A model for predicting copper runoff rates

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Summary

Based on both laboratory and field exposure results, a general model has been deduced which is able to predict the annual runoff rate from naturally patinated copper samples. Critical factors to determine annual copper runoff rates (R, g/m^2y) turn out to be annual precipitation volume (V, mm/y), precipitation pH and angle of inclination (θ), according to the following equation:

$$P(V,\theta,pH) = (0.97 + 0.95 * V * 10^{-0.62pH}) * COS(\theta)/COS45^{\circ}$$

The model can predict annual copper runoff rates during different urban and rural exposure conditions, with precipitation rates from 400 mm/y to 3200 mm/y and with precipitation pH from 3.9 to 5.8. In 80% of all reported cases, the predicted values of annual copper runoff rates are within 30% of the measured values.

Introduction

Copper is widely used in outdoor constructions as, e.g., roofing or facade materials. According to a Swedish survey, the building sector consumes one third of all produced copper in the country [1]. During its gradual evolution, the copper patina forms a number of compounds, always with an inner layer of cuprite, Cu_2O, the dominating patina constituent. Depending on actual exposure conditions, a variety of different copper hydroxysulfates form atop the cuprite layer, including posjnakite, $Cu_4SO_4(OH)_6 \cdot H_2O$ and brochantite, $Cu_4SO_4(OH)_6$ [2,3,4]. The patina formed possesses protective properties and generally results in a gradual decrease in copper corrosion rate with exposure time, at least during the first decade or so.

With the growing concern regarding possible environmental effects of copper as a building material, a few research projects started to measure not only copper corrosion rates, but also simultaneous runoff rates in different atmospheric environments [5-9]. In 1994 a research program was initiated by the Swedish Environmental Protection Agency with the aim to study the risks on the environment and on human health caused by the accumulation of metals in the urban society. It resulted in a number of field and laboratory studies of runoff rates of copper performed by the Division of Corrosion Science at the Royal Institute of Technology, Stockholm, Sweden [10-13]. Lately, other research groups have also reported copper runoff rates from exposure sites in various countries [14-17].

We report herein an effort to integrate most published copper runoff rates into one general model, which is based on both laboratory and field exposure results. This has been accomplished by first exploring the individual effect of different precipitation parameters (volume, pH, and angle of inclination) mainly through laboratory exposures in artificial rain. The insight gained has then been used to formulate a general equation, which takes previously reported field runoff rates into consideration.

Laboratory and field exposures

The effect of precipitation volume

Runoff rate data from copper, having a one-year old naturally formed patina prior to exposure, have been generated from both laboratory exposures (in artificial rain, pH=4.3) and from field exposures (in natural rain, pH in the range 4.1 to 5.6) in Stockholm [18]. All data originate samples with angle of sample inclination of 45^o. As shown in Fig. 1, it turns out that both laboratory and field data largely follow the same linear relationship between predicted annual runoff rate of copper (P(V), g/m^2y) and yearly precipitation volume (V, mm/y), expressed as follows:

$$P(V) = V/500 \qquad (1)$$

A similar linear relation was also found for copper with a 40-year old naturally formed patina (not shown in Fig.1). This suggests that equation (1) is independent of patina age.

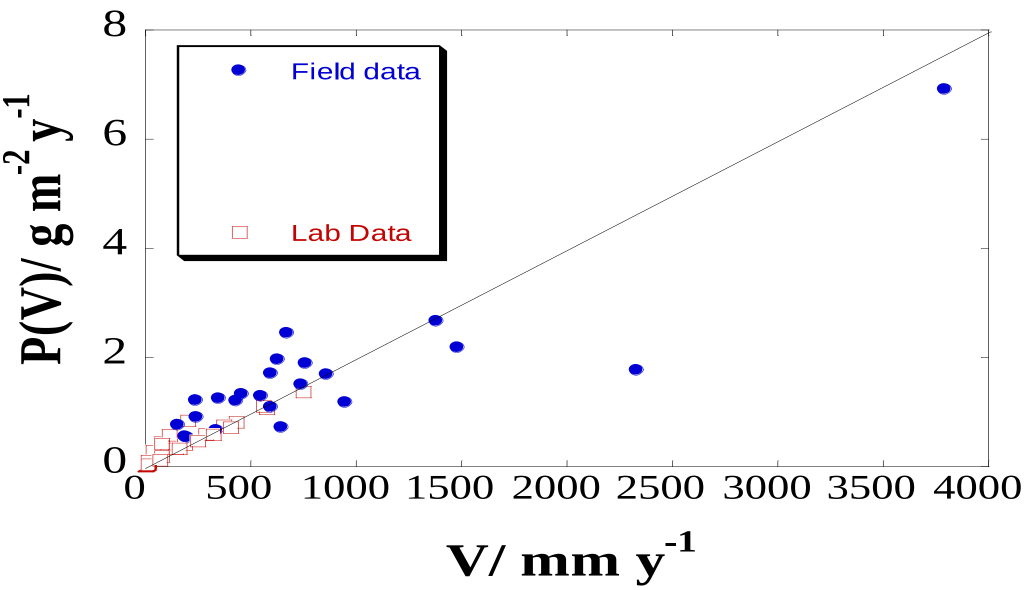

Fig.1. The relationship between annual runoff rate of one year naturally patinated copper and annual precipitation volume, based on both laboratory and field exposures [18].

The effect of inclination angle

While all copper runoff rate data presented in Fig. 1 originate from samples with a standard angle of inclination of 45^o, we next consider the influence of inclination angle on the copper runoff rate. By changing the inclination angle, the rain volume impinging on a given sample surface area unit will vary according to changes in trigonometry. Fig. 2 displays the ratio between the runoff rate of copper at selected angles (20^o and 70^o) of inclination and the runoff rate at the standard angle (45^o) of inclination angle. The data are based on 145-year old naturally formed patina on copper, which has been exposed to artificial precipitation [18]. The effect of inclination angle is clearly seen and follows the expected precipitation volume dependence, which is determined by the projected area onto which a given precipitation volume impinges. Hence, the resulting expression between predicted copper runoff rate at any given inclination angle, P(θ), and runoff rate at standard angle of inclination, P, is expressed as:

$$P(\theta) = P\ COS(\theta)/COS45 \qquad (2)$$

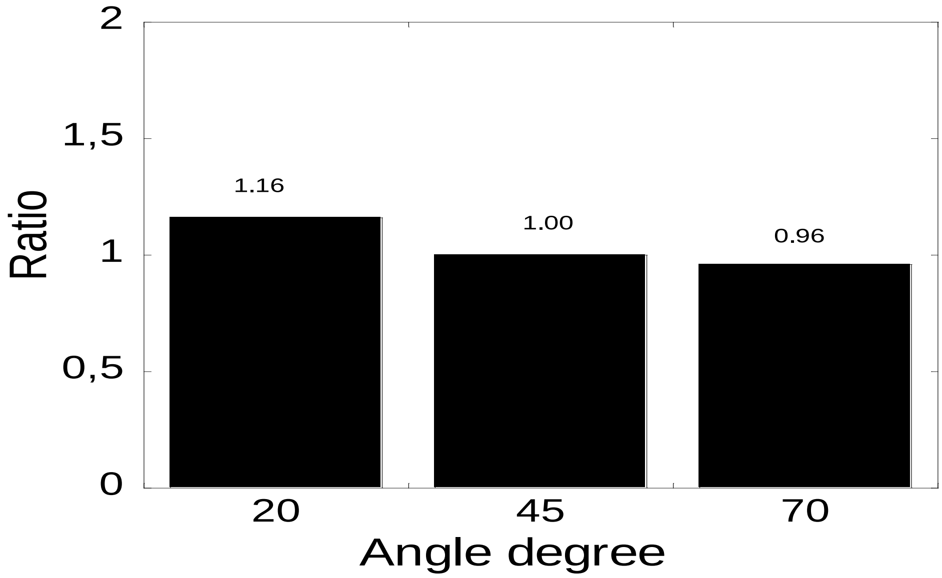

Fig.2. The effect of inclination angle on the ratio between the predicted runoff rate obtained at any given angle of inclination (P(θ)) and the predicted runoff rate obtained at 45^o of inclination (P).

The effect of precipitation pH

During any single precipitation event, the concentration of metal in runoff is initially high (the so-called first-flush region) and decreases to a lower but more constant value (the steady-state region) [18]. This behavior is schematically depicted in Fig. 3. In what follows the first-flush effect is regarded as minor and only the steady-state runoff effect will be treated. Table 1 summarizes the steady-state runoff rate when naturally patinated copper was exposed to artificial precipitation with different pH, 45^o inclination angle and 4.3 mm/h precipitation rate. Prior to laboratory exposure, the copper samples were pre-exposed in either an urban or a rural atmosphere for one year.

The effect of pH of precipitation, expressed as proton activity a_{H+}, on the predicted steady-state runoff rate, P(pH), is shown in Fig.4. By applying a regression analysis the following relation was obtained:

$$\log P(pH) = -0.031 - 0.6*pH \qquad R=0.89 \qquad (3)$$

$$P(pH) = 0.93*a_{H+}^{0.62} \qquad (4)$$

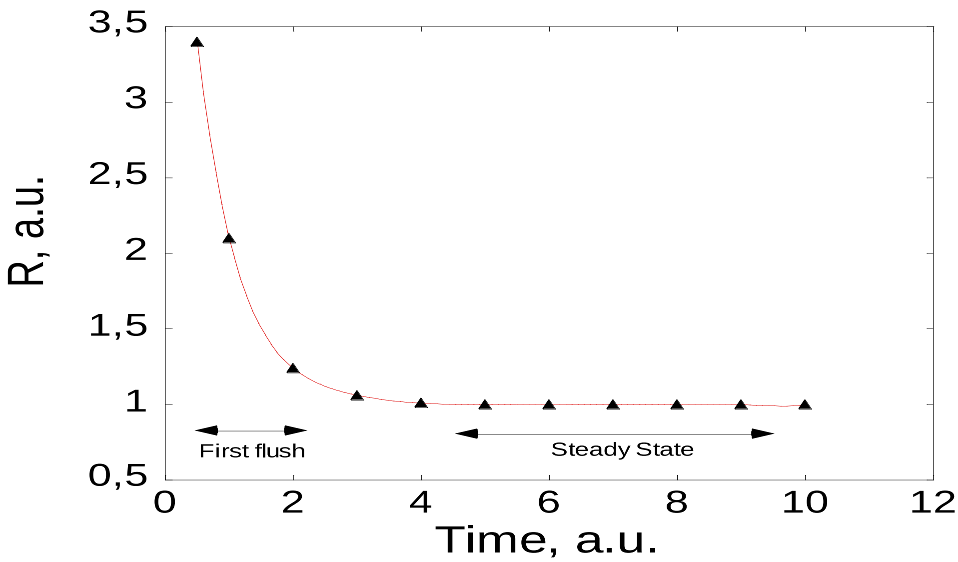

Fig. 3 Schematic description of how the copper runoff rate may change with time during a single precipitation event.

According to Graedel [19], equation 4 is representative of a proton-induced dissolution mechanism of any mineral layer and, hence, has a physical meaning.

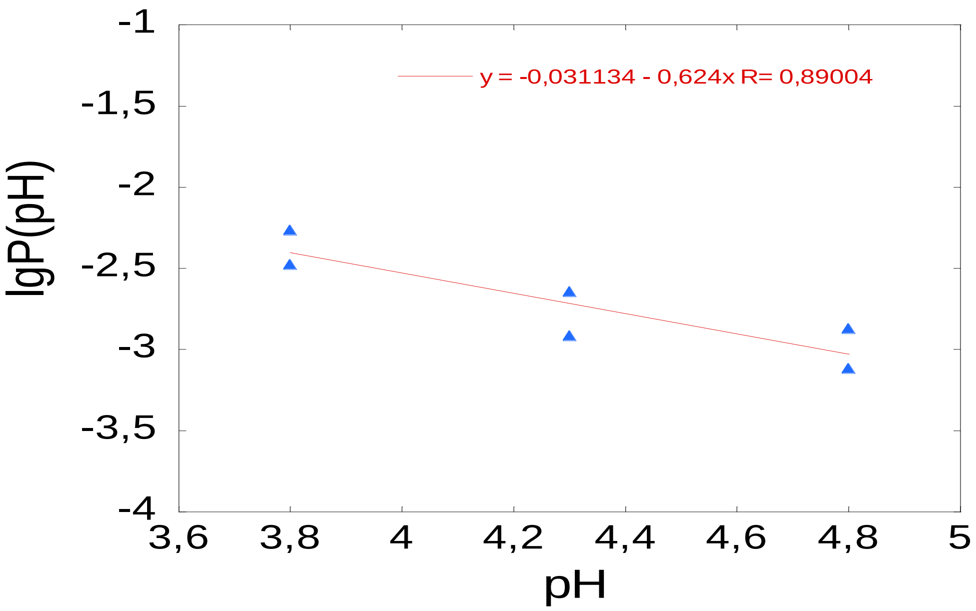

Fig.4 The effect of pH of precipitation on the predicted steady-state copper runoff rate.

<u>The combined effect of precipitation volume, inclination angle and precipitation pH</u>

From previous results it is obvious that precipitation volume, inclination angle and precipitation pH has significant effects on the predicted copper runoff rate, whereas the influence of other parameters, such as patina age and atmospheric pollutants, is less obvious.

In what follows these parameters are assumed to be independent of each other, i.e., their combined effect on the predicted copper runoff rate P(V, θ, pH) is separated into independent effects of each parameter:

$$P(V,\theta,pH) = P(V)*P(\theta)*P(pH) \qquad (5)$$

This assumption can be justified on physical grounds by regarding each water molecule, impinging on the patina surface, to act independently on the dissolution process of the copper patina. The combined effect of precipitation volume, inclination angle and precipitation pH is then expressed as:

$$P(V,\theta,pH) = 0.93*V*10^{-0.62pH}*COS(\theta)/COS45^{o} \qquad (6)$$

In most cases, the inclination angle is 45^o. From this follows that equation (6) is simplified as follows:

$$P(V,45^{o},pH) = 0.93*\mathbf{V}*10^{-0.62pH} \qquad (7)$$

Comparison with field runoff rate data

To check the validity of equation (7) for predicting field runoff rates, a comparison is made next in which *predicted* copper runoff rates (P, equation (7)) are compared with measured runoff rates (R). A majority of reported annual runoff rates (R, g/m^2y) of copper have been compiled in Table 2, most of them based on an angle of inclination of 45^o. A plot between measured annual runoff rates (R) and predicted annual runoff rates (P(V,45,pH)) is shown in Fig 5. A linear relationship can be discerned, and a regression analysis gave the following relation:

$$R = 0.97 + 1.02*P \qquad (R=0.91) \qquad (8)$$

The relatively high regression coefficient and the coefficient 1.02 close to 1, suggests that equation (7) is a very good predictor of copper runoff rates in different environments. The main difference between predicted and measured runoff rates is the addition of the term 0.97 to the predicted runoff rate. The term represents the average runoff rate caused by the first-flush effect, see Fig. 3. It was previously shown to be influenced by numerous factors including the environmental conditions prior to a rain episode, such as dry deposition of SO_2 and the length of the dry period [18].

A comparison between measured runoff rates (Table 2) and predicted runoff rates (equation (9)) shows that predicted values in 80% of the cases deviate less than 30% from the measured values. From Table 2 is also evident that the exposure sites investigated represent a broad spectrum of urban and rural environments, with a precipitation rate from 400 mm/y to 3200 mm/y and a with precipitation pH from 3.9 to 5.8. Although not seen in Table 2, the range in SO_2-concentration between the exposure sites is from 0.5 to 25 mikrogram/m^3.

Finally, by combining equation (8), which only considers field runoff rate data obtained at 45^o of inclination, with equation (6), which considers the influence of inclination angle, a general formula for predicting field runoff rates (P(V,θ,pH)) is obtained:

$$P(V,\theta,pH) = (0.97 + 0.95*V*10^{-0.62pH})*COS(\theta)/COS45^{\circ} \quad (9)$$

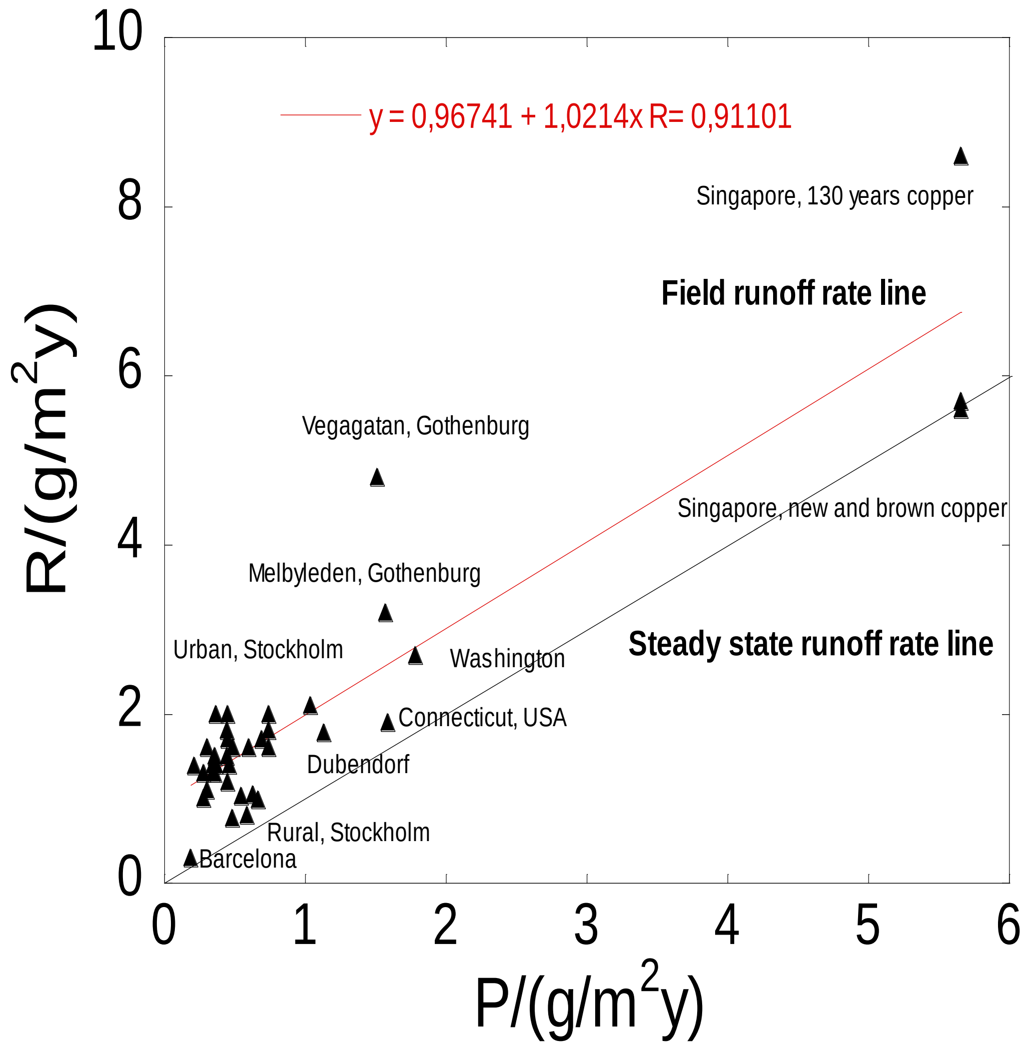

Fig. 5 The relationship between measured annual runoff rate, R, and predicted annual runoff rate, P, for most reported runoff data.

Conclusions

Based on both laboratory and field exposure data a general model has been deduced. It predicts the annual runoff rate from naturally patinated copper samples (P(V, θ, pH), g/m^2y) in a broad range of atmospheric environments with three parameters, precipitation volume (V, mm/y), precipitation pH and angle of inclination (θ), according to the following equation:

$$P(V, \theta, pH) = (0.97 + 0.95*V*10^{-0.62pH})*COS(\theta)/COS45^{\circ}$$

In 80% of all reported annual runoff rates, the predicted values are within 30% from the measured values.

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Table 1. The steady state runoff rate of one year aged copper exposed to artificial precipitation with intensity 4.3 mm/h, 45^o angle of inclination and different pH.

Site	Urban			Rural		
pH	3.8	4.3	4.8	3.8	4.3	4.8
P(pH)(g/m^2•mm)	0.005459	0.00227	0.001345	0.003331	0.001219	0.0007642
lg P(pH)	-2.263	-2.644	-2.871	-2.477	-2.914	-3.117

Table 2. Runoff rate of copper in different exposure sites

Exposure Site and environmental Type	Exposure period, copper age and inclination angle	Precipitation (mm/y) and pH of rainwater	Field runoff rate(g/m^{2}y)	Prediction runoff rate(g/m^{2}y)	Deviation percentage from Field runoff rate
Payerne, Switzerland. Rural atmosphere [21]	New copper for 1 year and 45˚ inclination	981 and 5.2	1.03	1.52	48
Dubendorf, Switzerland, Suburban atmosphere [22]	New copper for 4 years and 45˚ inclination	1000 and 4.7	1.78	2.13	20
Washington DC, USA Polluted Urban atmosphere[17]	New copper for 3 years and 30˚ inclination	958 and 4.21	3.3	3.42	3.7
Albany OR, USA Unpolluted atmosphere[17]	New copper for 3 years and 30˚ inclination	1084 and 5.78	1.7	1.46	20
Singapore, Urban atmosphere[23]	New copper for 1 year and 45˚ inclination Brown copper 130 years copper	3250 and 4.4 (between 3.9 and 4.9)	5.6-5.7 5.5-5.7 8.4-8.8	6.74 6.74 6.74	18 18 -22
Stockholm, Sweden Urban atmosphere[23]	Brown copper for 4 years and 45˚ inclination New copper 130 years copper	500 and 5.0	1.3-1.5 1.1-1.6 1.8-2.3	1.35 1.35 1.35	-3.6 -3.6 33
Barcelona, Spain[24]	New copper for 1 year and 45˚ inclination	526 and 5.5	0.3	1.16	287
Stockholm, Sweden Urban atmosphere[12]	New copper for 2 years and 45˚ inclination	410 and 4.7 430 and 4.7 530 and 4.6 461 and 4.6	1.40 1.60 1.70 1.60	1.44 1.47 1.68 1.59	2.9 -8.1 -1.2 6.3
Stockholm, Sweden Rural atmosphere[12]	New copper for 2 years and 45˚ inclination	450 and 4.6 510 and 4.6 480 and 4.6 370 and 4.6	0.8 0.99 1.05 0.77	1.57 1.65 1.61 1.46	96 67 53 90
Stockholm, Sweden Urban atmosphere[25]	New copper for 3 years and 45˚ inclination 30 years copper for 3 years and 45˚ inclination	488 and 5.0 395 and 5.03 498 and 5.04 488 and 5.0 395 and 5.03 498 and 5.04	1.3 1.0 1.3 1.5 1.3 1.4	1.34 1.25 1.32 1.34 1.25 1.32	3.1 25 1.5 10.7 3.8 5.7
Stockholm, Sweden Urban atmosphere[25]	New copper for 4 years and 45˚ inclination 30 years copper for 2 years and 45˚ inclination 130 years copper for 4 years and 45˚ inclination	399 and 4.7 591 and 4.63 602 and 5.0 430 and 5.03 399 and 4.7 591 and 4.63 399 and 4.7 591 and 4.63 602 and 5.0 430 and 5.03	1.2 1.6 1.5 1.1 1.7 1.8 2.0 2.0 1.8 1.6	1.43 1.73 1.42 1.28 1.43 1.73 1.43 1.73 1.42 1.28	19 8.1 -5.3 19 -16 -3.9 -29 -14 -21 -20
Connecticut, USA Urban atmosphere[16]	70 years copper roof for 1 year and 42˚ inclination	1400 and 4.7	2.0	2.72	36
Vegagatan, Gothenburg, Sweden Melbyleden, Gothenburg, Sweden Floda, Gothenburg, Sweden[5]	New copper for 1 year and 45˚ inclination	425 and 3.9 512 and 4.0 518 and 4.3	4.8 3.2 2.1	2.51 2.57 2.03	48 19.7 7