Critical Review: Copper Runoff from Outdoor Copper Surfaces at Atmospheric Conditions

Yolanda S. Hedberg,[‡] Jonas F. Hedberg,[‡] Gunilla Herting,[‡] Sara Goidanich,[†] and Inger Odnevall Wallinder*[,‡]

[‡]KTH Royal Institute of Technology, Department of Chemistry, School of Chemical Science and Engineering, Division of Surface and Corrosion Science, Drottning Kristinas väg 51, SE-100 44 Stockholm, Sweden

[†]Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, P.za Leonardo da Vinci 32, 20133 Milano, Italy

INTRODUCTION

Before the early 1990s, atmospheric corrosion of copper sheet used for roofing and facades was mainly investigated to make service life predictions and to study corrosion (oxidation) mechanisms and patina formation.[1−7] Since then, copper runoff (or release) from such surfaces has increasingly been investigated and assessed due to an increased awareness of potential environmental risks induced by the diffuse dispersion of metals from various sources in the society. Building and outdoor constructions were early identified as potential sources of metals, including copper, together with contributions from the transport sector and tap water systems.[8,9] As a consequence, restrictions and legal actions were implemented in different countries including Sweden, Germany, Switzerland, and some states in the US to limit the use of copper in outdoor constructions and thereby the dispersion of copper. Triggered by this environmental concern, a novel research area within atmospheric corrosion was implemented and directed toward metal runoff to assess the diffuse dispersion of copper from corroded surfaces and the environmental fate of released copper from an applied and a fundamental perspective. As a consequence, the topic has primarily been investigated for only a few decades by a limited number of research groups and with

the authors as one of the pioneering groups, as reflected in this review.

Copper runoff from outdoor surfaces is in this context defined as the amount of copper released, primarily by the action of rainwater, from naturally aged and corroded copper surfaces. It is governed by electrochemical and chemical corrosion and dissolution processes from a given copper surface into the environment either directly or via stormwater systems to different recipients. Copper runoff is sometimes referred to as "leaching".[10] However, as this term describes the transfer of a metal from a solid sample into an extraction solution,[11] often induced by chemical dissolution processes, it is not a sufficient or either a relevant description of the complex metal runoff processes at outdoor atmospheric conditions. The importance of copper roofs and facades as significant sources of the total amount of the diffuse dispersion of copper is largely debated in cities such as Stockholm, Sweden, having a long tradition of using copper in outdoor applications. Some studies claim copper released from copper roofing in Stockholm

(623,000 m^2)[12] to aquatic recipients as negligible[13] (based on measurements), whereas other findings entitle roofing as a major source for the diffuse dispersion of copper[14] (based on modeling). Due to metal concentrations exceeding drinking water directives, direct collection of runoff water from metal roofs (copper and many other metal roofs) should not be used for drinking purposes, a fact that historically has been unknown[15] and that recently has been elucidated for roof runoff water in Nigeria.[16] In the European Union, an environmental risk assessment agreed on a generic predicted no effect concentration of 7.8 μg L^{-1} for copper.[17] Frequent reports show a rapid reduction in total concentrations and bioavailable copper fractions of roof runoff water to background levels upon environmental interaction (contact with e.g. organic matter, solid surfaces such as soil, concrete, limestone, etc.).[18−22]

Data on the diffuse dispersion of copper runoff from outdoor constructions is crucial to *i*) assess potential environmental risks, *ii*) identify copper emissions at specific sites that may potentially cause adverse effects[8,15,23,24] and provide counter-measures if necessary, and *iii*) provide a scientifically based general understanding of the copper runoff process for the sustainable use of copper in outdoor constructions and for risk management. All these evaluations should be based on runoff data and not corrosion data.

The aim of this review is to provide an overview of *i*) influencing factors on copper runoff from copper outdoor surfaces at atmospheric conditions and *ii*) available literature and predictive runoff rate models for outdoor surfaces and *iii*) to critically discuss the importance of environmental fate and speciation for accurate risk assessment. The main focus is on *unsheltered naturally patinated copper* surfaces used for roofing and facade applications. However, general findings are also relevant for artificially patinated copper,[25,26] copper-based alloys,[27−29] zinc[6,30−44] and zinc-based alloys[30,33,34,36,39] and other metals,[44−48] and alloys[45,47−49] used in outdoor applications.

ATMOSPHERIC CORROSION AND RUNOFF
Several environmental and climatic parameters influence the extent of copper runoff from a given copper surface (Figure 1).
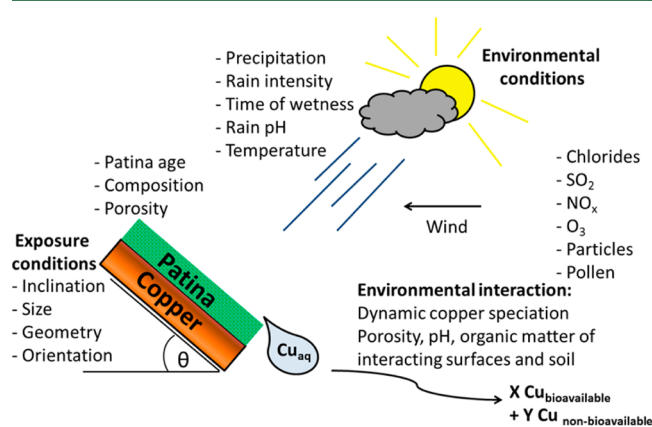

Figure 1. Main environmental, exposure, and surface parameters that influence the runoff process of copper from copper surfaces and its further environmental interactions (fate) at atmospheric conditions. "Bioavailable Cu" is defined as the released fraction that potentially can be absorbed by an organism, i.e. copper in a bioavailable chemical form.

Even though factors that influence atmospheric corrosion mechanisms and copper patina formation also influence the copper runoff process, corrosion data cannot be used to assess copper runoff. This has clearly been elucidated in several scientific publications, where corrosion rates (from mass loss measurements) and runoff rates from copper surfaces (continuous monitoring of the total amount of copper released from the corroded surface by the action of rainfall) were investigated in parallel.[26,32,35,45,50−56] Mass loss measurements require that the copper content within the patina, i.e. the oxidized mass of copper, is determined, hence the initial (unexposed) total mass of the copper sheet and the patina composition have to be known.[52] Since corrosivity measurements, following the ISO standard,[57] at different sites predominantly involve one-year corrosion rate measurements of fresh copper sheet, available corrosion rate data predominantly reflects the gradual evolvement of a protective patina and does not reflect its long-term rate of oxidation. Estimations based on patina composition and mass gain can be highly misleading, as prevailing exposure conditions prior to sample withdrawal govern generated findings and as corrosion product compositional assumptions (e.g., relative amounts) have to be made. Comparison of annual runoff rates and corrosion rates of copper sheet exposed at identical conditions at different sites (marine, rural, and urban) up to several years of exposure show that the corrosion rate is highly time-dependent with a strongly decreasing trend during the first years as the corrosion patina gradually evolves, while the annual runoff rate is relatively constant, or only slightly reduced with time. The runoff rate is significantly lower ($\leq$20%) compared with the corrosion rate during the first year(s) of exposure.[26,32,45,53,56] From this follows that most corroded (oxidized) copper remains within adhering corrosion products of the patina and is not released from the surface by the action of impinging rainwater directly into the environment or stormwater systems. Significantly lower corrosion rates compared with runoff rates have been estimated by means of electrochemical methods during single simulated rain events.[54] This is explained by the fact that copper is only released (by chemical and electrochemical processes) from the surface during a rain event, while corrosion processes are ongoing also under both dry and cyclic dry and wet (humid) periods. In another study, equal or lower corrosion rates compared to runoff rates were assumed based on total mass change measurements (not separately considering the patina weight),[44] which is an erroneous conclusion due to the contribution of noncopper patina constituents (e.g., O, S, Cl), the influence of particle deposition, and prevailing environmental conditions prior to sample withdrawal.[52] Recent unpublished long-term data for Stockholm, Sweden (urban, low-polluted) and different urban, marine, and industrial sites (Brest, France; Duisburg, Germany; Milan, Italy; Cadiz, Spain; and Madrid, Spain) all show that the annual copper runoff rate is significantly lower than the corrosion rate.[58] The copper runoff rate remains relatively constant or decreases with time for exposure periods up to 5 and 16 years (Stockholm) (see also Figure 2c), whereas the annual corrosion rate decreases with time (for exposure periods up to 5 years).[58] The runoff rate is still lower than the corrosion rate ($\leq$25%) for all sites and exposure time periods (up to 5 years) investigated.[58]
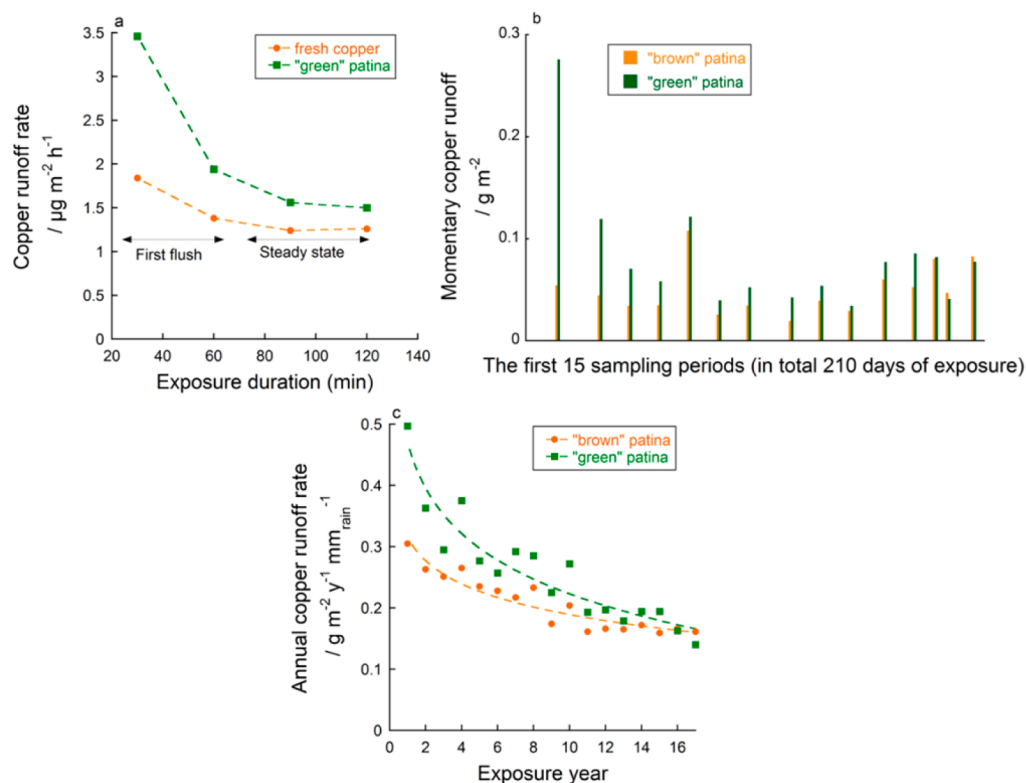
Figure 2. Momentary copper runoff rates within a rain event (a, rain intensity 7.8 mm h^{-1}, laboratory data, from ref 31), over several months (b, from ref 97 and unpublished data[58]), and over 17 years, 1996−2013 (c, normalized to annual rain precipitation, from refs 25 and 74 and unpublished data[58]), of outdoor exposure in Stockholm, Sweden. Patina color: Freshly exposed copper sheet ("brown" patina) and a 130 years old (pre-exposed in Stockholm, Sweden) with "green" patina.

■ INFLUENCE OF EXPOSURE CONDITIONS ON COPPER RUNOFF

Several on-site investigations have shown the extent of atmospheric corrosion of copper roofs and facades to be strongly influenced by the surface geometry, orientation, inclination, prevailing wind direction, and degree of sheltering.[4,7,59,60] For example, copper facades (vertical, 90° from the horizontal) were significantly less corroded compared with horizontal surfaces.[4] To this date, many studies have reported the importance of *building geometry*,[61] *size*,[38,62] *inclination*,[38,52,53,63] and *orientation*[6,38,62−64] on the extent of corrosion and copper runoff from roofs and facades, factors that all govern the time and amount of rainwater in contact with the corroded surfaces, Figure 1. Many studies and prediction models therefore conclude that the runoff rate must be normalized to the geometrical surface area[52,53,60,61,65,66] and the surface inclination.[52,53] Any comparison based on copper concentrations directly without such normalization is highly erroneous when comparing findings of different sites.[52,53,67] The comparison between different sites and years of exposure require further normalization to the annual rainfall quantity.[52,53] Most reported studies are conducted on surfaces inclined 45° from the horizontal facing south following the ISO standard for corrosion rate measurements,[57] lately also standardized for runoff rate measurements.[68] The surface orientation is mainly important due to the difference in prevailing wind directions and as a consequence the amount of rain impinging the surface,[38,64] and for dry deposition of corrosive species.[6]

■ INFLUENCE OF ATMOSPHERIC CORROSIVE SPECIES ON COPPER RUNOFF

Atmospheric aerosols containing sodium chloride, ammonium sulfate/chloride, and gaseous pollutants such as sulfur dioxide, ozone, hydroxyl radicals, hydrogen peroxide, hydroperoxyl radicals, nitrogen mon- or di oxide, and ammonia are well-known to strongly influence the atmospheric corrosion of copper.[1,3,51,62,69−73] Particle aerosols are deposited on any surface. Depending on exposure site, this may also involve deposition of metals transported from other natural or anthropogenic sources. Runoff measurements therefore require parallel reference measurements of an inert surface (blank).[68] Except for influencing the kinetics of the initial corrosion reaction, the pollutants also influence the patina composition, and hence the solubility and barrier properties of its corrosion products, and thereby subsequent copper runoff and corrosion processes. Most studies conclude sulfur dioxide to be the most potent pollutant for copper,[5,6,50,52,53,60,74] followed by its synergy effects together with ozone, and to a lower extent with nitrogen dioxide.[50,53,75,76] Gaseous SO_2 concentration levels at urban and rural sites of the western part of the world have during the last decades shown decreasing trends,[77] e.g. Stockholm, Sweden, and thereby significantly reduced corrosion rates and to some extent also reduced runoff rates. Predictions for the 21st century show even further reduction on SO_2 levels and corrosion rates in e.g. Europe and Northern America, however increasing trends in e.g. Asia and Africa.[77] Nitrogen dioxide has by itself no corrosive action.[70,78] However, enhanced corrosion is evident due to synergistic effects between SO_2 and NO_2 and even more pronounced between SO_2 and O_3.[50,53,75,76] The presence of chlorides (e.g.,

at marine sites) enhances the corrosion rate of copper compared with non-chloride environments.[1,26,79,80] However, when comparing the release of copper from copper sheet for a given rainfall quantity at a marine site and an urban site, the runoff process was not enhanced by the presence of chlorides. The release of copper was instead depressed due to long wet periods that resulted in rapid crystallization of corrosion products, limited first-flush contribution of released copper, and fewer dissolution reprecipitation events.[26] The effect was recently further confirmed in unpublished data comparing the annual copper runoff rate at two marine sites and three urban sites for up to 5 years of exposure (see also Figure 3).[58] Microorganisms such as bacteria and fungi have shown to influence copper corrosion.[81] However, no reports have elucidated biocorrosion in relation to copper runoff, a topic for further investigation. However, the fungicidal properties of copper have been shown to reduce the amount of fungal species compared with other metals,[82] which may imply that microorganisms play a minor role for copper runoff.

■ INFLUENCE OF PRECIPITATION AND RAIN CHARACTERISTICS ON COPPER RUNOFF

Both the relative humidity and the temperature largely influence atmospheric corrosion of copper by determining the thickness (and conductivity) of the aqueous adlayer, even during dry (nonrainy) periods.[1,3,69,75] A thicker aqueous adlayer will in general result in higher corrosion rates, which also are enhanced by repeated dry and wet cycles.[1] In contrast, copper runoff from outdoor surfaces mainly occurs by the action of rainfall (and during severe damp conditions), that transports dissolved copper from the patina (see also Figure 2b).[53] Without the action of rainwater, dissolved copper will reprecipitate as corrosion products during subsequent dry periods. Copper runoff is not only influenced by prevailing rain event characteristics (quantity, duration, frequency, pH, and intensity) and the presence of environmental pollutants but also by climatic (humidity, temperature) and environmental conditions during dry/wet periods preceding the rain event.[31] The quantity (mm), intensity (e.g., mm h^{-1}), and duration (min to h) of a rain event determine the contact period and hence the reaction time between the patina and the impinging rainwater.[5,6,26,29,31,32,38,42,50,51,53,63,64,83] If these parameters are unknown for a given rain event, but general rain and wind parameters are known, the orientation of the copper surface, its inclination, and the prevailing wind intensity and direction can be considered to estimate the amount and intensity of the rain actually impinging the surface.[52] When the temperature is below the freezing point of water at given conditions, atmospheric corrosion of copper is significantly reduced.[84] Snow and rainfall, to a lesser extent, are efficient scavengers of atmospheric pollutants, particles, and aerosols.[85] The water layer upon snow melting contains hence very high amounts of pollutants and particles[86] that may enhance the release of copper during the subsequent runoff event. When investigating the effect of the early spring snowmelt on the momentary copper runoff from copper sheet exposed up to 16 years in Stockholm, Sweden (exposure start in 1996), a slight to significant effect (up to 2-fold compared with average values) was observed for some years (6 out of 16) after long (>1 month) periods with snow. This effect was more pronounced for a 130-year old naturally patinated green copper sheet compared with a freshly exposed naturally brown patinated copper sheet.[58] The same effect is also evident during a rain

event that shows a lower pH of the first rainwater portion compared with the subsequent rain volume.[87] The pH and buffering capacity of rainwater hence vary during a rain event and depend on prevailing concentrations of gaseous pollutants, particle aerosols, and organic matter.[3,52,53] The rain pH has been reported to largely influence both copper corrosion and copper runoff, as a lower pH enhances both copper corrosion and runoff.[31,42,52,53,61,88] The annual rainfall quantity[52,53] and the rain pH[52,53,61] have been used in simplified predictive models of copper runoff from copper roofs and facades (discussed below).

■ INFLUENCE OF SEASON AND TEMPERATURE ON COPPER RUNOFF

Some studies have investigated the effect of starting season (winter, spring, etc.) on the copper runoff rate.[51,64] Short-term differences related to differences in relative humidity were observed, whereas no significant differences were observed on a long-term perspective.[51] Other important parameters that vary with the season are e.g. pollutant levels, number and duration of rainfall events, wet periods, and the deposition of organic matter such as pollen or pine needles. Pollen and pine needles are not directly involved in the corrosion reaction but can *i*) act as transport aerosols for other pollutants, *ii*) influence the rain pH and the pH of the runoff water, and *iii*) complex with released copper and reduce its bioavailability. The temperature, which is known to influence atmospheric corrosion of copper, is also related to the season.[6,84] So far, no systematic investigation exists on the effect of temperature on copper runoff.

■ INFLUENCE OF PATINA COMPOSITION AND CHARACTERISTICS ON COPPER RUNOFF

Several studies,[2,3,26,32,51,54,59,76,89−95] of which some are detailed reviews,[2,3,90] have reported on the copper patina composition at atmospheric conditions in dependence of site, gaseous pollutants, and chlorides. The most abundant stable patina constituents formed at unsheltered urban and rural outdoor conditions include cuprite (Cu_2O), posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$), and brochantite ($Cu_4SO_4(OH)_6$) (and antlerite, $Cu_3(SO_4)(OH)_4$, at highly SO_2-polluted conditions). Corresponding constituents at marine sites include atacamite/paratacamite ($Cu_2Cl(OH)_3$). Other sulfur- and/or chloride containing constituents (e.g., $CuCl$, $CuSO_4 \cdot nH_2O$) are less stable and therefore either transformed or released (washed) from the surface. They may however still be present in lower amounts. Besides aesthetic aspects,[28] the importance of the copper patina composition on the copper runoff process can be summarized by *i*) increased copper runoff (specifically during the first flush portion of a rain event) due to a gradually increased surface area (porosity, roughness)[25,31,42,47,53,54,63,96,97] and the formation of soluble copper corrosion products[44,60] and *ii*) reduced copper runoff with time due to the formation of stable and poorly soluble copper corrosion products of high barrier properties.[21,26,32,98] These two effects are illustrated in Figure 2, showing higher runoff rates for the thicker and porous green patina (pre-exposed for 130 years) compared with freshly exposed copper sheet during the first flush (discussed in the next paragraph) of single rain events (Figures 2a and 2b), and less evident differences and reduced rates after 12−17 years of parallel exposure (Figure 2c) as a result of improved barrier properties of the patina on both
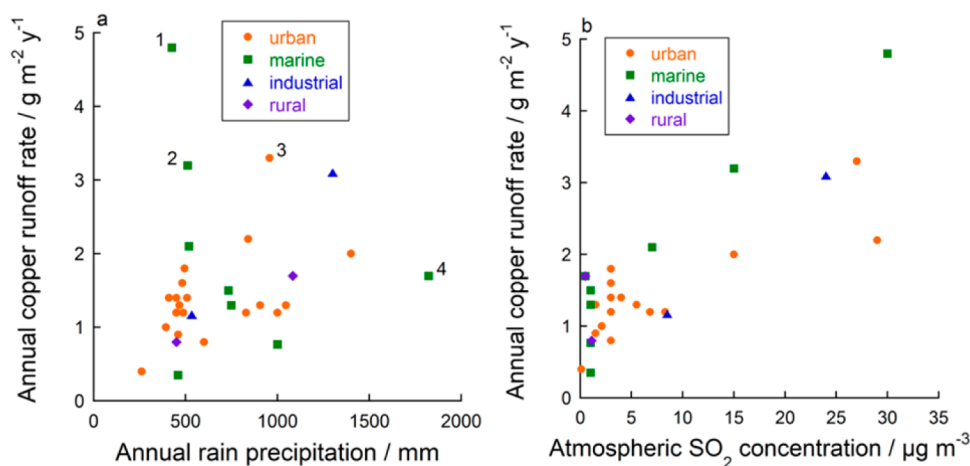
Figure 3. a) Literature data[5,6,21,25−27,35,44,45,51,58,60,64,74,89,97,106,107] on annual copper runoff rates in dependence of annual rain precipitation at different sites divided according to the ISO classification of test sites.[57] The strong outliers 1−4 are correlated to the atmospheric SO_2 concentration with 30 (1), 15 (2), 27 (3), and 0.5 μg m^{-3} (4). b) Literature data[5,6,21,25−27,35,44,45,51,58,60,64,74,89,97,106,107] on annual copper runoff rates in dependence of the atmospheric SO_2 concentration.

copper sheets. Whether the copper runoff from the copper patina is increased, reduced, or unchanged compared with a fresh non-corroded copper surface depends on the patina age and composition and on prevailing exposure conditions (e.g., the presence of pollutants and chlorides, humidity). This has for example been shown in a study comparing freshly exposed copper sheet with 40 and 100 years preaged copper surfaces exposed in parallel at a low-polluted urban site (Stockholm, Sweden). Both aged surfaces revealed initially higher annual runoff rates compared with fresh copper sheet. However, with time these differences were less pronounced. Significantly lower copper runoff rates were observed for the 100 year-old surface compared with the 40 year-old surface.[32] At other more polluted or marine sites, lower copper runoff was observed from aged copper compared with significantly less aged or freshly exposed copper surfaces.[21,26,99] When comparing different patina compositions, their solubility is not the only important factor for the copper runoff. This is exemplified by chloride-containing corrosion products formed at marine sites, of which some are highly soluble[2] and therefore often not, or only locally, observed at unsheltered conditions.[26,90] A recent long-term study comparing corrosion and runoff for copper sheet and copper alloys at three different sites of varying chloride deposition shows that some chloride-containing patina compounds, such as (par)atacamite, are relatively protective and poorly soluble, properties closely related to their adherence to underlying patina constituents.[55] Nevertheless, copper runoff was found to be significantly lower at given rainfall quantities at marine sites compared with other sites, e.g. low- or high-polluted urban sites, probably due rapid formation of a stable cuprite layer and with time basic copper chlorides of low solubility at the marine sites.[26,55,58,60]

COPPER RUNOFF KINETICS – IMPORTANCE OF FIRST FLUSH

Prevailing environmental conditions and deposition of particles/pollutants preceding a rain event govern the concentration (or rate) of released copper during the first flush portion of a rain event. Figure 2a illustrates the kinetics of copper runoff during a given rain event, with a typical first flush region of relatively high released concentrations (rates) followed by significantly lower, almost constant levels within

the steady state region during the remaining duration of the rain event. Several definitions and descriptions of the first flush region exist in the literature, from only considering dry atmospheric deposition,[10] to also consider higher concentrations of copper due to the release of soluble corrosion products.[31,99] The first flush region is either described by a strong reduction in copper runoff rates until steady state conditions (no significant change in the rate) are reached[31,63,64,99,100] or quantified based on rates within the first runoff volumes (1−2 mm,[100,101] 2−4 mm,[24] 4−5 mm[45]) or the first 3 h of the rain event.[15] Important factors that govern the magnitude of the first flush effect include i) the length of preceding dry periods,[31,99] ii) dry deposition,[31] iii) patina thickness and porosity, iv) rain intensity,[31] and v) any parameter that influences atmospheric corrosion during the preceding dry/wet periods, such as relative humidity, temperature, pollutants, season, and prevailing exposure conditions (previous paragraphs). Periods with repeated daily rainfall events will not show any large first flush effects.

AVAILABLE LITERATURE AND PREDICTIVE MODELS ON ANNUAL COPPER RUNOFF RATES

Available literature data of average annual copper runoff rates per surface area and per rain amount in dependence of exposure site, rain amount, rain pH, SO_2 atmospheric concentration, surface inclination, sample preage, initial year of exposure, and exposure length (up to 16 years) is compiled in Figure 3. Data on exposures of less than 1 year duration that later have been published after longer exposure times, or replicate data, are excluded from the figure.[29,32,38,50,102] Copper runoff data for up to 16 years of exposure in Stockholm, Sweden, and up to 5 years in Milan, Italy and Madrid, Spain (partly unpublished data)[58] is presented in Figure 3. Data published after shorter time periods is excluded.[28] Other available literature on copper runoff from copper surfaces has been excluded from the figure due to limited information on site, rainfall amount and pH, presence of pollutants, surface size, or limited study length.[6,16,83,99,103,104] Furthermore runoff data based on weight measurements and patina composition estimations has further been excluded, see discussion above,[71,105] even though they concluded similar annual copper

runoff values compared with actual measurements at the same site.[71,105]

The average annual copper runoff rate of all compiled data in Figure 3 is 1.5 g m^{-2} y^{-1} (0.35–4.8), equal to 0.25 g m^{-2} y^{-1} 100 mm$_{rain}$$^{-1}$ (0.04–1.3), representative for sites with annual rainfall quantities varying between 262 and 1822 mm and SO$_2$ levels between 0.1 and 30 μg m^{-3}. When performing linear regression analysis on annual runoff copper data, the most important single parameter is the atmospheric SO$_2$ concentration (R^2 = 0.54; 0.81 when excluding marine sites) with increasing copper runoff with increasing concentration, Figure 3b. Strongly connected to this parameter is the starting year of exposure (R^2 = 0.34) and length of exposure period (R^2 = 0.09), with reduced annual copper runoff rates with time. This is partly related to a reduction in SO$_2$ levels over time for most sites, e.g. in Europe, and partly related to the formation of gradually less soluble corrosion products (see also Figure 2c). The third most important parameter is the rain pH (R^2 = 0.17). Since the rain pH seldom is documented, but rather the pH in the blank runoff water (runoff from an inert surface and including dry deposited species), its effect may be even more important as evident from laboratory investigations.[31,53] When the effect of the rain pH on the log-transformed runoff rate normalized on rain amount is investigated, as in a previous investigation,[53] the effect is more apparent (R^2 = 0.38). The effect of the annual rain quantity has previously clearly been shown considering data from one site (Stockholm, Sweden) and for rainfall differences during single rain events.[53] However, its effect is non-significant (R^2 = 0.01) when considering all data, but more clearly pronounced (R^2 = 0.26) when excluding marine sites, where it is most probably overshadowed by the other parameters and the fact that the annual rainfall is presented as an average value, Figure 3a. The same is true for the inclination parameter (R^2 = 0.04), most probably due to a limited set of data and the effect of wind, changing the rain direction from vertical to other angles. A detailed long-term copper runoff study on the effect of different orientation and inclination is ongoing at two urban sites in Europe.[58]

A predictive runoff rate model with terms with physical meaning that describes the wet (rainfall quantity and rain pH) and dry (SO$_2$ concentration) contribution and the effect of surface inclination has previously been elaborated[53] and refined[52]

$$R = (0.37\ SO_2^{0.5} + 0.96\ rain\ 10^{-0.62pH})(\cos(\theta)/\cos(45°))$$

where R is the annual copper runoff rate (g m^{-2} y^{-1}), SO$_2$ is the atmospheric concentration (μg m^{-3}), rain is the annual rainfall quantity (mm y^{-1}), pH is the rain pH, and θ is the surface inclination/angle from the horizontal (degrees). This model does not take into account the effect of chloride deposition (i.e., marine conditions) or is able to predict copper runoff from gutters (described elsewhere[108]). Using this model, 63% of the data in Figures 3a-b (marine environments excluded) can be predicted within 30% of deviation (R^2 = 0.48). This model has been criticized for the limited amount of field data for surfaces of different inclination,[61,65] its lack of considerations related to roof dimensions (contact period for a given raindrop),[61,65] and that the first flush effect may be overestimated by the model, especially at very low annual rainfall quantities.[65] Experimental data has recently been published that suggests that a roof dimension (height length) parameter should be included in future models.[61] This may of course be important for copper surfaces, e.g. roofs of abnormal shapes, due to the importance

of the contact period between rainwater and the patina. Nevertheless, normalization on surface area seems to be sufficient enough in most cases.[38] An earlier model exists in the literature that also is based on rain quantity (precipitation volume), pH (hydrogen ion wet deposition), and SO$_2$ (dry deposition).[60] Both models attempt to predict the total copper runoff rate at the immediate release situation, i.e. without any environmental interaction or consideration toward chemical speciation or bioavailability aspects. Estimated rates do hence not reflect or cannot directly be used to assess potential adverse effects. A model that includes aspects of environmental fate and changes in speciation of copper has been developed for watersheds; however, this model is only based on a single field investigation.[66] Essential aspects to consider when assessing environmental risks are described in the following section.

■ ENVIRONMENTAL FATE AND SPECIATION OF COPPER RUNOFF FROM OUTDOOR SURFACES

When assessing any environmental risks induced by the dispersion of copper from outdoor constructions it is necessary to consider copper speciation and hence bioavailability aspects.[11,25,66,109,110] Copper speciation includes also the distinction between particles and aqueous species. This is important, as the mobility and stability of copper particles are very different compared to aqueous species or precipitates at solid surfaces. Literature on copper particles or byproducts released from copper roofs is rare; however, a study comparing the dissolved and total fraction of the copper runoff from a 10-years and 70-years old copper roof, respectively, showed the major fraction to be dissolved and no significant differences in patina ages.[21] In the case of marine sites, copper patina can flake off and may therefore release copper patina particles.[55] At the immediate release situation of copper from a copper roof (i.e., directly at the roof top, without any interactions with other solid surfaces adjacent to the building), between 40 to 100% of the total amount of released copper was present in its most bioavailable form (as free Cu^{2+} ions) at an urban site in Stockholm, Sweden.[51,74,97] Lower bioavailable fractions were determined at similar immediate release situations for copper surfaces at the urban site Storrs, Connecticut, US (42–48%)[21] and at the marine site Brest, France (14–54%).[26] Important factors governing the bioavailable fraction in the immediate runoff water are predominantly the presence of organic matter such as pollen, pine needles, and from sea aerosols.[25,26,51,74,97] However, the complexation (speciation) and bioavailability of released copper in runoff water changes rapidly and dramatically in contact with different solid surfaces, e.g. downspouts and drainage systems, or e.g. soils and pavement in the close vicinity of a building.[18–20,22,25,42,111,112] The largest irreversible retention of copper has been shown for surfaces such as concrete and limestone that increase the pH of the runoff water.[18,20,42,96,111,112] Different pavement systems and soils of varying characteristics have been reported to act as efficient sinks for copper, both via retention and by changing the speciation and hence the bioavailability.[19,22,25,113–116] The retention capacity of soils is strongly dependent on the soil pH, contact time, its depth and distance to groundwater, temperature, presence of carbonates, organic content, dissolved organic matter, particle size (surface area), and cation exchange capacity (presence of cations Fe, Mn, etc.) as well as on the initial copper concentration and bioavailability.[11,19,22,115,116] Soil column studies with realistic copper runoff concentrations, screening top-soils relevant for European urban/rural con-

ditions, showed high retention capacities (>99%) during 25 years of simulated exposure to copper-containing runoff water, with total concentrations of copper in the pore water similar to background levels.[19,25] The retention of copper increases with increasing soil pH, longer contact time, higher temperature, higher content of carbonates and total organic matter, lower dissolved organic matter, smaller particle size of the soil, higher cation exchange capacity, lower initial copper concentration, and higher initial bioavailability.[11,19,22,115−117] For example, the free copper ion fraction of the total copper in soil pore water of different soil pH has been shown to vary between 10% (soil pH 4) and 0.1% (soil pH 8).[116] When copper is complexed to organic matter (hence not bioavailable) its mobility is higher, since the mobility to a large extent is determined by the organic matter.[19,100,111,112] While the retention of free copper ions in urban stormwater is high for some surfaces (e.g concrete, limestone, soil), it is slightly lower for other surfaces such as asphalt, cast iron, and PVC.[20,96,114] In contact with stormwater drainage systems, the chemical form of copper in runoff water is most probably already complexed and not as free copper ions. A study investigating the interaction between copper runoff water and a stormwater system, after transport via a cast iron piping system, showed a significant reduction in the total, the dissolved, and the free cupric ion concentration.[21] Laboratory and field studies investigating the interaction between copper runoff water from a copper roof or artificial copper runoff solutions and concrete surfaces of varying length (thereby contact period) revealed pavement concrete to have a substantial retention capacity and parallel reduction of the free copper ion concentration and thereby the bioavailable copper fraction.[18] Predictions for a relevant scenario suggest a reduction in copper concentration to background concentrations already within 20 m from the building in contact with urban stormwater systems.[18] In all, literature findings conclude that solid surfaces in the near vicinity of buildings act as efficient sinks for released copper.

■ SYNTHESIS

Copper runoff from naturally patinated (corroded) copper surfaces at outdoor constructions is governed by electrochemical and chemical reactions and is highly dependent on prevailing exposure conditions (size, inclination, geometry, and orientation), patina age, composition and thickness, and site-specific environmental parameters such as atmospheric pollutants, chlorides, rain characteristics (amount, intensity, and pH), prevailing wind, temperature, and season. The extent of copper runoff varies largely between single rain events due to the importance of dry periods and prevailing environmental conditions prior to a rain event, which influence the amount of copper released during the first flush portion of the rain volume. This first flush effect is also highly related to patina characteristics being more pronounced for a thick porous patina compared with a thin compact patina. Interpretation and use of copper runoff data for e.g. risk assessment or life cycle analyses need therefore to consider the main influencing factors that govern the runoff process at a given site of interest and focus on average data generated during several years rather than on single event data (if available). Corrosion rates cannot be used to predict runoff rates. Predictive models on total copper runoff at the immediate release situation from copper surfaces of different inclination are available that reasonably well estimate the dispersion of copper from buildings. However, further refinements are recommended and ongoing. Additional long-term data relevant for different polluted sites and climatic conditions and data elucidating the effect of surface inclination on the extent of copper runoff should be generated including compilation of data on at least rain pH, SO_2 concentration, annual rainfall quantity, and annual runoff rates (normalized on volume and surface area) following the newly established ISO standard on metal runoff measurements.[68] Most important for future environmental risk assessment and management and for life cycle assessments of outdoor constructions is to consider copper roof runoff data combined with information on copper speciation and bioavailability changes as well as the irreversible retention on adjacent surfaces during its environmental interaction. Several studies are available on copper retention and changes in bioavailability in contact with different surfaces such as limestone, concrete, pavements, and soil. Without considering these aspects when assessing the environmental fate of copper released from outdoor constructions, there is an evident risk that any potential environmental impact of copper runoff from copper roofs or other copper release sources is overestimated.[11] Further scientific efforts are required to include effects of dewatering/drainage materials and distance from source to recipient into environmental fate models and to further include available information related to the copper source, e.g. available information on site (e.g., rain, pollutants, geochemical parameters), and on dewatering/drainage materials. Such a model would be applicable to assess environmental risks of copper runoff when planning new constructions/buildings or installations such as copper roofs and facades.

■ AUTHOR INFORMATION

Corresponding Author
*Phone: +46 8 790 6621. Fax: +46 8 208284. E-mail ingero@kth.se.

Author Contributions
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