Zinc and copper in roof runoff
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ABSTRACT
The zinc and copper content of roof runoff could originate from different sources such as dry and wet deposition and the corrosion of the material. The zinc runoff rate from a galvanized surface depends on the corrosion products formed during the dry days, the rain intensity and roof slope, which determines the contact time. In the present study the contact time dependence of zinc rate and the re-dissolution of the zinc were investigated with steeping tests and a pilot study. The average zinc runoff measured in the first 2.8 l of runoff was 3.8 mg m\(^{-2}\) (1.1–8.4 mg m\(^{-2}\)), while in the following samples 1.2 mg m\(^{-2}\) were detected. These results are in accordance with the 5–10 min, and 40–60 s contact time laboratory steeping test, respectively, which are realistic. The estimated specific yearly zinc runoff rate was 0.7 g m\(^{-2}\) y\(^{-1}\), while the dry and wet deposition rate of copper was 0.009 mg m\(^{-2}\) d\(^{-1}\) and 0.053 mg m\(^{-2}\) storm\(^{-1}\) respectively. The re-dissolution of the zinc from the evaporated then re-filled samples of leaching tests with high initial zinc content was just 60% after 60 min.

Key words | contact time, copper, deposition, dissolution, roof runoff, zinc

INTRODUCTION
Corrosion of metal roofing material and the atmospheric dry and wet deposition could be mentioned as a source of zinc and copper roof runoff.

Corrosion rate
Numerous researchers have studied relative humidity, temperature and air pollutant unique and synergic effects on the corrosion of zinc and copper materials (Oesch & Faller 1997; He et al. 2001; Castaño et al. 2007). Under natural environmental conditions the corrosion rate of zinc and copper showed decreasing tendency with time (He et al. 2001). After 8 weeks of exposure the corrosion rate of copper was 12.5 g m\(^{-2}\) y\(^{-1}\), and zinc was 18.6 g m\(^{-2}\) y\(^{-1}\). The copper material reached a steady-state condition after 24 weeks, while zinc showed a continuous decrease. The average corrosion rate after 48 weeks was 6.7 g m\(^{-2}\) y\(^{-1}\) (0.75 μm y\(^{-1}\)) for copper and 5.0 g m\(^{-2}\) y\(^{-1}\) (0.70 μm y\(^{-1}\)) for zinc.

Atmospheric deposition rate
Due to anthropogenic activity a high amount of heavy metals are emitted to the atmosphere, so zinc and copper are also measurable in non-metal roof runoff due to dry deposition. The main sources of atmospheric metal concentration are industry and transport. Dry deposition rates reported by international studies have large deviations due to the different degree of air pollution and meteorological conditions. The rates vary from 1.75 to 65.7 mg m\(^{-2}\) y\(^{-1}\), and from 0.35 to 28.85 mg m\(^{-2}\) storm\(^{-1}\) for zinc and copper respectively (Yi et al. 2001; Sabin et al. 2005; Lim et al. 2006; Sabin & Schiff 2008). Sweet et al. (1998) and Sabin et al. (2005) also studied the wet deposition rates, which were higher than the dry ones. The dry and wet deposition rates could not be generalized because of the numerous circumstances which affect them.

Runoff rate
The corrosion product, depending on its components, is soluble to a certain extent by rainwater. The specific runoff rate is lower than the corrosion rate (He et al. 2001; Odnevall Wallinder & Leygraf 2001; Schriewer et al. 2008; Veleva et al. 2009), but the difference varies with the exposure time and the type, material and protecting layer of the metal. The dissolubility of corrosion products on the surface
of copper shingle is lower than on the zinc surface under equal environmental conditions because of the different stability, solubility and adhesion capacity of the corrosion product. In the case of zinc shingles, the average specific runoff rate was 3.1 g m\(^{-2}\) y\(^{-1}\), which means that 60% of the corrosion products were washed off (He et al. 2001). Even higher ratios were measured by Veleva et al. (2009) in the first (82%) and second year (84%) of exposure with higher runoff rates (8.2 and 12.4 g m\(^{-2}\) y\(^{-1}\), respectively).

The metal concentration of runoff, among other things, depends on the rain intensity and the age, inclination and orientation of the shingles. The effect of rain intensity is high in zinc sheets. In research by He (2002) higher zinc concentration belonged to lower intensity (longer contact time), because the conditions to dissolve corrosion products, were more favourable. Schriewer et al. (2008) reported that the runoff concentration at a 14-year-old Zn roof is highest at the beginning of a normal rain event (0.5–5.1 mm h\(^{-1}\)).

Studying the effect of the age of the shingles, He et al. (2001) found that there was no difference between runoff rates of aged and new zinc panels, because a thick corrosion layer was formed on the surface on some days.

Odnevall Wallinder et al. (2001) and Bertling et al. (2006) studied the zinc runoff from different zinc-based materials. The highest average annual runoff rate was measured in the runoff from a general galvanized roof (2.5 g m\(^{-2}\) y\(^{-1}\)) (Bertling et al. 2006). Different surface protection layers (total organic carbon, chromate, paint) could decrease the zinc concentration of the runoff; however, only the painted surface during the 2-year experiment (Bertling et al. 2006).

The zinc and copper concentration from the different material roofs indicated high variance as the environmental conditions and roof characteristics changed (Quek & Förster 1995; Gadd & Kennedy 2001; Simmons et al. 2001; Rocher et al. 2004; Gnecco et al. 2005; Berndtson et al. 2009; Mendez et al. 2011; Lee et al. 2012). In research in Auckland, New-Zealand (Simmons et al. 2001), 125 collected roof runoffs were analysed without determining the roof types. The measured highest zinc concentration in harvested water was 5.2 mg l\(^{-1}\), and the average of the samples was 0.4 mg l\(^{-1}\). The average copper concentration was 0.060 mg l\(^{-1}\), and only three times exceeded 2 mg l\(^{-1}\).

Studies comparing heavy metal content of roof runoff from different roof types always reported significantly higher zinc concentration from galvanized roof than from other types (Chang et al. 2004; Göbel et al. 2007; Lamprea & Ruban 2008; Tobiszewski et al. 2010; Mendez et al. 2011; Lee et al. 2012). The measured minimum concentration was 0.005 mg l\(^{-1}\), and the maximum was 212.3 mg l\(^{-1}\). Some research handled the roofs with and without galvanized gutter separately (Göbel et al. 2007; Lamprea & Ruban 2008). They measured three to five times higher zinc concentration when just the gutters were galvanized, and eight to 16 times higher when the roof and the gutter too had a zinc coating layer. That indicates the main role of the dissolution of the corrosion products against the deposition.

In the present study zinc and copper emissions of galvanized roof were analysed. The main objective was to find a relation between contact time and zinc dissolution from a galvanized surface. In the case of copper emission, roof runoffs were measured to estimate dry and wet deposition rate.

**METHODS**

**Steeping test**

Steeping tests were applied in order to determine the role of contact time in dissolution of zinc from galvanized steel sheets (Herting et al. 2007). First, a 0.5 mm width shingle was disintegrated into pieces of 10 × 100 cm. These metal pieces were rolled into a loose spiral to assure high contact surface during the steeping test. Known mass of metals were put into 900 ml distilled water (average liquid-surface ratio 9.14 l m\(^{-2}\)). Samples were continuously mixed at approximately 150 rpm. The steeping time varied between 10 s and 8 h. After the elapsed time, dissolved Zn concentrations were measured. Knowing the surface of the shingles and the volume of the leaching water, the specific dissolved zinc rate could be calculated.

In real conditions the roof material is exposed to subsequent wetting and drying periods. The zinc solution on a wetted roof and gutter surface will be evaporated during the subsequent dry period and a certain portion of its zinc content as residuum is exposed to dissolution during the next rain event. It was supposed that solubility of residuum could significantly affect the change of runoff zinc concentration.

In order to determine the dissolution of zinc previously dissolved from galvanized steel, another test was carried out; 200 ml solutions of samples from the steeping tests were evaporated from three beakers. White material remained on the bottom of the cups. The crystallized zinc residuum was measured in every case, and then the cups were refilled with 200 ml distilled water. During continuous mixing (150 rpm),
the samples were taken out in the 1st, 5th, 10th, 15th, 30th and 60th minutes and their zinc concentrations were analysed.

**Roof runoff sampling**

A galvanized steel shingle sample roof was established on the top of our host building (Figure 1), which is situated in the centre of Budapest near to a busy street. It had a surface area of 1.98 m$^2$ with a 21.3° slope. During rain events sequential samples were collected from the roofs from the end point of the galvanized steel gutters into 2.8 l glass bottles between May and October 2011.

**Analytical procedure**

The weight of the sheets was measured with a KERN EWB 1200-1M type scale. The pH of the samples was measured with WTW inoLab device and the conductivity with WTW Cond 330i device. The dissolved zinc concentration of the solution after the steeping and re-dissolution tests was determined with photometrical method using NANOCOLOR Zinc Test 1–95 (Ref. 918–95) by Macherey-Nagel GmbH & Co. KG. The measuring range of the method is 0.02–1.50 and 0.1–3.0 using 50 and 10 mm cuvette respectively.

The total and dissolved zinc and copper concentration of the roof runoff samples was measured in an accredited laboratory. The concentrations were determined on the basis of the standard EPA 6020 with inductively coupled plasma mass spectrometry (ICP-MS). The preparation of the samples was based on the standard MSZ 1484–3:1998.

**Data analysis**

The Langmuir isotherm was developed to describe limited adsorption. As the results of the steeping test after 1.5 h reached a steady-state concentration, the Langmuir isotherm was selected to describe the process of dissolution. The applied equation was

$$q = \frac{q_0 \cdot C}{K + C}$$  

(1)

where $q_0$ [mg/m$^2$] is the highest specific value of dissolved zinc achieved in the experiments, $C$ [min] is the contact time, and $K$ is a constant.

**RESULTS AND DISCUSSION**

The results of the steeping tests showed limited zinc solubility from the surface of galvanized steel as well as dependence on the contact time (Figure 2). As Figure 2 demonstrates, the specific value of dissolved zinc approached the steady-state condition after 1.5 h, with a value of 8.6 mg m$^{-2}$. It did not exceed 9.2 mg m$^{-2}$ even after 8 h steeping. A possible explanation for the limited solubility could be the solubility of the zinc components present on the surface of the shingle.

Adjusting the Langmuir isotherm (1) to the measured zinc rates the parameters gained by the least squares method are the following: $q_0 = 9.2$ mg m$^{-2}$ and $K = 12.2$.

In real conditions the contact time is some seconds (at longest 1 min) on the roof surface; however, when runoff collects in the gutter, water could remain for a longer time.

Re-dissolution tests of crystallized zinc residuum resulted in a non-linear correlation between the initial zinc content and solubility. Samples with low initial zinc content (0.03–0.05 mg; 0.13–0.23 mg l$^{-1}$) could be re-dissolved totally from the cups in 10 min. As the initial zinc content increased, not even 60 min was long enough to re-dissolve the residuum (Figure 3). When the initial zinc content in the cups was approximately 0.38 mg, which corresponds to the maximum specific loss 8.4–9.2 mg m$^{-2}$ measured in the steeping test, the re-dissolved proportion was around 40–50% in 10 min.

In the roof runoff sampling the first bottle from the sequential samples was treated separately during the evaluation of the results because the contact time was longer than in the case of the other samples. Furthermore, the wash off from the atmosphere increased the zinc...
content of the samples. The average specific zinc runoff rate of the first samples was 3.8 mg m\(^{-2}\) (1.1–8.4 mg m\(^{-2}\)), which compared with the laboratory experiments shows a 5–10 min average contact time. The mean specific runoff rate of the following bottles varied between 0.3 and 3.6 mg m\(^{-2}\). One of the explanations for the different measured rates could be the varying contact time during the rain event because of the changes in the rain intensity. This affects the washed off amount of zinc (He 2002). The other reason could be that with the increasing antecedent dry days (Figure 3) the corrosion layer becomes thicker, so the runoff could wash off a higher zinc amount. The average concentration of these samples was 1.2 mg m\(^{-2}\). In the laboratory leaching test this rate was achieved after 40–60 s of steeping. The yearly specific zinc runoff rate, calculated with the average 550 mm amount of rain in Hungary, is 0.7 g m\(^{-2}\) y\(^{-1}\). Compared with data from the literature it is in the same order of magnitude (He et al. 2001; Bertling et al. 2006; Veleva et al. 2009).

Parallel with zinc, copper concentrations were also measured in roof runoffs. The average copper concentration per storm event was 0.03 mg l\(^{-1}\) and the rate was 0.073 mg m\(^{-2}\). The 0.009 mg m\(^{-2}\) d\(^{-1}\) dry deposition rate of copper in the study area was estimated from the measured emission after longer than 2 dry days. When the time between two rain events is shorter than 1.3 d, the effect of wash off from the atmosphere is greater than the dry deposition. From these six rain events the estimated wet deposition rate was 0.053 mg m\(^{-2}\) storm\(^{-1}\).
Dependence of runoff rates on the number of antecedent dry days and the volume of runoff water, for both metals, is demonstrated in Figure 4. It can be concluded from the estimated deposition rates and the diagrams that the copper runoff rate principally depends on wet deposition when the antecedent dry days are less than 1.3 d (Figure 4). In the case of zinc, the measured runoff rates increased with increasing dry days. However, the rates are too high to originate only from depositions. The reason for the correlation could be that with the increasing number of dry days the amount of soluble corrosion products increase. It indicates that besides wet deposition, the corrosion process affects the specific zinc losses of roof material. As the steeping test showed, the dissolution of zinc corrosion material is limited. On the right diagram of Figure 4 it can be seen that the specific zinc runoff rate per storm event increased with the volume of runoff water, but with the exception of one case it did not reach 10 mg m\(^{-2}\), which corresponds well with the leaching test results.

The specific copper runoff from a galvanized steel roof was two orders of magnitude lower than the zinc runoff, and principally originated from wet deposition.

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