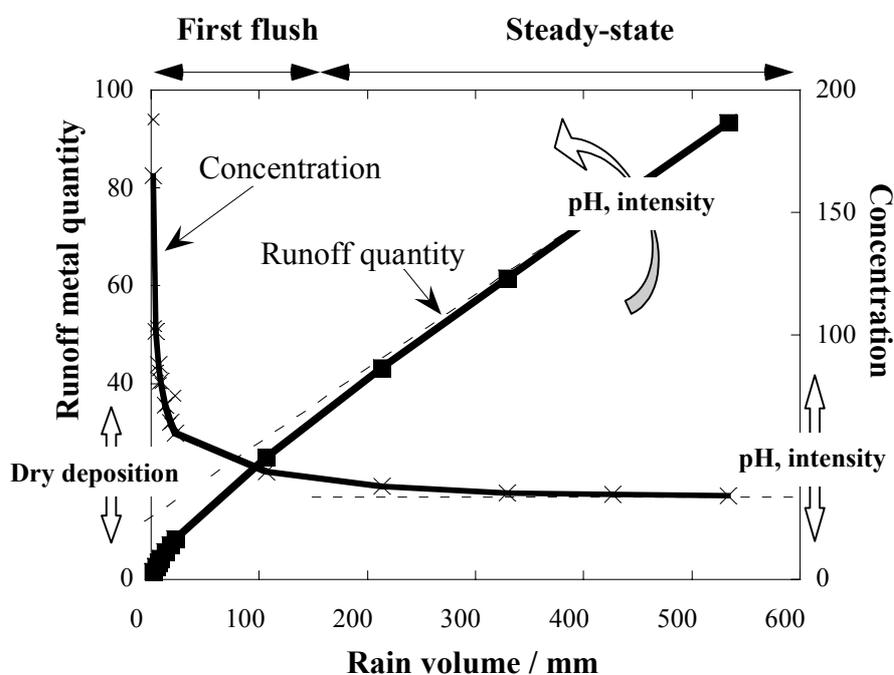




# Atmospheric Corrosion and Runoff Processes on Copper and Zinc as Roofing Materials



Wenle He

Doctoral Thesis

Department of Materials Science and Engineering  
Division of Corrosion Science  
Royal Institute of Technology  
SE-100 44 Stockholm, Sweden  
Stockholm 2002



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### **Abstract**

An extensive investigation with parallel field and laboratory exposures has been conducted to elucidate atmospheric corrosion and metal runoff processes on copper and zinc used for roofing applications. Detailed studies have been performed to disclose the effect of various parameters on the runoff rate including: surface inclination and orientation, natural patination (age), patina composition, rain duration and volume, rain pH, and length of dry periods in-between rain events. Annual and average corrosion rates and runoff rates have been determined consecutively during urban field exposures in Stockholm on naturally patinated copper and zinc of varying age and patina composition. The corrosion rate was found to decrease with time, amounting to 6.7 g Cu/(m<sup>2</sup>·y) and 5.0 g Zn/(m<sup>2</sup>·y) after 48 weeks of exposure, whereas the runoff rate was relatively constant with time on a yearly basis, being 1.3 g/(m<sup>2</sup>·y) and 3.1 g/(m<sup>2</sup>·y) for copper and zinc, respectively. The annual runoff rate was found to be significantly lower than the corresponding corrosion rate for both copper and zinc. Somewhat higher runoff rates of copper were determined from naturally green-patinated copper (> 40 years old, 2.0 g/(m<sup>2</sup>·y)) compared to brown-patinated copper (1 year old). The main reasons are specific environmental conditions combined with characteristics of the patina layer, which increase the magnitude of dissolved species flushed from the surface during the first flush volume of a rain event. No intrinsic effect of panel age on the runoff rate was seen for naturally patinated zinc. However, differences in prevailing environmental conditions during the initial exposure period and, hence, differences in formation rate and surface coverage of the corrosion patina, resulted in variations in runoff rate. This initial difference remained also during prolonged exposure periods and was referred to as a memory effect.

Model roof investigations and laboratory studies showed surface orientation and inclination to have a detrimental effect on the runoff rate with high runoff rates from surfaces of low inclination from horizon and surfaces exposed towards the wind direction.

Based on field exposures and literature data, a correlation was established between the runoff rate and the prevailing SO<sub>2</sub>-concentration. The runoff rate increases with increasing SO<sub>2</sub> level for exposure sites of similar annual precipitation quantities (500-1000 mm/y).

A rain device, using artificial rain, was shown to successfully simulate outdoor rain events of varying intensity and pH and result in realistic runoff rates of both copper and zinc. The device was used to monitor changes in metal concentration and quantity of runoff water during individual rain events. High metal concentrations are found in the initial rain volume flushing the surface (first flush), which decreased to rather constant metal concentrations during the subsequent rain volume (steady-state). The magnitude of first flush depends primarily on environmental conditions prior to a rain event and the characteristics of the corrosion patina. The metal concentration in runoff water increases with rain acidity, decreases with rain intensity and increases with length of the dry period preceding a rain event.

A comparison between instantaneous corrosion rates, monitored by electrochemical impedance spectroscopy using a 2-electrode set-up, and runoff rates during a continuous rain event was performed for naturally patinated copper panels. Corrosion rates were found to be approximately 10 (brownish patina) and 25 times (greenish patina) lower than corresponding instantaneous runoff rates.

A schematic description of the first flush and steady-state region of the runoff process was established. The magnitude of the concentration during first flush is primarily affected by prevailing environmental conditions prior to a rain event, while rain pH and intensity primarily affect the concentration during steady-state.

Key words: atmospheric corrosion, corrosion rate, runoff rate, copper, zinc, field study, laboratory study, roof, first flush, rain quantity, rain intensity, rain pH, dry and wet deposition, corrosion and runoff process.

## Preface

This thesis includes the following six papers, referred to in the text by their roman numerals.

- I. W. He, I. Odnevall Wallinder and C. Leygraf, “A comparison between corrosion rates and runoff rates from new and aged copper and zinc as roofing material”, *Water, Air and Soil pollution: Focus*, Vol. 1, (2001), pp. 67-82.
- II. I. Odnevall Wallinder, P. Verbiest, W. He and C. Leygraf, “The influence of patina age and pollutant levels on the runoff rate of zinc from roofing materials”, *Corrosion Science*, Vol. 40, No. 11, (1998), pp. 1977-1982.
- III. I. Odnevall Wallinder, P. Verbiest, W. He and C. Leygraf, “Effects of exposure direction and inclination on the runoff rates of zinc and copper roofs”, *Corrosion Science*, Vol. 42, No. 8, (2000), pp. 1471-1487.
- IV. W. He, I. Odnevall Wallinder and C. Leygraf, “A laboratory study of copper and zinc runoff during first flush and steady state conditions”, *Corrosion Science*, Vol. 43, No. 1, (2000), pp. 127-146.
- V. W. He, I. Odnevall Wallinder and C. Leygraf, “Runoff rates of zinc – a four-year field and laboratory study”, *Outdoor and Indoor Atmospheric Corrosion*, ASTM STP 1421, H. E. Townsend, Ed., American Society for Testing and Materials, West Conshohocken, PA, (2002), pp.216-229.
- VI. Xueyuan Zhang, Wenle He, Inger Odnevall Wallinder, Jinshan Pan and Christofer Leygraf, “Determination of instantaneous corrosion rates and runoff rates of copper from naturally patinated copper during continuous rain events”, *Corrosion Science*, Vol. 44, No. 9, (2002), pp. 2131-2151.

Paper I, III, and IV have been published in the licentiate thesis “Corrosion rates and runoff rates of copper and zinc as roofing materials – A combined field and laboratory study” (ISBN 91-7170-527-9, ISRN KTH/MSE/Korr/LA-00/1-SE).



## Contents

<b>1. Introduction</b>	1
1.1 Background	1
1.2 Atmospheric corrosion of copper and zinc	3
1.3 Metal runoff	7
<b>2. Experimental</b>	11
<b>3. Results and discussion</b>	14
3.1 Is the corrosion rate different from the runoff rate on a monthly and yearly perspective?	14
3.2 Is the corrosion rate different from the runoff rate during a single rain episode?	17
3.3 Which environmental parameters govern the metal runoff quantity?	19
3.4 What effect has natural patination on the runoff rate (panel age)?	29
3.5 Can laboratory and field runoff data be used to estimate the release of metals from existing buildings?	34
3.6 Can the runoff process be schematically described?	36
3.7 Can artificial rain really be used to simulate natural rain?	38
3.8 How can the data be used in the future work of environmental risk assessment and regulations?	40
<b>4. Concluding remarks</b>	41
<b>5. Acknowledgement</b>	43
<b>6. References</b>	44



## **1. Introduction**

### ***1.1 Background***

The first metals known to man were gold and copper. Early in the Bronze Age (3000-1300 B. C.) our forefathers started to hammer copper into various shapes for tools, weapons and jewelry. By melting copper, they found that almost anything could be produced. The addition of tin to copper (bronze) made e.g. the weapons much more durable and strong. With ongoing advances in metallurgy man was also later on able to refine zinc from its ores to produce e.g. brass. Ancient cultures in Greece, China and India, used zinc in jewelry and statuettes made of brass and bronze, alloys of zinc and copper, as early as 500 BC. The development of the human civilization implied the production and use of other metals and metal alloys. Aesthetic and status symbols in human history are e.g. copper roofs on churches and buildings as well as statues of bronze. Copper and zinc have been widely used on roofs and buildings, especially in Scandinavia and the European countries.

As a result of the early use of metals in the society, the science of corrosion was early established as a scientific discipline. The primary aim was to determine corrosion rates for materials in different environments in order to develop more durable metallic materials.

The increased use of metals also meant an increasing dispersion of metals in the environment and, hence, also an increase of metals in e.g. sediments. As a result, a debate has been evoked during the last decades in several European countries and the U.S.A. regarding the environmental effects of anthropogenic metal dispersion. Examples of anthropogenic sources are emissions from point sources such as industrial plants and diffuse emissions from highway runoff and buildings. Even though the industrial emissions in Sweden and Western Europe have decreased markedly since the 1970s as a result of an improved cleaning technology and altered industrial activities, legislators still believe the diffuse dispersion of metals to be a potential risk on the environment. “Man masters nature not by force but by understanding”[Bronowski (1965)]. Science should therefore form a base for legislative regulations and restrictions towards the use of metals, i.e., a base for human harmony with nature.

In 1995, the Swedish Environmental Protection Agency (SEPA) organized a five-year research program “*Metals in the urban and forest environment – ecocycles and critical loads*” with the aim to determine the accumulation and flow of seven metals (Hg, Cd, Pb, Cr,

Ni, Cu, and Zn) in the urban city of Stockholm, Sweden. One part of this research program aimed to quantify the diffuse dispersion of metals from roofs and buildings (Cr, Ni, Cu, Zn). An extensive research effort was therefore implemented at the division of Corrosion Science in order to determine and compare corrosion rates (degradation of metal) and runoff rates (metal release) from roofing materials of copper and zinc and to provide data to be used for future calculations and estimations of total metal flows from buildings in the society. Results from this investigation are presented in this thesis.

Data obtained within the SEPA investigation show total metal flows in the society without any consideration of the chemical speciation of the metals or its environmental interaction or effects, crucial information for environmental risk assessments. The field of corrosion science has therefore been confronted with a new challenge, i.e. it is not only a scientific challenge to investigate how the environment affects different materials but also how the environment can be affected by the release of metals induced by atmospheric corrosion. This new aspect requires an interdisciplinary approach, which includes other scientific disciplines such as atmospheric chemistry, electrochemistry, water chemistry, soil chemistry, biology, and ecotoxicology. The release of metals from roofing materials is one of the diffuse emission sources that have been indicated to be a potential risk on the ecosystem. An ecosystem is defined as a system formed by the interaction of a community of organisms with their physical environment. These systems may regionally and locally be disturbed by human activity. It is therefore crucial to describe the situation from the roof to the recipient and to provide quantitative data that range from the metal release situation through transport in soil and aquatic environments to the metal receptor situation. Research efforts have been conducted at the division of Corrosion Science including chemical speciation, bioavailability and ecotoxicity effects at the immediate situation when the runoff water leaves the roof [Karlén, *et al.* (2001, 2002), Heijerick, *et al.* (2002), Odnevall Wallinder, *et al.* (2001), Odnevall Wallinder and Leygraf (2002)<sup>a,b</sup>]. In addition, the interaction between runoff water and different sorbing surfaces has also been subject for investigation [Bertling, *et al.* (2002)<sup>a-c</sup>]. However, results from these investigations are not considered within this thesis.

This doctoral thesis includes data on copper and zinc from both field and laboratory exposures and contains the following main information: average outdoor corrosion- and runoff rates, instantaneous corrosion- and runoff rates during laboratory simulated rain events,

surface analysis, solution analysis, and effects of various parameters on runoff rates. The thesis also includes a theoretical approach to describe the metal runoff process for copper and zinc from roofing materials. Potential effects on the environment have not been part of this thesis and are hence not further discussed.

The following eight questions have been formulated during the course of this doctoral study, all believed to provide important basic knowledge on the diffuse flow of copper and zinc induced by atmospheric corrosion from roofing materials in the society.

1. *Is the corrosion rate different from the runoff rate on a monthly and yearly perspective?*
2. *Is the corrosion rate different from the runoff rate during a single rain episode?*
3. *Which environmental parameters govern the metal runoff quantity?*
4. *What effect has natural patination on the runoff rate (panel age)?*
5. *Can laboratory and field runoff data be used to estimate the release of metals from existing buildings?*
6. *Can the runoff process be schematically described?*
7. *Can artificial rain really be used to simulate natural rain?*
8. *How can the data be used in future work of environmental risk assessment and regulations?*

## ***1.2 Atmospheric corrosion of copper and zinc***

Atmospheric corrosion is a relatively old discipline in corrosion science. Extensive research has been carried out on copper and zinc with respect to e.g. corrosion product formation in various atmospheric environments, corrosion rate determinations, and theories of corrosion [Mattsson and Holm (1967), Rozenfeld (1972), Kucera and Mattsson (1987), Barton (1976), Holm and Mattsson (1982), Graedel (1987<sup>a,b</sup>, 1989), Graedel, *et al.* (1987), Feliu and Morcillo (1987), Zheng, *et al.* (1991), Granese, *et al.* (1992), Costas (1982), Slunder and Boyd (1986), Cramer, *et al.* (1988), Tsujino, *et al.* (1995), Leygraf (1995), FitzGerald (1995), Zhang (1996), Svensson and Johansson (1996), Gracia, *et al.* (1996), Oesch and Faller (1997), Leygraf and Graedel (2000), Rodríguez, *et al.* (2002)]. Also dose-response function models have been developed that describe the relation between the corrosion rate and various environmental parameters including e.g. temperature, time of wetness, exposure time, rain and air pollutants (SO<sub>2</sub>, Cl, NO<sub>x</sub>, O<sub>3</sub>, etc.) [Leuenberger-Minger, *et al.* (2002)<sup>a,b</sup>, Tidblad, *et al.*

(2001<sup>a,b</sup>), Haagenrud, *et al.* (1995), Reisener, *et al.* (1995), Knotková, *et al.* (1993), Spence, *et al.* (1992), Granese, *et al.* (1992), Cramer, *et al.* (1990, 1996), Kucera, *et al.* (1988), Baker and Kirk (1990)]. Common methods to describe the corrosion process have involved various surface analytical tools to determine phases of the corrosion patina and the morphology, whereas mass loss (ML) primarily has been used to determine corrosion rates. Recently, electrochemical measurements have been developed and applied in kinetics studies of corrosion processes and determination of instantaneous (in-situ) corrosion rates in thin aqueous films [Nishikata, *et al.* (1995<sup>a,b</sup>, 1996, 1997, 1999), El-Mahdy, *et al.* (2000)<sup>a,b</sup>, Katayama, *et al.* (2002)].

The corrosion process forms part of a natural cycle in which the metal is striving through spontaneous chemical and electrochemical processes to reach back to its most stable condition, i.e. as a mineral, from which it was refined. As roofing material, copper and zinc undergo processes of atmospheric corrosion during which wet and dry deposition [Edney, *et al.* (1988), Cramer, *et al.* (1990)] induce a gradual degradation of the metal. The atmospheric corrosion process is usually investigated in parallel unsheltered and sheltered exposures. The unsheltered exposure provides a process in which the metal is affected by both wet and dry deposition including gaseous and aqueous interactions, as well as salt and particle deposition, while predominantly dry deposition of gaseous and aerosol pollutants govern the corrosion attack in a sheltered exposure. A prerequisite for a corrosion process to occur is the presence of water, e.g. humidity, dew, fog, or precipitation. A minimum thickness of 5-10 monolayers [Aastrup (1999), Aastrup, *et al.* (2000)<sup>b</sup>] is required to reach bulk water properties in which electrochemical reactions take place on a metal surface. The prevailing environmental pollutants, e.g. SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, HCl, and NaCl, determine the formation rate and the composition of corrosion products (patina).

The thickness and the protective ability of the patina also determine the corrosion rate of the metal. The corrosion layer grows through a sequence of consecutive steps of dissolution, co-ordination and re-precipitation. A variety of corrosion products can form, depending on the type and amount of deposited species in the layer. A prediction of phases formed can be made using the concept of the hard- and soft acid-base principle (HSAB) [Jolly (1991)]. Since Zn(II)- and Cu(II) ions are classified as intermediate acids they are able to co-ordinate with a number of different bases, including e.g. OH<sup>-</sup>, O<sup>2-</sup>, and SO<sub>4</sub><sup>2-</sup>, and a number of different corrosion products are expected to form.

Recent research has deduced general reaction schemes that describe the evolution of both copper and zinc patina as a result of variations in environmental pollutants [Krätschmer, *et al.* (2002), Odnevall (1994), Odnevall and Leygraf (1994)]. Both schematic schemes are presented below, Fig. 1 and Fig. 2.

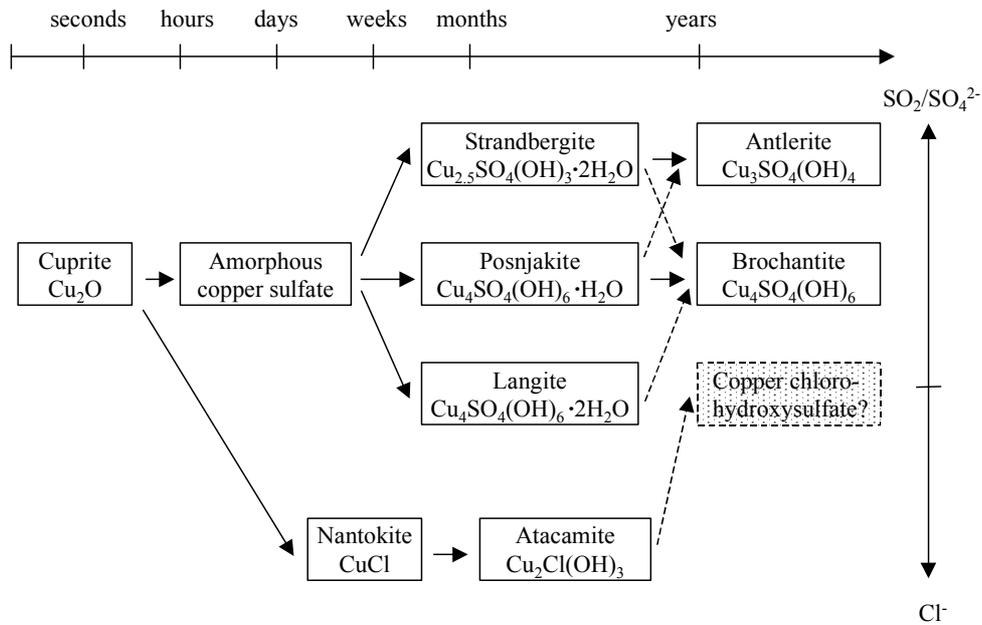


Fig. 1 A scheme for patina formation of sheltered copper, displaying the formation of different compounds as a function of exposure time in either sulfate- or chloride-dominated environments. The shaded box shows a postulated phase whereas the other boxes are based on phases observed in natural patina. [from ref. Krätschmer, *et al.* (2002)]

Figure 1 shows the scheme for patina formation on sheltered copper. The most common constituents of the patina (both unsheltered and sheltered) of a copper roof in an urban environment include cuprite ( $\text{Cu}_2\text{O}$ ) in the inner layer and posnjakite ( $\text{Cu}_4\text{SO}_4(\text{OH})_6\cdot\text{H}_2\text{O}$ ) and brochantite ( $\text{Cu}_4\text{SO}_4(\text{OH})_6$ ) in the outer layer. Strandbergite ( $\text{Cu}_{2.5}\text{SO}_4(\text{OH})_3\cdot 2\text{H}_2\text{O}$ ) and antlerite ( $\text{Cu}_3\text{SO}_4(\text{OH})_4$ ) can form in more polluted environments with higher levels of  $\text{SO}_2$  and sulfate-containing aerosols whereas nantokite ( $\text{CuCl}$ ) and atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) primarily form in chloride-containing environments such as traffic or marine atmospheres. The figure also includes langite ( $\text{Cu}_4\text{SO}_4(\text{OH})_6\cdot 2\text{H}_2\text{O}$ ), a precursor phase, that seems to exist in less polluted sites with more humid and wet conditions. The total thickness of the patina depends on age and environment and varies typically between 10 and 70  $\mu\text{m}$  [Graedel, *et al.* (1987), Odnevall and Leygraf (1996), Atrens, *et al.* (1996)].

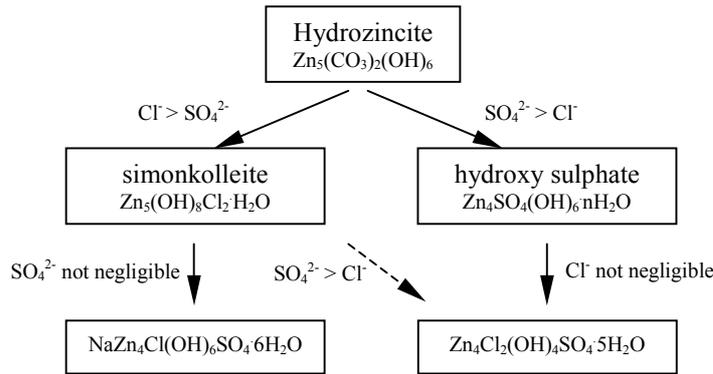


Fig. 2 A scheme for patina formation of sheltered zinc, displaying the formation of different compounds in either sulfate- or chloride-dominated environments [from Ref. Odnevall (1994), Odnevall and Leygraf (1994)]

The scheme for patina formation on sheltered zinc is shown in Fig. 2 [Odnevall (1994), Odnevall and Leygraf (1994)]. Hydrozincite ( $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ ) is the initial phase formed under outdoor atmospheric exposures (both sheltered and unsheltered conditions). This phase is also one of the most abundant phases of the corrosion patina formed on a zinc roof. Other common phases are basic zinc sulfates ( $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$ ,  $n=1-5$ ) in urban and rural environments or simonkolleite ( $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ ) in marine or traffic environments. Depending on prevailing environmental pollutants, also other phases such as  $\text{Zn}_4\text{Cl}_2(\text{OH})_4\text{SO}_4 \cdot 5\text{H}_2\text{O}$  or  $\text{NaZn}_4\text{Cl}(\text{OH})_6\text{SO}_4 \cdot 6\text{H}_2\text{O}$  can occur within the patina. The total thickness of these layers is typically 10-50  $\mu\text{m}$  [Odnevall (1994), Graedel (1989)].

Atmospheric corrosion rates can be determined and monitored either by gravimetric methods or by electrochemical techniques. The former is traditionally used to determine average corrosion rates during various exposure periods. The mass loss (ML) is hence determined as the difference in weight prior to exposure and after a chemical removal of the corrosion patina. The latter method refers to recently developed techniques to determine *instantaneous (in-situ)* corrosion rates under thin electrolyte films by evaluating the electrochemical signal response.

Corrosion rates have been extensively determined in different environments of varying conditions. Typical time intervals for these rate determinations have been one or several years. More recently, corrosion rates have also been determined on a shorter time-scale

including days, weeks and months [Odnevall and Leygraf (1996, 1999)]. The corrosion rate is generally high during the first year of exposure after which it decreases with prolonged exposure period. On a long-term scale it usually reaches an almost constant level [UN/ECE report (1998), Gullman (1993), Leuenberger-Minger, *et al.* (2002)<sup>a,b</sup>]. High corrosion rates can be induced by e.g. high concentrations of air pollutants such as SO<sub>2</sub>, NO<sub>2</sub>, NO, and O<sub>3</sub> [Zheng, *et al.* (1991), Cramer, *et al.* (1988), Svensson and Johansson (1996), Oesch and Faller (1997), Leuenberger-Minger, *et al.* (2002)<sup>a,b</sup>], low rain pH [Nassau, *et al.* (1987), Graedel (1993), Johansson and Linder (1993)], low degrees of surface inclination enabling pollutants to deposit on the surface [Vernon (1927), Fishman, *et al.* (1988), Hechler, *et al.* (1993)], and surface orientations in the prevailing wind direction [Carter, *et al.* (1987), Fishman, *et al.* (1988), Mendoza and Corvo (2000)]. Typical corrosion rates (expressed in µm/y) are 0.2-0.3 (rural), 0.5-8 (marine), 2-16 (urban, industrial) for zinc; and ≈ 0.5 (rural), ≈ 1 (marine), 1-2 (urban), ≤ 2.5 (industrial) for copper [Leygraf (1995)].

### **1.3 Metal runoff**

No attention was placed towards the diffuse emission of metals from various sources in the society, e.g. traffic highways, vehicles, drainage systems, and buildings, before high concentrations of metals and other species were detected in urban storm water [Malmqvist (1983), Gumbs and Dierberg (1985), Yaziz, *et al.* (1989), Good (1993), Boller (1997), Förster (1998), Gromaire, *et al.* (2001), Chebbo, *et al.* (2001), Davis, *et al.* (2001), Palm and Östlund (1996)]. Relatively high concentrations of organic and inorganic species were measured in storm water catchments from buildings with and without metal roofs [Good (1993), Förster (1998, 1999), Gromaire, *et al.* (1999, 2001)]. A first flush phenomena with a higher runoff concentration during the first collected volume of storm water and followed by a subsequent decrease in concentration was found for many species [Förster (1996), Zobrist, *et al.* (2000)]. The phenomena was described with a negative exponential function:  $C=C_0+C_1e^{-kR}$ , where R is the collected runoff volume, C the runoff concentration, C<sub>0</sub> the concentration in rain, C<sub>1</sub> the initial runoff concentration, and k a constant. Changes in runoff concentration were referred to as “first flush effects” and were significant within 2 mm of collected runoff water [Boller (1997), Förster (1996), Zobrist, *et al.* (2000)] from non-metallic roofs. The magnitude of the concentration of various species during first flush was shown to be affected by the rain intensity and increased after long dry periods without rain [Yaziz, *et al.* (1989), Good (1993), Thomas and Greene (1993)]. As a result of these findings and others, the concern towards the use and quality of urban storm water increased and regulations were introduced to treat the water before it was drained to storage of drinking

water. Water treatment was primarily focusing on the first flush volume (also called foul flush) that contained a large number of dissolved and suspended organic and inorganic matters, bacteria and organisms. Since many species present in roof runoff water were strongly reactive with soil, artificial infiltration became a popular, easy and effective method of low cost in many countries (e.g. Switzerland, Australia, France), instead of more expensive treatments for roof runoff [Thilo Herrmann and Uwe Schmida (2000), Bucheli, *et al.* (1998), Mason, *et al.* (1999), Legret, *et al.* (1996, 1999<sup>a, b</sup>)].

As a result of a general concern towards the diffuse flow of metals in the society, a number of investigations have recently been performed to monitor metal runoff rates from a number of different sources in the society. Runoff rates from roofing materials have until recently (the last decade) remained a significant gap of knowledge. Previous knowledge has not made any distinction between the corrosion rate and the runoff rate, but rather considered the two rates to be of equal magnitude. A corrosion process is complicated and consists of a number of processes such as corrosion film formation, dissolution, and re-precipitation. As a result of repeated cycles of e.g. dry and wet deposition, one part of the patina can be dissolved and be washed from the surface by precipitation (dew, rain, snow-melting etc) into the surrounding environment whereas the other part of the corrosion patina will retain on the surface during precipitation. The released metal fraction is within this concept referred to as the metal runoff or the metal release. Recent studies [see ref. in Table 1, Runoff rate/Corrosion rate] have shown the runoff rate to be considerably lower than corresponding corrosion rates, the quotient amounting to 50-90% for zinc and 20-50% for copper during exposures of up to five and two years, respectively.

The runoff process takes place if the volume and flow rate of precipitation (rain, snow thawing, dew etc) are sufficient to transport dissolved phases of the corrosion patina from the surface. Consequently, the runoff process is closely related to the characteristics of precipitation (volume, pH, intensity, flow rate etc) and corrosion processes prior to and during a rain event. Physical and chemical reactions as well as the mechanical action between precipitation and corrosion products within the patina will have an effect on the runoff process. The process is also closely related to prevailing pollutant levels. High concentrations of corrosive species in wet (e.g.  $H^+$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ) and dry (e.g.  $SO_2$ ,  $NO_x$ ,  $O_3$ ,  $CO_2$ ) deposition, accelerate the atmospheric corrosion process [Nassau, *et al.*, (1987), Graedel (1993), Johansson and Linder (1993), Zheng, *et al.* (1991), Strandberg (1997)<sup>a, b</sup>, Oesch and Faller (1997)]. The concentration of

corrosive species varies significantly for different forms of precipitation (e.g. rain, fog, dew, snow) and decreases usually with increasing rain quantity and duration [Graedel (1986, 1988), Mrose (1966), Beilke and GeorgII (1968)]. Corrosion rates are thus not always higher in unsheltered exposures (with direct rain impinging the surfaces) compared to sheltered conditions, since rain events of long duration can have a cleaning effect where deposited corrosive species are washed off the surface [Gullman (1993), Carter, *et al.* (1987)]. Prevailing pollutants determine the composition of the patina (see section 1.2). Corrosive species deposited within the patina and cycles of wet conditions interact and dissolve one part of the patina, even though most crystalline corrosion products of the patina formed on copper and zinc have relatively low solubility ( $pK_s > 14$ ). At high pollutant concentrations and in more acidic conditions other phases may also be common constituents of the patina.

A compilation of scientific papers and reports found in the literature on *i*) metal runoff rates, *ii*) comparisons between runoff rates and corresponding corrosion rates, *iii*) effects of various parameters on the runoff rate including solubility of corrosion products, precipitation chemistry (rain pH), rain intensity, exposure condition (inclination), air pollutants ( $SO_2$ ,  $Cl^-$ ,  $NO_x$ ,  $O_3$ , particles) and *iv*) the effect of first flush on the runoff rate (profile, concentration, dry period prior to rain event) are presented in Table 1. The papers in this thesis are also included in the table. In addition to copper and zinc, the compilation also includes data on other metals and alloys.

Table 1 A compilation of literature on metal runoff related issues, mainly on copper and zinc.

	References
<b>Runoff rate</b>	Malmqvist (1983)(F)(Cu, Zn, etc.), Von Franque and Weber (1984)(F)(Cu), Slunder and Boyd (1986)(F)(Zn), Cramer, <i>et al.</i> (1988)(F)(Zn), Kucera and Collin (1977)(F)(Cu, Zn, C-steel), Cramer and McDonald (1990)(F)(Zn, Cu), Lehmann (1995)(F)(Zn-Ti), Verbiest, <i>et al.</i> (1997, 1999)(F)(Zn), Svensson (1997)(F+L)(Cu, Zn), Odnevall and Leygraf (1997)(F)(Cu), Sundberg (1998)(F)Cu, Faller, <i>et al.</i> (1999)(F)(Zn, Cu, Al, SS), Faller (2000)(F)(Zn), Priggemeyer (1999)(F)(Cu), Costa, <i>et al.</i> (1999)(F)(Zn, Cu, SS), Odnevall and Leygraf (1999)(F)(Cu), Persson and Kucera (1999)(F)(Cu, Zn), TNO-report (1999)(F)Zn, Odnevall Wallinder, <i>et al.</i> (1999)(F)(Zn), Jouen, <i>et al.</i> (2000)(F)(Cu), Persson and Kucera (2001)(F)(Cu, Zn, Pd), Odnevall Wallinder, <i>et al.</i> (2001)(F)(Zn), Karlén, <i>et al.</i> (2001)(F)(Zn), Sundberg and Odnevall Wallinder (2001)(F)(Cu), Odnevall Wallinder and Leygraf (2001)(F)(Cu), Cramer, <i>et al.</i> (2002)(F)(Cu), Odnevall Wallinder, <i>et al.</i> (2002)(F)(L)(SS), Karlén, <i>et al.</i> (2002)(F)(Cu), Leuenberger-Minger, <i>et al.</i> (2002) <sup>b</sup> (F)(Cu, Zn), Matthes, <i>et al.</i> (2002)(F)(Pd), Odnevall Wallinder and Leygraf (2002) <sup>a</sup> (F)(Cu, Zn, SS), Odnevall Wallinder, <i>et al.</i> (2002)(F)(Cu), Paper I-VI (F)(L)(Cu, Zn).
<b>Runoff rate / Corrosion rate</b>	Kucera and Collin (1977)(F)(Cu, Zn, C-steel), Slunder and Boyd (1986)(F)(Zn), Cramer, <i>et al.</i> (1988)(F)(Zn), Lehmann (1995)(F)(Zn-Ti), Verbiest, <i>et al.</i> (1997, 1999)(F)(Zn), Sundberg (1998)(F)Cu, Odnevall Wallinder and Leygraf (1999)(F)(Cu), Costa, <i>et al.</i> (1999)(F)(Zn, Cu, SS), TNO-report(1999)(F)(Zn), Odnevall Wallinder, <i>et al.</i> (1999)(F)(Zn), Faller, <i>et al.</i> (1999)(F)(Zn, Cu, Al, SS), Cramer, <i>et al.</i> (2000)(F)(Zn), Jouen, <i>et al.</i> (2000)(F)(Cu), Odnevall Wallinder and Leygraf (2001)(F)(Cu), Cramer, <i>et al.</i> (2002)(F)(Cu), Leuenberger-Minger, <i>et al.</i> (2002) <sup>b</sup> (F)(Cu, Zn), Paper I, II, and VI (F)(L)(Cu, Zn).
<b>Solubility of corrosion products</b>	Stiles and Edney (1989)(L)(Zn), Cramer and McDonald (1990)(F)(Zn, Cu), Cramer and McDonald (1992)(F)(Zn), Cramer, <i>et al.</i> (1993)(F)(Cu, Zn), Oesch and Heimgartner (1996)(F)(Cu, Zn, Al, Steel), Strandberg (1997) <sup>a</sup> (L)(Cu), Oesch and Faller (1997)(L)(F)(Cu, Zn, Al), Fitzgerald (1995)(Cu), Fitzgerald, <i>et al.</i> (1998)(L)(Cu), Paper V (L)(Zn).
<b>Precipitation</b>	
Rain pH	Stiles and Edney (1989)(L)(Zn), Cramer and McDonald (1990)(F)(Zn Cu), Spence, <i>et al.</i> (1990) (L)(Zn), Zheng, <i>et al.</i> (1991)(F)(Zn), Spence, <i>et al.</i> (1990)(L)(Zn), Svensson (1997)(F+L)(Cu, Zn), Odnevall Wallinder, <i>et al.</i> (2002)(F)(L)(SS), Paper IV and V (F)(L)(Cu, Zn).
Rain intensity	Odnevall Wallinder, <i>et al.</i> (2002)(F)(L)(SS), Paper IV and V (F)(L)(Cu, Zn).
<b>Exposure condition</b>	
Inclination	Vernon (1927)(F)(Cu, Zn), Haynie, <i>et al.</i> (1990), Lehmann (1995)(F)(Zn-Ti), Paper III (F)(L)(Cu, Zn).
Orientation	Paper III (F)(L)(Cu, Zn).
<b>Air pollutants (SO<sub>2</sub>, Cl<sup>-</sup>, NO<sub>x</sub>, O<sub>3</sub>, particles, etc.)</b>	Slunder and Boyd (1986)(F)(Zn), Spence, <i>et al.</i> (1990)(L)(Zn), Spence, <i>et al.</i> (1990)(L)(Zn), Verbiest, <i>et al.</i> (1999)(F)(Zn), Odnevall Wallinder, <i>et al.</i> (1999)(F)(Zn), Leuenberger-Minger, <i>et al.</i> (2002) <sup>a,b</sup> (F)(Cu, Zn), Paper II (F)(Cu, Zn).
<b>During rain</b>	
First flush	Good (1993)(Zn, Al)(F), Quek and Förster (1993)(F)(Zn), Förster (1996, 1999), Paper IV-VI (L)(Cu, Zn).
Runoff profile	Quek and Förster (1993)(F)(Zn), Förster (1996), Paper IV-VI (L)(Cu, Zn).
Concentration	Good (1993)(Zn, Al)(F), Quek and Förster (1993)(F)(Zn), Costa, <i>et al.</i> (1999)(F)(Zn, Cu), Bertling, <i>et al.</i> (2002) <sup>a-c</sup> (Zn, Cu), Heijerick, <i>et al.</i> (2002)(F)(Zn), Paper IV-VI (L)(Cu, Zn).
Dry period	Good (1993)(F)(Zn, Al), Paper IV-VI (L)(Cu, Zn).

(F) = Field exposure, (L) = Laboratory exposure, SS = Stainless Steel.

## 2. Experimental

A schematic summary of all field- and laboratory investigations conducted within this thesis is shown in Fig. 3.

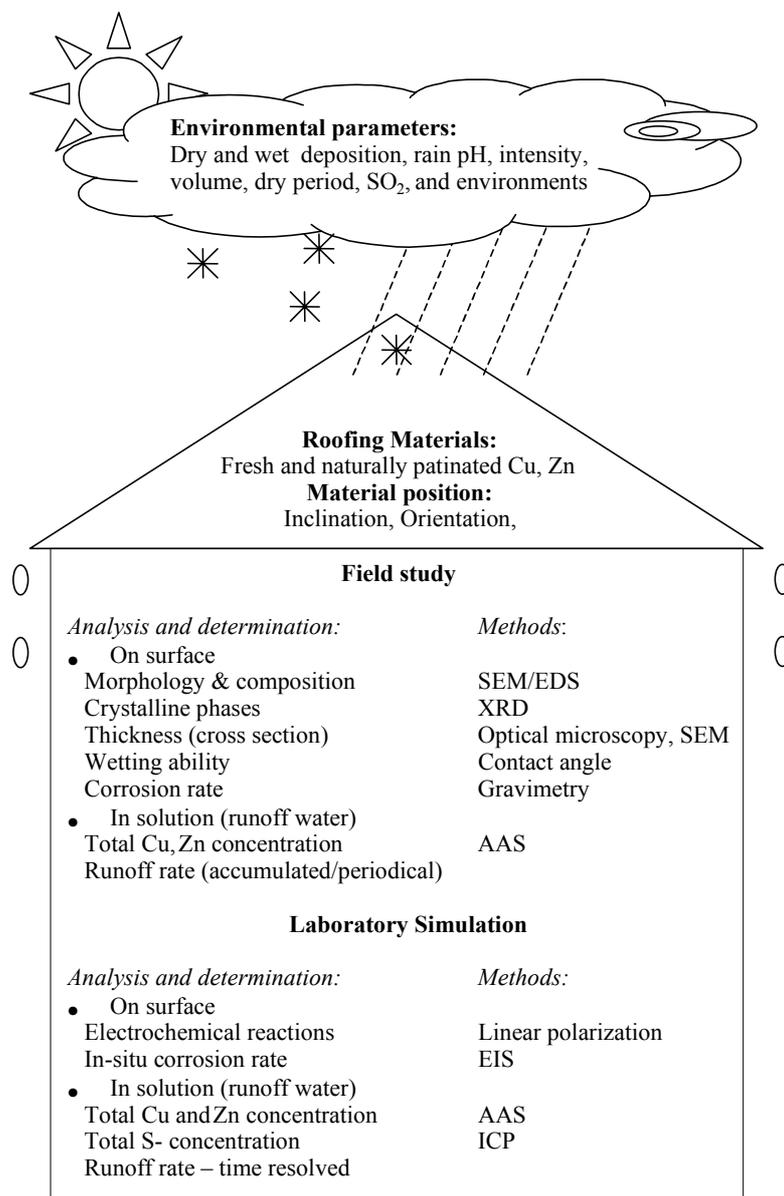


Fig. 3 Outline of the doctoral study. Abbreviations used; SEM: Scanning electron microscopy, EDS: Energy dispersive spectroscopy, XRD: X-ray powder diffraction, AAS: Atomic absorption spectroscopy, ICP: Inductively coupled plasma, EIS: electrochemical impedance spectroscopy.

All investigations aim at an increased understanding of the metal runoff process and the corrosion process as a result of precipitation on fresh and naturally patinated copper and zinc sheet used for roofing applications. This has been established by performing parallel field and laboratory investigations and through detailed studies show the effect of various parameters on the runoff rate; dry and wet deposition in different types of environments; rain pH, rain intensity, and volume of rain; SO<sub>2</sub> concentration, surface orientation and inclination, and different phases of the corrosion patina. During the field studies, panels were freely exposed with an inclination of 45° from horizon and directed south. Surface morphology, composition of the corrosion patina, film thickness and surface wetting ability were identified by means of surface analysis. Measurements of mass loss and metal concentration of the runoff water were performed to determine corrosion rates and runoff rates. In the laboratory studies, artificial rain was used to simulate real rain events on fresh and naturally patinated panels by varying the rain pH, amount, intensity and time-period in-between rain events. Prior to the laboratory investigation, the naturally patinated panels were either exposed under rain sheltered or unsheltered outdoor exposure conditions. The composition and pH of the artificial rain resembled rain of the central part of Sweden.

The different analytical methods seen in Fig. 3 and experimental set-up used are described in more detail in the papers (I-VI). In what follows only a definition is given on the most important concepts and how experimental data have been defined.

*Instantaneous* corrosion rates and runoff rates were determined during single rain events on copper by electrochemical impedance spectroscopy (EIS) and metal analysis in runoff water respectively.

The *corrosion rate* and the *runoff rate* were measured and calculated according to equation (1) and (2), in unit of g/m<sup>2</sup>, y or μm/y.

$$R_{\text{corr}} = 10^4 \cdot \text{ML} / (\rho \cdot A \cdot t) \quad (1)$$

$$R_{\text{runoff}} = 10^{-2} \cdot C \cdot V / (\rho \cdot A \cdot t) \quad (2)$$

Here,  $R_{\text{corr}}$  is the corrosion rate (μm/y),  $R_{\text{runoff}}$  is the runoff rate (μm/y), ML is the metal mass loss (g), i.e. the weight change before and after exposure and removal of the corrosion products, A is the exposed surface area (cm<sup>2</sup>), t is the exposure time (year) including dry and wet deposition, ρ is the density of the metal (g/cm<sup>3</sup>) (8.91 for copper; 7.14 for zinc), C is the

metal concentration in runoff water (mg/L, or ppm), and V is the volume of the collected runoff water (mL).

The *runoff profile* is usually presented as changes in runoff concentration or runoff rate as a function of increasing runoff volume or rain time. The unit of the runoff volume is L/m<sup>2</sup> (collected volume impinging the sample surface / sample area) and/or mm (collected volume / projected area of collector). A conversion between the units can easily be done; L/m<sup>2</sup> = mm·cosθ (θ is panel inclination from horizon).

Instantaneous (in-situ) corrosion rates and runoff rates have been determined for naturally patinated copper of varying age during single rain events. A 2-electrode system and electrochemical impedance spectroscopy (EIS) were used to evaluate the corrosion rate by using equation (3) and the Stern-Geary equation (4). The current density I<sub>corr</sub> represents the amount of corroded metal and R<sub>p</sub> the corrosion resistance.

$$R_{\text{corr}} = 3.15 \cdot 10^{11} \cdot M \cdot I_{\text{corr}} / (n \cdot F \cdot \rho) \quad (3)$$

$$I_{\text{corr}} = \beta_a \beta_c / [2.3 \cdot (\beta_a + \beta_c)] / R_p = K / R_p \quad (4)$$

Here, R<sub>corr</sub> is the corrosion rate (μm/y), M is the molecular mass (63.54 g/mol for copper), I<sub>corr</sub> is the corrosion density (A/cm<sup>2</sup>), n is the number of electrons transferred (assumed to be 2 for copper corrosion), F is Faraday constant (96500 A·s/mol), ρ is the metal density (g/cm<sup>3</sup>), and β<sub>a</sub>, β<sub>c</sub> are Tafel constants obtained from potentiodynamic polarization measurements in bulk rainwater using traditional 3-electrode electrochemical measurements. The units of rates can easily be converted by equation (5).

$$\text{Rate (g/(m}^2\text{·y))} = \rho \cdot \text{Rate (}\mu\text{m/y)} \quad (5)$$

A compilation of all field and laboratory investigations and type of information gained within each study is given in Table 2.

Table 2 A compilation of all investigations performed within this thesis

Paper	I	II	III	IV	V	VI	
Field exp.	Sheltered				x		x
	Unsheltered	x	x	x	x	x	x
	Urban	x	x	x	x	x	x
	Rural				x		x
	Marine				x		
	SO <sub>2</sub>		x				
	Inclination			x			
	Orientation			x			
Material	Cu-fresh	x		x	x		
	Cu < 2 y old				x	x	x
	Cu > 40 y old	x		x	x		x
	Zn-fresh	x	x	x	x	x	
	Zn < 2 y old			x	x	x	
	Zn > 15 y old	x	x			x	x
Lab exp.	pH				x	x	
	Intensity				x	x	
	Dry period				x	x	
	Inclination			x			
Evaluation	R <sub>corr</sub>	x	x				
	R <sub>corr-in-situ</sub>						x
	R <sub>runoff</sub>	x	x	x	x	x	
	R <sub>runoff-in-situ</sub>				x	x	x
	Corr. products	x					
	Morphology	x					
	Film thickness	x	x				
	Contact angle						x

### 3. Results and discussion:

The following eight questions have been formulated during the course of this doctoral study, all believed to provide important basic knowledge on the diffuse flow of copper and zinc induced by atmospheric corrosion from roofing materials in the society. Five different issues are mainly discussed; *i*) Comparison between corrosion rates and runoff rates (3.1 – 3.2), *ii*) effect of environmental parameters on the runoff process (3.3), *iii*) effect of surface morphology and patination on the runoff process (3.4 – 3.5), *iv*) mechanisms behind the runoff process (3.6), and *v*) validation and usefulness of data (3.7 - 3.8).

#### 3.1 Is the corrosion rate different from the runoff rate on a monthly and yearly perspective?

Corrosion rate determinations of fresh copper and zinc exposed during 8, 16, 24, 32, 40, and 48 weeks in the urban site of Stockholm, Sweden, showed decreasing rates with time while continuous measurements of the runoff rate showed relatively constant rates over the

same exposure period (Fig. 4). The continuous decrease of the corrosion rate with time (a decrease with more than 40% for copper and more than 70% for zinc between the 8<sup>th</sup> and the 48<sup>th</sup> week) reflects the gradual build-up of protective corrosion products. No steady-state condition was reached during the exposure period. Depending on the environment, literature data suggest time-periods of a few decades for copper and 3-5 years for zinc before reaching a relatively constant patina thickness and a relatively constant corrosion rate [Graedel, *et al.* (1987), Cramer and McDonald (1990)]. Annual corrosion rates (based on 48 weeks of exposure) of 6.7 g/(m<sup>2</sup>·y) and 5.0 g/(m<sup>2</sup>·y), were determined for copper and zinc, respectively. Corresponding annual runoff rates were 1.3 g/(m<sup>2</sup>·y) for copper and 3.1 g/(m<sup>2</sup>·y) for zinc exposed to a precipitation quantity of approximately 500 mm.

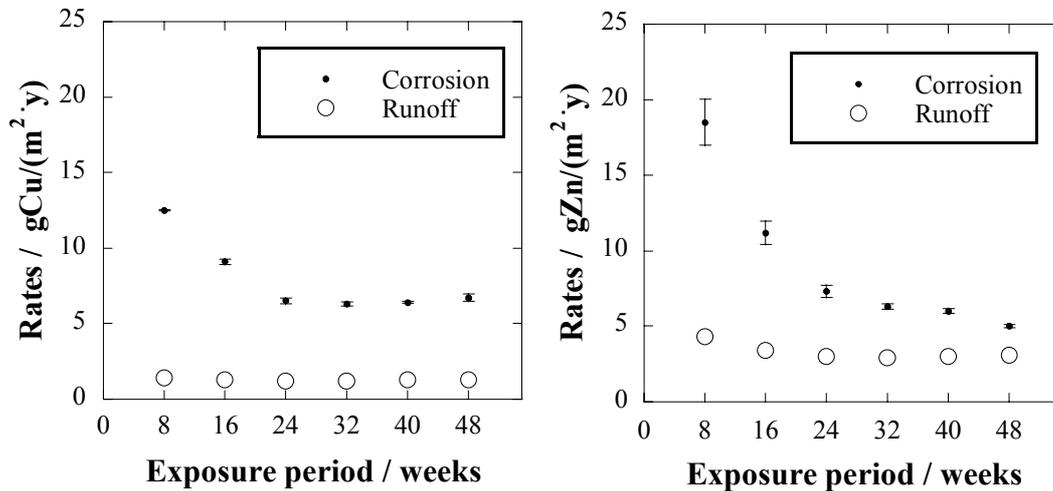


Fig. 4 Comparison between corrosion rates and runoff rates for copper (left) and zinc (right) exposed during 48 weeks at the urban site of Stockholm, Sweden.

The results show the runoff rate to be lower than the corrosion rate for both copper and zinc during exposure periods up to one year. The yearly metal runoff rate was determined to be approximately 20% and 60% of the yearly corrosion rate for copper and zinc, respectively. This means that a large fraction of the corroding metal is retained within the corrosion patina. Similar quotients between runoff rates and corrosion rates have been found in other investigations for exposure periods of up to five years (50-90% for zinc; 20-50% for copper) [Cramer, *et al.* (1988), Lehman (1995), Kucera and Collin (1977), Slunder and Boyd (1986), Verbiest, *et al.* (1997)]. Figure 4 shows the quotient between the runoff rate and the corrosion rate to increase from 10 to 20% for copper and from 40 to 60% between the 8<sup>th</sup> and the 48<sup>th</sup> week of exposure. The results are in agreement with findings by Leuenberger-Minger, *et al.* (2002)<sup>b</sup> showing an

increase of the same quotient from 2 to 15% for copper and from 30 to 65% for zinc after 0.5 and 4 years of exposure in Switzerland ( $\text{SO}_2 < 10 \mu\text{g}/\text{m}^3$ ). With prolonged exposure time it is anticipated that the annual corrosion rate and the annual runoff rate will reach similar values. This state will probably be reached faster for zinc than for copper. The magnitude of the corrosion rate and the runoff rate are closely related to the ambient environment including e.g. rain characteristics and prevailing pollutant concentration. Increasing rates are obtained with increasing pollutant levels and rainfall quantities.

More details are found in paper I.

*To summarize: a time dependence with initially high corrosion rates followed by a continuous decrease to lower corrosion rates obtained during steady-state conditions were observed, whereas the runoff rate showed to be relatively constant on a yearly basis for both copper and zinc. The data show the necessity of using yearly runoff rates rather than corrosion rates as a measure of the dispersion of metals from buildings and outdoor constructions in the society.*

On a yearly perspective, the runoff rate has been shown to be lower than the corrosion rate for both copper and zinc. However, on a much shorter time-scale (e.g. days, weeks, months) the situation can be different as a result of variations in environmental conditions, such as duration and length of dry and wet periods during the exposure period. A comparison between the actual rate of film formation or growth of the patina (i.e. the difference between the corrosion rate (ML) and the runoff rate during a specific time-period) and the dissolution rate of the patina (runoff rate) were monitored during 6 individual consecutive exposure periods. These periods, each being 8 weeks long, starting in November 1996 and illustrate the effect of different seasons. Some periods include a large number of rain events whereas others include only a few showers. The results, showing large variations between different exposure periods, are presented in Fig. 5. The formation rate of a patina was much faster than the dissolution rate during the initial 8 weeks for both copper and zinc. A similar trend could be seen on copper during all of six exposure periods indicating a relatively fast formation of compact and protective phases of the patina. For zinc, in this case, the 2<sup>nd</sup>, 3<sup>rd</sup> and 6<sup>th</sup> exposure period showed periods of corrosion patina thinning (negative film formation rates), most probably as a result of porous and poorly protective phases within the patina.

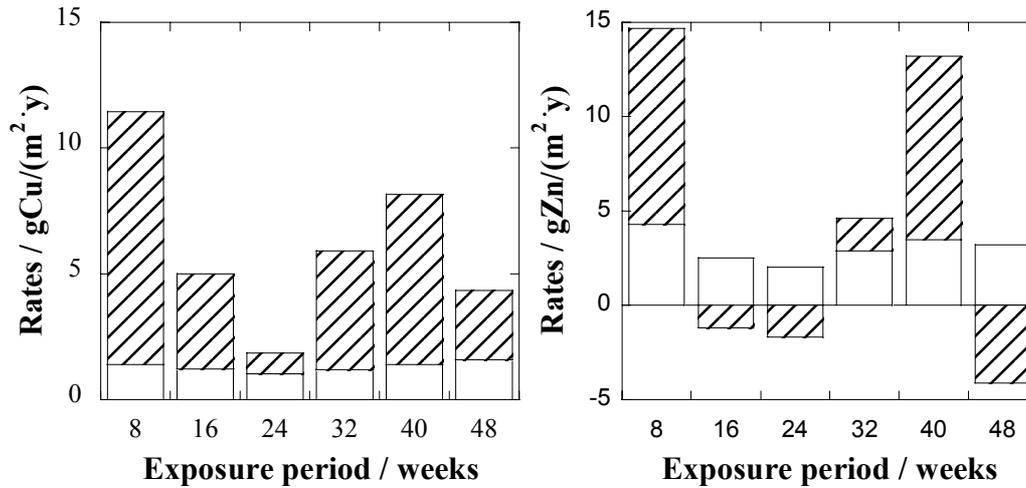


Fig. 5 Average rates of patina formation (dashed piles) and patina dissolution (unfilled piles) on copper (left) and zinc (right) during 6 eight-week exposure periods at the urban site of Stockholm, Sweden. The sum of the rate of film formation and dissolution corresponds to the total corrosion rate during each sampling period.

To summarize: as a result of the formation of relatively protective corrosion phases of the patina on copper, the patina formation rate was always dominating over the dissolution rate also on a monthly perspective. For zinc, however, periods occurred when the runoff rate was higher than the formation rate with a patina loss as a result, and vice versa.

### 3.2 Is the corrosion rate different from the runoff rate during a single rain episode?

Instantaneous corrosion rates and runoff rates were monitored during single successive rain episodes in the laboratory on naturally patinated copper panels of varying age by means of electrochemical impedance spectroscopy (EIS) using a 2-electrode cell and chemical analyses, respectively. The investigation involved both copper panels with brown (16 months of natural patination) and green patina (138 and 145 years of natural patination). No investigations have so far been made on naturally patinated zinc. The results, illustrated in Fig. 6, show relatively constant corrosion rates (between 0.2-0.4  $\mu\text{m}/\text{y}$  after 10 hours of continuous rain) for panels having a two-layer structure with an inner brownish layer of cuprous oxide and an outer greenish layer of basic copper salts (138, 145 years). Panels with cuprous oxide as the dominating phase of the patina (16 months) showed higher and

somewhat increasing corrosion rates during a rain event (from 0.6 to 1.2  $\mu\text{m}/\text{y}$  after 2 days of continuous rain).

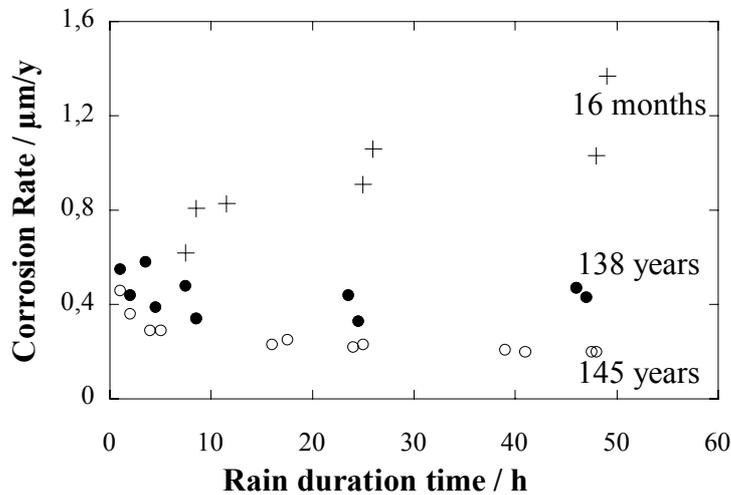


Fig. 6 Instantaneous corrosion rates of naturally patinated copper samples (brown-patinated Cu: 16 months (+), green-patinated Cu: 138 years (●), 145 years (○)) during a continuous rain event simulated in the laboratory (intensity 4-6 mm/h, pH 4.3)

The runoff process proceeds simultaneously, but independently of the corrosion process. Measurements of runoff rates during the same rain episodes show a decrease of an initially high rate in the initial rain volume flushing the surface (first flush) to a more constant rate with prolonged exposure (steady-state), Fig. 7. Runoff rates were found to be approximately 10 and 25 times higher compared to corresponding corrosion rates for naturally brown and green patinated panels, respectively. The decrease in runoff rate as a function of rain duration is a result of a number of interacting environmental and surface parameters such as rain pH, intensity, patina thickness and composition. The effect of these parameters on the metal runoff rate during first flush and steady-state is further discussed in section 3.3.

Higher runoff rates compared to corrosion rates during the rain event resulted in a diminishing of the patina thickness. However, on an annual basis the runoff rate is still lower than the corrosion rate since the time of rain duration on an annual basis is very short, approximately 2%, and the runoff rate is limited by the rain volume whereas the corrosion process occurs over a much longer fraction of the year and independently of the occurrence of rain.

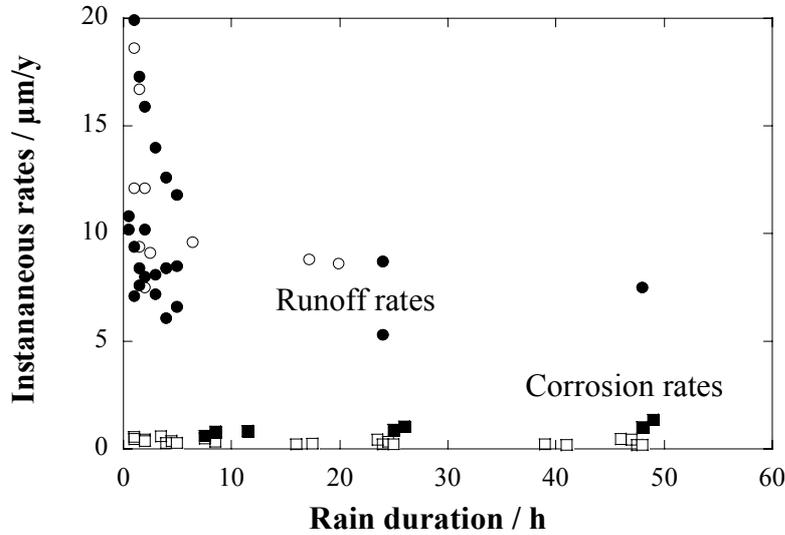


Fig. 7 Comparison between instantaneous runoff rates ( $\circ$ ,  $\bullet$ ) and corrosion rates ( $\square$ ,  $\blacksquare$ ) for naturally patinated copper of varying age during a continuous rain event of intensity 4 mm/h and pH 4.3. (green-patinated Cu (> 100 years old): unfilled symbols, brown-patinated Cu (16 months old): filled symbols.)

To summarize: corrosion rates were found to be substantially lower than the corresponding runoff rates of naturally patinated copper during single rain episodes with a diminishing of the corrosion patina thickness as a result.

### 3.3 Which environmental parameters govern the metal runoff quantity?

The metal runoff concentration and the runoff rate of copper and zinc was found to vary significantly between different outdoor sampling periods (typically days or a few weeks long depending on the actual rainfall quantity and frequency). Another general conclusion from the field exposures was that the runoff rate usually increased with increasing volume of collected runoff water. However, a significant variation in metal concentration was found for both copper and zinc when comparing different sampling periods of similar collected volumes of runoff water. This is illustrated in Fig. 8 for a number of sampling periods during a four-year urban field exposure of zinc. A total collected rain volume of approximately 20L characterizes each sampling period.

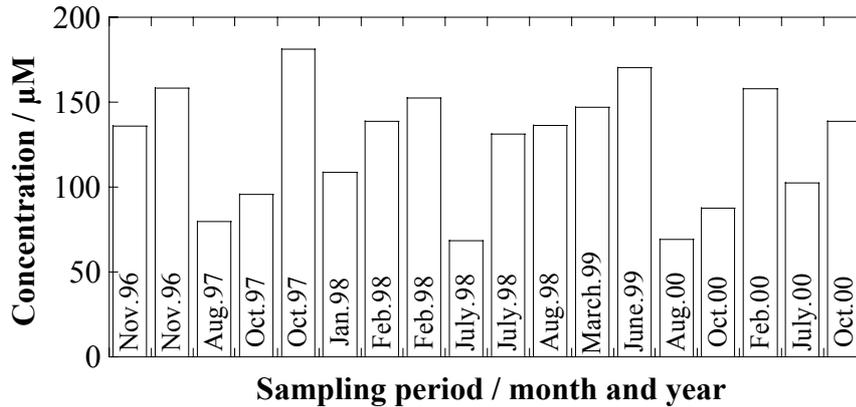


Fig. 8 Variation in zinc runoff concentration of different sampling periods of a collected rain volume of  $20 \pm 1 \text{ L/m}^2$  from fresh zinc panels. Sampling month and year is given in each stack.

The variation in concentration was believed to be a result of a number of interacting environmental parameters, including duration of rain events, intensity and pH, as well as length of dry periods in-between two rain events. The effect of each parameter on the runoff rate on both copper and zinc was separately investigated in the laboratory using artificial rain. This was accomplished by varying one parameter while keeping the other parameters constant, hence simplifying outdoor conditions. However, the results can still be used to explain variations in outdoor runoff concentrations.

More details are given in paper IV and V.

*Effect of rain volume.* The kinetics of metal runoff during single rain events was found to be similar for both copper and zinc, Fig. 9. Runoff water from each rain event showed a high metal concentration during the first volume of rain passing the surface (first flush), followed by a decreasing metal concentration with increasing rain volume, and a finally a region of a more or less constant metal concentration (steady-state). The magnitude of the concentration during first flush was influenced by changes in rain volume (or time) and by all other parameters investigated. However, the magnitude of the concentration during steady-state was only influenced by the rain intensity and pH. (These effects will be further discussed in the following sections).

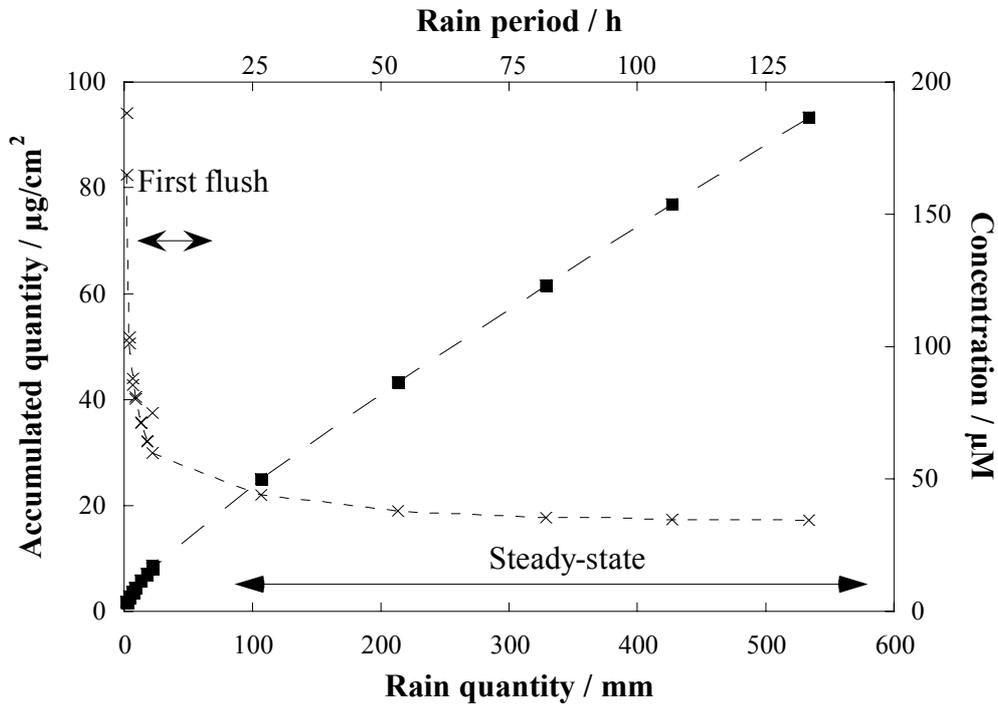


Fig. 9 Effect of rain volume and time on the accumulated runoff quantity (■) and concentration (×) of copper. The copper panel was pre-exposed under sheltered conditions in an urban environment for 16 months before the laboratory rain simulation (pH 4.3, 4 mm/h).

Effect of rain pH. The metal concentration and runoff quantity were found to increase with decreasing pH as a result of decreasing stability of corrosion products of copper and zinc within the patina. The effect was seen both during first flush and steady-state, Fig. 10. The change in concentration as a result of changing pH was of the same order of magnitude both during first flush and steady-state. This suggests the release of metal ions from corrosion products of relatively low solubility within the patina during both regions. A correlation could be discerned between the concentration of dissolved zinc and hydrogen ions in the steady-state region, Fig. 11, showing two hydrogen ions to dissolve one zinc ion into solution.

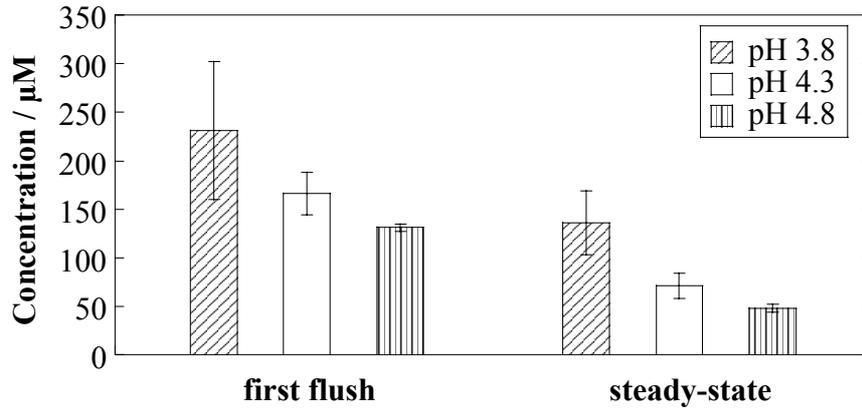


Fig. 10 Zinc runoff concentration from fresh zinc during first flush and steady-state of single rain events of varying pH at constant intensity (5 mm/h)

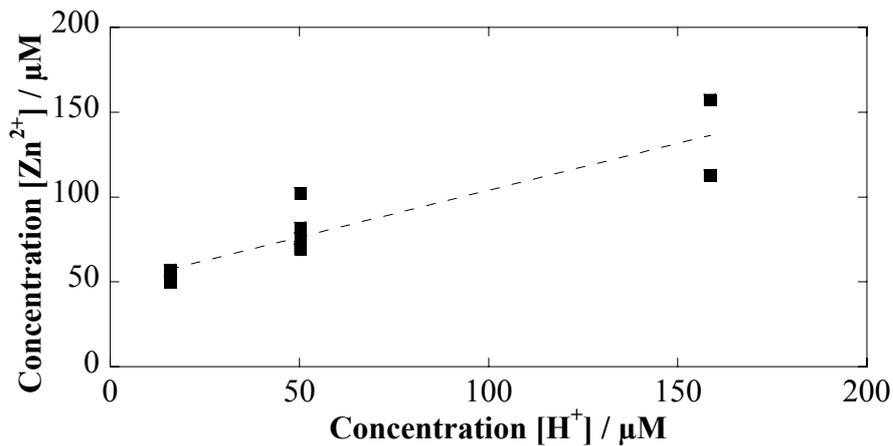


Fig. 11 Correlation between zinc ion concentration and hydrogen ion concentration during steady-state release from naturally patinated zinc (0.5 years).

The *effect of rain intensity* is illustrated in Fig. 12 for naturally patinated copper and zinc, respectively. A higher metal runoff quantity is obtained during drizzle (0.7 mm/h) compared to light- (4-6 mm/h) and moderate rain (14-22 mm/h) as a result of longer residence times for rainwater on the surface. The residence time is one major factor that determines the rate at which corrosion products are dissolved and released from the surface. If the residence time is very short at a given rain volume, i.e., a fast flow rate, a smaller fraction of the patina is dissolved and *vice versa*, see Fig. 13. Above a certain flow rate, the metal runoff

concentration will not change very much. This critical flow rate was determined to be approximately 10 L/(m<sup>2</sup>h) for zinc (Fig. 13). The term flow rate is more appropriate to use than the intensity since it can be used to describe the effect of rain intensity on panels of varying inclination. A transformation between the units can easily be performed with the equation  $L/(m^2h) = (mm/h)\cos\theta$ , where  $\theta$  is the degree of inclination from horizon and mm/h the intensity. The critical flow-rate for copper was estimated to be lower than 5.6 L/(m<sup>2</sup>h) since the runoff quantity reached similar levels both during light rain (7.8 mm/h) and moderate rain (20.5 mm/h). Unfortunately, no more measurements have been performed on copper to show the relation between the runoff concentration and the flow rate during steady-state.

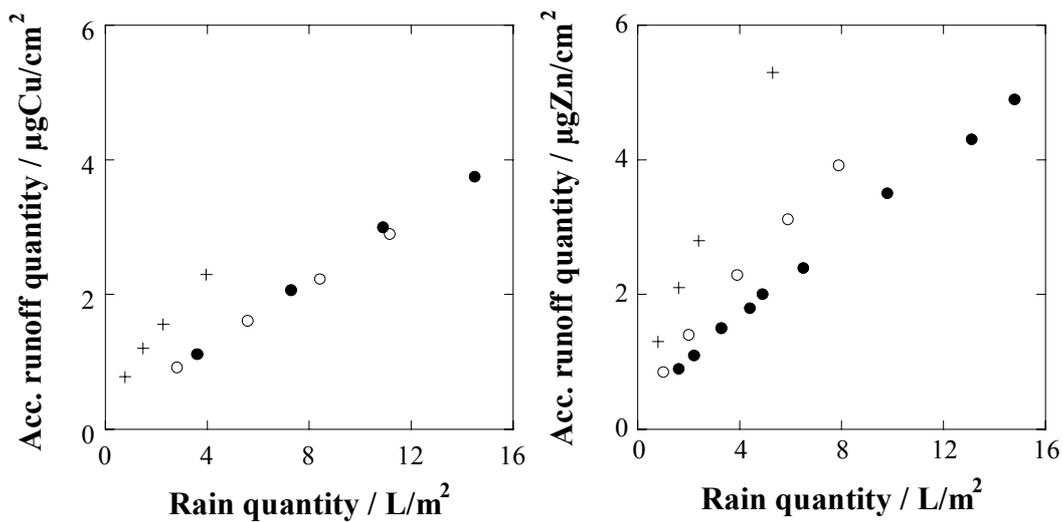


Fig. 12 Effects of rain intensity on naturally patinated copper (one year - left) and zinc (0.5 year - right) using artificial rain of varying intensity ((+) drizzle of 0.7 mm/h, (○) light rain of 4-6 mm/h, and (●) moderate rain of 14-22 mm/h).

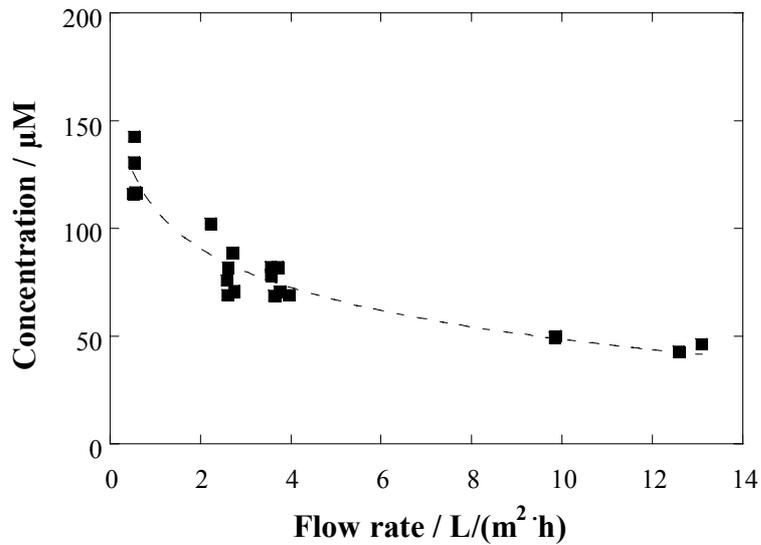


Fig. 13 Changes in zinc concentration during steady-state as a function of flow rate of impinging rainwater (pH 4.3, 40 year-old zinc panel).

The length of the dry period in-between rain episodes affects the runoff quantity and concentration primarily during first flush. A longer dry period in-between two rain episodes will induce a higher metal concentration during first flush but have no significant effect during steady-state. This is the result of a combination of interacting effects such as an increased deposition of corrosive species onto the corrosion patina and hence the formation of more easily soluble corrosion products, the formation of cracks, defects and porous corrosion products within the patina. The latter increase the specific reaction area and facilitates for corrosive species and water to be trapped and dissolved within the layer. The effect is illustrated in Fig. 14 for naturally patinated zinc (40 years). The zinc concentration in the first flush volume is approximately twice as high after a 1-month dry period compared to a one-day dry period in-between two rain events. Similar effects can be seen for naturally patinated copper with a more pronounced effect on copper having a green patina compared to copper with brown patina.

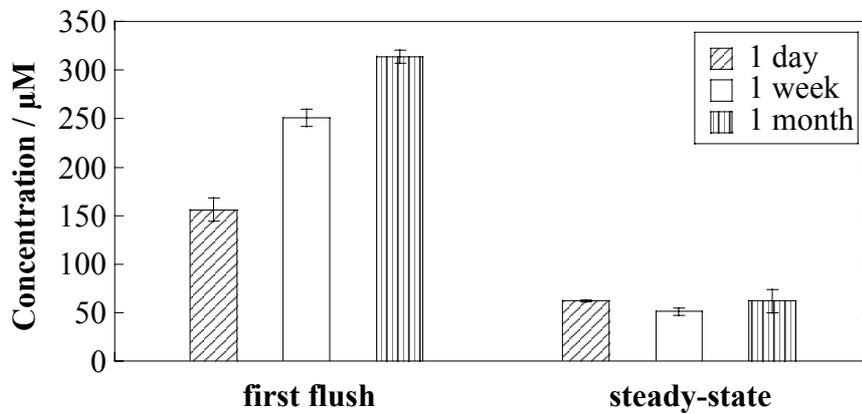


Fig. 14 Zinc runoff concentration (40- year old zinc panels) during first flush and steady-state during single rain events of constant pH and intensity (pH 4.3, 5 mm/h), preceded by dry periods of varying length.

To summarize: the runoff quantity and concentration of copper and zinc are affected by a number of environmental parameters including rain volume, pH, intensity, and length of dry periods in-between rain episodes. During a rain episode, the metal runoff concentration is higher during first flush compared to the steady-state region. The metal concentration in runoff water increases with increasing rain acidity (both during first flush and steady-state conditions), decreasing rain intensity (both during first flush and steady-state conditions), and increasing length of dry periods in-between two rain episodes (only during first flush).

One-year field exposures of fresh zinc sheet at three different test sites of varying  $SO_2$  concentration and compilation of literature data on runoff rates of zinc (1-5 years of exposure) were performed to investigate the *effect of  $SO_2$*  on the runoff rate. Results from the field exposures showed an increasing runoff rate with increasing  $SO_2$ -concentration, see Fig. 15.

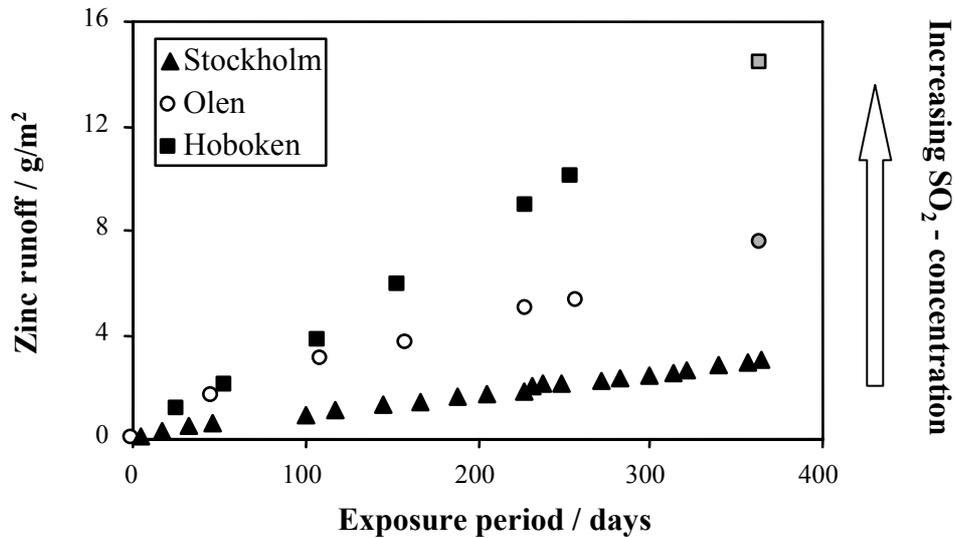


Fig. 15 Accumulated runoff data vs. exposure time for the three test sites. (The shaded circle and square after one year of exposure at Olen and Hoboken correspond to extrapolated data).

In agreement with previous observations, runoff rates were fairly constant on an annual basis. Previous findings have shown a strong relationship between the corrosion rate of zinc and the SO<sub>2</sub>-concentration [Zheng, *et al.* (1991), Cramer, *et al.* (1988), Oesch and Faller (1997)]. An attempt was therefore made to find a relationship also between the runoff rate and the SO<sub>2</sub>-concentration using data from outdoor field exposures of up to five years at test sites with annual precipitation quantities of the same order of magnitude. Experimental corrosion and runoff rate data and the calculated relations, based on regression analyses, are presented in Fig. 16. The correlations were described with equation (6) and (7).

$$\text{Corrosion rate } (\mu\text{m/y}) = 0.53 + 0.032[\text{SO}_2](\mu\text{g/m}^3) \quad R^2 = 0.98 \quad (6)$$

$$\text{Runoff rate } (\mu\text{m/y}) = 0.19 + 0.023[\text{SO}_2] (\mu\text{g/m}^3) \quad R^2 = 0.98 \quad (7)$$

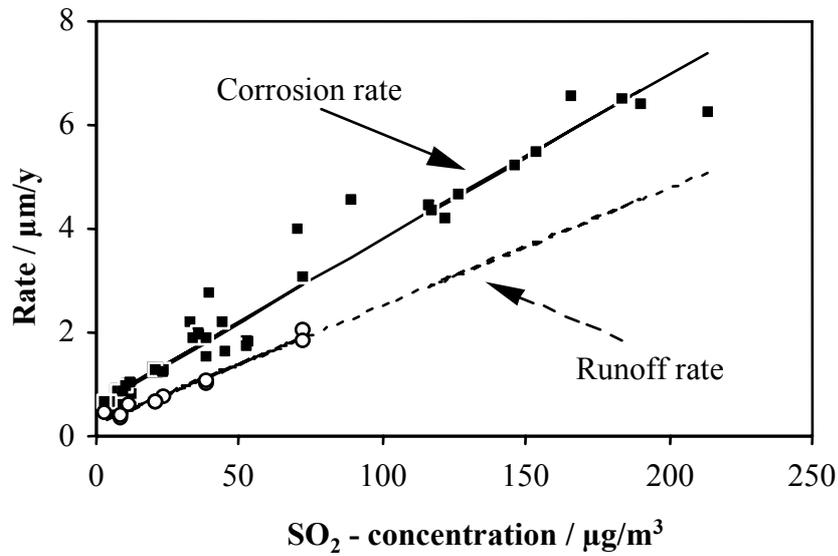


Fig. 16 Runoff rates and corrosion rates for fresh zinc sheet exposed to test sites of varying SO<sub>2</sub> - concentration and annual precipitation quantities of the same order of magnitude. The lines indicate calculated relations.

In agreement with previous findings (see paragraph 3.1) the results show annual runoff rates to be lower than corresponding corrosion rates for exposure periods up to five years.

Attempts are currently performed to establish correlations also for copper [Odnevall Wallinder, private communications (2002)].

*To summarize: a relationship between the runoff rate and the SO<sub>2</sub>-concentration has been established, which can be used to predict runoff rates of zinc in various polluted environments.*

The composition of corrosion products within the patina layer depends on the environment in which they are formed (see section 1.2). Differences in runoff behavior from *panels of different origin* (16 months of sheltered exposure in an urban, rural and marine site) were investigated during single rain episodes (pH 4.3, intensity 4-6 mm/h, and inclination 45°) in the laboratory. Higher metal runoff concentrations and metal quantities were released from panels being exposed in the marine and urban environment compared to the rural atmosphere, Fig. 17.

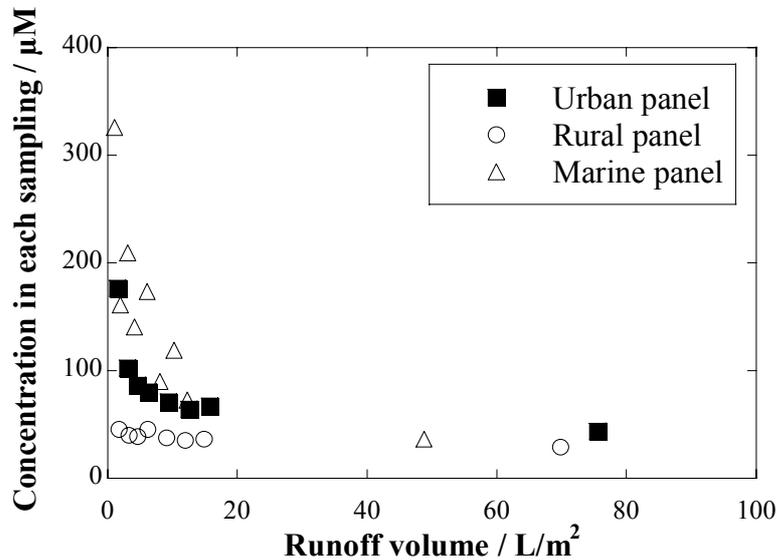


Fig. 17 Changes in copper concentration in each sampling during continuous rain events (4-6 mm/h, pH 4.3) on panels pre-exposed in marine, urban, and rural environments.

By assuming an annual precipitation quantity of 500 mm/y for each site, the data were used to calculate runoff rates for each site. These calculated rates; 1.7, 1.2, and 0.7 g Cu/(m<sup>2</sup>·y) and 3.7, 2.6, and 1.6 g Zn/(m<sup>2</sup>·y), for the marine, urban and rural site, respectively, were in excellent agreement with actual runoff rate measurements in the urban and the rural environment, being between 1.1-1.7 g Cu/(m<sup>2</sup>·y) and 2.1-3.1 g Zn/(m<sup>2</sup>·y) in the urban site, and between 0.6-1.0 g Cu/(m<sup>2</sup>·y) in the rural site [Paper I, Odnevall Wallinder and Leygraf (2001), Karlén, *et al.* (2001)]. Differences in runoff rates for samples of different origin were primarily a result of differences in runoff concentration during first flush. The main corrosion products of the patina were suggested to be of low and similar solubility, and mainly governed by rain properties. Higher runoff concentrations during first flush on samples originating from the urban site compared to the rural site were primarily a result of a more corrosive environment caused by increased concentrations of e.g. SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub>, see Table 3, and hence a higher deposition rate of species originating from these and other pollutants. A high metal runoff concentration and the large scatter in data on samples from the marine site were most probably a result of poorly protective and loosely adherent phases of the patina. The

corrosion accelerating effect of gaseous pollutants on copper and zinc has previously been shown in a number of investigations [Svensson (1996), Oesch and Faller (1997), Aastrup, *et al.* (2000)<sup>a</sup>].

Table 3 Concentrations of air pollutants at the urban and rural site (data during Nov. 1996 – Feb. 1998) (data-base at [www.slb.mf.stockholm.se](http://www.slb.mf.stockholm.se))

Pollutants	Urban site	Rural site
SO <sub>2</sub> (µg/m <sup>3</sup> )	3.5±3.2	0.7±0.9
NO <sub>2</sub> (µg/m <sup>3</sup> )	20.5±14.1	4.2±4.3
O <sub>3</sub> (µg/m <sup>3</sup> )	47.6±23.4	58.8±25.2

*To summarize: the runoff rate of copper and zinc depends on the prevailing pollutant levels of the environment to which the metals are exposed. Soluble and poorly adhesive corrosion products formed in more polluted environment will primarily be washed off during first flush and result in higher concentrations during first flush and, consequently, also higher runoff rates.*

### **3.4 What effect has natural patination on the runoff rate (panel age)?**

As previously shown, the metal runoff rate is governed by a large number of interacting parameters and can vary significantly between different sampling periods primarily as a result of prevailing characteristics of precipitation. Consequently, comparisons between runoff rates from different panels and exposures should preferentially be done in parallel exposures governed by the same environmental characteristics or otherwise be used with caution unless the specific environmental conditions are known.

Runoff rates were compared between naturally patinated copper and zinc panels of varying age during one year of urban exposure (Paper I). Fresh copper showed a lower runoff rate (1.3 g/(m<sup>2</sup>·y)) compared to naturally patinated (>40 years) copper (2.0 g/(m<sup>2</sup>·y)), Fig.18 (left).

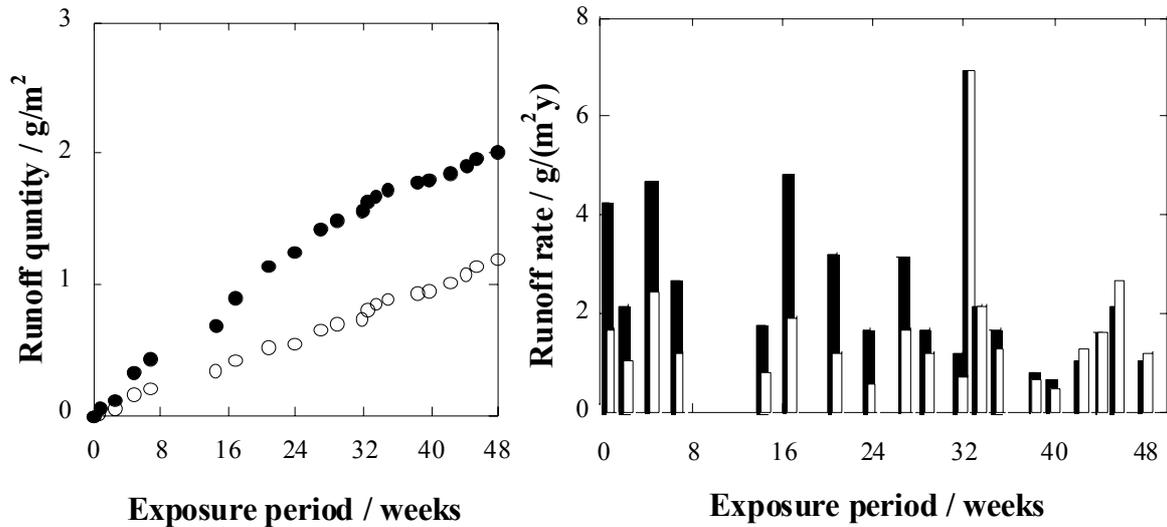


Fig.18 Left: Accumulated copper runoff data from fresh (unfilled circles) and naturally patinated copper (> 40 years old) (filled circles). Right: Runoff rates during different sampling periods from fresh (unfilled bars) and naturally patinated (filled bars).

The discrepancy in runoff rate between fresh and naturally patinated copper was large during the initial exposure period and the two rates became similar during the last 16 weeks of exposure, Fig. 18 (right). The large initial difference was partly explained by an indoor storage of the >40 year-panel, however the predominant reason was the prevailing environmental conditions. Long periods of dry deposition without any rain events and/or snow thawing were found to induce higher runoff rates from naturally patinated copper (> 40 year) compared to fresh copper, whereas no differences in runoff rates were found during periods of long lasting rain events. Similar results have been found by Karlén *et al.* (2002) for naturally patinated copper (fresh and > 30 years old) during a 3-year outdoor exposure, and no seasonal effects on the annual runoff rate of copper, as a result of different initial exposure conditions, were observed during four two-year exposures of fresh copper in Stockholm [Odnevall Wallinder and Leygraf (2001)]. Runoff rates of copper from the urban Stockholm site [Paper I, Karlén, *et al.* (2002), Odnevall Wallinder and Leygraf (2001)], varies between 1.0 and 1.7  $\text{g}/(\text{m}^2 \cdot \text{y})$  for fresh copper (< 5 years old) and between 1.3 and 2.0 for naturally patinated copper (>30 years old). The variation is mainly attributed to differences in annual precipitation quantities. The reason for the discrepancy in runoff rates (primarily during first flush) was due to the morphology and other surface characteristics of corrosion products

within the patina, see Table 5. Contact angle measurement of the surface of naturally patinated copper with brown and green patina layers, respectively, showed surfaces with green patina (>40 years) to possess a higher wetting ability compared to surfaces with brown patina, see Table 4. As a result, the absorption capacity of water was higher on green-patinated samples. Corrosion and dissolution can, hence, take place even during relatively dry periods during which water is trapped within the patina. Consequently, the first flush effect is more clearly pronounced on green-patinated copper compared to brown-patinated copper.

*Table 4. Contact angle measurements of naturally patinated copper of varying age*

Panel age	Origin	Patina color	Patina thickness (µm)	Contact angle (°)
Fresh	-	Pink	0	91
8 weeks	Urban site, Sweden	Brown	5-12	105
40 weeks		Brown	5-12	103
100 years		Green	14-70	43

No significant difference in runoff rate was seen between naturally patinated zinc panels (3.1 g/(m<sup>2</sup>·y)) during the one-year urban field exposure (Paper I), Fig. 19 (left). An extension of this exposure for another 5 years showed similar results (Paper II, V) with runoff rates between 2.6 and 3.5 g/(m<sup>2</sup>·y). This is illustrated for the 5<sup>th</sup> and 6<sup>th</sup> year of exposure in Fig. 19 (right). However, parallel exposures at the same site but with different starting dates suggested that differences in runoff rates can be seen as a result of variations in e.g. surface roughness and wetting ability of the zinc patina surface, due to variations in prevailing environmental conditions during the initial exposure period. Data to support this are displayed in Fig. 19 (right).

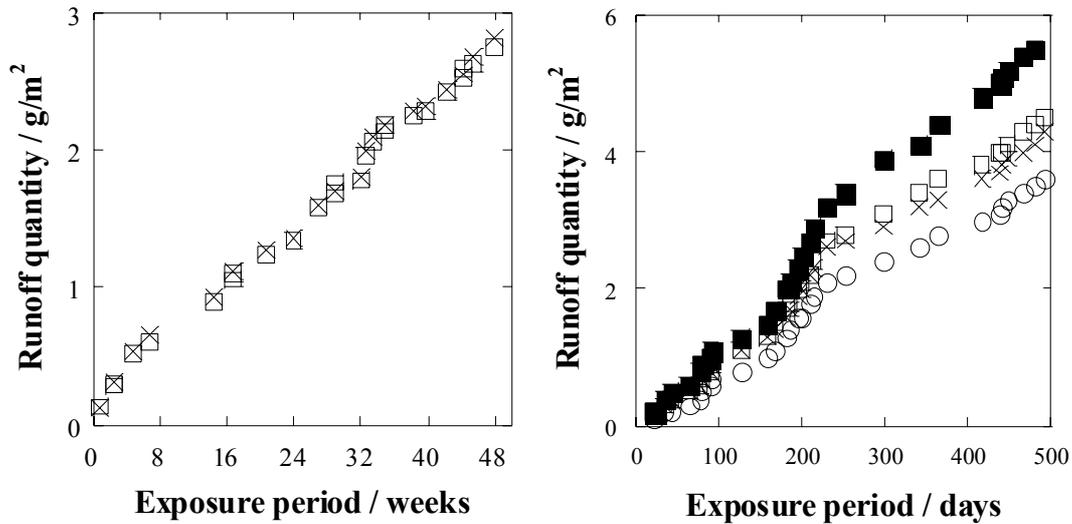


Fig. 19 Comparison between accumulated runoff quantities from fresh and naturally patinated zinc of varying age and initial exposure conditions.

Left figure: (×) fresh panel, (□) naturally patinated panel 39 years old, exposure start in November 1996 – a relatively wet and rainy period

Right figure: (×) and (□) same panels as in the left figure but during the 5<sup>th</sup> and 6<sup>th</sup> year of exposure, (○) fresh panel and (■) naturally patinated panel (originating from an industrial site, 26 years old), exposure start in April 2000 – a relatively dry and cold period.

The comparison is made during the same exposure interval in order to avoid the effect of differences in precipitation quantities and environmental conditions. It includes both fresh and naturally patinated zinc panels with an initial period of wet and long-lasting rain events (3.4 and 3.6 g/(m<sup>2</sup>·y)), a naturally patinated zinc panel originating from an industrial region of high pollutant levels and high deposition rates of soot and zinc dust from a zinc plant (4.4 g/(m<sup>2</sup>·y)), and a fresh zinc panel with an initial period of relatively dry and cold spring conditions (2.8 g/(m<sup>2</sup>·y)). The effect of prevailing initial exposure conditions on the runoff rate and the formation rate of corrosion products is shown in Fig. 20. The figures and a visual and microscopic inspection show a much slower formation rate of thin and non-uniform corrosion products on the zinc panel exposed to initial dry and cold exposure conditions (left figure) compared to a much faster formation rate of a relatively thick and porous dark-gray patina when exposed to initial wet and long-lasting rain events (right figure). The formation rate dominated in most cases over the runoff rate for the former case whereas the latter case

showed a much larger variation. The seasonal effect on corrosion product formation and morphology has previously been referred to as the “memory effect” [Ellis (1947), Guttman (1968), Odnevall (1994), Leuenberger-Minger, et al. (2002)<sup>b</sup>].

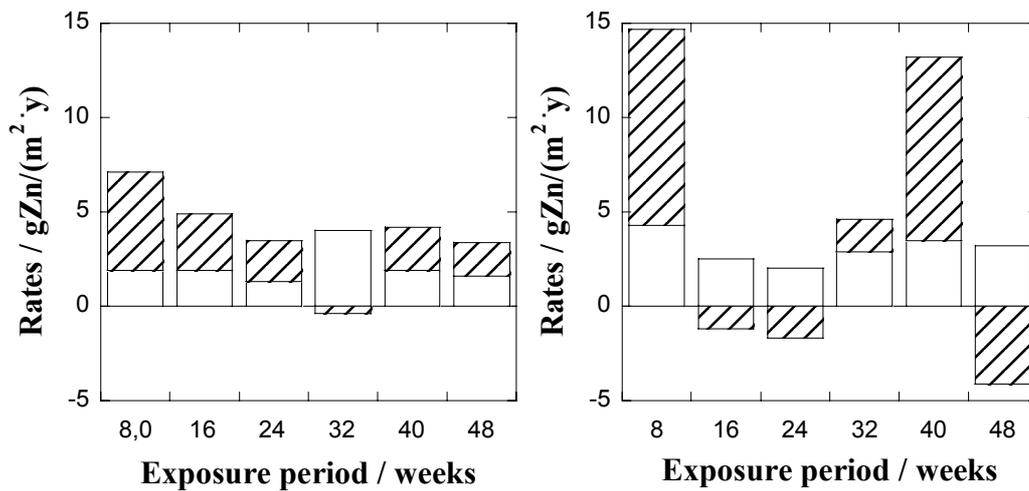


Fig. 20 Effect of initial conditions (left: dry and cold conditions, right: wet conditions) on the formation rate of a corrosion layer (dashed piles) and the runoff rate of zinc (unfilled piles) during the first 48 weeks of exposure.

A compilation of annual runoff rates determined within this thesis on naturally patinated copper and zinc panels of varying age and starting conditions are shown in Table 5 together with laboratory simulation data showing the contribution and effect of first flush on the runoff rate. The effect of first flush is higher on the 100-year copper panel compared to fresh copper and higher on the zinc panel starting its exposure during initial wet conditions in November compared to more dry and cold conditions in April.

Table 5 Annual runoff rates and the effect of first flush from naturally patinated copper and zinc of varying age and initial exposure conditions.

Material /Environment	Age (year)	Exposure period	Precipitation (mm/y)	Runoff rate (g/(m <sup>2</sup> ·y))			First flush contribution
				field	First flush	laboratory Steady state	
Zn / Urban	Fresh	April 00-April 01	659	2.8	1.6	2.0	20%
	1-40	Nov. 96-Nov. 01	587	3.3	1.6	2.5	36%
Cu / Urban	Fresh	Nov. 96-Nov. 97	575	1.3	0.8	1.0	18%
	100		575	2.0	0.9	1.6	44%

*To summarize, natural patination has an effect on the runoff rate of copper. Annual runoff rates from naturally aged copper showed a slight enhancement with copper patina age. The difference was mainly attributed to the first flush effect, with increased concentrations of copper in the runoff water from thicker patina layers.*

*Depending on the initial environmental exposure conditions but not panel age, natural patination on zinc can have an effect on the runoff rate.*

### ***3.5 Can laboratory and field runoff data be used to estimate the release of metals from existing buildings?***

A real building has usually a complex geometry with metal surfaces of roofs and facades of varying inclination, orientation, and degree of sheltering. As a result, large variations in the degree of dry and wet deposition and dry and wet periods will occur. All of these factors must be taken into account when estimating a total amount of released metal into runoff water. Runoff rate data collected within this thesis are primarily collected from a surface inclination of 45 degrees from horizon. The average runoff rate of a metal from a building is hence a weighed value of different exposure directions and inclinations. Effects of orientation and inclination on the runoff rate have been investigated for both copper and zinc during field exposures using model roofs and in laboratory investigations on smaller panels (0.3 m<sup>2</sup>) originating from real roofs and/or naturally patinated panels. Similar results were obtained during both investigations showing that smaller samples can be used when determining runoff rates from larger surfaces. The results show the volume of precipitation impinging on the metal surface to be the most important parameter affecting the annual runoff rate at a given pollutant level. The precipitation volume depends on the prevailing direction of wind, surface inclination and orientation. The effect of the latter two parameters on the runoff rate and on differences in collected rain volume from each surface is illustrated in Fig. 21, based on a one-year industrial exposure of a model roof of zinc.

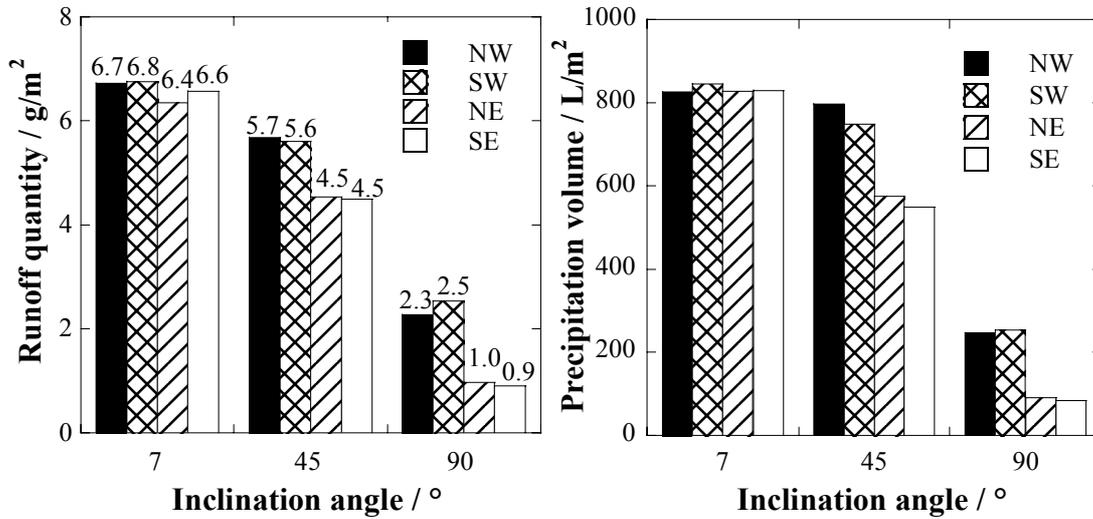


Fig. 21 Total zinc runoff quantity (left) and corresponding total precipitation volume (right) collected from various zinc faces (east-E, south-S, west-W, north-N) on a model roof after one year of exposure.

The results show higher runoff rates on surfaces facing the prevailing wind direction as a result of larger rain volumes. A low inclination from horizon and, hence, a slow flow rate of rain water over the surface induce high runoff rates during first flush in the next-coming rain episode as a result of longer residence times of moisture on the metal surface after rain. The effect of other environmental factors on the runoff rate has been discussed in section 3.3.

The total runoff rate of zinc or copper will be the sum of all runoff rates from each individual surface of the building. A comparison between the weighed average runoff rate from a real roof (typical for Europe), characterized by surfaces of different inclination, orientation and degree of sheltering, and runoff rates determined from panels exposed at 45° from horizon, facing south (as a standardized condition) shows the former rate never to exceed the latter rate. Runoff rates determined from the standardized conditions could, hence, be regarded as an upper limit. The weighed runoff rate from a given building with roofs and facades is at least 30% lower than rates from the standardized condition.

More information is given in paper III.

*To summarize: runoff rate data collected within this thesis can be used to estimate the release of copper and zinc from buildings in the society as long as the effects of surface inclination, orientation and degree of sheltering are considered.*

### 3.6 Can the runoff process be schematically described?

A schematic description of the metal runoff process during unique rain events has been established based on laboratory data (see section 3.2, 3.3 and 3.4) collected within this thesis, see Fig. 22

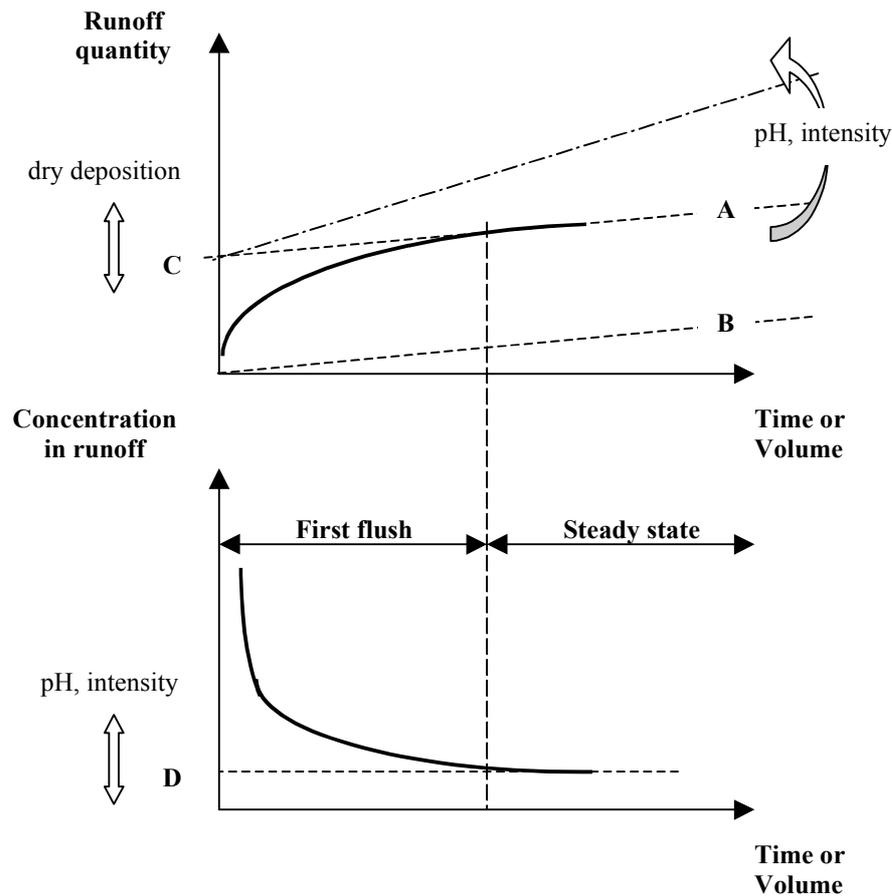


Fig. 22 A schematic description of a runoff process during a unique rain event.

The total metal runoff quantity increases and the total metal concentration decreases with increasing rain volume and/or time during a rain event. A linear increase in the runoff quantity with time and/or volume (line A) can be seen during steady-state conditions (relatively constant metal concentration - D) whereas an initial high and decreasing concentration is seen during first flush. In order to accurately determine the time and volume required to reach steady-state conditions, it is crucial that the concentration is measured in consecutive intervals. However, the accumulated average concentration can be used to compare the runoff process during different rain events. The intercept C (extrapolated from

line A) reflects the magnitude of first flush, which is a result of prevailing environmental conditions and corrosion processes occurring on the surface prior to a rain event. More detailed information of parameters affecting the runoff quantity and concentration during first flush is given in section 3.3. A parallel displacement of line A to line B (intercepting origo), reflects the quantity of metal released during steady-state, which primarily is a result of a corrosion and dissolution process of corrosion products of relatively low solubility. The concentration D increases with decreasing rain intensity and/or flow-rate and with decreasing pH, with an increase of the slope of lines A and B as a result, and *vice versa*. However the intercept C, will not be affected by the rain pH or intensity since the change in concentration is of the same order of magnitude both during first flush and steady-state.

In what follows, the schematic description of the runoff process is exemplified for pre-exposed samples of copper and zinc (16 months, urban exposure) during a 5-day continuous rain episode, Fig. 23. Zinc shows a high runoff concentration in the first flush volume (first sampling point) and reaches a relatively, fast and a fairly constant concentration during steady-state, Fig. 23a, and hence a linear increase in runoff quantity with increasing rain volume and/or time, Fig. 23b. The high and rapid decrease in concentration during first flush is the result of easily soluble and poorly adhesive corrosion products within the zinc patina. Copper also shows a high runoff concentration during first flush but a much slower decrease in concentration with increasing rain volume and/or time, Fig. 23c. As a result, the increase in runoff quantity with increasing rain volume and/or time is not perfectly linear, Fig. 23d. A relatively lower decrease in concentration during first flush suggests the presence of corrosion products within the patina of small quantity and relatively low solubility. During longer rain events, the slope of line A and B can during rain events of long duration and/or volume stay the same (Fig. 23b) or decrease (Fig. 23d). Changes of the slope depend upon whether the formation rate of a corrosion patina is dominating over the runoff rate or vice versa.

*To summarize: a schematic description of the runoff process has been established, which can be used for runoff analysis of individual rain events.*

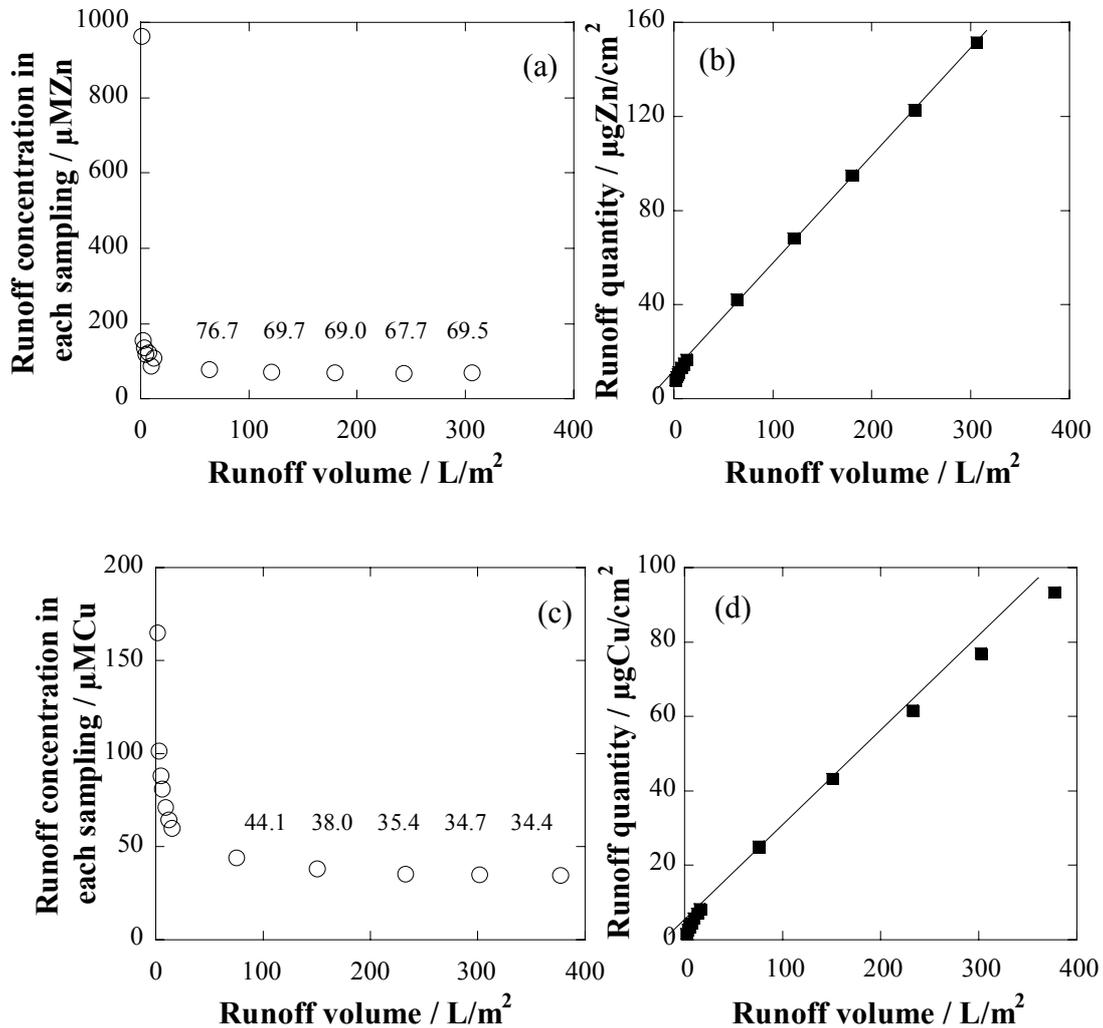


Fig. 23 Runoff processes during a 5-day artificial rain event of pH 4.3 and intensity 4-6 mm/h of zinc (a, b) and copper (c, d) panels being pre-exposed under sheltered conditions in an urban site for 16 months.

### 3.7 Can artificial rain really be used to simulate natural rain?

The aim of the laboratory investigations was to show the effect and importance of a single environmental parameters or a combination of parameters on the corrosion and the runoff behavior. Field conditions are of course more complex and contain a number of other factors (e.g. wind speed, wind direction, sun hours, temperature variations etc.) that will influence the runoff rate. However, in order to mimic field conditions as closely as possible, the artificial rain simulation study was designed to resemble rain properties (chemical composition, span in rain intensity, pH, and annual precipitation quantity) in the central part

of Sweden. Field exposures were conducted in parallel with the laboratory investigation. Comparisons between field runoff rate data and laboratory data are presented in Fig. 24 for copper (left) and zinc (right). The figures show runoff rates as a function of precipitation rates during different sampling periods in the field (circles) and during different rain episodes of varying characteristics in the laboratory (squares). The results show laboratory rain simulations to provide confident data in excellent agreement with field data.

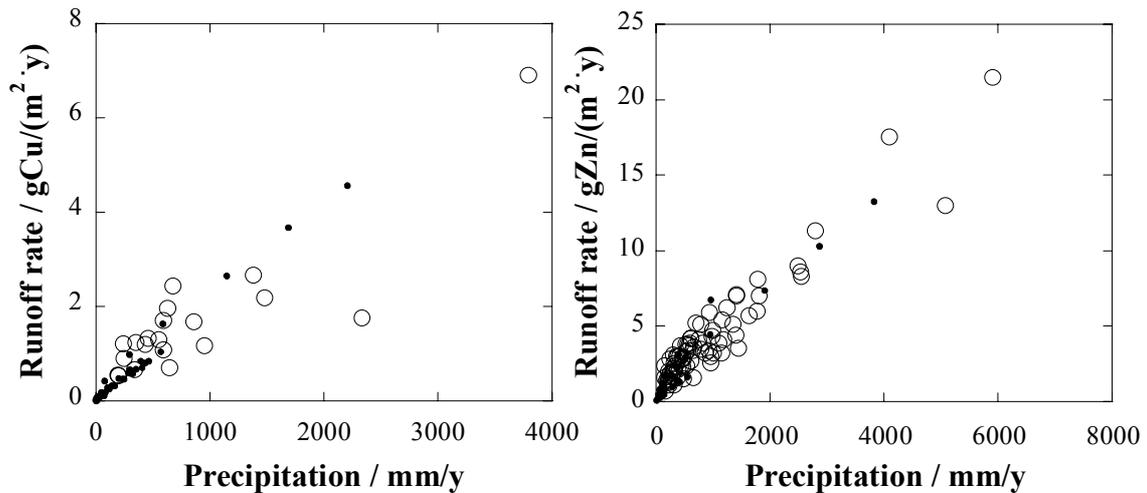


Fig. 24 Comparison between runoff rates measured in the field exposures (○) and laboratory simulations (●) for copper (one-year exposure) (left) and zinc (four-year exposure) (right).

In addition, Table 6 provides further evidence that rain simulations on pre-exposed copper and zinc result in runoff rates in reasonable agreement with observed runoff rates in field exposures.

Table 6 Comparison between runoff rates obtained in field exposures and predicted by laboratory simulations.

Materials	Field exposures			Laboratory simulations [ref. Paper IV]	
	urban site [ref. paper I]	urban site [ref. 1]	rural site [ref. 2]	Pre-exposed panels (urban site)	Pre-exposed panels (rural site)
Copper	1.3	1.1 - 1.7	0.6 - 1.0	1.2	0.7
Zinc	3.1	2.1 - 3.1		2.6	1.6

[ref. 1 Karlén, et al. (2001), ref. 2 Odnevall Wallinder and Leygraf (2001)]

To summarize: artificial rain can be used to reproduce runoff rates of copper and zinc exposed to natural rain.

### ***3.8 How can the data be used in the future work of environmental risk assessment and regulations?***

Corrosion- and runoff processes have been extensively investigated on naturally patinated copper and zinc of varying age. Annual runoff rates have been determined and compared with corrosion rates. The effect of environmental parameters (air pollutants, rain pH, intensity or flow-rate, and quantity), material parameters (surface properties, corrosion products, patination (age), and exposure parameters (inclination, orientation) on the metal runoff process has been thoroughly investigated and described within this thesis. Data can be used to estimate total metal flows of copper and zinc from buildings in the society and be utilized for e.g. the elaboration of models for metal runoff processes. A model for copper runoff estimations in environments of different characteristics is currently performed at KTH [Odnevall Wallinder, *et al*, private communication (2002)]. In addition, architects and constructors can use the increased knowledge on metal dispersion to design buildings of favorable geometry to minimize metal runoff. In all, the thesis hopefully forms a solid platform to be used when environmental aspects of metal runoff from buildings are of interest.

However, data within this thesis only show total metal runoff rates, quantities or concentrations, without considering the chemical speciation of the metal and changes in chemical speciation and bioavailability upon environmental entry, all crucial aspects within the framework of environmental risk assessment. Current activities are on-going at the division of Corrosion Science, KTH, with the aim to investigate the chemical speciation and bioavailability of metals (Cu, Zn, Cr, Ni) in runoff water from roofing materials, changes in metal speciation, bioavailability and ecotoxicity during transport, and metal retainment in and onto different sorbing surfaces including soil, limestone and concrete [Odnevall Wallinder, *et al*. (2001), Karlén, *et al*. (2001, 2002), Heijerick, *et al*. (2002), Odnevall Wallinder and Leygraf (2002)<sup>a,b</sup>, Bertling, *et al*. (2002)<sup>a-c</sup>]. Even though large efforts are made to map metal corrosion and runoff processes from roofing materials, it should be stressed that the annual dispersion of copper and zinc induced by atmospheric corrosion from roofing materials in the society is comparably low compared to other metal sources in the society, such as the traffic sector (brakes, tires, asphalt, car washes etc) and the tap-water system. [Bergbäck, *et al*. (2001)].

*To summarize: data within this thesis provide an extensive and thorough description of corrosion- and runoff processes of copper and zinc from roofing materials to be used in*

*future investigations and modeling of the runoff behavior of copper and zinc. However since the data reflect total copper and zinc runoff rates without any consideration towards changes in chemical speciation, bioavailability and ecotoxicity during environmental entry, they cannot be directly used for environmental risk assessments.*

#### **4. Conclusions**

In all, this extensive investigation with parallel field and laboratory exposures conducted to elucidate atmospheric corrosion and metal runoff processes on copper and zinc for roofing applications permit the following main conclusions to be drawn:

1. A time dependence was established for both corrosion rates and runoff rates. Corrosion rates are initially high followed by a continuous decrease to a lower rate during steady-state conditions for both metals. Runoff rates on the other hand are relatively constant on a yearly perspective for both copper and zinc. The data show the necessity of using yearly runoff rates rather than corrosion rates as a measure of the dispersion of metals from buildings and outdoor constructions. Field exposures in the urban city of Stockholm, Sweden showed corrosion rates of 6.7 g Cu/(m<sup>2</sup>·y) and 5.0 g Zn/(m<sup>2</sup>·y) after 48 weeks of exposure and annual runoff rates of 1.3 g Cu/(m<sup>2</sup>·y) and 3.1 g Zn/(m<sup>2</sup>·y).  
As a result of the formation of relatively protective corrosion compounds in the patina on copper, the patina formation rate is always dominating over the dissolution rate on monthly and yearly perspective. For zinc, however, periods may occur when the runoff rate is higher than the formation rate with a patina loss as a result, and vice versa.
2. Corrosion rates are substantially lower than corresponding runoff rates of naturally patinated copper during single rain episodes, with a diminishing of the corrosion patina thickness as a result.
3. A relation between the runoff rate and the SO<sub>2</sub>-concentration has been established, which can be used to predict runoff rates of zinc in various polluted environments.  
The magnitude of the runoff rate of copper and zinc depends on the prevailing pollutant levels of the environment (including e.g. SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, Cl<sup>-</sup>, and particles). Soluble and poorly adhesive corrosion products, formed in more polluted environments, will

primarily be washed off during first flush and result in higher concentrations during first flush and consequently higher runoff rates.

4. The runoff quantity and concentration of copper and zinc are affected by a number of precipitation parameters, including rain volume, pH, intensity, and length of dry periods in-between rain episodes. During a rain episode, the metal runoff concentration is higher during first flush compared to the steady-state region. The metal concentration in runoff water increases with increasing rain acidity (both during first flush and steady-state conditions), decreasing rain intensity (both during first flush and steady-state conditions), and increasing length of dry periods in-between two rain episodes (only during first flush).
5. Natural patination has an effect on the runoff rate of copper. Annual runoff rates from naturally aged copper showed a slight enhancement with copper patina age. The difference was mainly attributed to the first flush effect, during which increased concentrations of copper in the runoff water from thicker patina layers were observed. No intrinsic effect of panel age on the runoff rate was seen for naturally patinated zinc. However, differences in initial environmental exposure conditions can have an effect on the runoff rate of zinc.
6. Runoff rate data collected within various environments as long as the effects of surface inclination, orientation, degree of sheltering, SO<sub>2</sub>-concentration and total rain volume are considered, in order to estimate the release of metals from existing buildings.
7. A schematic description of the runoff process has been established, which can be used to analyze runoff process during individual rain events.
8. The use of artificial rain was shown to successfully simulate natural rain and able to reproduce runoff rates of copper and zinc observed in the urban site of Stockholm.
9. Data within this thesis provide an extensive and thorough description of corrosion- and runoff processes of copper and zinc from roofing materials, and can be used in future investigations and modeling of the runoff behavior of copper and zinc. However, since the data reflect total copper and zinc runoff rates without any consideration towards changes in chemical speciation, bioavailability and ecotoxicity during environmental entry, data should not directly be used within the framework of environmental risk assessments.

## **5. Acknowledgment**

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