

Field exposure study under sheltered and open exposure conditions at different test sites in Germany: First-year corrosion rate and atmospheric corrosivity

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Abstract

The corrosivity of atmospheres in Europe has changed significantly in recent decades. For the Federal Republic of Germany, no current values for the corrosion rate based on 1-year atmospheric exposure of standard specimens can be found in the scientific literature after 2000. This paper presents results from a field exposure study in the Berlin metropolitan area and Helgoland in 2016. Based on standard specimens, values for the corrosion rate and the corresponding atmospheric corrosivity category are determined for open exposure and indirect weathering in a ventilated enclosure as sheltering after 1 year of exposure. The results prove that determined corrosivity categories are material-specific. Sheltered exposure is a typical atmospheric situation for many building components. It allows statements on the effect of the concentration of airborne substances on the corrosivity beyond the normative requirements.

KEYWORDS

atmospheric corrosion, corrosivity category, ISO 9223, mass loss

1 | INTRODUCTION

The atmospheric corrosivity of exposure sites is classified according to the current edition of ISO 9223.^[1] According to Mikhailov et al.,^[2] the foundations for today's ISO 9223 were already laid in the 1970s and 1980s. Rural, urban, industrial and marine atmospheres were qualitatively described before the introduction of ISO 9223. ISO 9223 contained the first classification system that could quantitatively describe corrosivity categories. However, the first version of ISO 9223 was mainly based on data obtained in the temperate climates of Europe and North America. In 2004, the first efforts were made to revise ISO 9223 with data obtained in cold, subtropical, and

tropical climates.^[2] The revision included the long-term results of the ISOCORRAG program^[3] and the MICAT program.^[4–7]

ISO 9223 distinguishes between the determination and estimation of the corrosivity of an atmosphere. ISO 9226^[8] is used as the basis for determining corrosivity. It describes a procedure by metal standard specimens utilizing corrosion losses (mass losses) after 1 year of atmospheric exposure. Estimating the corrosivity is based on material-specific dose–response functions or via a table in the informative annex in ISO 9223 with a verbal description of the environmental conditions. Estimating the corrosivity results from investigations according to ISO 9225^[9] is required. These include the time of

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wetness (TOW) of a metal surface, the annual mean temperature, the deposition rate of sulfur dioxide (SO₂), and the deposition rate of chloride as decisive atmospheric parameters for the corrosivity. The result of the determination and estimation of the corrosivity is classifying an atmosphere into corresponding corrosivity categories from C1 (very low corrosivity) to CX (extreme corrosivity). However, according to ISO 9223, corrosivity determination based on standard specimens is the preferred method.

In addition to the classification system according to ISO 9223, the qualitative distinction of atmospheres into rural, urban, industrial, and marine is still widespread and accepted in scientific articles.^[2,10–13] Tidblad et al.^[14] describe that these designations often correlated with atmospheric corrosivity in the past. However, this is no longer the case as they cannot quantify the corrosivity. Nevertheless, the designations are still useful to indicate the type of contamination (e.g., dominated by SO₂ or chloride).

The estimation of the corrosivity category using dose–response functions is often the subject of scientific studies. Odnevall Wallinder and Leygraf describe in their review article^[15] that dose–response functions for zinc obtained during an exposure program are often not applicable or valid for exposure sites from other exposure programs. Differences in environmental conditions at the respective sites are considered to be the reason. Since this problem was also found for the other metal standard specimens,^[13] dose–response functions for steel, zinc, copper, and aluminum are subject to updating and adapting. For example, an adaptation for cold climate regions,^[2] continental regions,^[16] and tropical locations^[17] was carried out.

Besides chloride, SO₂ is the most important air pollutant for atmospheric corrosion of metals and is therefore used as a basis for estimating the corrosivity of an atmosphere. The influence of SO₂ is based on the fact that it will lower the pH value if it is dissolved in rainwater or moisture film. This reaction is often associated with accelerated corrosion processes.^[18] Hudson^[19] showed as early as 1964 that the amount of SO₂ contamination directly influences atmospheric corrosion, especially for zinc.

Kreislová and Knotková^[20] confirmed that a significant correlation between the atmospheric corrosion of steel, zinc, and copper with the SO₂ concentration exists, based on data from 1970 to 2016 from extensive exposure campaigns at an industrial and urban site in the Czech Republic. The SO₂ concentration decreased significantly at all sites during the studied period and led to a significant decrease in the corrosion rate of these metals within the first year of exposure. Kreislová and Knotková

assume that the influence of SO₂ has overridden the influence of other environmental factors in recent decades. However, dose–response functions are derived from field exposure studies from 1986 to 2004, during which high levels of SO₂ were detected at urban and industrial sites.

In a study from 2017, Tidblad et al.^[14] clarified the influence of SO₂ on atmospheric corrosion. They looked at a wide range of European rural, urban and industrial exposure sites. They found that SO₂ concentrations in 1987 were higher in industrial areas (70 μg m⁻³) than in urban areas (~40 μg m⁻³) and significantly higher than in rural areas (5 μg m⁻³). In 2014, however, SO₂ pollution at industrial sites was only about 10 μg m⁻³. At urban sites, the low level in rural areas in 1987 was reached with a value of 5 μg m⁻³. The corrosion rate of steel, zinc, and copper within the first year of atmospheric exposure followed the decreasing trend and was significantly lower in 2014 than in 1987.

The explanations show that the corrosivity of atmospheres in the European area has changed significantly due to a change in atmospheric conditions. As a result, the dose–response functions listed in ISO 9223 may lose their relevance and are no longer applicable to many types of atmospheres. Therefore, an estimation of the corrosivity for exposure sites and atmospheres would lead to erroneous values for the corrosion rate and the corrosivity category. For the Federal Republic of Germany, no current values for the corrosion rate after 1 year of atmospheric exposure can be found in the scientific literature based on the exposure of standard specimens, especially after 2000. Current values for the corrosion rate of steel, zinc, copper, and aluminum in the first year of atmospheric exposure are needed for the Federal Republic of Germany to design economic corrosion protection measures and for regulatory work.

For the new federal states/eastern Germany area, values describing the atmosphere's corrosivity are compiled in^[21] for the four standard metals from 1989 to 1994. A direct correlation between the decreasing SO₂ concentration of the air and the decreasing corrosion rate of the standard metals was also proven. In Ungermann et al.,^[22] helix specimens were attached to the underside of bridges within the Federal Republic of Germany. The corrosivity category was determined after 1 year of exposure. On the bridges investigated, the corrosivity was lower in 2012 (C2 to C4) compared to 1983 (C3 to C4). However, values for the corrosion rate are not given, and there is no breakdown of the corrosivity categories according to the type of metal.

With the publication of the Exposure Site Catalogue of Working Party 25 “Atmospheric Corrosion” of the European Federation of Corrosion,^[23] steps are being taken to achieve the networking and connection of

exposure sites operated within Europe and to create a broad database. The exposure sites within the Federal Republic of Germany focused mainly on the marine sector, particularly on testing in the surf zone and close to the waterline. In some cases, the corrosivity categories C5 and CX for steel and copper are reached. The few rural and urban exposure sites listed for the Federal Republic of Germany are described in more detail in this study.

This study presents results from an exposure campaign from 2016 to 2017 at a rural, three urban sites in the Berlin metropolitan area and a marine site in Helgoland. The study focuses on the determination of the atmospheric corrosivity category at each exposure site by standard specimens. The exposure racks have the unique feature that weathering is possible under open exposure (normative) and in an indirect exposure situation in a ventilated enclosure as sheltering (non-normative). Sheltered exposure is a typical atmospheric situation for many building components. It allows statements on the effect of the concentration of airborne substances on the corrosivity beyond the normative requirements.

2 | EXPERIMENTAL

2.1 | Materials investigated and preparation of standard specimens

Cold-rolled sheet material of aluminum, zinc, copper, and unalloyed steel was used for the investigations according to the specifications in ISO 9226.^[8] The chemical composition of copper, aluminum, and unalloyed steel was determined using X-ray fluorescence spectroscopy (XRF). The chemical composition of zinc was determined by wet chemistry. In the following, the chemical composition is listed by indicating the most important elements (data in wt.%):

- unalloyed steel: 99.36% Fe/0.49% Mn/0.03% Cr/0.03% S/0.02% Cu,
- zinc: 99.95% Zn/0.04% Cu,
- copper: 99.81% Cu/0.09% Ni/0.04% Zn/0.03% Fe,
- aluminium: 99.57% Al/0.27% Fe.

The sheet material with a thickness of 0.8 mm was cut into sheet sections with dimensions of 150 × 100 mm. These values correspond to the dimensions of standard specimens for atmospheric exposure according to ISO 9226^[8] and ISO 8565.^[24] The sheets were solid material (bulk material). Before exposure, the sheets were degreased with petroleum ether and

cleaned with acetone and ethanol. Metal sheets in the initial state were metallic bright without visible corrosion products and had an average roughness Rz of 3.6 μm (steel), 2.8 μm (zinc), 1.1 μm (copper), and 2.3 μm (aluminum).

2.2 | Exposure on standard exposure racks under open exposure and sheltering

The atmospheric corrosion tests were carried out on various exposure sites of the Bundesanstalt für Materialforschung und -prüfung (BAM). Exposure tests were conducted according to specifications in ISO 8565.^[24] The standard specimens were adjusted to the exposure racks on-site using plastic fasteners. They were exposed to natural weathering for 1 year. The test racks had the option of exposing the standard specimens under sheltered conditions (rainfall excluded) and under open exposure (unhindered rainfall). The standard specimens were fixed at 90° to the horizontal in the sheltered area and 45° under open exposure conditions. Specimens were exposed with an inclination angle of 90° in the sheltered area to avoid uneven deposition of chloride and SO₂ on both sides of the specimens. With an inclination angle of 90° both sides of the specimens experience the same level of deposition. Three standard specimens per metal were stored in the open exposure and sheltered area. An overview of the exposure sites in this study is given in Table 1. In addition, the exposure periods are listed.

The exposure sites listed in the table are distributed over various locations in the Berlin metropolitan area and Helgoland. In addition to the information in Table 1, the exposure sites have the following special features:

- HW—Horstwalde:
The exposure site is located at the BAM Test Site for Technical Safety in Horstwalde (TTS), in the federal state of Brandenburg. It is a forest area in a rural environment. The exposure rack is set up at ground level and is located above naturally grown sandy soil with turf.
- BAM—Rooftop main building:
The exposure site is located on the rooftop of the main building at BAM Headquarters in Berlin-Steglitz at a height of 17 m above street level. The distance (direct distance) to the B1 federal road is 25 m. The exposure rack was set above a stone pavement with a drainage layer.
- B1—national road B1:
The exposure site is located at BAM Headquarters in Berlin-Steglitz at a distance of 8 m from the national

TABLE 1 Exposure sites, exposure conditions, and period of exposure for atmospheric exposure testing of standard specimens

Abbreviated designation	Exposure site and exposure conditions	Type of atmosphere	Informative estimation of corrosivity according to ISO 9223, Annex C ^[1]		Exposure direction of specimens	Start of exposure	End of exposure
			C2	C3			
HW	Test Site for Technical Safety in Horstwalde (TTS), open exposure/sheltered	Rural	C2		52° 05' 53.0" N 13° 25' 04.3" E	3 August 2016	August 3, 2017 365 days
BAM	BAM Headquarters, rooftop of main building, open exposure/sheltered	Urban	C3		52° 26' 34.4" N 13° 17' 14.6" E	Open exposure: 25 May 2016 Sheltered: 31 May 2016	29 May 2017 369 days 29 May 2017 363 days
B1	BAM Headquarters, national road B1, open exposure/sheltered	Urban, close to road	C3/C4		52° 26' 32.4" N 13° 17' 06.3" E	9 August 2016	9 August 2017 365 days
A103	Berlin, motorway A103, open exposure/sheltered	Urban, close to road	C4		52° 27' 41.5" N 13° 19' 45.0" E	10 June 2016	12 June 2017 367 days
HL	Helgoland, port area, open exposure/sheltered	Marine, North Sea island	C5		54° 10' 30.8" N 7° 53' 33.4" E	14 June 2016	19 June 2017 370 days

road B1 (six lanes) and is elevated at road level. The exposure rack is aligned parallel to the road and is located above natural ground with turf.

- A103—motorway A103:
The exposure site is located in Berlin-Steglitz at a 3 m distance from the motorway A103 (six lanes) at street level. The exposure rack faces the road at 45° and is located above a stone pavement.
- HL—Helgoland:
The exposure site is located in the port area in the southern part of the North Sea island Helgoland. Helgoland has a distance of about 49 km from the coast. The exposure rack is positioned 40 m from the harbor edge and 300 m from the southwestern breakwater wall and is located above a gravel layer.

Figure 1 shows the installation situation of the standard specimens on the exposure racks at the various exposure sites investigated in this study.

The exposure racks were of the same design at all exposure sites. They offered the possibility of open exposure and indirect weathering (sheltered exposure) in an air-permeable, ventilated enclosure at the bottom. The exposure sites B1 and HW* in Figure 1 show examples of the sheltered area of the exposure racks in the open state. The enclosure protects the sheltered area except for the floor opening and thus differs from a typical sheltering. Three ventilation slots are arranged in the side walls, which, together with the floor opening, allow air exchange in the sheltered area with the surrounding atmosphere. The sheltering prevents cleaning effects caused by rainfall and thus enables the accumulation of airborne substances on the standard specimens. The sheltered area had dimensions of 1500 × 700 × 700 mm. The sheltered area of the exposure racks was made from stainless steel 1.4301 (AISI 304/X5CrNi18-10) with rolled surface finish.

2.3 | Determination of chloride and SO₂ deposition rate

The amount of chlorides and sulfates deposited on a metal surface was determined at the exposure racks for the exposure periods. This investigation was carried out as described in Babutzka et al.^[25] on separate test areas on the exposure racks made of stainless steel 1.4301 with rolled surface structure in the sheltered area. The amount of deposits was determined on horizontal surfaces in the sheltered area to obtain a statement about the supply of chloride and sulfate at the different exposure sites.

For this purpose, the test areas were rinsed with a sponge and double-distilled water, and the eluate was

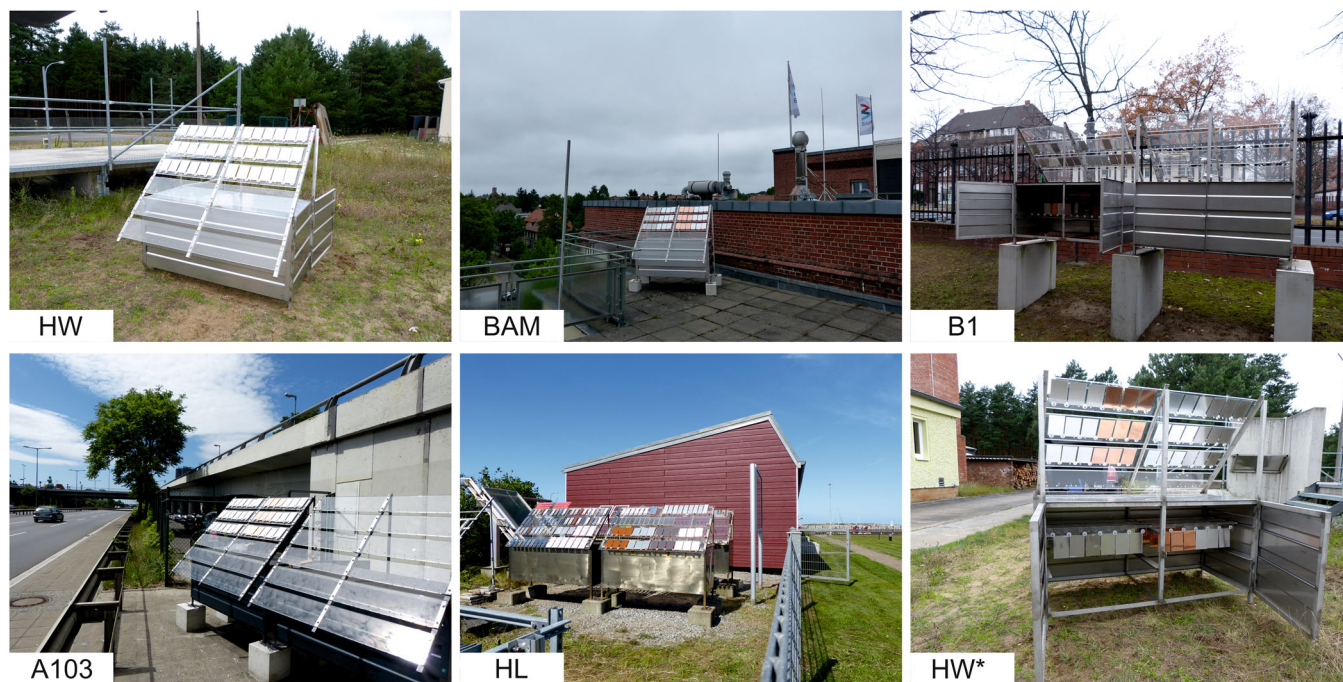


FIGURE 1 Exposure racks at the different exposure sites from Table 1 with installed standard specimens at the beginning of exposure, HW* shows exemplarily the specimen arrangement in the indirectly weathered area in the open state of the shelter [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.202213582)]

TABLE 2 Determined values of the effectively deposited amount of chlorides and sulfates on horizontal metal surfaces from rolled stainless steel in the enclosed area for the different exposure sites after 1 year of exposure

Exposure site type of atmosphere	Effectively deposited amount of chloride mg m^{-2}	Effectively deposited amount of sulphate mg m^{-2}
Horstwalde (HW) rural	13	<1
Rooftop (BAM) urban	26	26
National road (B1) urban	103	64
Motorway (A103) urban	282	192
Helgoland (HL) marine	533	142

collected. In the laboratory, the sponge was washed several times with double-distilled water. The collected solution was transferred to a 250 ml volumetric flask and filled to total volume. The solution was filtered through a $0.45 \mu\text{m}$ syringe filter, and then the chloride and sulfate content was analyzed using an 883 IC Basic Plus from Metrohm AG (Herisau, Switzerland). The values in mg m^{-2} are related to a volume of 1000 ml. Table 2 gives an overview of the chloride and sulfate deposition in the sheltered area at the different exposure sites.

Further details on climatic conditions and environmental parameters at the exposure sites are listed in the corresponding entries of the Exposure Site Catalogue^[23] for further information.

2.4 | Determination of corrosion rate and corrosivity category by standard specimens

For the determination of the corrosion rate using standard specimens after 1 year of atmospheric exposure according to ISO 9223^[1] and 9226,^[6] the metal specimen sheets were first weighed in their initial state using an analytical balance CPA324S-OCE from Sartorius (Sartorius Lab Instruments GmbH & Co. KG). After 1 year of exposure, the corrosion products were removed according to the specifications in ISO 8407:2009, Table A1^[26] and the specimens were then weighed again. The following solutions were used for the chemical cleaning of the different metals:

- unalloyed steel: C.3.1 (based on hydrochloric acid and hexamethylenetetramine),
- zinc: C.9.4 (based on ammonium acetate),
- copper: C.2.2 (based on hydrochloric acid),
- aluminum: C.1.1 (based on nitric acid).

Longer chemical cleaning treatment times of up to 20 min, deviating from the standard, were necessary to remove all corrosion products from the surfaces of some zinc and aluminum specimens. For zinc, the chemical cleaning agent C.9.4 was used, which was still permissible according to the 2009 version of ISO 8407,^[26] but is no longer listed in the current version of ISO 8407 from 2021.^[27]

The corrosion rate r_{corr} was obtained as the area-related mass loss during the exposure period, expressed in $\text{g m}^{-2} \text{y}^{-1}$, according to Equation (1):

$$r_{\text{corr}} = \frac{\Delta m}{A \cdot t}, \quad (1)$$

where m is the mass loss in gram (g), A is the specimen surface area (0.03 m^2 : front and back of the sheet), and t is the exposure time (1 year). The corrosion rate after 1 year of atmospheric exposure is used to evaluate the corrosivity of the different atmospheres. It was assigned to the corresponding corrosivity categories according to ISO 9223^[1] for each metal based on the mean values of the corrosion rate from three specimen sheets in each case.

2.5 | Determination of pit depths

The standard specimens from zinc and aluminum showed localized corrosion in the form of pits after 1 year of atmospheric exposure. Therefore, pit depths were determined using metallographic cross-sections. After chemical cleaning, samples were taken from the middle of the standard specimens and embedded in epoxy resin. At least 10 pits were observed and measured

in the cross-section and the maximum depth of the local corrosion phenomena was determined. An Axioplan 2 microscope with an AxioCam HRc from Zeiss (Carl Zeiss Jena GmbH) was used for optical microscopy.

3 | RESULTS

3.1 | Corrosion rate after 1-year exposure of standard specimens

3.1.1 | Unalloyed steel

The results of the 1-year atmospheric exposure of unalloyed steel specimens are shown in Figure 2 in dependence on the exposure site and exposure conditions.

Differences between the corrosion rate of unalloyed steel under open exposure and sheltered conditions were determined. For open exposure, the corrosion rate of unalloyed steel tended to be twice as high as under sheltered conditions at all exposure sites. In a direct comparison of the sites, the HW, B1, and BAM sites showed corrosion rates of unalloyed steel in the same order of magnitude under open exposure and sheltered conditions, respectively. Atmospheric exposure of unalloyed steel at site A103 resulted in a significantly higher corrosion rate under open exposure and sheltered conditions. Under sheltered conditions, the corrosion rate of unalloyed steel was about three times higher than at the HW, B1, and BAM sites. Atmospheric exposure at the marine site HL showed the highest values for the corrosion rate of unalloyed steel. The corrosion rate was five times higher than at the HW, B1, and BAM sites.

3.1.2 | Zinc

Figure 3 summarizes the corrosion rate of zinc at the different exposure sites after 1 year of atmospheric exposure.

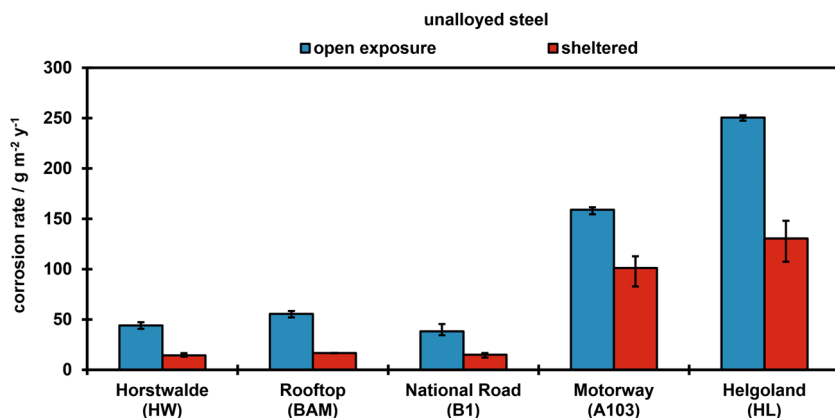


FIGURE 2 Corrosion rate of unalloyed steel at different exposure sites under sheltered and open exposure after 1 year of atmospheric exposure, exposure period 2016–2017 [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/terms-and-conditions)]

FIGURE 3 Corrosion rate of zinc at different exposure sites under sheltered and open exposure after 1 year of atmospheric exposure, exposure period 2016–2017 [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

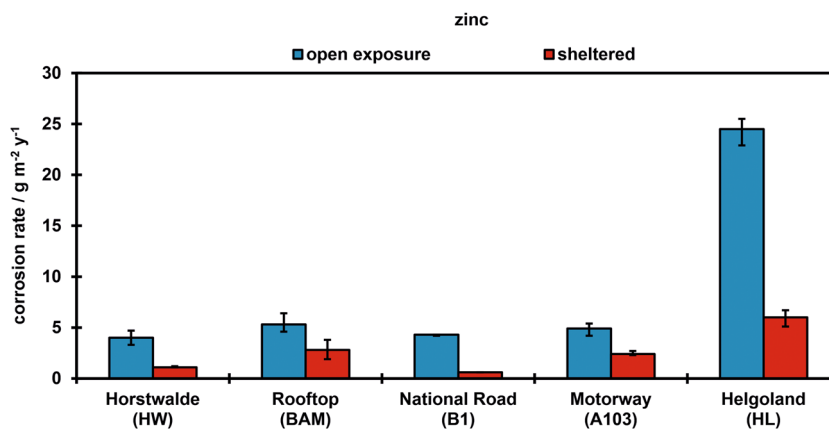
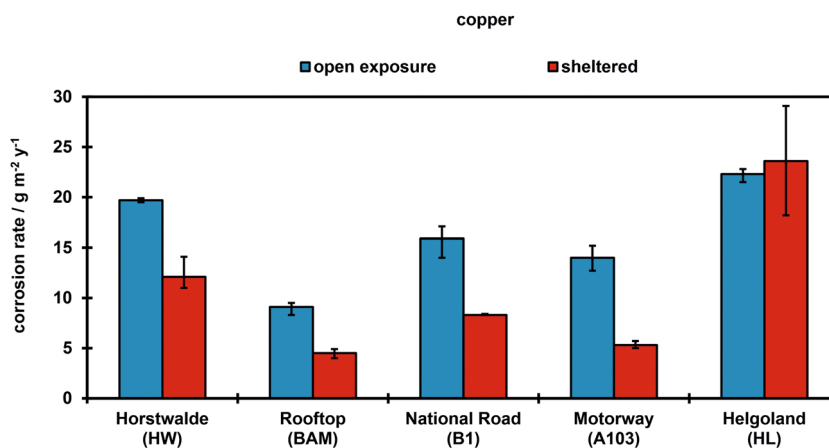


FIGURE 4 Corrosion rate of copper at different exposure sites under sheltered and open exposure after 1 year of atmospheric exposure, exposure period 2016–2017 [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]



Apparent differences between the various exposure sites and between open and sheltered exposure can be seen when comparing the corrosion rate of zinc. In the case of open exposure, the corrosion rate of zinc tended to be two to five times higher than in the case of sheltered exposure. Exposure sites HW and B1 showed corrosion rates for zinc of the same order of magnitude in a direct comparison of the sites under open exposure and sheltered conditions, respectively. Exposure sites BAM and A103 showed higher values for the corrosion rate of zinc under sheltered exposure compared to sites HW and B1. Atmospheric exposure at site HL showed by far the highest values for the corrosion rate of zinc. These were two (sheltered exposure) to five (open exposure) times higher than at the other exposure sites.

3.1.3 | Copper

The corrosion rate of copper after 1 year of atmospheric exposure is shown in Figure 4.

The corrosion rate of copper tends to be higher under open exposure than under sheltered conditions. An exception was the marine exposure site HL, where

specimens occasionally showed a higher corrosion rate under sheltered conditions, although the values are subject to high scattering. The lowest corrosion rate for copper, regardless of the exposure conditions, was determined at the urban site BAM. The near-road urban sites B1 and A103 had higher corrosion rates for copper than the BAM site. At the rural site HW, twice as high copper corrosion rate values were determined than at the urban site BAM. The highest corrosion rate for copper of all sites was determined at the marine site HL.

3.1.4 | Aluminum

Figure 5 summarizes the corrosion rate of aluminum at the different exposure sites after 1 year of atmospheric exposure.

For aluminum, differences were found between the corrosion rate under open exposure and sheltered conditions. The corrosion rate tended to be higher under open exposure. However, at the rural exposure site HW, the same corrosion rate was determined under open exposure and sheltered conditions, although very low. On the other hand, at the marine site HL, a significantly

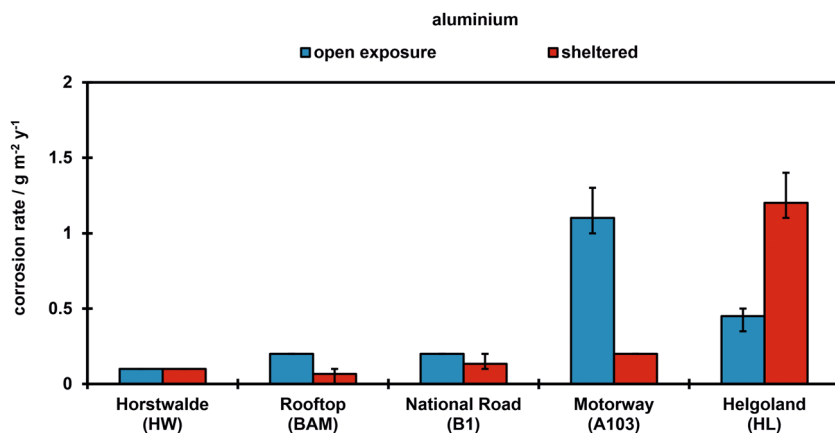


FIGURE 5 Corrosion rate of aluminum at different exposure sites under sheltered and open exposure after 1 year of atmospheric exposure, exposure period 2016–2017 [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.202213582)]

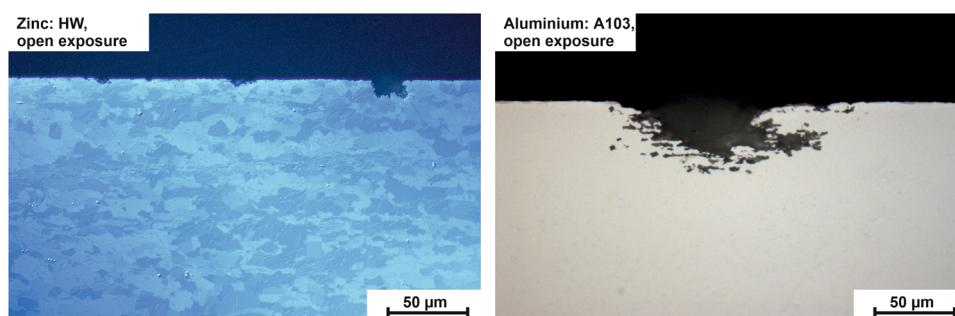


FIGURE 6 Cross-sections of zinc and aluminum specimens at a rural (HW) and urban (A103) exposure site after 1 year of atmospheric exposure; corrosion products were removed [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.202213582)]

higher corrosion rate was determined for aluminum in the sheltered area than under open exposure. The lowest corrosion rate of all exposure sites was determined at the rural site HW. The highest corrosion rate for aluminum was determined under sheltered exposure at the marine site HL and open exposure at the urban site A103.

3.2 | Localized corrosion on zinc and aluminum

Localized corrosion phenomena were found on zinc and aluminum surfaces after 1 year of atmospheric exposure. Pit depths were measured and determined in a metallographic cross-section. Images of the morphology of localized corrosion phenomena on zinc and aluminum are shown exemplarily in Figure 6.

Figure 7 shows the results of pit depth determination by means of metallographic investigations.

For zinc, localized corrosion was observed at all exposure sites. Under open exposure, the pit depths were significantly higher at all sites than under sheltered conditions. The deepest pits were determined under open exposure at sites A103 and HL. Pit depths at sites HW,

B1, and BAM showed similar values in a direct comparison of the three sites.

No assessable pit depths were determined for aluminum specimens at exposure sites HW (open exposure), BAM, and A103 (both under sheltered conditions). Pit depths with a mean value of $\sim 1 \mu\text{m}$ were determined at sites HW and B1 (both under sheltered conditions) and site BAM (open exposure). Pit depths with a mean value of ~ 20 to $25 \mu\text{m}$ were determined at sites B1 and A103 (affected by de-icing salt) under open exposure and at the marine site HL under sheltered conditions. At marine site HL, the pit depth was higher in the sheltered area than under open exposure.

3.3 | Determination of corrosivity categories according to ISO 9223

The first-year corrosion rate was assigned to the corresponding corrosivity categories according to ISO 9223^[1] for each metal and each exposure site, considering the exposure conditions (open or sheltered exposure). The assignment was made using the mean values of the corrosion rate from three standard specimens in each

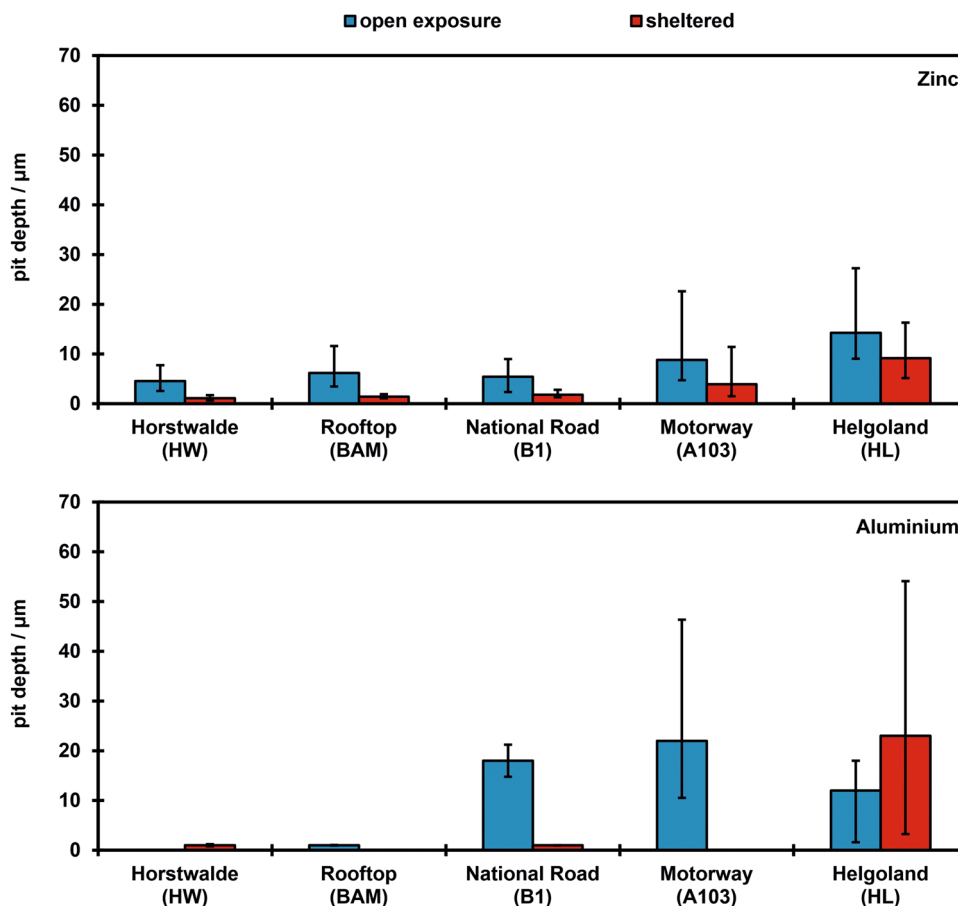


FIGURE 7 Pit depths of zinc (top) and aluminum (bottom) determined at different exposure sites under sheltered and open exposure after 1 year of atmospheric exposure, exposure period 2016–2017, mean pit depth and deviation range from 10 measured pits [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.202213582)]

case. The corrosivity categories of the investigated exposure sites are compiled in Table 3.

The table shows the differences regarding corrosivity categories in dependence on the exposure site and the standard metal examined. Since an allocation of the sheltered area is not regulated in ISO 9223, the corrosivity categories have been placed in brackets. Nevertheless, they will be used in the following discussion as a guide based on ISO 9223. Figure 8 illustrates graphically the location of the corrosion rate within the individual corrosivity categories for all exposure sites and standard metals.

Figure 8 shows the importance of indicating the value of the corrosion rate in addition to the corrosivity category. For example, the corrosivity category C2 and thus low corrosivity was determined for unalloyed steel at all locations except for HL under open exposure and sheltered conditions. Due to the broad range of corrosion rates for C2 between 10 and $200 \text{ g m}^{-2} \text{ y}^{-1}$, the existing differences in the corrosion behavior of the unalloyed steel are not represented based on the corrosivity

category. For example, unalloyed steel at site A103 has a corrosion rate three times higher than at site BAM. Nevertheless, both are assigned to the corrosivity category C2.

For zinc, the corrosivity category C2 was determined at most of the exposure sites under open exposure and sheltered conditions. At site B1, the sheltered area had a lower category for zinc with C1 than the openly exposed area with C2. The value of the corrosion rate for the sheltered area is $0.6 \text{ g m}^{-2} \text{ y}^{-1}$ for zinc, which is close to the limit of category C2 at $0.7 \text{ g m}^{-2} \text{ y}^{-1}$. Category C3 was determined for zinc under open exposure at the BAM site. With a corrosion rate of $5.3 \text{ g m}^{-2} \text{ y}^{-1}$, this is slightly above the upper limit of category C2 ($5.0 \text{ g m}^{-2} \text{ y}^{-1}$). HL was the only site that showed high corrosivity (C4) for zinc under open exposure and medium corrosivity (C3) in the sheltered area and thus differed significantly from the other exposure sites.

For copper, predominantly high corrosivity categories in the range of C4 were determined under open exposure. The corrosivity with the categories C2 to C3

TABLE 3 Corrosivity categories C1...C4 of the investigated exposure sites and mean corrosion rate of the standard metals ($n = 3$) in $\text{g m}^{-2} \text{y}^{-1}$ in dependence of the exposure conditions, exposure period 2016–2017, determined after 1-year exposure of standard specimens

Exposure site type of atmosphere	Exposure condition	Unalloyed steel	Zinc	Copper	Aluminium
Horstwalde (HW) rural	Open exposure	C2 44.0	C2 4.0	C4 19.8	C2 0.1
	Sheltered	(C2) 14.4	(C2) 1.1	(C3) 12.1	(C2) 0.1
Rooftop (BAM) urban	Open exposure	C2 55.6	C3 5.3	C3 9.1	C2 0.2
	Sheltered	(C2) 16.6	(C2) 2.8	(C2) 4.5	(C2) 0.1
National Road (B1) urban	Open exposure	C2 38.2	C2 4.3	C4 15.9	C2 0.2
	Sheltered	(C2) 15.0	(C1) 0.6	(C3) 8.3	(C2) 0.1
Motorway (A103) urban	Open exposure	C2 159.0	C2 4.9	C4 14.0	C3 1.1
	Sheltered	(C2) 101.1	(C2) 2.4	(C3) 5.3	(C2) 0.2
Helgoland (HL) marine	Open exposure	C3 250.6	C4 24.5	C4 22.3	C2 0.5
	Sheltered	(C2) 130.4	(C3) 6.0	(C4) 23.6	(C3) 1.2

Significance of colors:

	C1
	C2
	C3
	C4

(BAM site) tended to be lower for copper in the sheltered area than under open exposure. At the HL site, the mean value of the corrosion rate in the sheltered area corresponded to the value under open exposure. However, one of three comparative specimens in the sheltered area had a corrosion rate of $29.1 \text{ g m}^{-2} \text{ y}^{-1}$ and can thus be assigned to corrosivity category C5. The corrosion rate for copper is unexpectedly high and lies outside the expected horizon. This applies in particular to the rural site HW, where the corrosion rate of copper reaches the highest values under open exposure and which thus has similar corrosivity for copper as the marine site HL.

For aluminum, the corrosivity category C2 was determined at almost all sites except for open exposure at site A103 and sheltered exposure at the marine site HL. A higher corrosivity category (C3) was determined on these sites for the aluminum specimens.

The corrosivity categories C5 (very high corrosivity) and CX (extreme corrosivity) were not determined at any of the investigated exposure sites (Table 3).

4 | DISCUSSION

4.1 | Corrosivity categories of exposure sites and atmospheres

A detailed examination of Table 3 and Figure 8 shows that the corrosivity categories of the sites determined using standard specimens are often material-specific. Unalloyed steel and aluminum are classified by the corrosivity category C2, zinc by category C1, and copper by category C3 under sheltered conditions at exposure site B1. Another example of the material dependency of the corrosivity categories is the location HL under open exposure.

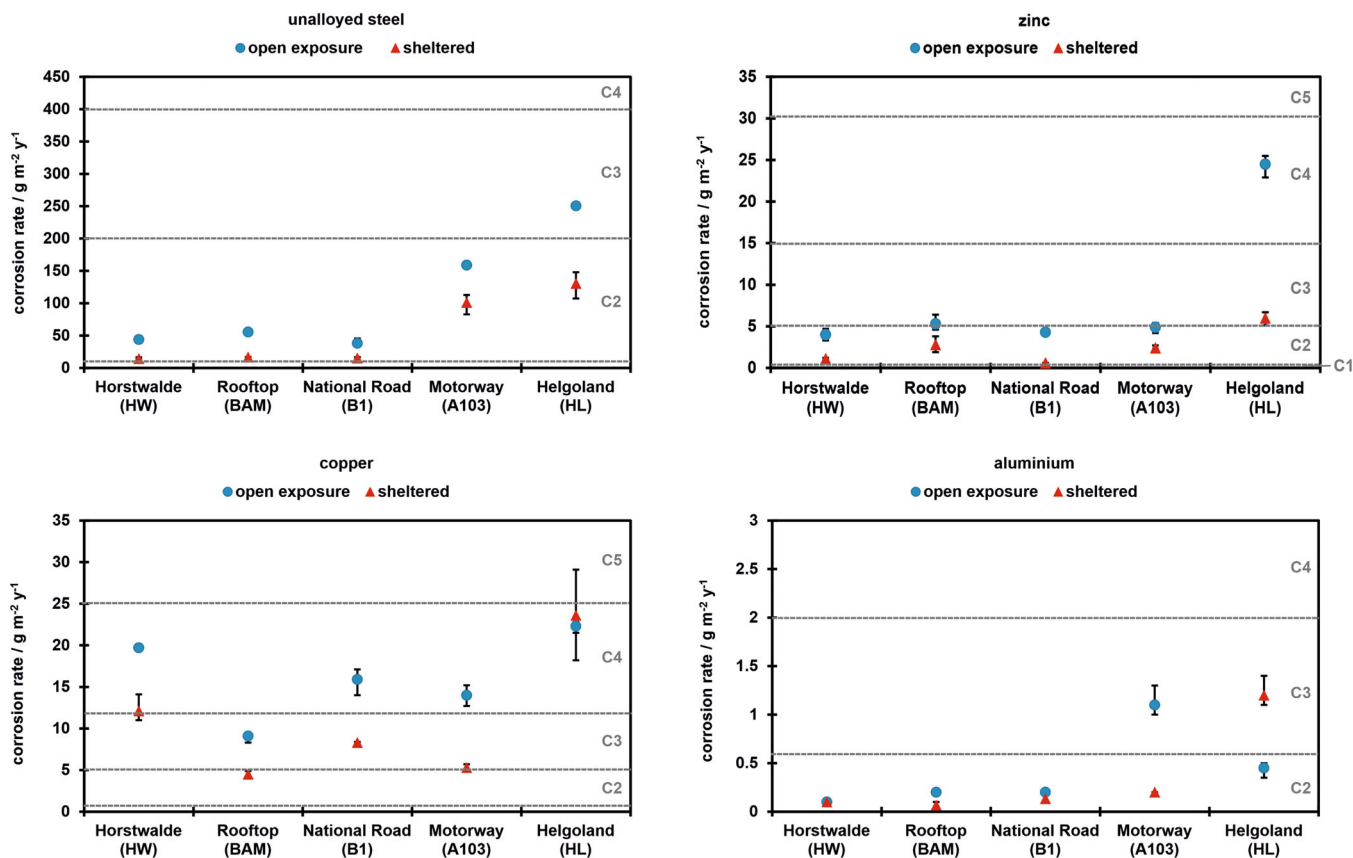


FIGURE 8 Location of the corrosion rate within the respective corrosivity category of the standard metals, exposure period 2016–2017 [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

Unalloyed steel is classified by corrosivity category C3, zinc and copper by C4, and aluminium by C2.

The differences with regard to the corrosivity categories are based on the different properties of the metals examined: Aluminium forms a passive layer and tends to localized corrosion under the influence of chlorides. Zinc forms protective layers of corrosion products, whose stability and properties are based on the factors influencing the environment. The most stable layers form on zinc surfaces due to the influence of carbon dioxide. In the case of copper, patina formation occurs, whereby permanently stable layers can only form in the atmosphere through the influence of SO_2 and chloride. Unalloyed and low-alloyed steels do not form protective top layers in the true sense but porous layers of corrosion products that do not have a significant protective effect. In the case of unalloyed steel, humidification cycles (changes in TOW) and rainfall play a prominent role.

An exposure site can thus have different corrosivity categories according to ISO 9223. For the reasons described, a determined corrosivity category should always be accompanied by the comment to which exposed standard metal it refers.

Table C1 in the informative annex of ISO 9223 estimates the corrosivity category derived from comparing exposure conditions with the description of typical atmospheric environments.^[1] The corrosivity categories of the sites in this study estimated from Table C1 in the informative annex of ISO 9223 are listed in Table 1. Figure 9 compares the estimated corrosivity category and the corrosivity category determined by standard specimens.

Comparing corrosivity categories determined by standard specimens shows that these are often one to two categories lower than the estimated ones. This is particularly significant in the case of unalloyed steel. In the case of copper, on the other hand, the corrosivity category determined via standard specimens is higher than the estimated one at the sites HW and B1. Copper thus has a higher corrosion rate at the sites than expected.

Based on the estimation of the corrosivity category, no reference to the respective standard metal is available. The informative Table C.1 in the informative annex of ISO 9223 does not take into account the material-specific peculiarities with regard to corrosion behavior. Since sheltered exposure is not considered as normative, sheltered areas cannot be evaluated from the estimation of the corrosivity via Table C.1 in the informative annex of ISO 9223.

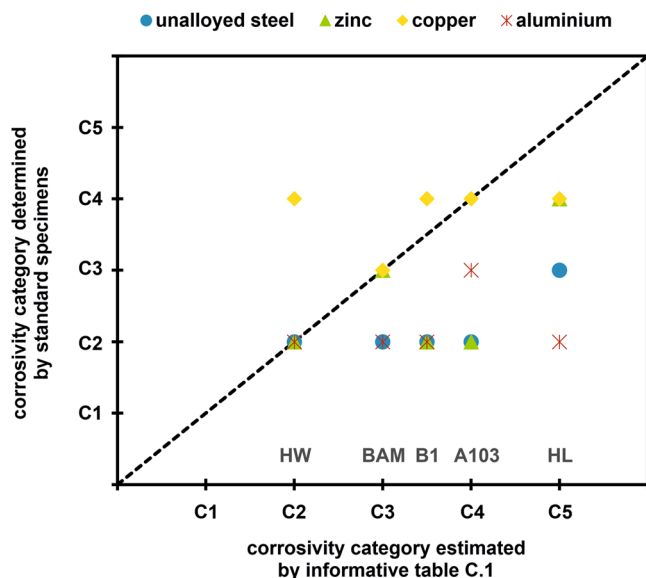


FIGURE 9 Comparison of the corrosivity category estimated on the basis of informative table C.1 of ISO 9223^[1] and the corrosivity category determined by standard specimens under open exposure [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

4.2 | Difference in corrosivity category between open exposure and sheltering

Due to the different exposure conditions under open exposure and sheltered conditions, differences in corrosion rate and corrosivity categories can be determined at an exposure site for the same standard metal.

For unalloyed steel, the corrosion rate tends to reach only half as high values in the sheltered area as under open exposure. For zinc, a corrosion rate four times lower than under open exposure is achieved at some exposure sites under sheltered conditions. The exceptions to this tendency are aluminum and copper at the HL site, with corrosion rates of similar magnitudes for open and sheltered exposure.

Under sheltered conditions, the surface is protected from direct precipitation, such as rainfall and solar radiation. Furthermore, sheltering and enclosure can affect the transport and deposition conditions of chlorides and SO₂ on metal surfaces. For the marine site HL, for example, a dependence of the amount of chloride deposited on the specimen inclination angle in the sheltered area was found in a previous study.^[25] With a horizontal specimen inclination angle of the metal surface, about 5–10 times more chlorides are deposited on a metal surface in a marine atmosphere than with a vertical inclination angle.

Chloride and SO₂ deposition conditions, lack of solar radiation, protection from precipitation, and the specimen inclination angle have a mutual effect of interaction

on the TOW of the metal surfaces in the sheltered area. This leads to a deviating corrosion behavior, although the specifics of the corrosion behavior of the respective metals must be taken into account. It can be assumed that the corrosion rate in the sheltered area is higher at surface inclination angles of 45° or 0° (horizontal) than at an inclination angle of 90°, as investigated in this study.

It must be noted that prognoses regarding the corrosion progress based on the corrosivity category determined after the first year of exposure cannot be made with certainty without further investigations for a sheltered area. The differences between openly exposed and sheltered areas could lead to the assumption that sheltered areas are much less critical for most metals than openly exposed areas. However, using zinc as an example, it was confirmed in Babutzka^[28] that corrosion products on zinc are less protective and stable in the sheltered area than in the openly exposed area. Under sheltered conditions, the corrosion product formation on zinc surfaces occurs under different conditions whereby corrosion products with chloride or sulfate components are formed. Under open exposure, on the other hand, corrosion products containing carbonate form on zinc surfaces. These are stable over a long time, do not change significantly regarding their chemical constituents, and significantly inhibit the corrosion rate after the first year of exposure.

4.3 | Classification of studied exposure sites in European comparison

The exposure sites described in the European Exposure Site Catalogue of the EFC^[23] predominantly show corrosivity categories in the range of C2 and C3 for the standard metals. It should be noted that, except for the sites described in this study, the Exposure Site Catalogue only lists openly exposed sites. The corrosivity categories C4, C5, and CX are predominantly determined at marine sites—C5 and CX predominantly in the area of splash water and sea surf. The corrosivity category C1 is determined negligibly rarely.

The exposure sites investigated in the present study confirm these open exposure trends except copper. The corrosivity categories for steel, zinc, and aluminum are within the trend ranges in European comparison for the rural (HW) and urban (BAM, B1, A103) atmospheres. However, it can be seen that unalloyed steel only has a corrosivity category C3 at the investigated marine site HL (no splashing water or sea surf). This trend is also recognizable in European comparison for marine locations, whereby the category C5 is also determined for steel at some locations affected by splash water.

As described in Section 4.1, the values for the corrosion rate of copper are relatively high and, especially for the rural site HW, well outside the horizon of expectation. This site is characterized by the absence of significant air pollutants such as SO₂ and chloride (Table 2), which prevents the most stable form of copper patina from forming, according to common scientific opinion. Based on the investigations in this study, no conclusive answer can be given for this deviating corrosion behavior. However, based on the standard scientific literature,^[29] it can be stated that the values for the urban sites BAM, B1, and A103 are within the expected range, so a systematic error, for example, in the determination of mass losses, can be excluded. In Leygraf et al.,^[29] it is stated that the natural copper patina is characterized by a very porous structure and thus can absorb significant amounts of water. Due to the high water absorption, the corrosion rate of copper could be increased at the HW site.

The open questions about the corrosion behavior of copper in rural locations under the climatic conditions currently prevailing in the Federal Republic of Germany can only be clarified by further studies.

4.4 | Localized corrosion phenomena

The corrosion rate is determined via the area-related mass loss to determine the corrosivity category. In the case of zinc and aluminum, however, localized corrosion phenomena were preferentially determined after 1 year of atmospheric exposure. Figure 10 contrasts the corrosivity category to the pit depths for aluminum and zinc.

No correlation between the pit depth after 1 year of exposure and the corrosivity category can be proven for aluminum. There is a wide scattering of individual pit depths within categories C2 and C3. For zinc, there is a tendency for deeper pits to be measured in higher corrosivity categories for open and sheltered exposure, respectively. However, the comparatively large deviation ranges must be taken into account.

By looking at the pit depths in Figure 7 and the chloride deposition in the sheltered area in Table 2, a dependence of the pit depth on de-icing salt influence and chloride influence in the marine area is recognizable for aluminum. Pits are deeper under sheltered conditions with a mean value of 45 μm than under open exposure with 20 μm at the HL site, see Figure 7. This relationship is a known phenomenon for passive layer-forming metals in marine atmospheres and is described as exemplary for stainless steel.^[30] As already stated in Section 4.2, the surface inclination angle in the sheltered area influences the amount of chloride deposited on a metal surface. At exposure sites B1 and A103, no significant pit depths are observed for sheltered conditions compared to the openly exposed area. However, a significant amount of chloride was detected on horizontal surfaces (Table 2). Further investigation of the deposition mechanisms for chlorides and other contaminants in the road is necessary to clarify the issue.

For zinc, localized corrosion is detected at all sites, regardless of the chloride supply of the surrounding atmosphere. The zinc specimens show similar pit depths at the rural and urban sites HW, BAM, and B1. However, there is a tendency for the pits to be deeper at sites with

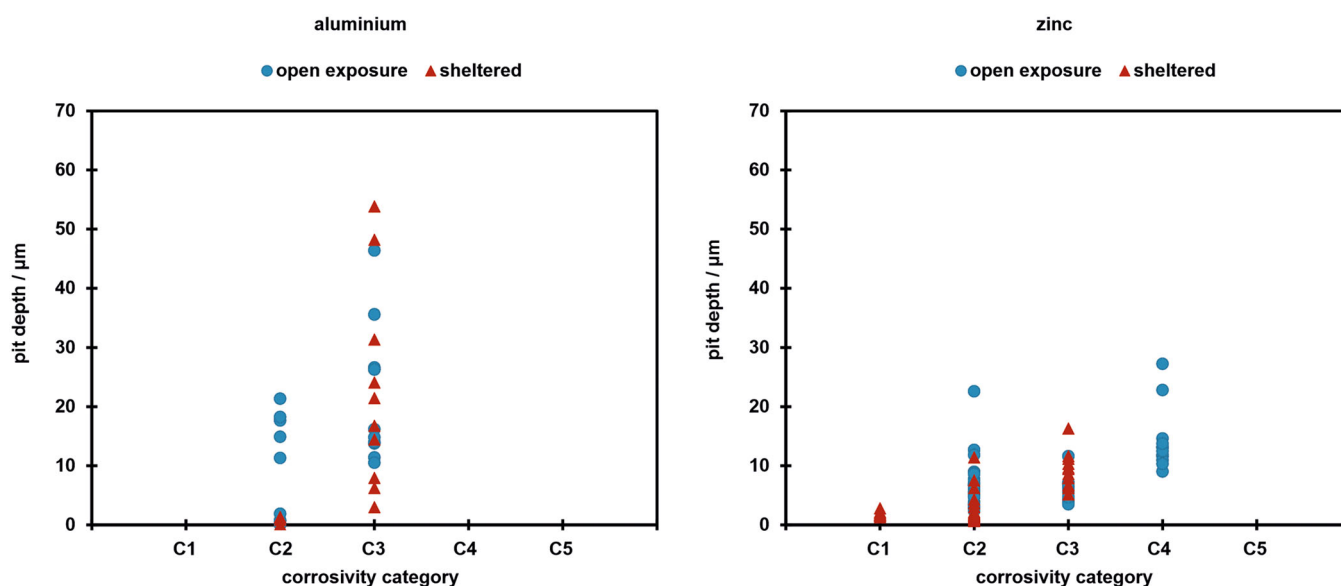


FIGURE 10 Comparison of corrosivity category (determined via standard specimens) and individual values of pit depths for aluminum and zinc under open and sheltered exposure, exposure period 2016–2017 [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.202213582)]

significantly increased chloride influence (A103 and HL) under open and sheltered exposure, respectively.

Localized corrosion on zinc, even under near chloride-free conditions, is a recent phenomenon that needs to be specifically investigated in further studies. In a comprehensive review article, Cole^[31] describes the state of knowledge in 2009 on the subject of localized corrosion on zinc and developments after 2009. Until 2009, the general opinion was that zinc was subject to uniform corrosion. However, more recent findings show that localized zinc corrosion is not an exception. However, Cole et al.^[32] suggest that the degree of contamination of the atmosphere influences the type of corrosion (uniform or localized corrosion). There seems to be a direct correlation to the SO₂ content of the atmosphere. They describe that pitting corrosion cannot be detected in atmospheres with high SO₂ content. A rather uniform corrosion results at low pH values (due to high SO₂ contents) in deposited aerosols. At lower SO₂ contents and only slightly acidified aerosols, on the other hand, the corrosion appears needle-shaped and localized. For low SO₂ and sulfate contents, this correlation can be confirmed in the present study for the HW site. No significant amounts of sulfate deposits were found at the HW site, see Table 2. Pits were correspondingly needle-shaped and localized, as shown in Figure 6. Furthermore, a correlation between the amount of sulfate deposition and pit depth cannot be proven. As the amount of deposited chlorides increases analogously to the sulfate content at the different sites (Table 2), these two influencing factors cannot be distinguished from each other in their effect.

5 | SUMMARY AND CONCLUSIONS

Results from an exposure study in the Berlin metropolitan area and Helgoland were presented to determine current values for the corrosion rate after 1 year of atmospheric exposure and the associated corrosivity categories. Values were determined for open and sheltered exposure by using standard specimens according to ISO 9223 and 9226. The most important findings of the exposure study are listed below:

- The corrosivity category of an exposure site is often material-specific. Therefore, the corrosivity category should always be specified with reference to the standard metal.
- A lower corrosion rate and lower corrosivity category tend to be determined under sheltered exposure conditions compared to open exposure. However, this tendency does not allow prognoses about atmospheric durability. No sufficiently reliable statements can be

made about the protective effect of corrosion products and passive layers based on mass loss values from 1-year exposure tests.

- The respective corrosivity categories determined in this study are predominantly within the expected range for rural, urban, and marine atmospheres in Europe under open exposure conditions, except for unalloyed steel at the marine site and copper at the rural site.
- For zinc, localized corrosion phenomena were detected at all exposure sites. These were not significantly linked to chloride and SO₂ influence.
- Aluminum shows localized (pitting) corrosion. Pitting is related to de-icing salt influence and the marine atmosphere.
- The corrosion rate of copper is significantly increased at the investigated rural site and deviates from expectations. The causes could not be elucidated within this study.

Some unexpected results were obtained in the course of this study. These require more in-depth investigations to clarify the causes and mechanisms. However, it cannot be excluded that they are based on the fundamentally changed atmospheric conditions during the last decades. Therefore, the effects of the changed environmental conditions on the formation of corrosion products or passive layers must be reconsidered for the different metals.

The determined corrosivity categories only indicate the corrosivity of an atmosphere. They are subject to annual fluctuations. Statements and prognoses on durability based on first-year values must be viewed critically. Only a more extensive exposure campaign can provide reliable statements on durability. For this reason, a subsequent study will focus on the corrosion progress at the various exposure sites over 5 years.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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