

Review

Copper and Zinc as Roofing Materials—A Review on the Occurrence and Mitigation Measures of Runoff Pollution

Susanne Galster and Brigitte Helmreich * 

Chair of Urban Water Systems Engineering, School of Engineering and Design, Technical University of Munich, Am Coulombwall 3, 85748 Garching, Germany; susanne.galster@gmx.de

* Correspondence: b.helmreich@tum.de; Tel.: +49-89-2891-3719

Abstract: Stormwater runoff from metal roofs has been a significant subject of discussion, especially when it comes to its treatment and the target concentrations that need to be achieved prior to discharge into the aquatic environment. To raise further awareness on this issue, occurrence, characterization, and also mitigation measures for metal roof runoff were analyzed using the example of copper and zinc roofs. These stormwater runoffs were found to contain metals in significant concentrations, mainly due to the wash-off of corrosion products by precipitation. Factors influencing metal corrosion and runoff concentrations were compiled. As Cu and Zn mainly occur in dissolved and thus bioavailable forms in roof runoff, harmful effects on the environment were detected. Therefore, adequate treatment of the runoff before discharge to groundwater or surface water is necessary to protect the aquatic environment. Vegetated infiltration swales as a sustainable urban drainage system enable a reduction in pollution loads. However, especially in densely built-up urban areas, stormwater quality improvement devices (SQIDs) offer an attractive alternative for pre-treating metal roof runoff, as they are mostly located underground. There is not yet a uniform legal approval system for SQIDs in Germany, but the German state of Bavaria has approved four types of SQIDs according to its own developed test criteria.

Keywords: metal roof runoff; stormwater pollution; runoff rate; corrosion rate; drainage; urban stormwater management



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1. Introduction

The use of the metals Cu and Zn for constructions goes back to the Middle Ages, and is still very significant for different elements of roof constructions, e.g., roof surface, chimneys, gutters, and dormers [1–3]. When Cu and Zn are exposed to the atmospheric environment, both metals are subject to a corrosion process (mostly chemical corrosion), which is influenced by various climatic and polluting atmospheric factors. The resulting corrosion products lead to the formation of a surface layer preventing further corrosion, a so-called patina [4–6]. Mainly due to precipitation, parts of the corrosion products can be dissolved or become detached and washed off, expressed by the runoff rate of Cu and Zn in $\text{g}/(\text{m}^2 \cdot \text{a})$, and discharged into the environment [5]. At the beginning of exposure, corrosion rates for Zn and Cu are higher than their runoff rates, but they decrease over time as the patina is formed [4–11]. Meanwhile, the runoff rate is much higher for Zn compared to Cu [4,6]. The runoff rates vary not only in dependency of the metal (Cu or Zn), but also of the weathering time, the local situations and the atmospheric conditions [4,5,12]. At the beginning of the weathering period, resulting corrosion rates are clearly higher than runoff rates for both metals, therefore a distinction between the two rates is required. After approximately ten years for Zn [8] and longer periods (e.g., fifty years) for Cu [5,8], the corrosion rate and runoff rate equalize [4,8,13]. With the exception of opposing statements by the metal industry [14], e.g., [4,5,8,15] have observed a fairly constant temporal behavior of the metal roof runoff during studies. Although the test periods have been relatively

short, [16,17] stated that the metal abrasion from Cu and Zn roofs is not to be neglected even after many years. In addition, it must be considered that even if both metals are essential for most organisms, they can have harmful effects, especially for aquatic life, depending on their chemical form and concentration [2,4,6].

With the knowledge of existing, constantly remaining runoff concentrations, the advantages of their longevity and good processability of Cu and Zn as construction material must be seen critically, as metal runoff may enter the environment (soil, groundwater, surface water).

Traditionally, urban stormwater runoff is drained into the sewage system and discharged somewhere into surface water bodies. In the case of combined sewer systems, where wastewater and stormwater are mixed and drained together, mixed water can enter the surface waters untreated as overflow, if the sewer system is overloaded by heavy rain events [2]. Additionally, Cu and Zn are not completely retained in the sewage treatment plant. Therefore, Cu and Zn are also released into surface waters by sewage treatment plant effluent [2]. In the case of separate sewer systems, where stormwater runoff is discharged directly into surface waters, sometimes after treatment by a sedimentation unit, high loads of Cu and Zn enter surface waters [2,6,7,17–19].

Currently, stormwater runoff is more and more often managed on-site in order to maintain the local water balance in urban areas in equilibrium (water-sensitive cities). Therefore, an increasing amount of stormwater runoff is infiltrated on-site. Prior to infiltration, the runoff must be treated in order to protect soil and groundwater from contamination. This can be done by sustainable urban drainage systems (SUDS), e.g., in a vegetated infiltration swale, where the filter and sorption function of the topsoil is used to retain heavy metals from runoff [20]. However, if there is only little space available at the urban site to pre-treat the stormwater runoff before infiltration via vegetated infiltration swales, space-saving technical stormwater quality improvement devices (SQIDs) which also provide a treatment and are often located underground, must be applied [21].

There are currently many discussions about what requirements must be placed on stormwater treatment devices or whether it is entirely better to forego Cu and Zn as building materials in order to avoid contamination from the start.

Hence, the goal of this review is the analysis of stormwater runoff pollution from Cu and Zn roofs considering legal and technical aspects. The chemical runoff composition and its temporal behavior, as well as reasons for differences in quantity and metal load level are also discussed, as the selection of a suitable treatment method for metal roof runoff requires precise knowledge of its chemical characteristics and changes in quality with time [22,23]. An overview of treatment options for Cu and Zn roof runoff that are currently available in Germany and their performance should help to discuss possible limit values.

2. Characterization of Metal Roof Runoff

2.1. Primary and Secondary Stormwater Pollution

The polluting load of stormwater runoff is composed of a primary load on the one hand and a secondary load on the other hand. During a rain event, atmospheric pollutants are washed out leading to a primary contamination of stormwater even before it reaches the ground (wet deposition). Known as dry deposition, atmospheric pollutants can also settle on the earth's surface, rinsing off with subsequent precipitation and thus leading to a further primary contamination. From the primary contamination, stormwater has ions like Cl^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , and NO_3^- dissolved, to name just a few [7]. For those ions, different concentrations in natural or artificial stormwater are given in [5,12,24,25], but their concentrations are mostly lower than 10 mg/L. Exact concentrations differ with type and location of the test site [20]. In general, their concentrations in stormwater are higher at urban sites compared to rural ones, as for example industry and traffic means are main sources of SO_2 , which is oxidized to SO_4^{2-} [7]. Besides those ions, organic compounds like polycyclic aromatic hydrocarbons and heavy metals such as Cu, Zn, Pb, Cd, or Cr can be also present as a result of primary load, even if in concentrations 10 times lower

than the ions mentioned. In addition, a secondary pollution has to be considered, when stormwater gets in contact with surfaces, e.g., metal roofs, where it can dissolve or detach further substances. The secondary pollution leads to much higher concentration levels in the runoff compared to the primary pollution [7,20].

2.2. Chemical Forms of Cu and Zn in Stormwater

Cu and Zn in roof runoff are mainly present as dissolved ions (Zn^{2+} , Cu^{2+}) or they are adsorbed on particles (undissolved) [26–28]. The quantities and therefore the ratios in which these forms appear, depend mostly on the pH value of the runoff as well as on its content of dissolved organic matter (DOM) and the environmental conditions [2,26–28].

With an increasing pH value and concentration of DOM in the runoff, the proportion of the free ions is decreasing [28–30]. While in a pH range of approx. 4.5–7 Zn is mostly in dissolved form as Zn^{2+} , the formation of undissolved carbonates and hydroxides such as $ZnCO_3$ or $Zn(OH)_2$ rises from a pH of 7 and higher, resulting in a smaller proportion of free Zn^{2+} ions [29]. Percentages higher than 90% for dissolved Zn^{2+} and higher than 70% for dissolved Cu^{2+} have been found in different studies depending on various circumstances [8,9,22,29,30]. However, changes of the pH value and thus the percentage of dissolved ions in the runoff may occur due to contact with other materials, e.g., soil or concrete surfaces [9,20,29].

It is stated in many articles that the free ions provide harmful impacts on the ecosystem and are therefore in the “bioavailable” form [4,8,31,32]. In a study on algae, for example, up to 100% of Zn has been measured as Zn^{2+} in the Zn roof runoff resulting in observable toxic effects [31]. As these detected values are valid for the runoff immediately released from the roof, the study advises against simply generalize the results for the environment. Due to changes in metal concentrations and generally in the composition of the runoff through contact with different surfaces (esp. concrete) and processes such as dilution, reactions with various (in-)organic matter and complexation, a decrease of bioavailability may still occur. In a study on the interaction between concrete and Cu runoff, a reduction of 20–95% in the concentration of free Cu^{2+} ions was observed after contact with concrete, depending on factors such as the moisture of the concrete and the pH of the runoff [32]. In any case, it must be noted that dissolved and undissolved metals in the runoff have to be considered when assessing impacts on the environment and the runoff treatment to protect the ecosystem [9,22,32–36].

2.3. Metal Corrosion and Runoff Rates

The corrosion rate as well as the runoff rate will naturally vary dependent on the type of roofing material and its surroundings. In several studies, equations for the prediction of runoff rates for various sites have been elaborated. Ref. [37] gives a linear equation for calculating the Zn mass loss at given parameters of the roof surrounding such as the amount of SO_2 and Cl^- in the atmosphere. A model for the prediction of Cu runoff rates is stated in [38], depending on the pH value and the amount of rain, as well as SO_2 concentrations. However, in the case of Cu corrosion rates, even characteristics of the Cu patina are influencing factors [9]. The influences affecting corrosion and runoff rates are explained in the following two chapters. Tables 1 and 2 provide an overview of the corrosion rates and runoff rates for Cu and Zn roofs from various studies.

2.3.1. Properties of the Roof Material and Building Characteristics

Building characteristics of the roof such as inclination and orientation, and the age of the roof respective to its exposure time, as well as the type of the roofing material, are important factors for corrosion and runoff rates [7,8,12,15,23,27,38,39].

It is stated in many articles, e.g., [12,33], that with increasing inclination, the runoff rate is decreasing enormously. A study on different roof inclinations [12] confirms this correlation, as values in the range of 6.4–6.8 g/(m²·a) have been measured for total accumulated Zn in the runoff from a roof with an inclination of 7°, 4.5–5.7 g/(m²·a) from an

inclination of 45° and $0.9\text{--}2.5\text{ g}/(\text{m}^2\cdot\text{a})$, and from an inclination of 90° , depending on the exposure direction, respectively. This is because, as the slope increases, a smaller amount of stormwater impinges on the roof surface, and a reduced contact time between precipitation and roof surface occurs, thus the stormwater runs off faster. Hence, the amount of corrosion products washed off is less [7,12,27,33]. The roof orientation additionally has an influence on runoff rates. It was observed that the Zn runoff from a Zn roof inclined at 45° increases for a southeast exposure, being nearly the same as for a northeast exposure, to a southwest respectively northwest exposure. This was also confirmed by [12] for inclinations of 7° and 90° .

As Cu roof runoff rates increased for a western direction of exposure to north, to east, and to south, it can be concluded that, primarily, it is not the orientation itself but the wind direction that has a direct impact on the runoff rate (wind driven rain). With the wind carrying rain to the respective roof orientation, the rain amount is the crucial factor. Hence, given a fixed rain amount, the factor “orientation” is only of minor importance [12,27,40]. This is also confirmed by [41], where highest rain amounts, and thus also highest runoff rates were observed for the west site of a Cu roof, from where the wind primarily came. Furthermore, in this context, minor effects due to slipstream, resulting from other parts of the building have to be considered [12,41]. However, inclination as well as orientation are rather influencing factors on runoff rates, whereas corrosion rates are quite independent of them [27].

In addition, a study investigated the influence of the length of the roof surface from which the stormwater comes into contact with and runs off on Cu runoff concentration [42]. Tests were carried out on a specially built test system made of Cu roofing material measuring 9.14 m long and 40.6 cm wide. Synthetic rainwater flowing over it was collected and analyzed after different roof lengths (3.05 m ($\hat{=}$ 1.2 m² area) and 9.14 m ($\hat{=}$ 3.7 m² area)). The pH values of the synthetic water and the inclinations of the system also varied. The Cu concentration (39 $\mu\text{g}/\text{L}$) was lowest at a length of 3.05 m, an inclination of 20° , and pH of 6.4 and highest (426 $\mu\text{g}/\text{L}$) at a length of 9.14 m, an inclination of 60° , and pH of 4.5 (see also Table 2). The study concluded that the roof surface length is an important parameter, as Cu concentrations rise significantly with increasing contact time. However, further analysis is needed here, including investigations of the combined impact of roof age and run length, as only new roofing material was used in the study.

An analysis regarding the influence of different roof ages on corrosion runoff rates, respectively, is more difficult, as only a few investigations can be found, and they are partly even contradictory. In [2] it is mentioned that the age is an important factor as the corrosion rate of bare metals is highest (see also Section 1). However, the extent to which the corrosion rate decreases over time due to the formation of a patina is disputed. Regarding runoff rates, [27] stated that the runoff of metal surfaces is independent of the age of the material, whereas results obtained from a study in Sweden [5] show that naturally aged Cu panels (40–100 years) caused higher runoff rates than unaged panels (see Table 2). Here, cracks or pores, which are able to retain stormwater on the surface and are leading to an enlargement of the effective area, were also contributing to higher runoff rates of aged panels. However, for Zn no significant dependence between age and runoff rate could be observed [5], whereas [30] detected higher Cu concentrations in the runoff from an eight year old Cu roof compared to a 37-year old roof of the same location and orientation (see Table 2); another study in New Zealand [23] presented higher Zn concentrations of older (22 respectively older than 25 years) than of new (younger than one year) roofs which differ only by age (see Table 2). As [30] classifies its findings as contradictory to others, the results of other studies stating higher metal concentrations in the runoff from older roofs compared to newer ones, e.g., [5], explained by the formation of a patina that becomes more soluble with time. However, lower Zn concentrations of older, coated roofs compared to new, uncoated roofs have also been observed [23], leading to the next influencing factor.

The type of the roofing material respectively various coatings, as well as their appropriate maintenance, can be effective for a reduction of metal concentrations in roof runoff [23].

Besides pure Cu- and Zn-, respectively, and titanium-Zn-roofs (pure Zn would be too brittle) [1], there are different coatings and pre-treatments for metal surfaces under application. Possible coatings are Galfan and Galvalume, for instance. Both are Zn-aluminum (Al)-based coatings, composed of 95% Zn and 5% Al, and 55% Al and 45% Zn, respectively. They provide lower Zn runoff rates compared to galvanization, which will be explained later [43]. Annual Zn runoff rates of test panels coated with Galfan and Galvalume ($1.2 \text{ g}/(\text{m}^2 \cdot \text{a})$ and $0.55 \text{ g}/(\text{m}^2 \cdot \text{a})$, respectively) are lower than those of nearly pure Zn sheets (approx. $2.6 \text{ g}/(\text{m}^2 \cdot \text{a})$, see Figure 1), observed in a study in France [43]. The reason for this is the formation of Al rich corrosion products, which increase the polarization resistance. Hence, this leads to a slower corrosion rate for Zn, as it is inversely proportional to the polarization resistance [43,44].

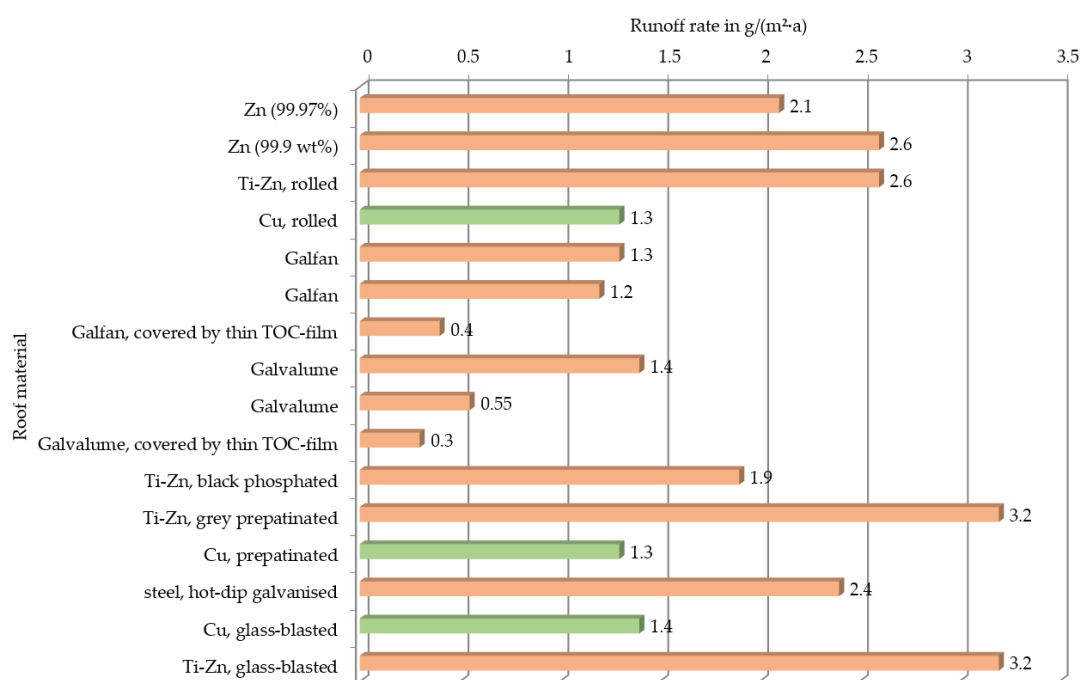


Figure 1. Overview of various runoff rates for different roof materials, different values for the same roof materials result from different test conditions (data according to [15,29,43]).

The study also tested the application of organic coatings on Zn-based materials. In this case, the increase of the corrosion resistance respectively the reduction of Zn runoff rates depends mainly on the thickness of the coating. Thicker coatings result in lower runoff rates if the coatings are undamaged and in good condition [43]. Another method of corrosion protection and thus influencing runoff rates is the phosphating of metals. For example, black phosphated Ti-Zn had, with a total runoff rate of $1.9 \text{ g}/(\text{m}^2 \cdot \text{a})$ after five years of exposure, a lower runoff rate than Ti-Zn without any pre-treatment ($2.6 \text{ g}/(\text{m}^2 \cdot \text{a})$, see Figure 1) during a project in Switzerland [15]. Galvanization is also a possible pre-treatment of metals. In this case, Zn was not used as primary roofing material, but as a substance covering steel with a thin layer. This layer results in a higher corrosion resistance as well as in a smaller mass loss of Zn from galvanized steel compared to pure Zn samples (see Figure 1) [25,37]. It is stated that even new, uncoated galvanized roofs had Zn concentrations in higher ranges than older, painted galvanized roofs confirming the advantages of coatings [23].

In contrast, there are also methods of pre-treatment resulting in rather negative impacts like higher runoff rates. An example is the method of pre-patination of Cu and Zn. According to [15], grey pre-patinated Ti-Zn had the highest runoff rate ($3.2 \text{ g}/(\text{m}^2 \cdot \text{a})$) of all investigated Zn-samples, and thus a higher runoff rate than pure, rolled Ti-Zn ($2.6 \text{ g}/(\text{m}^2 \cdot \text{a})$, see Figure 1). A reason may be the formation of corrosion products of other crystallinity and specific surface during the industrial patination process. In the case of pre-patinated

Cu, neither advantages nor disadvantages can be stated, as runoff rates of pure Cu as well as runoff rates of pre-patinated Cu are at $1.3 \text{ g}/(\text{m}^2 \cdot \text{a})$ (see Figure 1). Finally, a further possible treatment of metals influencing corrosion respectively runoff rates is the glass-blasting technology. Corrosion rates of glass-blasted Cu respectively Ti-Zn are higher than those of the only rolled variant in the first years of exposure. This may be explained by a higher roughness of the surface of glass-blasted metals compared to rolled ones. As this influence decreases with time, after approximately eight years, corrosion rates of both variants are equalizing.

Differences in runoff rates between glass-blasted respectively rolled Cu, however, are comparatively low (see Figure 1). This finding shows that runoff processes take place mainly on the surface of the corrosion products and, therefore, runoff processes are quite independent of the surface structure of Cu and Zn. Nevertheless, differences between runoff rates of untreated and glass-blasted Zn (see Figure 1) are more significant than the differences in the case of Cu, as just explained [15]. Hence, further factors are likely to have an influence causing these disparities. An overview of the various runoff rates resulting from different coatings as well as from further pre-treatment methods in comparison with pure Zn respectively Cu roof materials can be seen in Figure 1.

2.3.2. Influence from the Surrounding Environment and Climate

The process of corrosion is influenced by several climatic and polluting factors. Furthermore, the pH value of precipitation and the so-called “time of wetness” (TOW), which is the period during which a metallic surface is covered by adsorptive and/or liquid film of electrolyte [37]. Roof runoff rates and respective metal concentrations are rather dependent on the characteristics of rain events and the location of the roof (air pollutant content, climate zone) [2,27,45,46].

Relating to the characteristics of rain events, impacts of the factors rain intensity, amount of rain, and the time between two rain events have to be considered. When analyzing the influence of the rain quantity on releasing metal amounts from roofs, for which a clear connection was detected in [5], the factor of the rain intensity has to be included. Higher rain intensities result in lower metal concentrations in the runoff because of dilution effect due to shorter residence times between water molecules of precipitation and the roof and therefore shorter wet periods, in which corrosion products can be dissolved from the roof surface. A further reason may be the formation of multiple layers of runoff water, which are leading to a partial contact of the water with the roof only. A lower rain intensity, in comparison, results in higher metal concentrations. Hence, for the washed off metal, the duration of the contact time between the rain drops and the metal surface is of higher importance than the mechanical force, that would be more intensive in the case of higher rain intensities [5,22,37,46].

The impact of the time that passes after a rain event until the next one (dry period) on Zn and Cu concentrations, respectively, in roof runoff is discussed controversially, whereas [22,37] could not observe a dependency between Zn concentrations in the runoff and the time duration of the preceding dry period; [30,46] stated that the length of the dry period has an impact on released metal amount at the beginning of a rain event. Ref. [30] measured higher concentrations of particulate Cu in a Cu roof runoff after a long dry period. Hence, with increasing time between two rain events, the dry deposition of pollutants on the metal surface could increase, the formation of cracks in the corrosion layer is introduced, resulting in a removal of corrosion products, thus leading to higher metal concentrations in the runoff [46]. However, existing discrepancies on this issue are addressed in [7] and justified by further influencing factors, which have to be considered. For example, the age of the roof respectively the SO_2 content of the air must be considered, as after a certain time a stable corrosion layer has been formed respectively higher SO_2 contents are leading to higher corrosion rates. Sulphur dioxide contents in the atmosphere, as well as other air polluting substances, are identified to be some of the most important factors influencing corrosion as well as runoff rates [6,7]. Due to more industry as well as a higher traffic

volume, urban areas and regions near a highway generally have higher SO₂ and nitrogen oxide (NO_x) levels than rural areas [4,47]. An increasing acidification of the atmospheric rainwater (rising SO₂ content), associated with a falling pH value, leads to increasing corrosion [24,47]. Hence, corrosion as well as runoff rates are mostly higher in an industrial urban area compared to rural areas due to higher SO₂ concentrations in the atmosphere, confirmed by several studies [4,24,48].

Besides SO₂ and NO_x, Cl⁻ is also known to influence corrosion mass loss and runoff rates [6,25]. However, this could not be verified by [43] at a marine test site in France, classified as a Cl⁻-rich environment due to the proximity to the sea. The corrosivity of the marine test site varies, as the deposition of Cl⁻ and SO₄²⁻ changes due to different wind speeds and rain characteristics, but not even in October, the month of highest Cl⁻ deposition rates, could any increased runoff rates be observed. It should be mentioned again that the prevailing climate has an influence on runoff rates of metal roofs. A marine climate leads to higher runoff rates (see Tables 1 and 2), but this is mainly due to higher rainfall amounts and not due to the high deposition rates of Cl⁻ [43,49].

Table 1. Overview of corrosion and runoff rates (respectively concentrations in runoff) from Zn roofs under different test conditions, see respective source.

Zn Corrosion Rate [g/(m ² ·a)]	Zn Runoff Rate or Concentration	pH Value of the Rain [-]	Roof Age [a]	Roof Size [m ²]	Test Site	Source
n.a.	6.3 g/(m ² ·a)	4.3	1	0.02	Stockholm, Sweden	[12]
n.a.	3.7 g/(m ² ·a)	6.7	14	238	Garching, Germany	[22]
n.a.	3 g/(m ² ·a)	n.a.	30	950	St. Gallen, Switzerland	[27]
5 (after 48 weeks of exposure)	3.1 g/(m ² ·a)	4.7 ± 0.6	new	0.03	Stockholm, Sweden	[5]
n.a.	98 µg/L (Zn ²⁺)	6.57	<1	n.a.	Christchurch, New Zealand	[23]
n.a.	640 µg/L (Zn ²⁺)	6.57	22	n.a.	Christchurch, New Zealand	[23]
n.a.	8.72 g/(m ² ·a)	6.1	n.a.	1	Rouen, France	[24]
8	2.6 g/(m ² ·a)	5.9	n.a.	0.03 resp. 0.0048	Brest, France	[43]
n.a.	7800 µg/L	<5.6	n.a.	(744–1339) 10 ⁴	Paris, France	[50]

n.a. = not available.

Table 2. Overview of corrosion and runoff rates (respective concentrations in runoff) from Cu roofs under different test conditions, see respective source.

Cu Corrosion Rate [g/(m ² ·a)]	Cu Runoff Rate or Concentration	pH Value of the Rain [-]	Roof Age [a]	Roof Size [m ²]	Test Site	Source
n.a.	1.1 g/(m ² ·a)	4.3	145	0.03	Helsinki, Finland	[12]
n.a.	1 g/(m ² ·a)	n.a.	29	400	Zurich, Switzerland	[27]
6.7 (after 48 weeks of exposure)	1.3 g/(m ² ·a)	4.7 ± 0.6	new	0.03	Stockholm, Sweden	[5]
attempts were unsuccessful	1.9 g/(m ² ·a)	4.7 ± 0.6	100	0.03	Stockholm, Sweden	[5]
n.a.	2130 µg/L (Cu ²⁺)	6.45	8	384	Auckland, New Zealand	[30]
n.a.	519 µg/L (Cu ²⁺)	6.45	37	102	Auckland, New Zealand	[30]
n.a.	3.93 g/(m ² ·a)	6.1	n.a.	1	Rouen, France	[24]
8.5–13.3 (first year), 4.9–7.8 (second year)	0.6–0.8 g/(m ² ·a) (first year), 0.8–1 g/(m ² ·a) (second year)	4.6	n.a.	0.03	Stockholm, Sweden	[9]

Table 2. Cont.

Cu Corrosion Rate [g/(m ² ·a)]	Cu Runoff Rate or Concentration	pH Value of the Rain [-]	Roof Age [a]	Roof Size [m ²]	Test Site	Source
8.9–9.8 (first year), 3.6–6.4 (second year)	1.1–1.4 g/(m ² ·a) (first year), 1.4–1.7 g/(m ² ·a) (second year)	4.6–4.7	n.a.	0.03	Stockholm city, Sweden	[9]
n.a.	255–359 µg/L at inclination 20–60°, resp.	4.5	new	1.2	New York, USA	[42]
n.a.	403–426 µg/L at inclination 20–60°, resp.	4.5	new	3.7	New York, USA	[42]
n.a.	39–47 µg/L at inclination 20–60°, resp.	6.4	new	1.2	New York, USA	[42]
n.a.	149–231 µg/L at inclination 20–60°, resp.	6.4	new	3.7	New York, USA	[42]
73 (after 2 weeks of exposure), 19 (after 1 year of exposure)	1.38 g/(m ² ·a)	5.7	new	0.03 resp. 0.0016	Brest, France	[49]
n.a.	1.23 g/(m ² ·a)	5.7	200	0.03 resp. 0.0016	Brest, France	[49]
n.a.	3340 ± 1520 µg/L (Cu ²⁺)	4.7	11	65.8	Connecticut, USA	[51]
n.a.	1340 ± 760 µg/L (Cu ²⁺)	4.7	72	12.6	Connecticut, USA	[51]
n.a.	5.7 g/(m ² ·a)	4.4	new	0.03	Singapore, Singapore	[52]
n.a.	0.66–1.9 g/(m ² ·a)	6.9	0–2	500	Munich, Germany	[53]

n.a. = not available.

Furthermore, a humid tropical climate has aggressive effects on metals, as values for the prevailing TOW, are high in this climate zone [25]. As humidity is another influencing factor on atmospheric corrosion [47], corrosion rates are influenced by TOW, which is defined as the time during which temperature is >0°, relative humidity is >80% [4], and therefore the time when corrosion occurs [37]. With high values of TOW and thus shorter times of drying, more corrosion products can be formed on the metal roof surfaces, as wet conditions are necessary for this [54]. Values of 64–73% for TOW occurring at 25–30 °C [37] and 80% for TOW occurring at 20–25 °C [25], respectively, are cited as specifics of a humid tropical climate, determining this climate as highly aggressive for metals compared to the prevailing climates in Europe or the USA.

As relative humidity is declared by [9] as the most important parameter for corrosion, the findings of this study in Sweden should be mentioned too. The authors investigated decreasing corrosion rates after two years of exposure with decreasing values of relative humidity for a rural test site. However, since for the urban test site this behavior could not be observed, further parameters must have an influence. The impact of the relative humidity is declared as a seasonal influence on corrosion rates, as different seasons are characterized by different values of relative humidity (relative humidity is usually lower in summer than in winter). Another occurrence that can also be declared as a seasonal influence is the frequency of precipitation events of certain intensities in different months. Snow melting (low intensities) occurs in winter only, whilst rain events of high intensities are mostly in summer and early autumn [7]. Since snow is an effective scavenger of atmospheric pollutants, the water layer upon snow melting contains high amounts of pollutants that may enhance the release of metals from roofs during the subsequent runoff event [39]. The temperature itself could also have an influence. While the corrosion rate of Cu is significantly reduced at temperatures below the freezing point [55], there are no systematic studies on the effect of temperature on Cu runoff concentrations or runoff rates [39].

In general, it can be seen that corrosion and runoff rates are influenced by a huge number of factors. Theoretically, an evaluation of the studies (Tables 1 and 2) would result in a median value for Cu runoff rate of $1.3 \text{ g}/(\text{m}^2 \cdot \text{a})$ and for Zn runoff rate of $3.4 \text{ g}/(\text{m}^2 \cdot \text{a})$. However, various interdependencies between the individual factors must be considered, which may not yet be fully known. This fact as well as the individuality of every metal roof including its surrounding circumstances and the difficulty of scaling up given results to gain long-term findings are only several reasons [23,30] why stated values in the literature are difficult to compare and to transfer to other roofs. It must also be noted that there are few studies with sampling on a technical scale. Additionally, many studies worked only with small metal surfaces with an area of less than 1 m^2 (laboratory to pilot scale). More studies under real conditions would be helpful to clarify open questions and to prove a statistical difference between the influences and the corrosion and runoff rate. Therefore, only a few values have been quoted, which can be regarded as examples. Exact values for a particular roof must be investigated individually. Nevertheless, for a brief overview of corrosion and runoff rates measured under different test conditions, see Tables 1 and 2.

2.4. Runoff Concentrations

Corrosion rates of metal roofs have already been described as high at the beginning of exposure and then decreasing with time, while roof runoff rates have been classified as time-independent, showing a more or less constant behavior [9]. However, looking at metal concentrations in the roof runoff, temporal differences in their levels can be observed. In most studies [8,9,22,23,27,30,46], higher metal concentrations were found in the runoff at the beginning of the rain event, followed by decreasing concentrations that remain constant over time. The high concentrations at the beginning are called “first flush”, defined as an initial period of storm flow during which the concentration of pollutants was significantly higher than those observed during the latter stages of the storm event [56]. In addition, further definitions of the first flush can be found, see e.g., [8,22,30]. This effect is justified by the fact that at the beginning of a precipitation event, mainly atmospheric particles that have accumulated on the roof before the stormwater as well as corrosion products that are highly soluble, thus easily mobilized are washed off, resulting in higher concentrations [30,37,46]. Such soluble and poorly adhering corrosion products are Cu_2O (cuprite) and amorphous Cu compounds and amorphous Zn hydroxides, respectively, which are mainly formed at the beginning of the patination process [8,37]. The concentrations occurring in the first flush are described to be often five to ten times higher than average concentrations, sometimes even up to 100 times higher. The exact differences between the concentration values of the first flush compared to the following, more stationary values depend on the properties of the corrosion layer, and the rain intensity and amount, as well as the length of the dry period prior to the rain [27,46]. However, in [41] the dependence of the first flush on rain intensity, rain amount and the preceding dry period could not be confirmed, but an influence of the roof aspect. The course of concentrations in roof runoff is stated to be very individual and thus difficult to describe with average values and general statements [2]. It should be briefly mentioned at this point that it is also possible that no first flush can be detected during a rain event. This can be explained on the one hand by dilution effects that occur when corrosion products cannot be solved from the roof surface or by a too high rain intensity [41]. On the other hand, different lengths of the preceding dry periods, as well as different degrees of dry deposition on the metal roof are given as reasons [8].

Although Cu and Zn concentrations are usually higher in the first flush, respectively, the metal concentrations in the further roof runoff are still high and may cause harmful effects on the environment if the runoff is not treated. Hence, it is not sufficient to focus only on the treatment of the first flush, but on the total runoff. Regarding treatment methods, they must be designed to treat the entire roof runoff, especially if it is followed by infiltration into the groundwater [23,41].

3. Metal Roof Runoff Management and Regulation

From Section 2, it can be concluded that there are too many different influencing factors to calculate individual solutions for treating Cu and Zn roof runoff. It should be emphasized that the entire stormwater runoff must be treated and that both particulate and dissolved Cu and Zn must be removed before being released into the environment. However, in order to calculate the minimum performance of a treatment device, legal aspects must first be clarified. This is performed using Germany as an example.

3.1. Legal Requirements in Germany

The European Water Framework Directive (WFD) serves as a regulatory framework for the protection of surface waters and groundwater, and must also be implemented in Germany [57]. With regard to stormwater, the WFD not only calls for its quantitative management, but above all for an immission-oriented approach for the disposal of stormwater runoff, since it may contain various forms of pollutants, as described above [57]. In addition to the WFD, the European Groundwater Directive, which contains criteria for the characterization of the groundwater status and measures to reduce pollution in order to protect groundwater, is legally binding [58]. In Germany, the provisions were implemented by the Groundwater Ordinance (GrwV) [58] and the Surface Water Ordinance (OGewV) [59]. However, the WFD also had to be transposed into national law, which was achieved in Germany through amendments to the Water Resources Act (WHG) [60]. In accordance with the WHG (§ 54 WHG) [60], collected stormwater from sealed surfaces, as is the case with metal roof runoff, is wastewater. Hence, according to § 55 WHG [60], stormwater should be infiltrated on-site, trickled away, and discharged directly or via a sewer system into a water body without being mixed with sewage. In addition, the discharge of substances into water bodies (§ 9 WHG) [60] or measures that are likely to cause adverse changes in the water quality (§ 9 WHG) [60] are considered as uses and therefore require a permit or authorization pursuant to § 8 WHG [60].

3.1.1. Groundwater

The threshold values of the GrwV apply to the assessment of the good chemical status of groundwater bodies according to the WFD. Since they are valid in the groundwater body itself [61], they cannot be used directly as “limit values” for seepage of SUDS or SQUIDs effluents into groundwater. The Working Group of the Federal States on Water (German: Bund/Länderarbeitsgemeinschaft Wasser (LAWA)) has therefore drawn up insignificance threshold values for inorganic parameters (German: Geringfügigkeitsschwelle, GFS), which are defined as concentrations at which no relevant ecotoxic effects occur even with an increase in the content of the respective substance [62]. The LAWA has suggested that these insignificance threshold values must be adhered to in the effluent of SQUIDs and SUDS. However, dilution by the groundwater itself or retention by a further soil passage is not considered yet.

Currently, the LAWA insignificance threshold values for Cu and Zn are 5.4 µg/L and 60 µg/L, respectively [62]. However, the LAWA threshold values are not legally binding in Germany, and therefore it is currently being discussed whether these values are valid in order to assess the performance of SQUIDs and SUDS. So far, SQUIDs and SUDS had to comply with the threshold values of the Federal Soil Protection and Contaminated Sites Ordinance (German: Bundesbodenschutz- und Altlastenverordnung; BBodSchV) for the soil-groundwater pathway (50 µg/L for Cu and 500 µg/L for Zn) [63]. In 2023, the BBodSchV will be replaced by the so-called “Shell” Ordinance (German: Mantelverordnung; MantelV) which, among others, contains the revised BBodSchV and will have threshold values of 50 µg/L for Cu and 600 µg/L for Zn. A leachate prognosis according to § 14 of the MantelV [64] takes into account the degradation and retention effect of the water-unsaturated zone.

3.1.2. Surface Water

Regarding surface water bodies, the discharge of collected stormwater runoff may only be permitted if the conditions set out in § 57 WHG [61] are met. The state of the art given in the technical guidelines of the German Association for Water, Wastewater and Waste (DWA) DWA-A 102-2/ /BWK-A 3-2 [65] are currently used in practice in Germany. Hence, there are no nationwide legally binding requirements for discharging stormwater runoff into surface waters in Germany [66]. However, in addition, based on § 23 WHG [61], the OGewV [60] is valid for the protection of surface waters [60] and contains regulations regarding the ecological as well as the chemical state of surface waters [60]. Regarding Cu and Zn runoff discharge, Annex 6 of the OGewV [60] should be mentioned, which lists values of 160 mg Cu/kg suspended matter or sediment and 800 mg Zn/kg suspended matter or sediment that must be complied with. However, these values must be viewed critically for metal roof runoff, since Cu and Zn are predominantly dissolved in roof runoff.

3.2. Mitigation Strategies

On-site management of stormwater runoff is recommended for sustainable stormwater management. Therefore, decentralized SUDS and SQIDs are also becoming increasingly prevalent for the treatment of stormwater runoff at the source in order to reduce pollutant levels before discharging into water bodies [21].

As an example for SUDS, vegetated infiltration swales [67–71] are applied to protect groundwater. According to the technical guideline DWA-A 138 [20] which is valid in Germany, a minimum topsoil layer thickness of at least 30 cm has to be applied in vegetated infiltration swales to retain Cu and Zn roof runoff prior to infiltration. During the percolation of the stormwater runoff over the topsoil layer, Zn and Cu are retained in the soil through filtration and physicochemical processes, including sorption, complexation, and precipitation [72]. The removal capacity for metals depends not only on the type and quantity of accessible soil, but also on the metal concentration, the type of complexing organic and inorganic ligands in soil, the texture, the soil pH value as well as the organic content [73,74]. A possible transport of metals through the topsoil layer also depends on soil characteristics like organic content, micro-organic activity, porosity, and infiltration capacity [68,72,74].

The aforementioned processes retaining metals in the soil thereby also lead to changes in the chemical bonding forms of the metals when the runoff enters the soil (see also Section 2.1). Due to the fixation of the metals in the soil, the proportion of freely hydrated Cu and Zn ions (Cu^{2+} , Zn^{2+}), which are considered bioavailable, decreases. Metals in emerging complexed forms, on the other hand, are much less often available [75]. However, in addition to the fixation processes, the process of desorption, i.e., the release of the metals in the soil, must also be considered. Although this is a slow process, it cannot be disregarded in terms of a possible risk to groundwater [75]. The desorption rate is mainly influenced by the concentration of dissolved organic matter and the pH value of the soil [76–78]. Through low-molecular, little decomposed organic complexing agents (e.g., humic and fulvic acids) occurring in the soil solution (aqueous phase of the soil), fixed heavy metals can be remobilized through the formation of metal-organic complexes [76]. During an investigation of the retention capacity of a soil, [79] was also able to establish that Zn forms complexes with mobile organic ligands. As a result, it is released again and, contained in the leachate, may enter the groundwater. The influence of the pH value on desorption is different for Cu and Zn. The solubility of Zn increases strongly at $\text{pH} < 5.5$ and decreases strongly at $\text{pH} > 5.5$. Cu has its lowest solubility at pH 6, which increases at pH values above or below [80]. The lack of degradation processes for metals, as well as slow desorption rates, lead to an accumulation of heavy metals in the soil and thus to a contamination of the soil material. Hence, it must be considered that the topsoil's absorption capacity for Cu and Zn is limited [7,20,75].

There are many studies on the retention of Cu and Zn from traffic area runoff, e.g., [21,69,81–83]. In comparison, studies on the treatment of metal roof runoff are

few. However, [67] assesses the risks of groundwater contamination due to infiltration of stormwater runoff of a Zn roof over vegetated infiltration swales. The spatial horizontal and vertical distribution of the Zn content in four infiltration swales showed high Zn contents in the topsoil layer (up to 27.9 g/kg dry mass) only for spatially limited areas at the inflow zones of the infiltration swales. In an analysis of the horizontal Zn distribution in the topsoil, the highest Zn contents were measured directly at the inlet points in the first 5 cm depth. The content decreased rapidly from the inlet point to the utmost periphery of the swale. However, due to unevenness and preferential flow directions, the horizontal Zn distribution varied. Taking those highly contaminated zones, it demonstrates, on the one hand, the high retention capacity of the soil but, on the other hand, also that the soil is quickly saturated, which is why maintenance of the infiltration system is necessary. Regular inspection every three years combined with a replacement of the contaminated soils is therefore recommended to protect the groundwater. Depending on the contamination, the required measures of the Federation/State Working Group on Waste (German: LAGA) must be observed when disposing of the contaminated soils [67].

However, even though retention capacities of topsoils amounting to 99% for Zn [79] and up to 100% for Cu and Zn [75] were obtained and consequently the removal rate for Cu and Zn in soils is classified as very high, the above-mentioned preconditions and hazards must not be neglected in the case of infiltration of Cu and Zn contaminated runoff. In addition to the retention capacities in %, runoff concentrations must also be considered. In a study, Zn concentrations of 22 mg/L were measured in the effluent of a vegetated infiltration swale treating Zn roof runoff which clearly exceed the values of the BBodSchV as well as of the MantelV (see Section 3.1) [84]. Furthermore, it must also be considered that vegetated infiltration swales have high land requirements. However, these areas are not always available in densely built-up urban areas [7]. Although vegetated infiltration swales should be used as a priority over SQIDs to treat polluted stormwater, as they also include stormwater storage and evapotranspiration, which helps to maintain the local hydrological cycle, SQIDs, which are mostly located below the surface, offer the possibility of on-site treatment, even in densely built-up areas [20,21]. SQIDs apply different treatment processes based on physical-chemical adsorption, precipitation, and other chemical processes for a reduction of Cu and Zn [21,66,70,71].

In general, there are a large number of different SQIDs currently available in Germany. However, most of them are for traffic area runoff [66], whereas only a few are for metal roof runoff. While the focus of SQIDs for traffic runoff treatment is mainly on the separation of fine particles [85], the main task of SQIDs for metal roof runoff is the separation of solids such as leaves etc., and above all the removal of dissolved metals through adsorption, ion exchange or precipitation combined with filtration [66]. A selection of materials respectively components through which the respective mechanism can be used to treat metal roof runoff is given in Table 3.

Table 3. Overview of mechanisms and components to remove Cu and Zn from runoff. (data according to [18,26,62,86–95]).

Mechanism	Materials and Components	Achievable Cleaning Performance	Comments	Examples
Density separation	silt trap, hydrodynamic separator	n.a.; pretreatment step	for the retention of undissolved stormwater constituents; usually preceding the following mechanisms	[18,26,86]
	activated carbon (fixed bed)	n.a.	also, for the retention of organic trace substances contained in runoff	[26,87,88]
(Ad-) Sorption	granulated Fe hydroxide (GEH)	Cu: approx. 38%	especially suitable for Cu roof runoff	[18,86–89]
	Fe sludge	Cu: approx. 47%	especially suitable for Cu roof runoff	[89]
	GEH + concrete rubble (50:1)	Cu: approx. 43%	addition of concrete rubble to GEH at low ratio (1:50) improves cleaning performance slightly, opposite effect at higher ratio	[89]
Ion exchange	clinoptilolite (natural zeolite)	Zn: 92% for first flush, 97% for remaining stormwater; Cu: 97% (combined with hydrodynamic separator and subsequent infiltration ditch)	increase in ion exchange capacity possible through pre-activation	[18,86,90–92]
	zeolites	Cu: 99% (combined with silt trap and subsequent infiltration) → compliance with BBodSchV limit value possible	ion exchange capabilities of zeolites are only usable if pollutants are dissolved → in the case of previous precipitation, however, they are in particulate form	[18,26,86]
	chabazite-philipsite (natural zeolite)	Cu: approx. 99% (combined with hydrodynamic separator and subsequent infiltration ditch)	-	[18,86]
	biocalith K	proven cleaning performance fulfilling the requirements of BBodSchV and LAWA	high-performance substrate	[93]
Precipitation	clay + GEH	f Zn: approx. 70%	especially suitable for Zn roof runoff	[89]
	zeolites	Zn: approx. 40%	especially suitable for Zn roof runoff; besides sorption of heavy metals, also sorption of protons of water → pH increase → precipitation of Zn hydroxides	[89]
	porous concrete with high CaCO ₃ content	Cu: approx. 99% (combined with hydrodynamic separator, Fe hydroxide coating and infiltration ditch)	high concentration of CaCO ₃ increases the pH in the runoff of the plant → precipitation of dissolved heavy metals as hydroxides or carbonates	[18,86]
Filtration	Geotextile filter	n/a	No removal of dissolved metals, just pre-treatment	[92]
	two-layer, needle-punched geotextile fleece	Zn: almost 80% (particulate bound)	due to fine pores, fleece can remove particulate bound pollutants	[94]

n.a. = not available.

In Germany, there is no general approval system for SQIDs for metal roof runoff. However, the state of Bavaria has developed test criteria for the preliminary assessment of infiltration systems for the retention of metal ions from precipitation runoff from metal roofs, in which such SQIDs are tested and evaluated for the retention of Cu or Zn on a Cu or Zn roof runoff over a period of one year for three different rain event classes (I: ≤ 4 l/(s·ha), II: >4 to ≤ 10 l/(s·ha), and III: >10 l/(s·ha)) at real weather conditions [66,96]. According to these criteria [96], the test is considered to have been passed if both of the following criteria are met:

- (1) The calculated annual mean value of the concentration in the filter drain does not exceed the specified limit value of 50 $\mu\text{g/L}$ for Cu or 500 $\mu\text{g/L}$ for Zn, respectively (according to BBodSchV), and
- (2) if all measured concentrations within a single class I, II, or III exceed the specified limit value, the mean value of this class must not exceed twice the limit value.

Although many SQIDs would be suitable for treating metal roof runoff, only a few are currently commercially available that have been tested according to these criteria (see Table 4) [26,66].

Table 4. Currently approved SQIDs for treating metal roof runoff (data according to [97–101]).

SQIDs Name	Manufacturer	Suitable Metal Roofing Material	Description of the Plant	Cleaning Performance
Metal roof filter “Tecto” type MVS 70–600	Mall GmbH	Cu and Zn	1. slotted sieve stainless steel cylinder 2. geotextile filter bag 3. metal ion adsorption substrate	>97%
3P Hydrosystem 400 metal (Cu)	3P Technik Filtersysteme GmbH	Cu and Zn	1. sedimentation (hydrodynamic separator) 2. precipitation + adsorption 3. filtration	>90% for Zn, >98% for Cu
3P Hydrosystem 1000 metal	3P Technik Filtersysteme GmbH	Cu and Zn	see above	>90% for Zn, >98% for Cu
RAUSIKKO HydroClean type M	REHAU AG + Co.	Cu and Zn	1. sedimentation (hydrodynamic separator, silt trap) 2. precipitation + adsorption 3. filtration	>90% for Zn, >98% for Cu

The SQIDs all consist of a shaft structure made of concrete or plastic in appropriate dimensions. A roof area of between 130 and 650 m^2 can be connected to the SQIDs, depending on the system. Some manufacturers recommend installing up to five systems in one shaft to increase the connection area. Therefore, up to 3250 m^2 roof area can be connected [97–101]. All of the systems listed in Table 4 have mechanical coarse removal as the first treatment stage. For example, the “Tecto” type MVS metal roof filter [98] has a geotextile filter bag in addition to the filter cartridge, and the 3P Hydrosystem metal [99,100] and RAUSIKKO HydroClean type M [101] have a hydrocyclone for removing leaves and particles. As a second treatment stage, the systems each have a filter cartridge filled with natural or synthetic cation exchanger material to remove the dissolved heavy metals. For example, there are Ca^{2+} , Mg^{2+} , Na^+ , and K^+ ions on the surface of cation exchange materials, which balance the negative charge on the surface. These metal ions can be exchanged by Cu^{2+} and Zn^{2+} ions from the metal roof runoff, whereby the heavy metals are retained [66,91].

A possible cation exchange material is e.g., zeolite (see Table 4). The use of natural zeolites as cation exchangers for the treatment of metal roof runoff has been known since

over a decade [91,92]. The ion exchange capacity of the zeolites can be enhanced through targeted pre-treatment [91,102–105]. When pre-treated with sodium chloride (NaCl) solution, Na⁺ ions exchange the K⁺, Ca²⁺, and Mg²⁺ ions of the natural zeolite due to their high concentration. Na⁺ can be exchanged more easily than Ca²⁺ and Mg²⁺ by Cu²⁺ and Zn²⁺, as Na⁺ has a lower binding energy to the zeolite compared to Ca²⁺ and Mg²⁺ [102]. The pre-treatment also releases clogged pores, since fine particles are washed out of the pores during the treatment process and more surface area is available for the adsorption processes. In investigations with clinoptilolite, a natural zeolite, pre-treatment with a one molar NaCl solution was able to remove 8% fine fraction (based on the mass) [91]. Associated with this was an almost doubling of the sorption capacity for Zn²⁺ from 0.067 mmol/g to 0.12 mmol/g (at pH 5) and an increase in the sorption rate of 15% [91]. Ion exchangers that are selectively loaded with Cu or Zn can later easily be regenerated with a NaCl solution and thus reduce the amount of waste for loaded sorbent materials [91]. Theoretically, back-flushed Cu and Zn could be recovered from the salt concentrates.

4. Conclusions

The level of pollution of Cu and Zn roof runoff depends on many factors such as the properties of the roofing material and building characteristics as well as the surrounding environment and climate. While findings on the influences of factors such as roof inclination and orientation, atmospheric pollutant content (esp. SO₂ content), as well as rain amount and intensity on corrosion and runoff rates, respectively, are quite clear, their dependence on roof age and on the length of the previous dry period before precipitation is still controversial. Moreover, there are also various coatings and pre-treatment methods influencing metal concentrations in the roof runoff. Due to a lot of influencing factors, no median or average Cu or Zn runoff concentrations can be given from a scientific point of view; the exact values must be determined individually for each roof.

However, in any case, metal roof runoff must be taken seriously as containing metal concentrations that do not really decrease throughout the duration of exposure. It contains Cu and Zn mostly in dissolved form, which are bioavailable and therefore harmful especially to aquatic life when entering the environment. Therefore, adequate treatment of the entire runoff is required.

Various systems are available for on-site pre-treatment of stormwater before infiltration such as vegetated infiltration swales and space-saving SQIDs. In Germany, however, there is no general test system for SQIDs for the treatment performance for metal roof runoff. Therefore, the state of Bavaria has defined its own test criteria to evaluate various SQIDs regarding their Cu and Zn retention capacity. According to these criteria, four SQIDs are currently approved for the pre-treatment of roof runoff. Moreover, SQIDs still lack construction and operation regulations, although already under operation since years. Therefore, further research on metal roof runoff and its treatment measures as well as binding regulations, especially a general approval system for SQIDs, are needed.

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