightarrow \text{NO} + \text{O}_2 \]  

(15)

In addition, \text{NO} and \text{NO}_3 can react to regenerate \text{NO}_2 using Eq. 16.

\[ \text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2 \]  

(16)

Nitrous acid is generated by using Eq. 17.

\[ \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HONO} \]  

(17)

And can react bimolecular to regenerate the original reactants, using Eq. 18.

\[ \text{HONO} + \text{HONO} \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \]  

(18)

Photolysis of nitrous acid in the wavelength range 280-400 nm guide to producing hydroxyl radical and \text{NO}, using Eq. 19.

\[ \text{HONO} + \text{hv} \rightarrow \text{OH}^- + \text{NO} \]  

(19)

The hydroxyl radical may react with \text{NO} and \text{NO}_2 to yield nitrous and nitric acid using Eqs. 20 and 21, respectively.

\[ \text{OH}^- + \text{NO} \rightarrow \text{HONO} \]  

(20)

\[ \text{OH}^- + \text{NO}_2 \rightarrow \text{HONO}_2 \]  

(21)

**Applied method**

Mapping of the corrosion rates was carried out through the following procedure: Integration of the available data from measurements of concentrations of sulfur dioxide (SO\textsubscript{2}), estimated nitric acid (HNO\textsubscript{3}), relative humidity (RH), rainfall, or amount of precipitation (PP), temperature (T) and the acidity of the rain [H\textsuperscript+]. The data and results were applied in suitable mathematical functions to construct, by interpolation, maps of their spatial distribution. Subsequently, with these values, the multi-pollutant function corresponding to zinc is applied to obtain the corrosion layers. A description of these steps is presented in the following paragraphs.

**Damage function parameter database**

The database was integrated with the multi-pollutant function parameters to calculate the corrosion rate in the period 2015-2019. These parameters are obtained from the different monitoring stations as described below. For this study, SO\textsubscript{2} data generated by the Red Automática de Monitoreo Atmosférico (Automatic Atmospheric Monitoring Network, RAMA) for the period (2015-2019) are used. The estimation of HNO\textsubscript{3} required annual average values per hour of the parameters: Nitrogen dioxide (NO\textsubscript{2}) and ozone (O\textsubscript{3}) from the (RAMA); in addition to temperature (T) and relative humidity (RH) from the databases of the Red de Meteorología y Radiación Solar (Atmospheric Monitoring Network and the Meteorology and Solar Radiation Network, REDMET). The values of the acidity of the precipitation [H\textsuperscript+] and the amount of rainfall or rain (PP) included in the multi-pollutant function were obtained from data reported by the Red de Depósito Atmosférico (Atmospheric Deposit Network, REDDA) for the period (2015-2019). The values of temperature (T) and relative humidity (RH) included in the dose-response function were obtained from the database of the Red de Meteorología y Radiación Solar (Meteorology and Radiation Network, REDMET) for the period (2015-2019) (SEDEMA, 2020a).

**Creating layers using geographic information systems**

**Selecting the interpolation method**

Geographic information systems (GIS) are an indispensable technology for capturing, storing, analyzing, modeling and displaying spatially
referenced data (Moreno, 2006a). Conesa (1996) indicated that GIS could process large databases with information about the land surface globally and globally. One of a GIS’s purposes is to provide a spatial framework to support decisions about the efficient use of the earth’s resources and manage the anthropogenic environment (Zeiler, 1999). The kriging method combined with deterministic modeling improves the spatial analysis of acid deposition (Venkatram, 1988). Modeling temperature and relative humidity were interpolated using the kriging method, and the standard deviation (SD) was used to measure the spatial uncertainty (Phillips and Marks, 1996). The inverse distance weighting (IDW) and kriging spatial interpolation techniques are regularly used to estimate pollutant concentration levels in areas with limited sample points. The value of each parameter is determined by cross-validation until the least mean square error (RMSE) is obtained (Rojas-Avellaneda, 2007; Diem and Comrie, 2002). Pollutant concentration maps using the kriging method are used in the European Monitoring and Evaluation Materials Program (EMEP) (Denby et al., 2005). Modeling the temporal behavior of \( \text{SO}_2 \) using the ordinary kriging method provides an estimate of the air quality in Europe. It is suggested to use a semivariogram with a spherical model to obtain the \( \text{SO}_2 \) layer (Denby et al., 2010). In this study, spatial representation was developed using Aeronautical Reconnaissance Coverage Geographic Information System (ArcGIS) software (ArcGIS, 2014). ArcGIS uses the extension called “geostatistical analysis”. It employs advanced tools to perform exploratory analysis of spatial data and a wizard with which statistical surfaces are constructed. The layers’ construction was decided to build vector layers with both IDW and ordinary kriging for each of the parameters. The selection of the interpolation method for each parameter was based on obtaining the lowest value of the Root Mean Square (RMS) of the cross-validation. The coefficient of determination \( R^2 \) of the relationship observed value vs. predicted value resulting from the cross-validation is obtained. The ordinary kriging interpolation method was used to obtain the layers of the following parameters, with their corresponding annual coefficient of determination \( R^2 \): [\( \text{SO}_2 \)]: 2015 = 0.60; 2016 = 0.52; 2017 = 0.76; 2018 = 0.71 and 2019 = 0.67. [\( \text{HNO}_3 \)]: 2015 = 0.55; 2016 = 0.76; 2017 = 0.73; 2018 = 0.60 and 2019 = 0.60. HR: 2015 = 0.02; 2016 = 0.17 and 2018 = 0.15. T: 2015 = 0.44; 2016 = 0.60; 2017 = 0.41; PP: 2016 = 0.67; 2017 = 0.87; 2018 = 0.70 and 2019 = 0.72. \([\text{H}^+]\): 2017 = 0.01; 2018 = 0.20 and 2019 = 0.21. The IDW interpolation method was employed to obtain the following parameters’ layers, with their corresponding annual coefficient of determination \( R^2 \): HR: 2017 = 0.03 and 2019 = 0.01. T: 2018 = 0.40 and 2019 = 0.32. PP: 2015 = 0.26. \([\text{H}^+]\): 2015 = 0.09 and 2016 = 0.52.

RESULTS AND DISCUSSION

Layer maps of the parameters of the dose-response function and the corrosion rate

The representation of the maps of the dose-response function parameters focuses mainly on \( \text{SO}_2 \) as one of the main factors in the corrosion process and \( \text{HNO}_3 \) regarding corrosion in the urban atmosphere. The sulfur dioxide [\( \text{SO}_2 \) ] layers for the period 2015-2019 are shown in Fig. 2. The figure indicates spatially that the highest [\( \text{SO}_2 \) ] levels are located to the “northwest” and the lowest to the “east, northeast” and “southeast” and a lesser extent south of the MCMA. From a temporal perspective, the highest levels of [\( \text{SO}_2 \) ] are present in 2017 and 2018, while the lowest levels occur in the year 2019, followed by 2015 and 2016. The [\( \text{HNO}_3 \) ] layers for the period 2015-2019 are represented in Fig. 3. The figure shows spatially that the highest [\( \text{HNO}_3 \) ] levels are located in the “central” and “southwest” areas and the lowest in the “east” and “northeast” areas of the MCMA. From a temporal viewpoint, the highest [\( \text{HNO}_3 \) ] levels are in 2015 and 2016, while the lowest levels are in 2016, followed by 2018. The importance of the annual change in the levels of \( \text{HNO}_3 \) concentration observed in the maps allows visualizing the urban atmosphere’s complexity in relation to its acidity.

The corrosion layers for zinc used in the evaluation were constructed using the “raster calculator” tool included in the ArcGIS 10.2.2 spatial analysis extension. It performs analysis operations with mathematical functions. The process consists of applying the multi-pollutant function, introducing the raster layers of the corresponding parameters. These layers represent the terrestrial space’s property through a set of square cells of the same size, called pixels. The raster model is appropriate to represent continuous variables in space, such as meteorological variables and air pollution (Moreno, 2006b). The corrosion rate maps construction results are shown in Figs. 4 and 5.
The layers of the corrosion rates employing the multi-pollutant function of equation 2 for 2015-2019 are shown in Fig. 4. The images show a corrosion rate of 5.81-8.19 of mass loss (g/m²). Spatially, the highest corrosion rates are located in the “southwest” of the MCMA. On the other hand, the lowest corrosion rates are seen in the “northeast-southeast” of the MCMA. The highest corrosion rates present in 2015 and 2016, while the lowest corrosion rate occurs in the year 2019. Likewise, the corrosion rates’ layers using the
multi-pollutant function of equation 2, without the component that includes HNO$_3$ for 2015-2019, are shown in Fig. 5. The images establish a corrosion rate interval of [4.86-6.64] of mass loss (g/m$^2$). Spatially, the corrosion rates represent the same trend as in Fig. 4. The highest rates are located in the “southwest” of the MCMA, although the area covered is smaller. Meanwhile, the lowest corrosion rates are seen in the “northeast-southeast” of the MCMA, covering larger areas. In the same way, temporarily, the highest

![Maps of concentration layers of the annual average of HNO$_3$ (µg/m$^3$) for the period 2015-2019 in the MCMA](image-url)
corrosion rates present in 2015 and 2016, while the lowest corrosion rate occurred in 2019. The highest corrosion rates are presented in the years 2015 and 2016. It is probably due to the high levels of [HNO₃] observed in Fig. 3. In contrast, the lowest corrosion rate occurred in 2019. The above is probably due to both sulfur dioxide and nitrogen dioxide, which present the lowest concentration levels in the 2015-2019 period. However, the fact that the corrosion rate for 2019 is the lowest in magnitude compared...
to other years, in percentage terms, has a significant influence on the corrosion rate for this year. The low per determination coefficient values $R^2$ were obtained mainly in constructing the climatic parameters' layers, possibly due to the nature and variability of the data obtained from the monitoring networks. The HNO$_3$ percentage contribution layers to the annual zinc corrosion rate are shown in Fig. 6. The impact is determined by combining the layers of corrosion rates of Figs. 4 and 5 in a percentage relationship.
for 2015-2019. The images indicate a % contribution interval of 12.23-32.15. Spatially, the areas with the greatest contribution are located in the “center”, and the areas with the least contribution are to the “east” of the MCMA. Temporarily the areas with the highest contribution are presented in the years 2015, 2016, and 2019. This is mainly due to the decrease in [SO$_2$] levels and the oxidation process of NO$_2$ to HNO$_3$ that occurs in the complex urban atmosphere of the MCMA, while the areas with the lowest contribution

![Maps of the contribution (%) of HNO$_3$ to the annual zinc corrosion rate (g/m$^2$) of zinc, for a multi-pollutant situation for the 2015-2019 period in the MCMA](image)

Fig. 6: Maps of the contribution (%) of HNO$_3$ to the annual zinc corrosion rate (g/m$^2$) of zinc, for a multi-pollutant situation for the 2015-2019 period in the MCMA
Table 2 Environmental data including temperature (T), relative humidity (RH), precipitation (Rain and pH) and gaseous pollutants (HNO₃ and SO₂). (Tidblad et al., 2007)

<table>
<thead>
<tr>
<th>Country</th>
<th>Test site name</th>
<th>SO₂ (μg/m³)</th>
<th>Temperature (°C)</th>
<th>Relative humidity (%)</th>
<th>Rain (mm)</th>
<th>pH</th>
<th>HNO₃ (μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>India</td>
<td>Bhubaneswar-u</td>
<td>4</td>
<td>26.5</td>
<td>69</td>
<td>425</td>
<td>6.0</td>
<td>1.3</td>
</tr>
<tr>
<td>India</td>
<td>Bhubaneswar-r</td>
<td>3</td>
<td>26.5</td>
<td>69</td>
<td>425</td>
<td>6.0</td>
<td>1</td>
</tr>
<tr>
<td>Thailand</td>
<td>Bangkok</td>
<td>11</td>
<td>29.3</td>
<td>76</td>
<td>1,371</td>
<td>6.8</td>
<td>2.3</td>
</tr>
<tr>
<td>Thailand</td>
<td>Phra Pradaeng</td>
<td>59</td>
<td>29.3</td>
<td>73</td>
<td>1,335</td>
<td>6.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Vietnam</td>
<td>Hanoi</td>
<td>15</td>
<td>24.7</td>
<td>79</td>
<td>1,556</td>
<td>5.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Vietnam</td>
<td>Ho Chi Minh</td>
<td>21</td>
<td>28.3</td>
<td>74</td>
<td>1,441</td>
<td>6.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Vietnam</td>
<td>Myito</td>
<td>2</td>
<td>27</td>
<td>81</td>
<td>1,222</td>
<td>6.4</td>
<td>0.3</td>
</tr>
<tr>
<td>China</td>
<td>Chongqing</td>
<td>99</td>
<td>18.5</td>
<td>70</td>
<td>1,162</td>
<td>4.5</td>
<td>1.3</td>
</tr>
<tr>
<td>China</td>
<td>Tie Shan Ping</td>
<td>51</td>
<td>18.5</td>
<td>90</td>
<td>1,133</td>
<td>4.2</td>
<td>1.8</td>
</tr>
<tr>
<td>China</td>
<td>Hong Kong</td>
<td>16</td>
<td>22.9</td>
<td>78</td>
<td>2,092</td>
<td>4.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Malaysia</td>
<td>Kuala Lumpur</td>
<td>12</td>
<td>28</td>
<td>78</td>
<td>2,776</td>
<td>4.3</td>
<td>3.8</td>
</tr>
<tr>
<td>Malaysia</td>
<td>Tanah Rata</td>
<td>0</td>
<td>18.1</td>
<td>91</td>
<td>2,433</td>
<td>5.1</td>
<td>0.1</td>
</tr>
<tr>
<td>South Africa</td>
<td>Johannesburg</td>
<td>18</td>
<td>17.2</td>
<td>78</td>
<td>417</td>
<td>4.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Zambia</td>
<td>Kitwe</td>
<td>92</td>
<td>22.6</td>
<td>58</td>
<td>1,083</td>
<td>4.7</td>
<td>0.9</td>
</tr>
<tr>
<td>Zambia</td>
<td>Magoye</td>
<td>0</td>
<td>22.2</td>
<td>62</td>
<td>826</td>
<td>7.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Zimbabwe</td>
<td>Harare</td>
<td>16</td>
<td>18.9</td>
<td>63</td>
<td>798</td>
<td>6.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 3. Estimation of the % contribution of HNO₃ to the zinc corrosion rate (g/m²) for different test sites

<table>
<thead>
<tr>
<th>Country</th>
<th>Test site name</th>
<th>ML (g/m²) of zinc, for a multi-pollutant situation</th>
<th>ML (g/m²) of zinc, for a multi-pollutant situation without the HNO₃ component</th>
<th>Contribution % HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malaysia</td>
<td>Tanah Rata</td>
<td>4.46</td>
<td>4.32</td>
<td>3.17</td>
</tr>
<tr>
<td>Vietnam</td>
<td>Myito</td>
<td>5.61</td>
<td>5.20</td>
<td>7.90</td>
</tr>
<tr>
<td>Zimbabwe</td>
<td>Harare</td>
<td>6.73</td>
<td>5.77</td>
<td>16.61</td>
</tr>
<tr>
<td>Zambia</td>
<td>Kitwe</td>
<td>8.43</td>
<td>7.19</td>
<td>17.14</td>
</tr>
<tr>
<td>Vietnam</td>
<td>Hanoi</td>
<td>7.33</td>
<td>6.23</td>
<td>17.58</td>
</tr>
<tr>
<td>Zambia</td>
<td>Magoye</td>
<td>4.22</td>
<td>3.53</td>
<td>19.39</td>
</tr>
<tr>
<td>China</td>
<td>Chongqing</td>
<td>10.63</td>
<td>8.85</td>
<td>20.12</td>
</tr>
<tr>
<td>Vietnam</td>
<td>Ho Chi Minh</td>
<td>7.17</td>
<td>5.94</td>
<td>20.75</td>
</tr>
<tr>
<td>China</td>
<td>Tie Shan Ping</td>
<td>13.66</td>
<td>11.19</td>
<td>22.04</td>
</tr>
<tr>
<td>India</td>
<td>Bhubaneswar-r</td>
<td>6.39</td>
<td>5.02</td>
<td>27.31</td>
</tr>
<tr>
<td>China</td>
<td>Hong Kong</td>
<td>10.84</td>
<td>8.38</td>
<td>29.44</td>
</tr>
<tr>
<td>Thailand</td>
<td>Phra Pradaeng</td>
<td>8.49</td>
<td>6.43</td>
<td>31.96</td>
</tr>
<tr>
<td>India</td>
<td>Bhubaneswar-u</td>
<td>6.89</td>
<td>5.11</td>
<td>34.84</td>
</tr>
<tr>
<td>South Africa</td>
<td>Johannesburg</td>
<td>9.79</td>
<td>6.91</td>
<td>41.61</td>
</tr>
<tr>
<td>Malaysia</td>
<td>Kuala Lumpur</td>
<td>16.71</td>
<td>11.50</td>
<td>45.25</td>
</tr>
<tr>
<td>Thailand</td>
<td>Bangkok</td>
<td>8.78</td>
<td>5.63</td>
<td>55.98</td>
</tr>
</tbody>
</table>

% are located in the year 2016. The difference is due to the annual concentration levels of HNO₃ compared to SO₂ and the other climatic parameters of the dose-response function.

On the other hand, in the latitudinal position of the MCMA, solar radiation is intense and accelerates photochemical reactions of pollutants in the atmosphere such as ozone and aerosols. Since ozone is involved in the formation of nitric acid, empirical equation 3 derived for other conditions must be reevaluated. There are limitations modeling atmospheric corrosion by empirical equations obtained in other situations. For example, in many cases, the weather when the exposure starts is relevant. It is different to start an atmospheric exposure in summer than in winter. Also, using annual mean temperature values for the MCMA has temperatures below 10 °C for many periods throughout the year. This effect is probably related to the time of wetness (TOW), an important variable that is not explicitly
considered in the MULTI- ASSESS equation. Table 2 shows gaseous pollutant and environmental data from a network of test sites that includes 12 sites in Asia (India, Vietnam, Thailand, Malaysia, and China, including Hong Kong) and four test sites in Africa (South Africa, Zambia, and Zimbabwe). Implemented by the RAPIDC program and funded by the Swedish International Development Agency (SIDA), in order to obtain corrosion values for materials including zinc after one year of exposure (2002-2003) (Tidblad et al., 2007).

Table 3 shows the estimate of the % contribution of HNO₃ to the zinc corrosion rate (g/m²). This is possible, using the values from Table 2 in equation 2 and combining in a percentage relationship the corrosion rate (g/m²) of zinc in a multi-pollutant situation with the multi-pollutant situation without the HNO₃ component. Table 3 shows a contribution interval % HNO₃ of 3.17 - 55.98 with a great difference in the climatic and pollution values of the test sites. Johannesburg 41.61%, Kuala Lumpur 45.25% and Bangkok 55.98% show the highest HNO₃ contribution % values corresponding to the highest measured HNO₃ values. While Tanah Rata 3.17% and Mytho 7.90% have the lowest % contribution values of HNO₃ in relation to the lowest values of HNO₃ measured.

Comparing the interval of % contribution of HNO₃ of 12.23-32.15 observed in fig. 6 with the interval of values of 3.17-55.98 of Table 3, it is highlighted that it is possible to place it at an intermediate level with respect to the values of Table 3. However, the values in Table 3 are from more than a decade ago; there was already evidence of a significant contribution % of HNO₃ to the zinc corrosion process. However, at that time there was an important attention to SO₂.

CONCLUSION

Most studies on atmospheric zinc corrosion and galvanized steel carried out in Mexico and the Mexico City Metropolitan Area have focused on contaminants such as sulfur dioxide, relative humidity, amount of precipitation, temperature, and the acidity of the rain. The construction of corrosion rate maps using dose-response functions for a multi-pollutant situation in equation (2) provides a spatial and temporal estimate of the variation in corrosion rates in 2015-2019. This estimate allows visualizing areas where zinc materials are at risk corrosion due to the dispersion of atmospheric pollutants and climatic parameters. The construction of percentage maps shows the contribution (%) of HNO₃. HNO₃ contributes at least 12% and up to 32% to the zinc corrosion rate. These layers show that the years 2015, 2016, and 2019 present the highest contribution percentages. The equation (2) is applicable in geographic areas without the influence of chlorides and countries with tropical and subtropical climates, characteristic of the MCMA. Therefore, it is likely that the corrosion rate values obtained with the multi-pollutant dose-response function in this work are overestimated. It is desirable to have specific multi-pollutant dose-response functions for the MCMA that adequately represent the dispersion of pollutants and climatic parameters of the study area’s urban atmosphere. It would be possible to implement an Exposure Program on the effects of atmospheric zinc corrosion, with specific attention to HNO₃. There is a relatively good correlation between the extrapolated loss of zinc mass resulting from laboratory exposures and the dose-response function based on statistical analysis. Therefore, the corrosion rates estimated for zinc in this work are very likely to represent an approximate value of the corrosion rates for zinc that can be found in field tests. This due to the absence of field tests.

AUTHOR CONTRIBUTIONS

J.O. Castillo-Miranda conceived the original idea, performed the literature review, analyzed and interpreted the data, prepared the manuscript text, and manuscript edition. F.J. Rodríguez-Gómez worked out the technical details, analyzed and interpreted the data, prepared the manuscript text, and manuscript edition. J. Genescá-Llongueras encouraged to investigate a specific aspect, helped in the literature review and manuscript preparation. L.G. Ruiz-Suárez developed the theoretical formalism and supervised the findings of this work. J.A. García-Reynoso helped shape the study, analysis and contributed to the interpretation of the results.
ACKNOWLEDGMENTS

J.O. Castillo-Miranda is grateful to “PROGRAMA DE BECAS POSDOCTORALES UNAM-DGAPA” for the postdoctoral scholarship and the authors (J.O. Castillo-Miranda and F.J. Rodríguez-Gómez) would like to thank the UNAM Facultad de Química, Departamento de Ingeniería Metalurgica. The authors want to acknowledge the contribution of Carlos Arroyave, Professor Emeritus University of Antioquia and Dr. Farid Samie, Shell Global Solutions, Houston Texas, USA (TA2 Materials and Corrosion Engineering).

CONFLICT OF INTEREST

The authors declare no potential conflict of interest regarding the publication of this work. In addition, the ethical issues including plagiarism, informed consent, misconduct, data fabrication and, or falsification, double publication and, or submission, and redundancy have been completely witnessed by the authors.

ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>Percentage</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>µg/L</td>
<td>Micrograms per liter</td>
</tr>
<tr>
<td>µg/m³</td>
<td>Micrograms per cubic meter</td>
</tr>
<tr>
<td>ArcGIS</td>
<td>Aeronautical reconnaissance coverage Geographic Information System</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Calcium ion</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Chlorides</td>
</tr>
<tr>
<td>CLRTAP</td>
<td>Long-range Transboundary Air Pollution</td>
</tr>
<tr>
<td>cm/s</td>
<td>Centimeters per second</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>DGAPA-UNAM</td>
<td>Dirección General de Asuntos del Personal Académico de la Universidad Nacional Autónoma de México</td>
</tr>
<tr>
<td>EMEP</td>
<td>European Monitoring and Evaluation Materials Program</td>
</tr>
<tr>
<td>Eq.</td>
<td>Equation</td>
</tr>
<tr>
<td>Fig.</td>
<td>Figure</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform spectroscopy</td>
</tr>
<tr>
<td>g/m²</td>
<td>Grams per square meter</td>
</tr>
<tr>
<td>GIS</td>
<td>Geographic information systems</td>
</tr>
<tr>
<td>h/y</td>
<td>Hour per year</td>
</tr>
<tr>
<td>H⁺</td>
<td>Hydrogen ion</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>H₂S</td>
<td>Hydrogen sulfide</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrogen chloride</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Nitric acid</td>
</tr>
<tr>
<td>ICP materials</td>
<td>Co-operative programme on effects on materials, including historic and cultural monuments</td>
</tr>
<tr>
<td>IDW</td>
<td>Inverse distance weighting</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>ISOCORRAG</td>
<td>The International Testing Program</td>
</tr>
<tr>
<td>ISO/TC 156</td>
<td>International Organization for Standardization/Technical Committees 156</td>
</tr>
<tr>
<td>K⁺</td>
<td>Potassium ion</td>
</tr>
<tr>
<td>km</td>
<td>Kilometres</td>
</tr>
<tr>
<td>m/s</td>
<td>Meters per second</td>
</tr>
<tr>
<td>MCMA</td>
<td>Mexico City Metropolitan Area</td>
</tr>
<tr>
<td>mg/L</td>
<td>Milligrams per liter</td>
</tr>
<tr>
<td>mg/m²/day</td>
<td>Milligrams per square meter day</td>
</tr>
<tr>
<td>Mg/y</td>
<td>Megagrams per year</td>
</tr>
<tr>
<td>MICAT</td>
<td>Ibero-American Map of Atmospheric Corrosiveness</td>
</tr>
<tr>
<td>ML</td>
<td>Corrosion rate</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeters</td>
</tr>
<tr>
<td>mmHg</td>
<td>Millimeters of mercury</td>
</tr>
<tr>
<td>mol/L atm</td>
<td>Mole per liter atmosphere</td>
</tr>
<tr>
<td>MULTI-ASSESS</td>
<td>Model for multi-pollutant impact and assessment of threshold levels for cultural heritage</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Sodium ion</td>
</tr>
<tr>
<td>NO₂</td>
<td>Nitrogen dioxide</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>Nitrate ion</td>
</tr>
<tr>
<td>NOx</td>
<td>Nitrogen oxides</td>
</tr>
<tr>
<td>O₃</td>
<td>Ozone</td>
</tr>
<tr>
<td>pH</td>
<td>Hydrogen potential</td>
</tr>
<tr>
<td>PP</td>
<td>Precipitation or rain</td>
</tr>
<tr>
<td>ppb</td>
<td>Parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>R²</td>
<td>Coefficient of determination</td>
</tr>
<tr>
<td>Rain</td>
<td>Amount of precipitation</td>
</tr>
<tr>
<td>RAMA</td>
<td>Automatic Atmospheric Monitoring Network</td>
</tr>
<tr>
<td>RAPIDC</td>
<td>Regional Air Pollution in Developing Countries</td>
</tr>
</tbody>
</table>
Atmospheric Deposit Network

Atmospheric Monitoring Network and the Meteorology and Solar Radiation Network

Relative humidity

Root Mean Square

Least mean square error

Standard deviation

Swedish International Development Agency

Sulfur dioxide

Sport utility vehicle

Temperature

Time of Wetness

Convention of the United Nations Economic Commissions for Europe

Deposition rate

Zinc nitrate

Basic nitrate o essential nitrate

REFERENCES


Seinfeld, J.H., (1980). Lectures in Atmospheric Chemistry. Am. Insti-
J.O. Castillo-Miranda et al.

AUTHOR (S) BIOSKETCHES

Castillo-Miranda, J.O., Ph.D., Postdoctoral stay, Departamento de Ingeniería Metalúrgica, Facultad de Química, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, C.P. 04510, Ciudad de México, México. Email: jrechateau@yahoo.com.mx

Rodríguez-Gómez, F.J., Ph.D., Professor, Departamento de Ingeniería Metalúrgica, Facultad de Química, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, C.P. 04510, Ciudad de México, México. Email: fxavier@unam.mx

Genescá-Llongueras, J., Ph.D., Professor, Polo Universitario de Tecnología Avanzada, Universidad Nacional Autónoma de México, Vía de la Innovación 410 PIIT Autopista Monterrey-Aeropuerto Km. 10 C.P. 66629, Apodaca, Nuevo León, México. Email: genesca@unam.mx

Ruiz-Suárez, L.G., Ph.D., Professor, Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Circuito de la Investigación Científica, Ciudad Universitaria, C.P. 04510, Ciudad de México, México. Email: ruizs@unam.mx

García-Reynoso, J.A., Ph.D., Professor, Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Circuito de la Investigación Científica, Ciudad Universitaria, C.P. 04510, Ciudad de México, México. Email: agustin@atmosfera.unam.mx

COPYRIGHTS

©2021 The author(s). This is an open access article distributed under the terms of the Creative Commons Attribution (CC BY 4.0), which permits unrestricted use, distribution, and reproduction in any medium, as long as the original authors and source are cited. No permission is required from the authors or the publishers.

HOW TO CITE THIS ARTICLE


DOI: 10.22034/gjesm.2021.04.0*

url: http://gjesm.net/***