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Surface–rain interactions: Differences in copper runoff for copper sheet of different inclination, orientation, and atmospheric exposure conditions

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A R T I C L E I N F O

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A B S T R A C T

Predictions of the diffuse dispersion of metals from outdoor constructions such as roofs and facades are necessary for environmental risk assessment and management. An existing predictive model has been compared with measured data of copper runoff from copper sheets exposed at four different inclinations facing four orientations at two different urban sites (Stockholm, Sweden, and Milan, Italy) during a 4-year period. Its applicability has also been investigated for copper sheet exposed at two marine sites (Cadiz, Spain, for 5 years, and Brest, France, for 9 years). Generally the model can be used for all given conditions. However, vertical surfaces should be considered as surfaces inclined 60–80° due to wind-driven effects. The most important parameters that influence copper runoff, and not already included in the model, are the wind and rain characteristics that influence the actual rainfall volume impinging the surface of interest.

1. Introduction

Copper (Cu) can potentially be dispersed into the environment from societal sources such as buildings and outdoor structures, the transport sector, and tap water systems (Bader et al., 2011; Bergbäck et al., 2001; Sörme and Lagerkvist, 2002). For buildings and outdoor constructions with copper surfaces in contact with precipitation, many parameters influence the amount of released copper. Its environmental fate and bioavailability were recently summarized in a review (Hedberg et al., 2014). When predicting the load of copper that can be released from naturally aged copper roofs and facades of a given building, or of buildings in a city, an existing predictive model has previously been developed (Hedberg et al., 2014; Odnevall Wallinder et al., 2007, 2004), and field data on copper runoff in dependence of site, inclination, surface area, and average rain characteristics have been generated and published, summarized in Hedberg et al. (2014).

However, the predictive model has mostly been verified with data for surfaces inclined 45° from the horizontal facing south, *i.e.* standardized conditions for corrosion and runoff rate monitoring (ISO 9226, 2012; ISO 17752, 2012). To be accessible and useable for *e.g.* architects and environmental agencies, the model consists of parameters that can easily be obtained for a given site. The model considers the inclination parameter mainly as a measure of the total amount of precipitation impinging vertically on the surface (*i.e.* the meteorological measure of precipitation), without considering any wind-driven effects, varying rain contact durations for different inclinations, or different water sliding/dropping velocities. The model has been criticized for its lack of source data of different inclinations at field conditions (Arnold, 2005; Bielmyer et al., 2012).

Extensive 4-year field exposures were therefore implemented to determine copper runoff rates for copper sheet exposed at four different inclinations (10, 45, 60, and 90° from the horizontal) facing four orientations (north, east, west, and south) at two different urban sites (Stockholm, Sweden, and Milan, Italy). Observed copper runoff rates were compared with corresponding corrosion rates. Copper runoff data from copper sheet (inclined 45° from the horizontal) was further investigated for two marine sites of different characteristics (primarily humidity and chloride deposition) in Brest, France, for 9 years exposure, and Cadiz, Spain, for 5 years exposure. The aim of this study was to elucidate the

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effect of inclination and orientation on copper runoff rate at different sites, compare generated data with the existing copper runoff model, and investigate its applicability for chloride-rich conditions.

2. Methods

2.1. Material

Bare Cu sheet (99.98 wt%) was exposed to determine copper runoff rates (300 cm^2) and corrosion rates (54 cm^2). Single sided samples (reverse side covered with an adhesive Nitto tape) were exposed as-received after being degreased with acetone/isopropyl alcohol and dried with nitrogen gas. Detailed information on the mounting of the samples is given in Goidanich et al. (2011) and ISO 17752 (2012).

2.2. Exposure sites

Cu sheet was exposed for up to 4 years at two urban sites, Stockholm, Sweden (starting May 2009), and Milan, Italy (starting Sept. 2009), *c.f.* Table 1. Environmental conditions of each exposure site are given in Table 1. The sheets were exposed facing north, south, west, and east at an inclination of 45° and 90° from the horizontal. In addition, surfaces were exposed at inclinations of 10° and 60° from the horizontal facing south. Most available literature data reflects exposures of surfaces inclined 45° from the horizontal facing south in agreement with the ISO standards for corrosion rate and metal release rate measurements (ISO 9226, 2012; ISO 17752, 2012). Copper runoff from Cu sheet (45° facing south) was in addition investigated at two marine sites. The exposure at the marine site (300 m from the sea-shore) in Cadiz, Spain started in April 2007 and ended April 2012 (5 years). The exposure in Brest, France (5 m from the sea-shore), started in June 2004 and continued until June 2013 (9 years). Available pollutant-, rain-, and exposure conditions are given in Table 2. The deposition of chlorides was more than 10 times higher compared with the urban sites, see Table 1. Detailed information on chloride deposition rates and seasonal variations in Brest is given elsewhere (Odnevall Wallinder et al., 2014). No exact rain pH values are available for Cadiz. The average annual pH value measured in the blank runoff water (Plexiglas surface) was pH 7.3 ± 0.9. Since the runoff model has only been validated for rain pH values up to pH 6.0 (Odnevall Wallinder et al., 2007, 2004), pH 6.0 was used as the input value to the model for Cadiz, with error bars showing the corresponding difference between pH 6.0 and pH 8.2. For Brest, rain pH data are available for the years 2008–2011 with values of pH 5.7 ± 0.5 (French Corrosion Institute, 2008, 2009, 2010, 2011). Annual average values have been used as input values for the model, and an average value of 5.7 when no data was available. The standard deviation of the annual pH is reflected in error bars of predicted data. The pH value in collected blank runoff water samples in Brest was pH 5.80 ± 0.26.

Table 2
Rain, pollutant, and particulate matter data for Cadiz, Spain, and Brest, France.

Site	Cadiz, Spain (April 2007–April 2012)	Brest, France (June 2004–June 2013)
mm_{rain}	421 ± 129	674 ± 105
Number of rain days	N/A	261 ± 21
Rain intensity (mm/day)	N/A	8.5 (0.2–102)
RH (%)	71 ± 15 (April 2007–April 2008)	84.2 (23–100)
T (°C)	19 ± 5 (April 2007–April 2008)	11.2 (0–32.5)
SO_2 (µg/m^3)	9 (4–46) (2007–2009)	N/A[a]
O_3 (µg/m^3)	53 (2–118) (2007–2009)	N/A[a]
NO_2 (µg/m^3)	22 (3–116) (2007–2009)	N/A[a]
PM_{10} (µg/m^3)	33 (1–697) (2007–2009)	N/A[a]
Chlorides (mg/L)[b]	7.1 (1–20)	618 (4–5030)
Nitrates (mg/L)[b]	2.5 (0.07–23)	46 (0–2030)
Sulfates (mg/L)[b]	3.2 (1.2–9.5)	85 (1–861)

N/A – no data available.

[a] No data available for Brest. Brest is a marine site without any significant influence from industrial sources, or busy streets.

[b] Measured in the blank runoff water (rain water impinging a Plexiglas surface inclined 45° from the horizontal).

Table 1
Rain, pollutant, particulate matter, and wind characteristics during the four-year urban exposure in Stockholm, Sweden, and Milan, Italy.

Site	Stockholm, Sweden				Milan, Italy			
Year	May 2009–2010	May 2010–2011	May 2011–2012	May 2012–2013	Sept 2009–2010	Sept 2010–2011	Sept 2011–2012	Sept 2012–2013
mm_{rain}[a]	399	344	334	277	971	816	502	862
pH_{rain}[b]	5.7 ± 0.7				5.12 ± 0.5			
Number of rain days	136	84	147	130	113	103	75	137
Rain intensity (mm/day)	2.7 (0.2–35.4)	3.3 (0.2–29.6)	2.5 (0.2–19.6)	3.3 (0.03–25.2)	8.8 (0.2–50.2)	8.2 (0.2–42.8)	7.0 (0.2–32.8)	6.5 (0.2–35.0)
RH (%)	74 (15–100)	72 (15–100)	74 (22–100)	71 (21–100)	64 (21–97)	65 (11–99)	62 (21–97)	66 (16–98)
T (°C)	7.3 (−20 to 31)	9.0 (−18 to 30)	8.5 (−15 to 29)	9.2 (−16 to 26)	13 (−9 to 33)	16 (−6 to 36)	14 (−8 to 35)	15 (−2 to 35)
SO_2 (µg/m^3)	1.1[c]	1.1[c]	0.8[c]	N/A	3.1 (1–47)	3.0 (1–93)	3 (1–40)	5 (1–86)
O_3 (µg/m^3)	53 (max. 135)[c]	51 (max. 140)[c]	53 (max. 132)[c]	49 (max. 121)[c]	45 (1–213)	43 (2–205)	44 (1–204)	40 (1–178)
NO_2 (µg/m^3)	13 (max. 80)[c]	14 (max. 84)[c]	11 (max. 88)[c]	12 (max. 90)[c]	61 (1–264)	56 (1–276)	33 (1–185)	36 (3–148)
NO_x (µg/m^3)	N/A				75 (2–804)	72 (1–1005)	48 (1–482)	39 (3–549)
$PM_{2.5}$[d] (µg/m^3)	N/A				29 (1–104)	27 (1–148)	33 (1–171)	30 (1–110)
PM_{10}[d] (µg/m^3)	14 (max. 52)[c]	14 (max. 53)[c]	14 (max. 53)[c]	14 (max. 50)[c]	41 (2–139)	40 (5–157)	50 (2–213)	38 (5–126)
Chlorides (mg/L)[e]	0.6 (0.1–2.0)	0.9 (0.1–2.8)	0.8 (0.4–1.4)	0.7 (0.2–2.1)	0.4 (0–1.1)	0.7 (0.1–2.8)	1.6 (0.5–7.8)	0.5 (0.1–1.0)
Nitrates (mg/L)[e]	1.6 (0.5–3.3)	2.0 (0.8–3.2)	1.5 (0.9–2.7)	1.4 (0.9–3.2)	3.0 (0–9.4)	2.6 (0.9–4.8)	2.9 (1.3–6.6)	2.0 (0.9–3.2)
Sulfates (mg/L)[e]	1.1 (0.3–2.3)	1.1 (0.6–2.0)	1.0 (0.6–1.5)	0.8 (0.4–2.2)	1.4 (0–4.2)	1.1 (0–2.1)	2.2 (0.8–6.5)	1.1 (0.4–2.1)
Wind direction[f]	W > S ≈ N > E	W > S > N ≈ E	W > S > N > E	W > S > N > E	S > E > N ≈ W	S > E > N ≈ W	S > E > N ≈ W	S > E > N ≈ W

N/A – no data available.

[a] Average annual amount of rain (mm) measured at the test site.

[b] Average pH of rain, before interactions with pollutants and particles deposited on surfaces of Cu sheet or Plexiglas, from Grøntoft et al. (2011) and Grøntoft and Ferm (2014). Uncertainties are discussed in the text. pH values in runoff water impinging a Plexiglas blank surface facing south at 10° from horizontal were 5.4 (4.0–6.5) in Stockholm and 6.0 (4.9–6.9) in Milan.

[c] Based on data for Stockholm (urban background) from IVL (2014).

[d] Particulate matter smaller than 2.5 ($PM_{2.5}$) or 10 (PM_{10}) µm.

[e] Measured by means of ion chromatography in runoff water impinging a Plexiglas blank surface facing south at 10° from horizontal.

[f] S – south; E – east; N – north; W – west.

2.3. Runoff rate and corrosion rate measurements

Runoff water from the Cu sheets and the bare Plexiglas fixture (blank) was collected in parallel. The runoff water was continuously collected approximately once a month throughout each 4-year exposure. The reproducibility of Cu runoff measurements from bare Cu sheet has been proven to be sufficient with an approximate error of 5% (exposure of triplicate Cu sheets inclined 45° facing south during the first exposure year in Milan, Italy) (Goidanich et al., 2011). The runoff water was acidified (65% ultra-pure HNO_3) to a pH less than 2 to prevent potential complexation and adsorption, and to dissolve particulate Cu. The total Cu in the runoff water was measured by means of atomic absorption spectroscopy, AAS (Perkin Elmer AAnalyst 800). The detection limit was 0.010 mg/L Cu (three times the highest blank standard deviation). Measured copper concentrations in solution were based on five replicate readings of each runoff water sample. The accuracy of the analysis was assured by continuous verification of the calibration curve and re-calibration if the error was larger than 5%. Corrosion rate measurements were conducted after 1, 2, and 3 years of exposure by stripping corrosion products from the surfaces by using amidosulfonic acid. The experimental procedure is described elsewhere (He et al., 2001a).

3. Results and discussion

3.1. The copper runoff rate is significantly lower compared with the corrosion rate. Both rates depend on surface inclination and orientation

In the following is the immediate total copper release at the copper roof or facade discussed, *i.e.* without any environmental interaction or consideration towards chemical speciation or bioavailability aspects. Estimated rates do hence not reflect, or cannot directly be used to assess any potential adverse effects (Bertling et al., 2006; Boulanger and Nikolaidis, 2003; Gnecco et al., 2008; Hedberg et al., 2014; Kiaune and Singhasemanon, 2011; Pettersen and Hertwich, 2008).

Fig. 1 displays annual copper runoff rates and momentary annual copper corrosion rates for different inclinations and orientations in Milan and Stockholm during the first and third year of exposure. It can be seen that the corrosion rate is significantly higher compared with the runoff rate, independent of site, inclination, or orientation. This is in agreement with previous findings (Faller and Reiss, 2005; He et al., 2001a; Odnevall Wallinder et al., 2004; Odnevall Wallinder and Leygraf, 1997; Sandberg et al., 2006). Corrosion rates are similar in Milan and Stockholm during the first and third year of exposure, despite higher rain amounts and pollution in Milan. However, observed copper runoff rates are higher in Milan compared with Stockholm (factor 1.9, 1.8, 1.2, and 2.3 for the first, second, third, and fourth year of exposure, respectively). This is predominantly explained by approximately twice as high annual rainfall amount in Milan compared with Stockholm, Table 1, as the release of copper into runoff water only takes place during rain events, while atmospheric corrosion also takes place during dry periods (Hedberg et al., 2014).

The surface inclination affects both the copper runoff rate and the corrosion rate, Fig. 1. Generally, a steeper inclination results in lower corrosion and runoff rates due to less amount of water in contact with the surface, observations in agreement with literature findings (Fishman et al., 1987; FitzGerald et al., 2006; Förster, 1996; Odnevall Wallinder et al., 2007, 2004, 2000). The copper runoff rates are more similar for different inclinations, when normalized to the amount of water that actually impinges the surface (the sampled water volume), Fig. 2b. The amount of rain per given time (rain intensity, or rain volume in contact with the surface) is important in addition to the actual water amount impinging the copper surface, Fig. 2b. A higher amount of copper runoff per sampled rain volume is apparent for the vertical surface (90°) that is in contact with the lowest amount of rain water. This finding is in agreement with previous investigations on the effect of rain intensities and inclination on the copper runoff rate (He et al., 2001b), where higher copper runoff rates were observed for lower rain

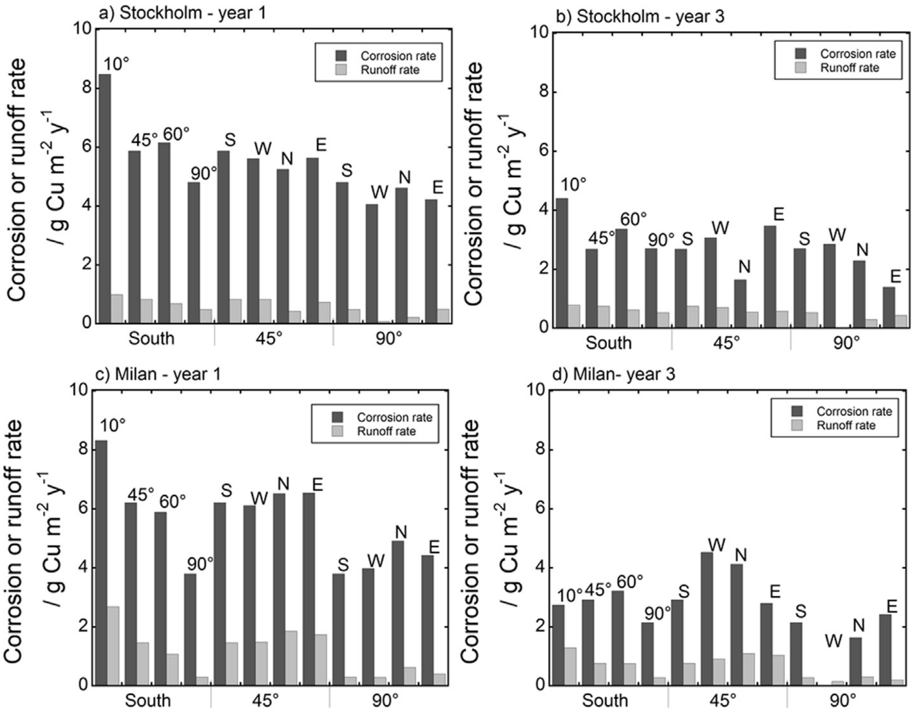

Fig. 1. Annual momentary corrosion and runoff rates in Stockholm (a–b) and Milan (c–d), shown for exposure years 1 and 3 (S – South, W – West, N – North, E – East).

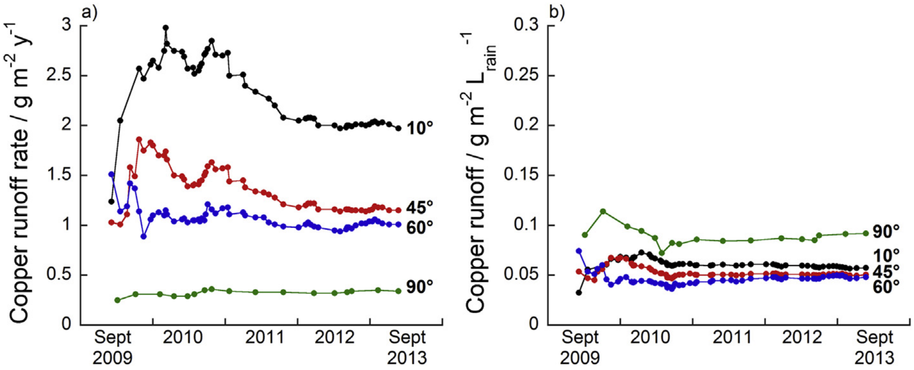

Fig. 2. Changes in copper runoff rate with time per surface area (a) compared with copper runoff normalized to the rain amount actually impinging each surface (b), for copper sheets exposed at different inclinations facing south in Milan, Italy. The lines are only for guidance of the eye.

intensities due to longer contact and interaction time between the copper surface and the rain. The effect of surface inclination on the runoff rate of copper sheet is more pronounced for surfaces exposed in Milan compared with Stockholm, Fig. 1. This might be related to the coastal location of Stockholm with relatively high wind intensities, further discussed in section 3.2.

The relative influence of the orientation was most pronounced after longer exposure time for the observed corrosion rates (deviation from the mean value of all orientations of <15%, <50%, <100%, for the first, second, and third year of exposure, respectively, in Stockholm and Milan). This could be explained by the fact that the corrosion rates decrease with time due to the formation of a protective patina of poorly soluble corrosion products and hence an increased relative influence of the prevailing wind direction and deposition of pollutants. No similar trend was observed for annual copper runoff rates, which depend more on the annual rain amount and wind directions during rain events (discussed in section 3.2.).

3.2. Prevailing wind characteristics during rain events affect the copper runoff mainly by the rainfall volume that impinges the surface

Annual wind directions did not correlate with the copper runoff of the different orientations in neither Milan nor Stockholm. In Milan, the copper runoff followed the trend N > E > W > S for copper surfaces inclined 45° (all four years), and N > S > E > W for surfaces inclined 90° (years 2–4), despite annual average wind directions of S > E > N ≈ W (Table 1). In Stockholm, the copper runoff followed different trends for the different inclinations and years, but never correlated with the average wind directions of W > S > N > E (Table 1). The effect of wind speed and rain amount during rain events in dependence of the wind direction in Stockholm was therefore investigated during the four-year period (monitored continuously with a resolution of 0.5 h), Fig. S1 (supporting information). Fig. 3a shows the annual copper runoff in Stockholm in dependence of surface orientation (45 and 90°). It is evident that the orientation has a larger impact on vertical surfaces, with nearly no copper runoff for surfaces facing west, in contrast to surfaces inclined 45° from the horizontal, Fig. 3a. This is mainly explained by significantly lower precipitation volumes (3 L for vertical surfaces facing west compared with 13–19 L for surfaces facing east, south, or north, for the entire 4-year exposure). This is reflected by higher rain amounts from east, north, and south, compared with west (Fig. S1, bottom). The difference between orientations is much smaller when normalized on the rain amount actually impinging each surface (sampled volume), Fig. 3b. Some single rain events and westerly winds after long dry periods, Fig. S1 top, and dry deposition of particles and pollutants predominantly taking place on surfaces orientated towards west, Table 1, can possibly explain relatively higher copper runoff values normalized to the rain amount (Fig. 3b) of westerly facing surfaces during the second to fourth year of exposure compared with the first year.

In all, the precipitation volume actually impinging each surface is the single most important factor, but strongly depends on surface orientation and inclination, and on prevailing wind characteristics. The wind characteristics during single rain events are important and not necessarily identical with dominating annual wind directions. For example, westerly winds were dominating in Stockholm throughout the four-year exposure, Table 1, whereas this wind direction was not typical during rainy episodes characterized by large rainfall quantities, Fig. S1.

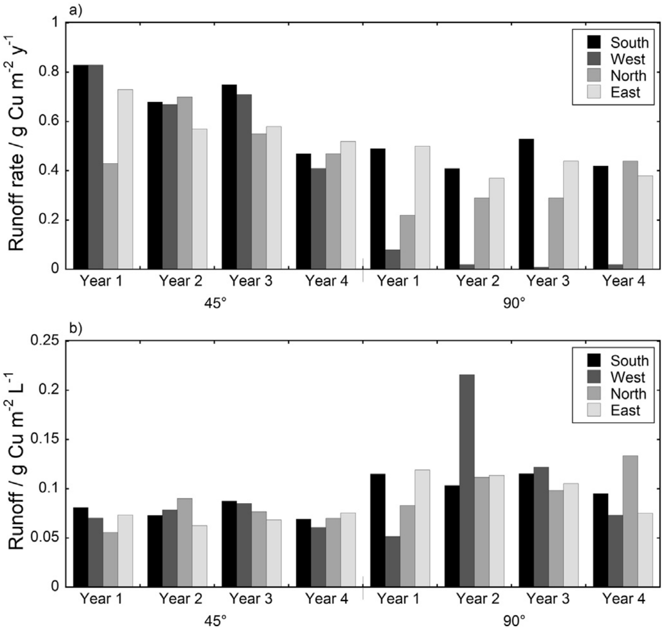

Fig. 3. Annual runoff rates (a) and runoff rates normalized on the rain amount actually impinging the surface (b) during four years of exposure of copper sheets inclined 45 and 90° from horizontal in Stockholm, Sweden.

3.3. The effect of surface inclination on copper runoff depends on rain amount, interaction (contact) time, and patina characteristics

Several studies conclude that the rain amount (rainfall volume), rain pH (hydrogen ion wet deposition), and SO_2 (dry deposition) are important parameters to consider when predicting total copper runoff rates from copper surfaces (Cramer et al., 2002; Odnevall Wallinder et al., 2007, 2004). The amount of rain that actually impinges a copper surface is often unknown, and is therefore estimated from known annual rainfall quantities. Since the amount of rain that interacts with the copper surface is dependent on surrounding buildings, prevailing wind conditions, surface orientation and inclination, the estimated annual rainfall quantity may be erroneous. Variations in rainfall quantities in contact with a copper surface due to differences in surface inclination (proportional to cos (θ)), based on geometry, have been taken into account in the model by Odnevall Wallinder et al. (2007):

$$R = \left(0.37\ \mathrm{SO}_2^{0.5} + 0.96\ \mathrm{rain}\ 10^{-0.62\mathrm{pH}}\right)\ \left(\cos(\theta)/\cos(45^\circ)\right) \qquad (1)$$

where R is the annual copper runoff rate (g m^{-2} y^{-1}), SO_2 the atmospheric concentration of sulphur dioxide (μg m^{-3}), rain the annual rainfall quantity (mm y^{-1}), pH the rain pH, and θ the surface inclination/angle from the horizontal (degrees). 1 mm rain equals 1 L rain per a 1 m^2 horizontal surface area (meteorological term).

This model has mostly been verified for European sites (due to scarce data from other global sites) and does not consider the contribution of chlorides (marine sites) (Hedberg et al., 2014). It may however be applicable for marine sites, as discussed in section 3.4. Its consideration of inclination is mostly based on the assumption that the rain quantity is the most important parameter affected by inclination, and primarily verified by few laboratory data (Hedberg et al., 2014; Odnevall Wallinder et al., 2007, 2004, 2000). The model does not take into account the effect of wind, and predicts no copper runoff for vertical copper surfaces. This is however, as stated, not representative for windy conditions, *c.f.* Figs. 1–3.

As previously discussed, the wind affects the amount of rain that actually impinges the surface. This influences both the copper runoff from surfaces of different orientation, Fig. 3, and surfaces of different inclination, Fig. 4a and b. In Milan the copper runoff is

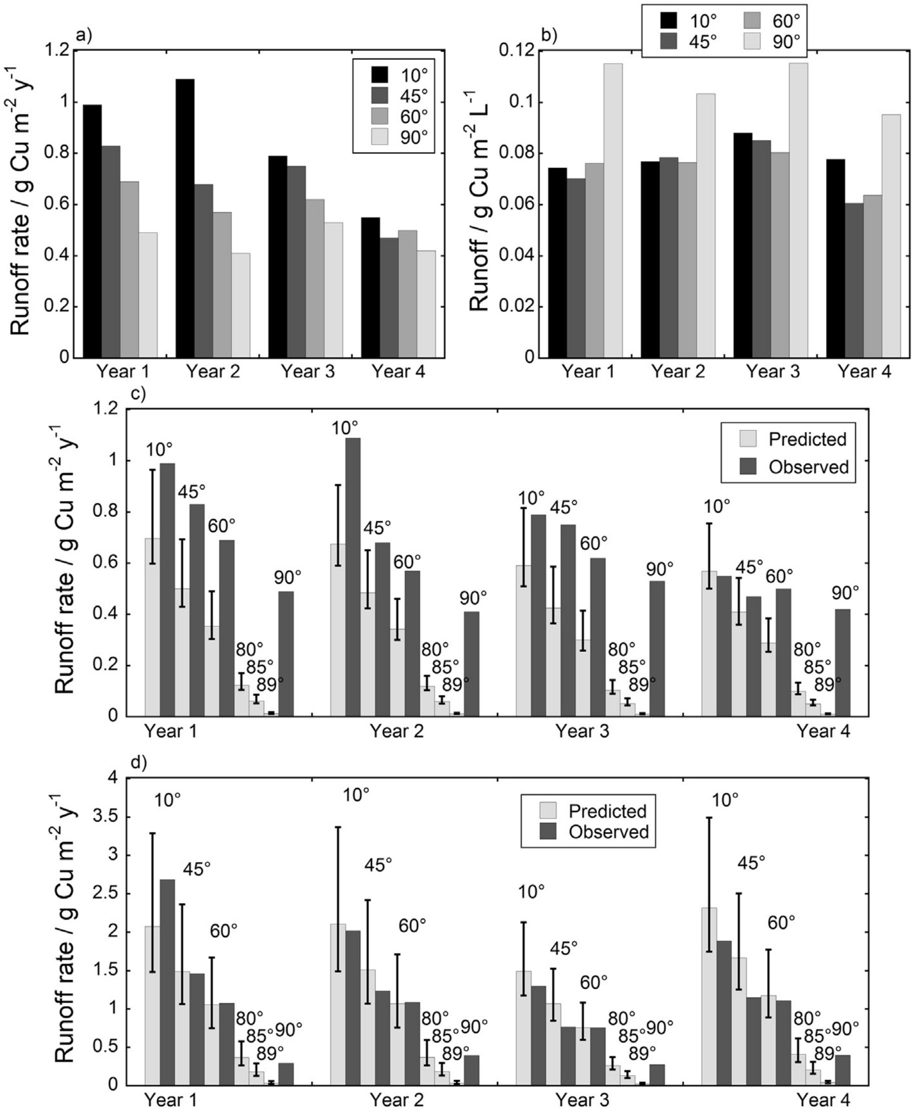

Fig. 4. Annual copper runoff rate (a) and annual copper runoff normalized to the actual rain amount impinging each surface (b) in Stockholm for surfaces inclined 10, 45, 60, and 90° facing south. Comparison of predicted (eq. (1), input values in Table 1) and measured annual copper runoff rates from copper sheets facing south in Stockholm (c) and Milan (d). The error bars of the predicted data reflect the standard deviation of the pH values (Table 1).

higher per given rainfall volume for vertical surfaces compared with surfaces inclined 10, 45, and 60°, due to lower rain intensity on these surfaces. Since the wind had a stronger influence on the amount of impinging rain in Stockholm compared with Milan, model predictions of copper runoff compared with observed data are expected to be more erroneous for Stockholm compared with Milan, and more erroneous for vertical surfaces compared with inclined surfaces. Fig. 4c and d shows a comparison of predicted and observed copper annual runoff rates for Stockholm and Milan, respectively. While the model underestimates the annual copper runoff in Stockholm and for vertical surfaces (Stockholm and Milan), it overestimates the annual copper runoff in Milan. This is explained by the fact that the model does not account for rain intensities. Rain intensities in Stockholm are on average 50% lower compared with Milan, indicated by the same number of raining days, but half the annual rain amount in Stockholm compared with Milan, Table 1. The vertical surfaces are partially underestimated due to the same reason (lower rain intensities, see Figs. 2b and 4b) and mostly because that the model assumes that the rain impinges vertically, which is often not the case. We propose therefore that an inclination of 90° is not used as input value for the model for unsheltered vertical surfaces, but rather 60–80° as a maximum inclination, depending on wind characteristics.

Observed annual copper runoff rates decrease with time in both Milan and Stockholm compared to predicted values. This is predominantly related to the formation of a more protective patina of less soluble corrosion products with time. This has recently been shown for copper sheet exposed in Stockholm up to 17 years (Hedberg et al., 2014), and was most significant for naturally aged surfaces (130 years in Stockholm). The model is hence more valid for short (<10 years) exposure compared with longer (>10 years) exposures, for which the model overestimates the runoff rate.

Despite the amount of precipitation, surface inclination might theoretically also affect the contact time and sliding/dropping properties of the rain, aspects that have not previously been investigated in this context. The copper patina might affect these parameters as well. For an ideal surface and a single water drop, the contact time of a water droplet is proportional to $\sqrt{(1/\sin\theta)}$, and after approximately one second, proportional to $1/\sin\theta$ due to friction (*c.f.* supporting information). However, the copper patina surface is non-ideal and often porous. Static contact angle values of 91° (fresh copper surface), 103–105° (8–40 weeks aged brown patina), and 33–43° (100–145 years aged green patina) have been measured (Zhang et al., 2002), indicative of largely varying wetting properties depending on the patina type, thickness and age. The droplet height was further unchanged for 10 s for fresh copper, but changed significantly for aged copper (mostly for 145 years aged green patina) (Zhang et al., 2002), showing significant differences in porosity. For a water droplet in contact with the patina surface, the porosity and surface wettability will affect its sliding velocity and the critical inclination, where it starts to slide (Kim et al., 2002). Furthermore, the copper surface is not in contact with single water droplets but exposed to rain events of varying intensity. Intense rain events will result in a relatively lower number of water droplets in direct contact with the copper surface due to rolling and spreading drops, and a bulk water film. This results in relatively higher amounts of copper in the runoff water per given precipitation volume for vertical surfaces, and hence higher observed copper runoff rates in Stockholm compared with Milan from these surfaces.

The rain pH is largely influencing predicted values (Cramer et al., 2002; Odnevall Wallinder et al., 2007, 2004). Due to dissolution of particles and gaseous species in collected rain water, it is often changed when compared to the initial rain pH impinging the surface. Standard deviations of the annual pH (0.7 for Stockholm and 0.5 for Milan) are largely affecting predicted values, as evident from the error bars in Fig. 4c and d. Care should therefore be taken with pH input values, and uncertainties need to be considered in any runoff prediction.

3.4. The copper runoff at marine sites can be predicted despite different chloride deposition rates

At marine sites, high chloride deposition rates result in higher corrosion rates compared with lower chloride-rich environments. For example, observed momentary annual corrosion rates in Cadiz, Spain, and in Brest, France were approximately four times higher compared with the urban sites Stockholm, Sweden, and Milan, Italy (4.9 ± 1.7 (Stockholm), 3.7 ± 1.9 (Milan), 11.7 ± 8.3 (Cadiz), and 11.1 ± 4.5 (Brest) $g\ m^{-2}\ y^{-1}$). However, observed copper runoff rates are not as strongly affected as corrosion rates by high deposition rates of chloride. This is further elucidated by lower copper runoff rates per given rainfall volumes (in mm, see above) at the marine sites compared with the urban sites: 0.0009 $g\ m^{-2}\ mm_{rain}^{-1}$ in Cadiz, 0.0012 $g\ m^{-2}\ mm_{rain}^{-1}$ in Brest, 0.0020 $g\ m^{-2}\ mm_{rain}^{-1}$ in Stockholm, and 0.0013 $g\ m^{-2}\ mm_{rain}^{-1}$ in Milan, for each exposure period. These results elucidate that the presence of chlorides does not enhance the extent of copper runoff at these sites and that the model can be used also for such sites for long-term predictions.

This is illustrated in Fig. 5 by observed annual copper runoff rates and corresponding predicted rates by the model (Eq. (1)). In Cadiz (significantly lower chloride deposition rates compared with Brest), the model overestimates the measured copper runoff throughout the 5-year exposure (133 ± 24%). In Brest, the model underestimates the copper runoff during the first three years of exposure (39 ± 12%), while it estimates the runoff sufficiently during the following four years (within ±22%), and overestimates the copper runoff the last two years (50 and 99%). This is explained by the fact that higher initial corrosion results in a fast formation of a more protective patina of poorly soluble corrosion products (Graedel et al., 1987; Graedel, 1987; Hedberg and Odnevall Wallinder, 2011; Hedberg et al., 2014; Krätschmer et al., 2002),

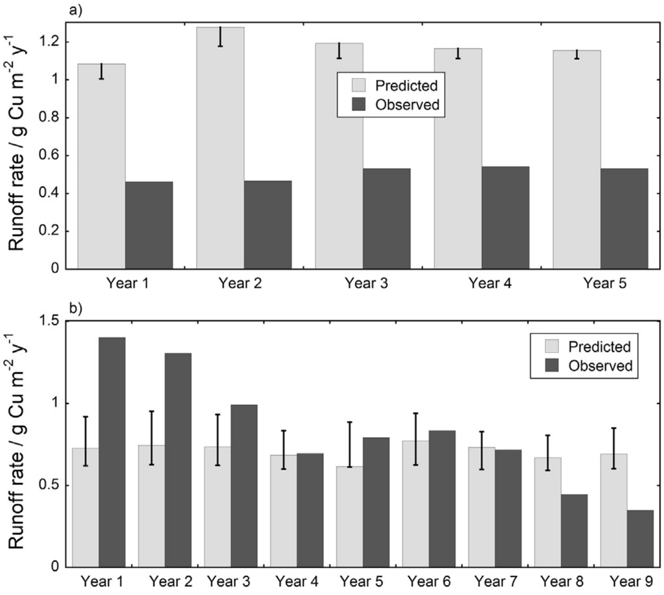

Fig. 5. Comparison of predicted (eq. (1)) and observed annual copper runoff rates from copper sheet (inclined 45° from the horizontal, facing south) at the marine sites of Cadiz, Spain, for 5 years exposure (a) and Brest, France, for 9 years exposure (b). The error bars of the predicted data reflect the standard deviation of the pH values (+ pH 1.2 for Cadiz and ± pH 0.50 for Brest).

with the consequence of lower copper runoff. This is in agreement with the observation that the model tends to overestimate the copper runoff after some years of exposure for surfaces that are exposed to the highest initial corrosion (for example 10° inclined surfaces in Milan and Stockholm).

4. Conclusions

Copper runoff from copper sheets exposed at atmospheric conditions at four different inclinations (10, 45, 60, and 90° from the horizontal), facing four orientations (north, east, west, and south) at two different urban sites (Stockholm, Sweden, and Milan, Italy) has continuously been monitored during a 4-year period. Observed rates were compared with corrosion rates and with predictions using an existing predictive copper runoff rate model. The applicability of the model to predict copper runoff rates for copper sheet exposed at marine conditions was investigated using long-term runoff rate measurements of copper sheet (45° from the horizontal, facing south) in Cadiz, Spain, for 5 years exposure, and Brest, France, for 9 years exposure. The following main conclusions were drawn:

1. Runoff rates were significantly lower compared with corrosion rates, 53–99.6%, and did not necessarily follow the same trends. Corrosion rates can therefore not be used to predict copper runoff rates.
2. The actual precipitation volume impinging the copper surface was the single most important parameter affecting the copper runoff.
3. The actual precipitation volume was strongly dependent on inclination, orientation, and wind characteristics during rain events.
4. General annual wind information can not directly be used to predict the dependence of orientation on the precipitation volume. For example, westerly winds were predominating in Stockholm during the entire investigated period, but the actual precipitation volume was lowest for surfaces facing west compared with other orientations.
5. The rain intensity (precipitation amount per given time) was the second most important parameter resulting in relatively higher copper runoff for vertical surfaces, and for the low rain intensity site of Stockholm when compared with predicted values.
6. The existing copper runoff model overestimates the copper runoff for sites with high rain intensity (Milan) and long-term exposures (<45%), but underestimates the copper runoff for vertical surfaces (<98%) and sites of low rain intensity (<49%).
7. Predictions of copper runoff from facades (vertical surfaces) should, due to wind-driven effects, be considered as surfaces inclined 60–80°.
8. The existing copper runoff model is applicable also for marine sites although it tends to overestimate the copper runoff at marine sites (<156%) due to high corrosion rates and rapid formation of a patina of high barrier properties and poorly soluble corrosion products at these sites. At sites of very high chloride deposition rates (Brest), the model underestimates the copper runoff only during the first years of exposure (<48%).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.11.003.

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