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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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ABSTRACT

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.