REPORT

Copper in storm water runoff from a naturally patinated copper roof and a parking space – variations in fluxes during a rainfall in Stockholm, Sweden

For Scandinavian Copper Development Association

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Contents

Abstract

The present study has three aims. The first is to simultaneously study the time dependence of concentrations of copper (Cu) in storm water from a copper roof and a parking space during a specific rain event and to estimate emissions of Cu from the two sources as a function of area and time during rain events. The second aim is to estimate yearly fluxes of Cu based on these emission numbers and precipitation data for the Stockholm area. The third aim is to assess the capacity of storm water to complex copper. The major conclusions were:

- A Cu runoff value derived for the parking space during a single rainfall (10 mm) was 48 mg $mm^{-1}m^{-2}$. This number corresponds to an annual Cu runoff value from parking spaces of 29 mg m^{-2} by multiplying with the annual precipitation in Stockholm, 585mm.
- A Cu runoff value derived for the copper roof during the rainfall was 2.4 mg $mm^{-1}m^{-2}$ after expected retention in downpipes of cast iron and concrete. This value corresponds to an annual Cu runoff value from copper roofs (representative for a surface inclined 5° from the horizontal) of 1.4 g m^{-2}. For a surface inclined 45° from the horizontal, which is representative for Stockholm, this number equals 1 g m^{-2}.
- For the roof samples, the total copper concentration was too high for any complexation capacity measurement using DPASV.
- A substantial part of the copper in the storm water from the parking space was complexed to ligands, compared to the total concentrations of copper in the samples.

1 Introduction

Metals are natural and in many instances essential (e.g. copper and zinc) constituents of the environment. In population centres the additional loads of metals from infrastructure, industrial activities and human consumption to surface waters and sediments have frequently caused concern for environmental risks. These concerns have motivated studies and monitoring programs aiming at estimating the loads from diffuse or background sources such as atmospheric deposition and land use (infrastructure, buildings and soil), point sources such as wastewater treatment plants (WWTP), effluents from industrial activities and contaminated sites such as landfills. The city of Stockholm, with a population of 0.87 million, is no exception. Several studies have looked at the emissions of metals from various sources to the environment in Stockholm. These sources include road traffic (Furusjö et al., 2007; Hjortenkrans et al., 2007); copper in building materials (Ekstrand et al., 2001; Bertling et al., 2006; Odnevall Wallinder et al., 2009) and WWTPs (Pettersson and Wahlberg, 2010). Finally, some studies have estimated the atmospheric deposition of metals (Stockholm Stad, 2000) and some the combined, total load of metals from all sources (Sörme and Lagerkvist, 2002; Cui et al., 2010; Jönsson, 2011). However, considering the fact that all metals naturally exist in the aquatic environment with large variations in concentrations it is also important to study the speciation and bio-availability of these metals in the aquatic environment (Benjamin and Honeyman, 1998).

Copper is among the metals which are the most commonly monitored in the aquatic environment due to its potential toxicity and large anthropogenic loads in relation to background fluxes in the environment (Benjamin and Honeyman, 1998). Specifically, the concentrations of this metal in the aquatic environment are of interest since it has many important sources in the urban environment such as runoff from buildings and roads (Göbel et al., 2007; Jartun et al., 2008). The wear of brake linings is a major source of Cu from road traffic (Sternbeck et al., 2001; 2002; Sanders et al., 2003; Furusjö et al., 2007).

The present study has three aims. The first is to study the time dependence of released concentrations of copper (Cu) in the storm water from a naturally aged copper roof simultaneously with the release of copper from a parking space during a single rainfall and to estimate emissions of Cu from the two sources as a function of area and time. The second is to estimate annual fluxes of Cu based on these emission numbers and precipitation data for the Stockholm area. The third aim is to assess the capacity of storm water to complex Cu.

2 Materials and methods

The study site is at a shopping centre in the suburb Farsta Centrum (59.25 deg N; 18.08 deg E) south of Stockholm (Figure 1) at the same site as the study by Odnevall Wallinder et al. (2009).

Figure 1. Storforsplan at Farsta centrum with the copper roof directly north of the parking space.

The precipitation at Farsta for the year 2011 (Figure 2) was estimated from gridded (4x4 km) SMHI data (from a meteorological station in Tullinge (59.18 deg. N; 17.91 deg. E), about 10 km southwest of Farsta. As can be seen from the precipitation data (Figure 2), there were only minor (< 5 mm) rainfalls during the 38 day period prior the sampling event (Dec. 3, 2011) of the present study.

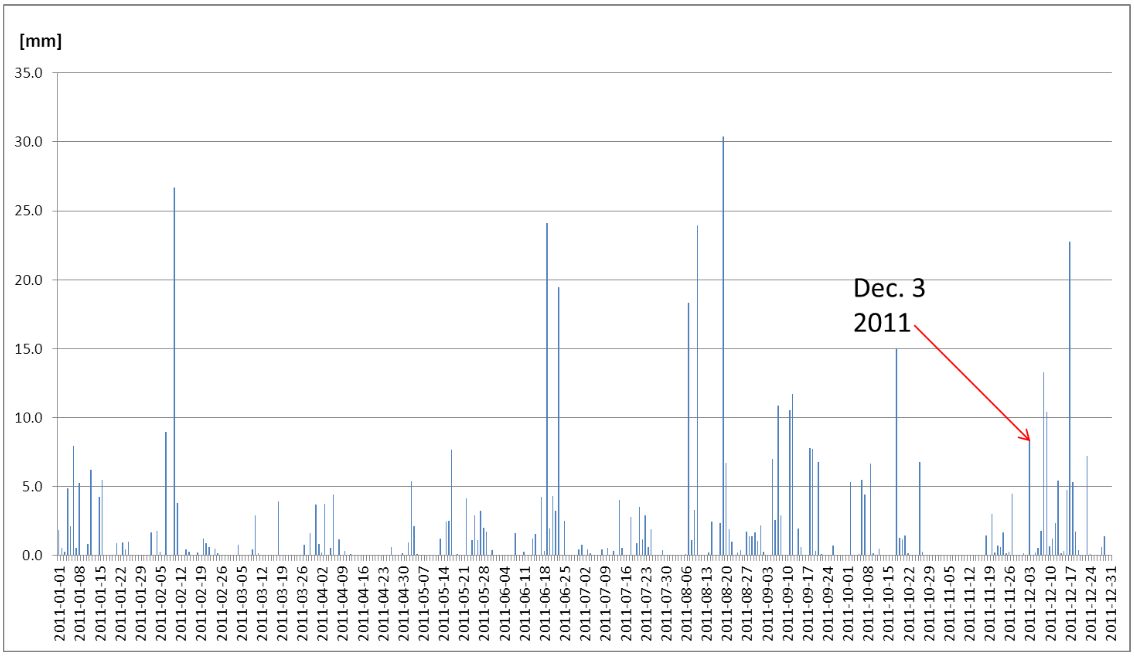

Figure 2. Daily precipitation in mm, in Farsta during 2011.

2.1 Hydrology and hydraulics

Both the copper roofs and the parking space can be considered to be impervious surfaces from a hydrological perspective, with runoff coefficients of 0.95 (Shaw, 1994). The storm water runoff from a copper roof with a projected surface of 2 330 m^2 (Odnevall Wallinder et al., 2009) on the shopping centre was sampled and its flow measured in the underground concrete storm drain pipe with a diameter of 300 mm. The sampling and measurement point is located about 20m downstream from where the storm drain system of the roof is connected, c.f. site B in Fig. 3. At this point only storm water from the roof is measured. The storm drain system of the roof is made of cast iron and has a 40m horizontal section under the roof and a 30 m vertical section connection to the sewers. Simultaneously, the storm water runoff from a parking space adjacent to the building with the copper roof (Figure 1) was sampled and its flow measured. The precipitation was measured using a RGP (Rain wise Inc.) rain-gauge meter of tipping bucket type (size 0.25mm) with a Rain log unit (Rain wise Inc.) placed on the copper roof. Sampling was conducted using a vertical shaft giving access to the underground storm drain pipe at location where the total runoff from the majority (14 000m^2) of the parking space of approximately 15 000 m^2 (Odnevall Wallinder et al., 2009) entered the storm water system without any contribution from other sources (Figure 4). The storm drain pipe is made of concrete and has a diameter of 300 mm. The rest of the parking space (1 000 m^2) is drained to the south on map (Figure 4). The parking space has a capacity of about 415 cars within the area which is drained to the sampling point. It is estimated that about 1 000 cars use the parking space on a typical day (Odnevall Wallinder et al., 2009).

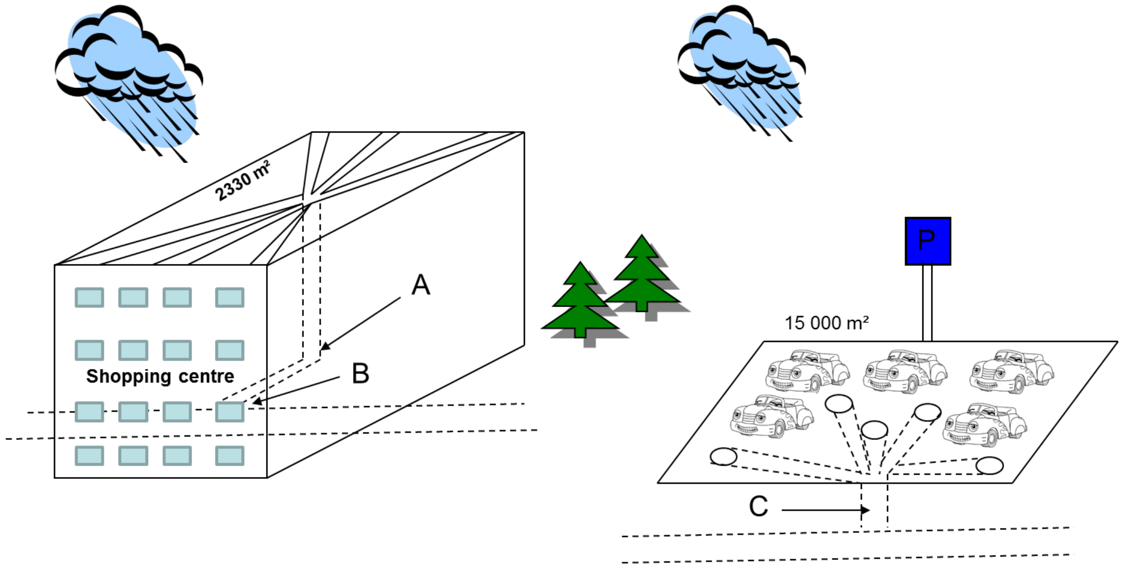

Figure 3. Schematic drawing (by Y. Hedberg, KTH) of sampling sites: this study – roof: site B; Parking space: site C, compared with the study of Odnevall Wallinder et al. 2009. The storm water pipes of the parking space are only schematically illustrated. Technical drawings are given in Fig. 4.

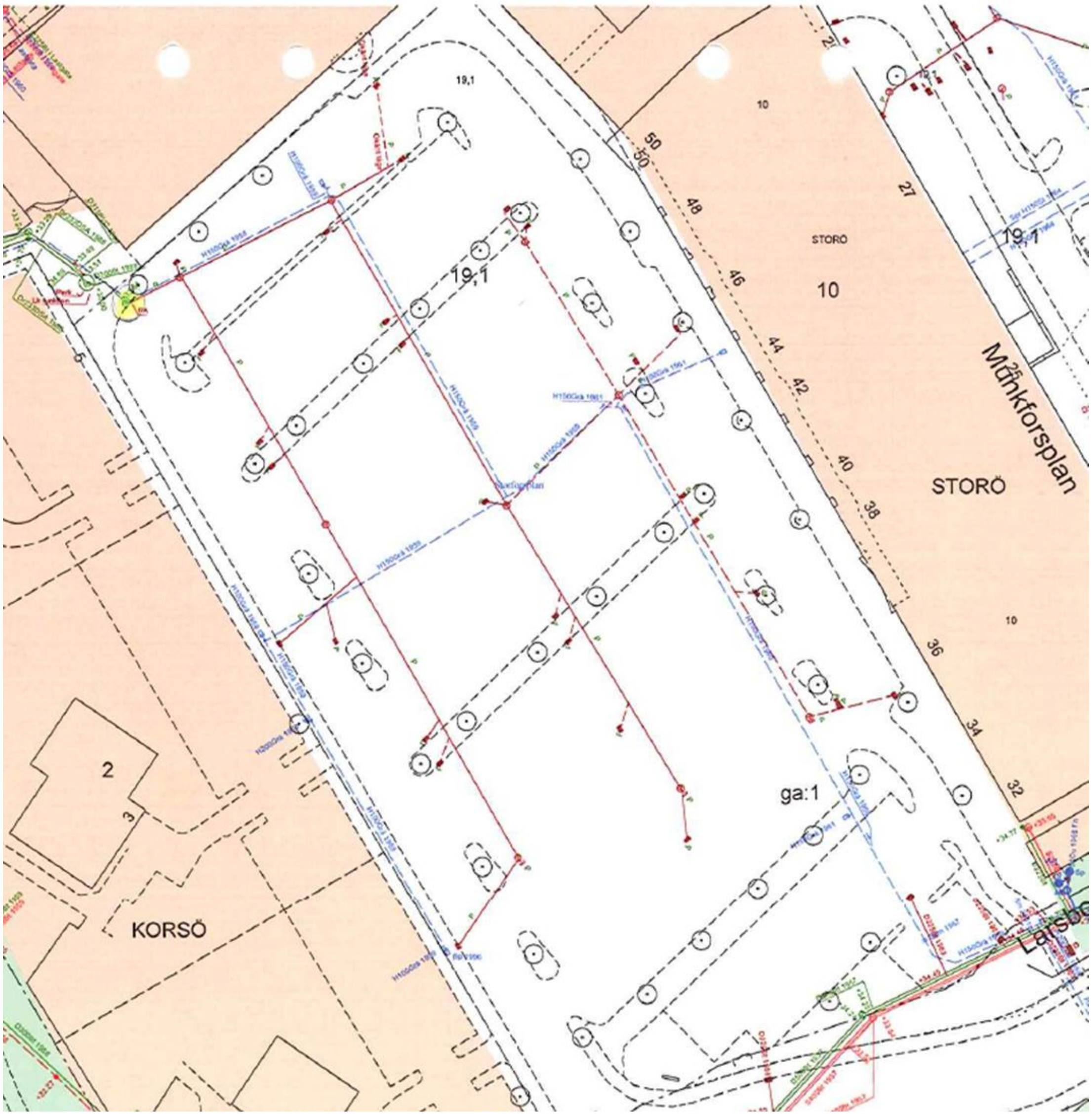

Figure 4. Layout of the storm water system of the parking space.

According to technical drawings, the storm water system of the roof has a slope of 0.04 – 0.05 at the sampling point, whereas the corresponding slope for the parking space is 0.018. At both locations storm water was sampled using a hand operated pump as soon as the maximum depth of the flow in the storm water pipe was 4 cm. Sampling started about 12 minutes earlier of the storm water from the roof compared to the parking space. Samples were collected every 10th minute. For every fifth sample an extra sample was collected speciation studies. At both locations, the storm water depth and average speed was measured by using a VeALogg unit (VeAInfo – Norconsult AB) equipped with a pressure sensor and ultrasound receiver/transmitter. The average speed of the flow is estimated by the shift in frequency between the outgoing and incoming sound signal (Doppler Effect). The sensor unit was fastened by a stainless steel ring in the storm water pipe a few centimetres downstream from the manhole at the parking space. When measuring the storm water flow from the roof, the sensor unit was placed on a wooden pole standing on the bottom of the storm water pipe. Additional samples of the Storm water from the parking space were also collected during the following rain fall on December 9.

Due to problems with the ultrasound receiver/transmitter, which indicated too low average velocities, the storm water flows at the two samplings locations were estimated using a method combining the Darcy-Weisbach and Colebrook-White equations (Chadwick and Morfett, 1998).

Flow in pipes can be divided into three categories (Chadwick and Morfett, 1998):

Laminar flow. Surface roughness has no influence on the shear stress transmission.

Transitional turbulence. The presence of the laminar sub-layer 'smooths' the effect of surface roughness. In practice, most of pipe flow lies in this region.

Rough turbulence. The surface roughness is large enough to break up the laminar sub-layer giving turbulence right across the pipe.

The relative roughness of the storm water pipe, relates the roughness of the interior of the pipe, expressed as equivalent sand-roughness size, k_s, with the diameter of the pipe (D). For a slimed concrete pipe, the equivalent sand-roughness size, k_s, can be set to 6.0mm (Chadwick and Morfett, 1998).

For laminar flow, the friction factor, λ, is independent of the surface roughness of the pipe and is only dependent on the Reynolds number, Re

$$\lambda = \frac{64\mu}{\rho DV} = \frac{64}{Re} \qquad (1)$$

The Reynolds number is in turn dependent on the diameter of the pipe (D) and the average velocity (V), density (ρ) and absolute coefficient of viscosity or dynamic viscosity (μ) of the fluid. The ratio μ/ρ is referred to as the kinematic viscosity, ν. For a pipe flowing full, laminar flow will exist if Re<2 000. There is an unstable region between Re=2 000 and 4 000 where transition from laminar to turbulent flow occurs. Normally, pipe flows lie outside of this region. The limiting line of turbulent flow, approached by all values of relative roughness as Re decreases, is referred to as smooth turbulence. Transitional turbulence is the region in which λ varies with both Re and k_S/D, where k_S is the equivalent sand-size roughness. Most of pipe flow lies within this region. It has a limit which varies with k_S/D. Rough turbulence is the region where λ remains constant for a given k_S/D and is independent of Re.

The storm water flow is estimated by multiplying the speed (V) of the uniform flow with the cross sectional flow area

$$Q = V*A \qquad (2)$$

Where the cross sectional flow area (A) is calculated by using the diameter D of the storm water pipe and the angle ϕ (Figure 5) of the formula

$$A_d = \left(\frac{\phi - \sin\phi}{8}\right) D^2 \qquad (3)$$

The wetted perimeter will be $P_d = \phi D/2$.

The proportional ($A_p = A_d/A_D$) cross sectional flow area is expressed as

$$A_p = \left(\frac{\phi - \sin\phi}{2\pi}\right) \qquad (3')$$

By measuring the depth of flow, d, the angle Φ is calculated by:

$$\phi = 2\arccos\left(1 - \frac{2d}{D}\right) \qquad (4)$$

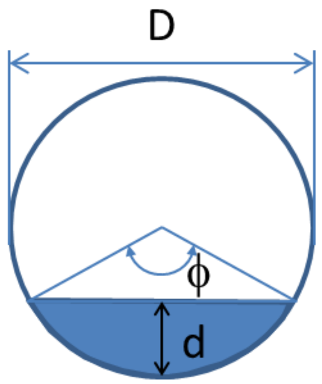

Figure 5. The geometrical relationship between the diameter D of the storm water pipe and the depth of flow, d.

Since the measured flow in a storm water pipe in this study was not completely full and not pressurised, the water surface is parallel to the pipe invert so the hydraulic gradient (h_f/L) equals the pipe gradient, S_0. Thus, the head loss (h_f) due to viscous effects is related to the length of the channel or slope, *L*. The head loss due to viscous effects is also related to the uniform velocity (V) of the flow in the Darcy-Weisbach equation. The Darcy-Weisbach equation for a full pipe is given by:

$$h_f = \frac{\lambda L V^2}{2gD} \qquad (5)$$

in which the diameter, D, of the storm water pipe needs to be known together with its pipe friction factor, λ (Chadwick and Morfett, 1998) and g is the acceleration due to gravity ($9.81 ms^{-2}$).

In the case of pipe running partially full, the hydraulic radius, R, needs to be known

$$R_d = \left(1 - \frac{sin\phi}{\phi}\right)\frac{D}{4} \qquad (6)$$

The proportional hydraulic radius is expressed as:

$$R_p = \left(1 - \frac{sin\phi}{\phi}\right) \qquad (6')$$

By replacing h_f/L by S_0, the Darcy-Weisbach equation reduces to:

$$V = \sqrt{2g4RS_0/\lambda} \qquad (7)$$

The corresponding proportional velocity can be expressed as:

$$V_p = \sqrt{\lambda_D R_p/\lambda_d} \qquad (7')$$

Similarly, the proportional flow is given by:

$$Q_p = \sqrt{\lambda_D A_p R_p/\lambda_d} \qquad (8)$$

The Colebrook-White transition law relates the Reynolds number with the friction factor and geometry of the pipe in the region of transitional turbulence. For a pipe flowing partially full the Colebrook-White transition law becomes

$$\frac{1}{\sqrt{\lambda}} = -2log\left(\frac{k_S}{3.7\times 4R} + \frac{2.51}{Re\sqrt{\lambda}}\right) \qquad (9)$$

where Re=$4RV/\nu$.

In the case of rough turbulence and the pipe flowing full the Colebrook-White equation becomes

$$\frac{1}{\sqrt{\lambda}} = 2log\left(\frac{3.7D}{k_s}\right) \qquad (10)$$

hence:

$$\frac{\sqrt{\lambda_D}}{\sqrt{\lambda_d}} = \frac{2log(3.7\times 4R_d/k_s)}{2log(3.7D/k_s)} \Leftrightarrow \frac{\sqrt{\lambda_D}}{\sqrt{\lambda_d}} = 1 + \frac{logR_p}{log(3.7D/k_s)} \qquad (11)$$

Equation (9) can be substituted into equations (7') and (8) to yield:

$$V_p = \left(1 + \frac{logR_p}{log(3.7D/k_s)}\right)\sqrt{R_p} \qquad (12)$$

and

$$Q_p = \left(1 + \frac{logR_p}{log(3.7D/k_s)}\right) A_p \sqrt{R_p} \tag{13}$$

The equivalent expressions for the transition regions are:

$$V_p = \left(1 + \frac{logR_p}{log3.7\theta}\right) \sqrt{R_p} \tag{14}$$

and

$$Q_p = \left(1 + \frac{logR_p}{log3.7\theta}\right) A_p \sqrt{R_p} \tag{15}$$

where

$$\theta \simeq \left(\frac{k_s}{D} + \frac{1}{3600DS_0^{1/3}}\right)^{-1} \tag{16}$$

As can be seen from Equations 13 and 14, neither Q_P nor V_P are particularly sensitive to θ. Therefore, as a first approximation only Equations 10 and 11 were used to estimate the velocity and flow, respectively, although conditions for rough turbulence might not have been met. If λ can be evaluated by Equation 1, the Darcy-Weisbach equation (Eq. 5) can also be applied to laminar flows.

2.2 Chemical analyses

The copper concentration was measured by flame atomic absorption spectroscopy (AAS) using a Perkin Elmer Analyst 800. Calibration standards at 1, 3, and 10 ppm were prepared from a 1 g/L stock solution standard from Perkin Elmer. The samples were acidified to a pH <2 with 65% HNO_3 after sampling. Triplicate readings were analysed for each sample.

Differential pulse anodic stripping voltammetry (DPASV) was used (Metrohm 797 VA Computrace) to determine the complexation capacity of runoff water to copper, A hanging mercury drop served as working electrode, an Ag/AgCl (3 M KCl) electrode as reference electrode, and a platinum rod as auxiliary electrode. A 1M EPPS (Sigma Aldrich) buffer (in 0.5 M NH_3) at pH 8.0 was used (0.5-1 mL added to 10 mL of sample solution). The solution was purged with argon for 3 min before the measurements. The deposition time of copper onto the mercury electrode was 90 s and the deposition potential set to -0.9 V (vs. Ag/AgCl). During the stripping measurement the potential was scanned from -0.5 V to 0.05 V at a scan rate of 0.015 V/s. The applied pulse amplitude was 0.05 V and the pulse time 0.04 s. In the complexation capacity measurements, standard additions of copper were applied and changes in peak height of stripping peak of copper were observed. For comparison, UV digested samples were also tested using DPASV, so that measurements on solutions without any complexation capacity were conducted. The UV digestion method consisted of 10 mL sample with 10 µL 30 wt.% HCl (puriss p.a., Sigma Aldrich) and 50 µL

30 wt.% H_2O_2 (puriss p.a., Sigma Aldrich) added, and subjected to 1 h of UV treatment at 95°C (Metrohm 705 UV digestor).

3 Results

3.1 Hydrology and hydraulics

The precipitation data is presented in Table A1 in the appendix and in Figure 6 below.

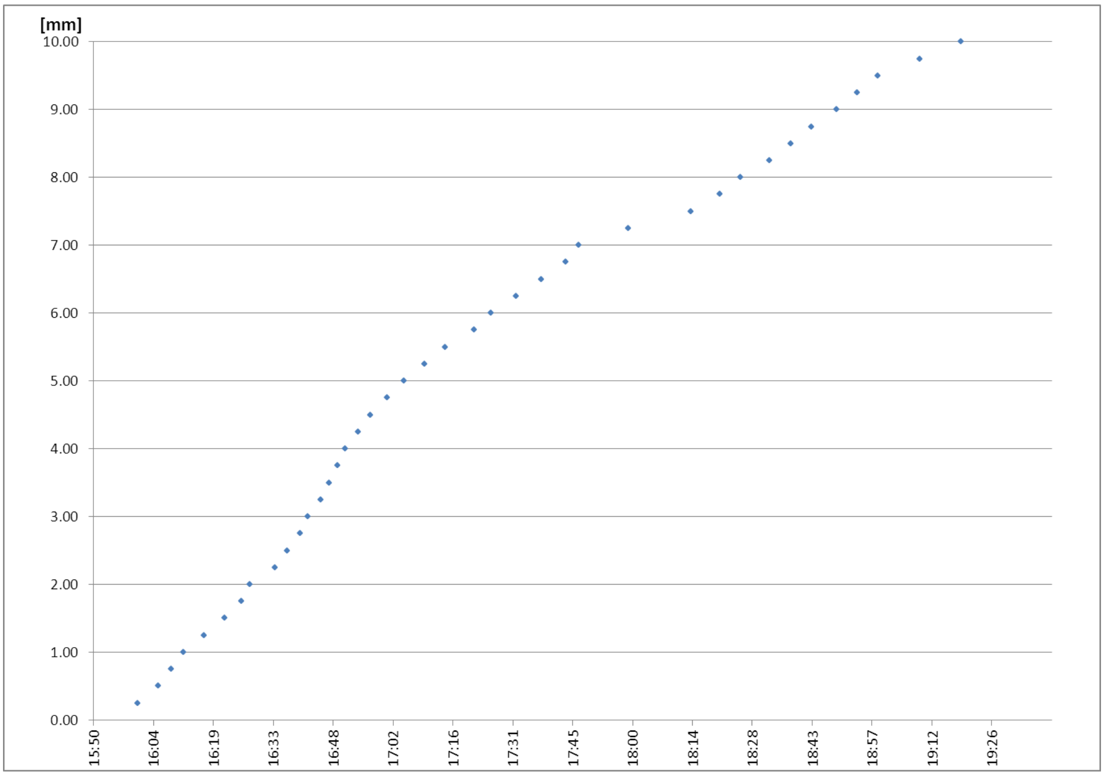

Figure 6. Cumulative amount of precipitation recorded, in mm, on the copper roof during the rainfall on December 3, 2011.

Data on the flow (Q) of storm water from the parking space and roof presented in Tables A2 and A3, respectively, in the appendix and in Figures 7 and 8, respectively. The accumulated storm water flow generated by the rainfall sums up to 30.8 m^3 from the copper roof and 220 m^3 from the parking space. The reduction in measured average speed to zero in the storm water pipe from the parking space at 16:51 during high flow (Table A2) is probably caused by surcharging. The surcharging was probably caused by lower flow velocities downstream due to fuller pipes which lead to increased friction (Chadwick and Morfett, 1998).

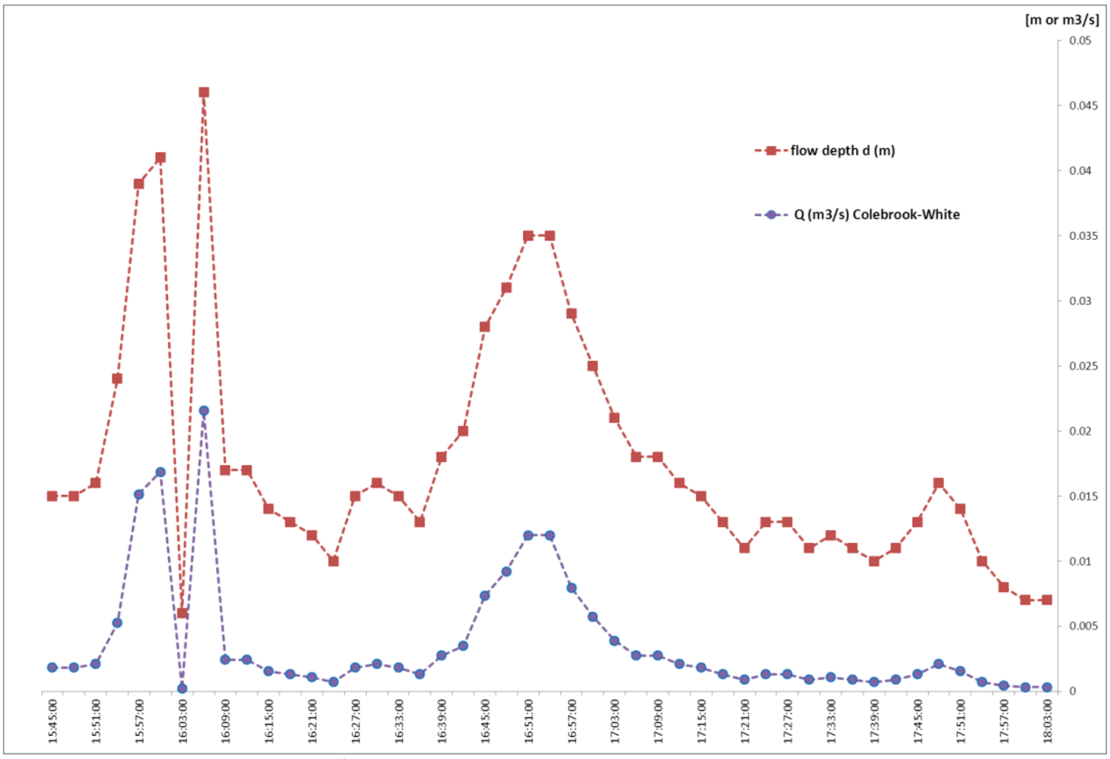

Figure 7. Storm water flow (m^3/s) from the roof during the rain event on December 3, 2011.

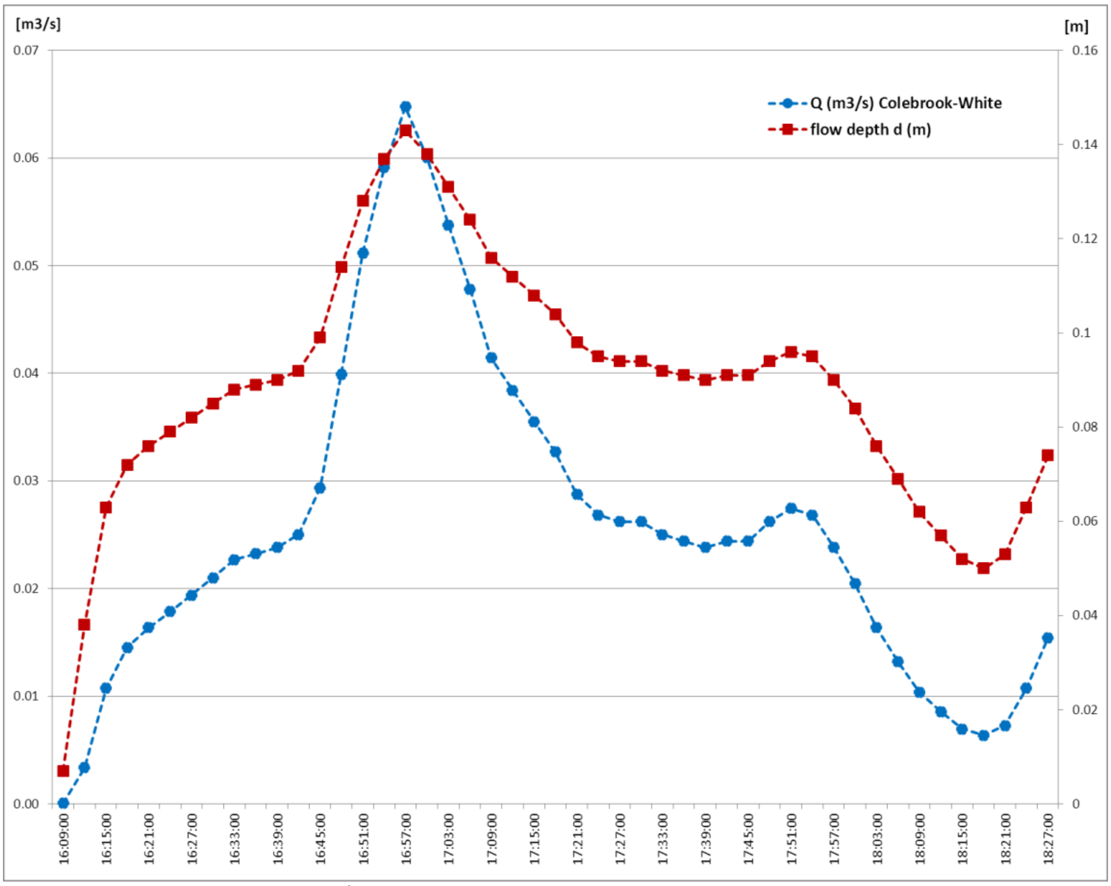

Figure 8. Storm water flow (m3/s) from the parking space during the rain event on December 3, 2011.

Measured concentrations of total copper (Cu) in the storm water samples collected from the parking space and the copper roof are presented below in Figure 9 and in Tables A4 and A5, respectively, in the appendix. The estimated loads of Cu in the storm water from the parking space and roof, respectively, are also shown in Figures 10 and 11.

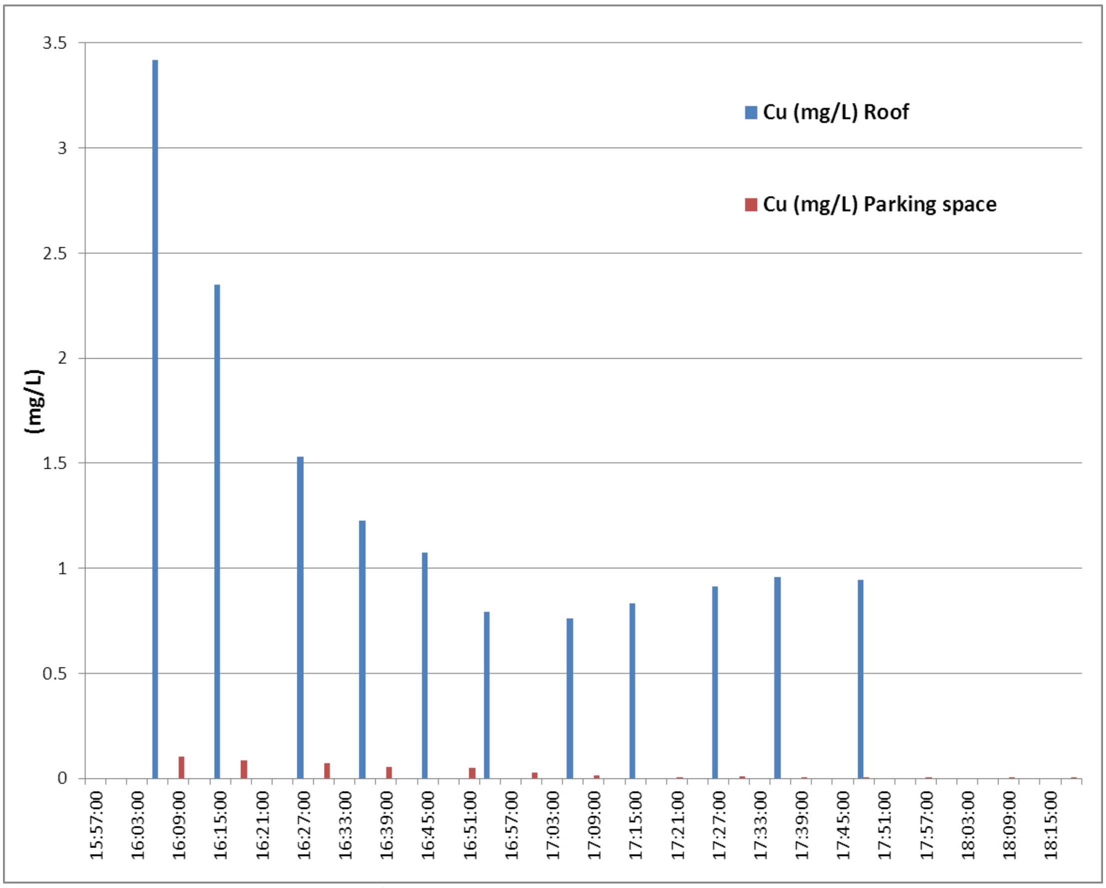

Figure 9. Concentration of Cu (mg/L) in storm water from the roof and parking space on Dec. 3, 2011.

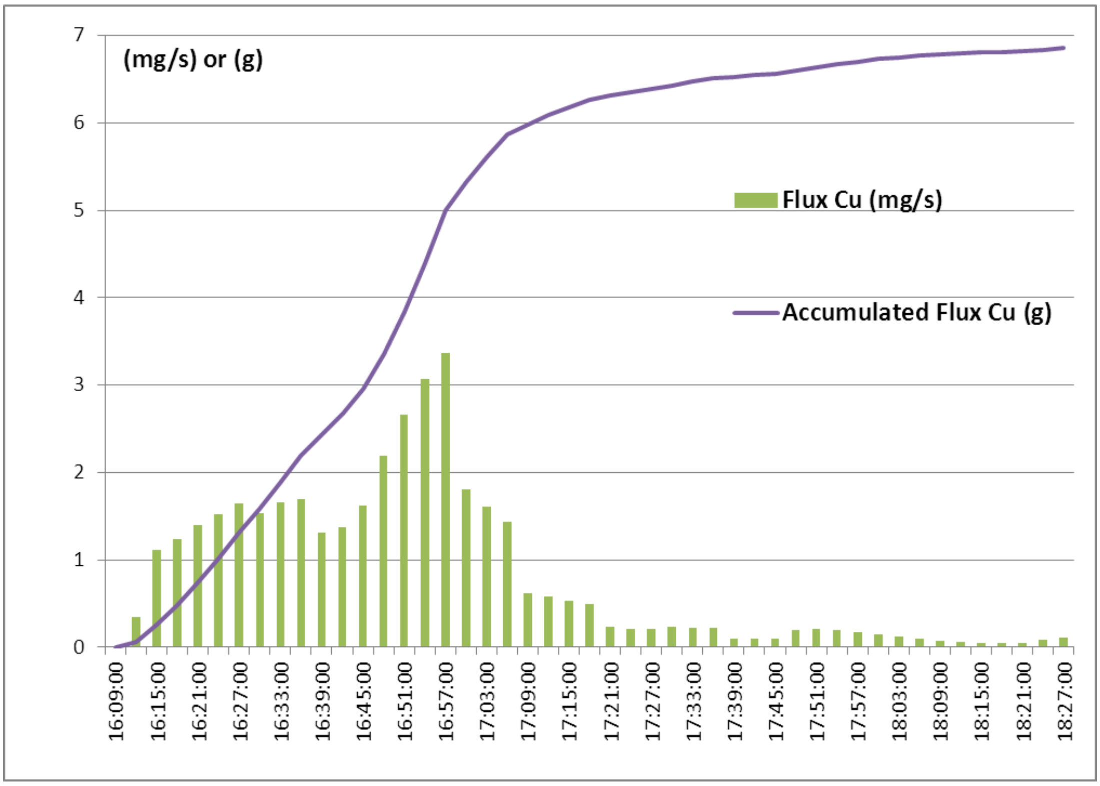

Figure 10. Flux and accumulated flux of copper from the parking space during the rainfall on Dec. 3, 2011.

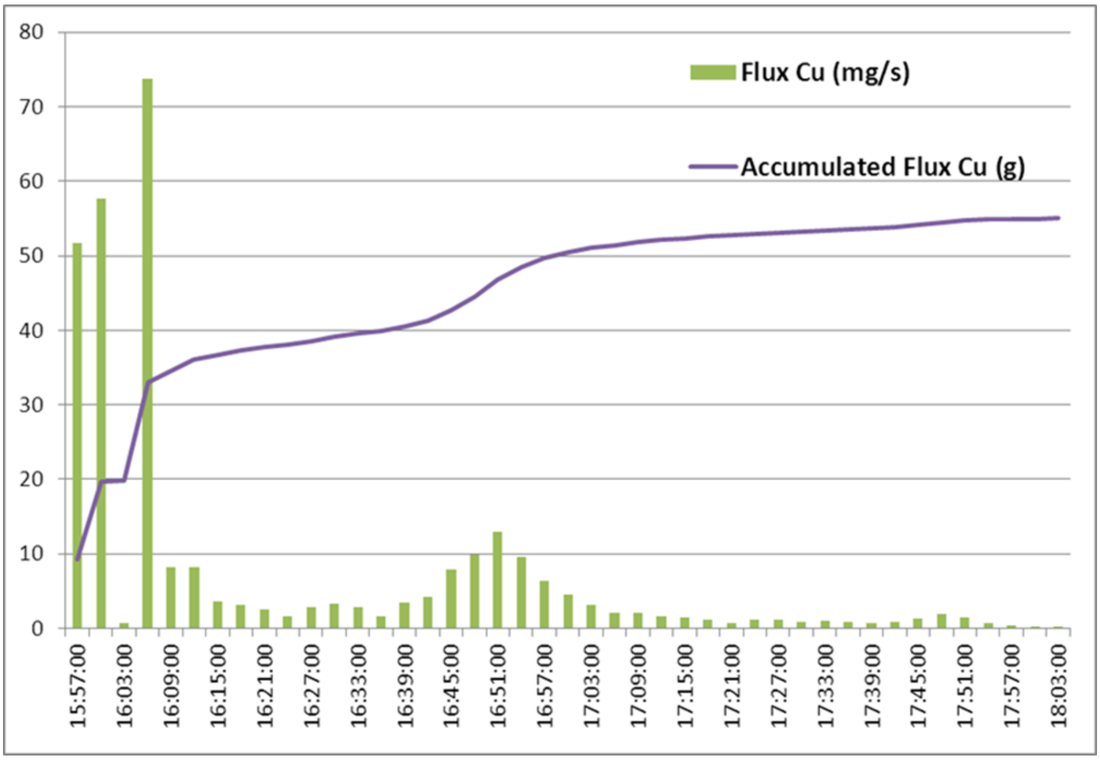

Figure 11. Flux and accumulated flux of copper from the roof during the rainfall on Dec. 3, 2011.

Data in tables A2 to A5 (Figures 10 and 11) were used to estimate both the accumulated fluxes and emission factors during this rainfall expressed as mass of Cu per unit time and area for both types of land use. The accumulated fluxes of Cu from the copper roof and parking space were during this rainfall 55g and 6.9g, respectively. Emission factors expressed per surface area and rainfall quantity were calculated based on a total surface area of 2 330 m^2 for the copper roof and 14 000 m^2 for the parking space and a total precipitation quantity during the rainfall of 10 mm (10 L m^{-2}, c.f. Figure 6). These deliberations resulted in calculated emissions factors during this single rainfall of 2.4 mg $mm^{-1}m^{-2}$ and 49μg $mm^{-1}m^{-2}$ for the roof and parking space, respectively.

3.2 Chemical analyses

3.2.1 Total concentrations of Cu in collected storm water samples – AAS

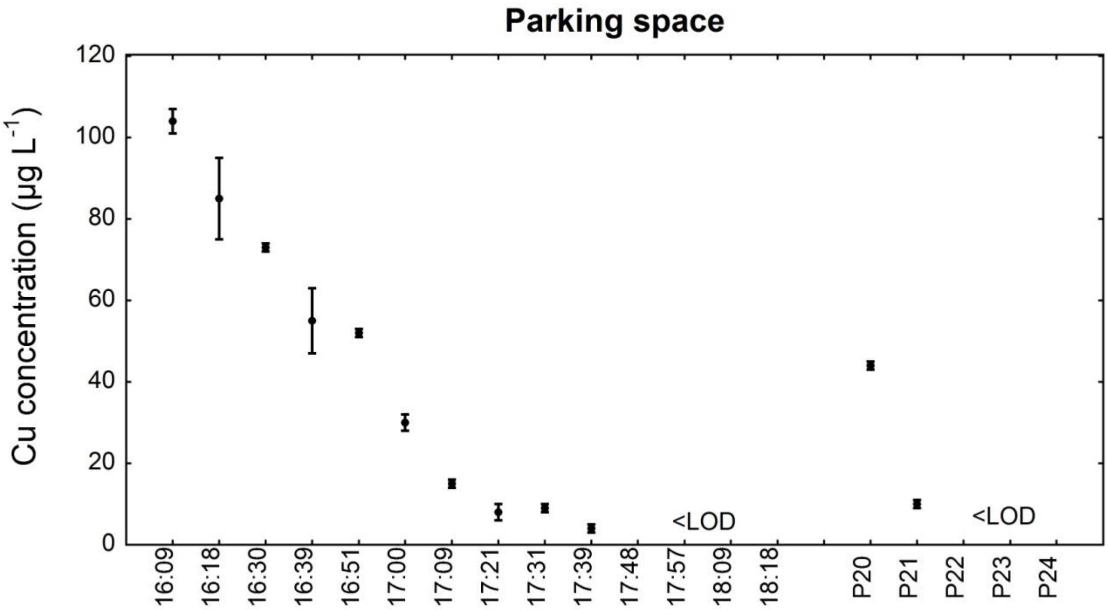

Figure 12. Concentrations of copper measured in acidified samples collected from the parking space during the rainfall on December 3, 2011 measured by means of AAS. The samples P20 – P24 are from the following rain fall on Deccember 9, 2011.

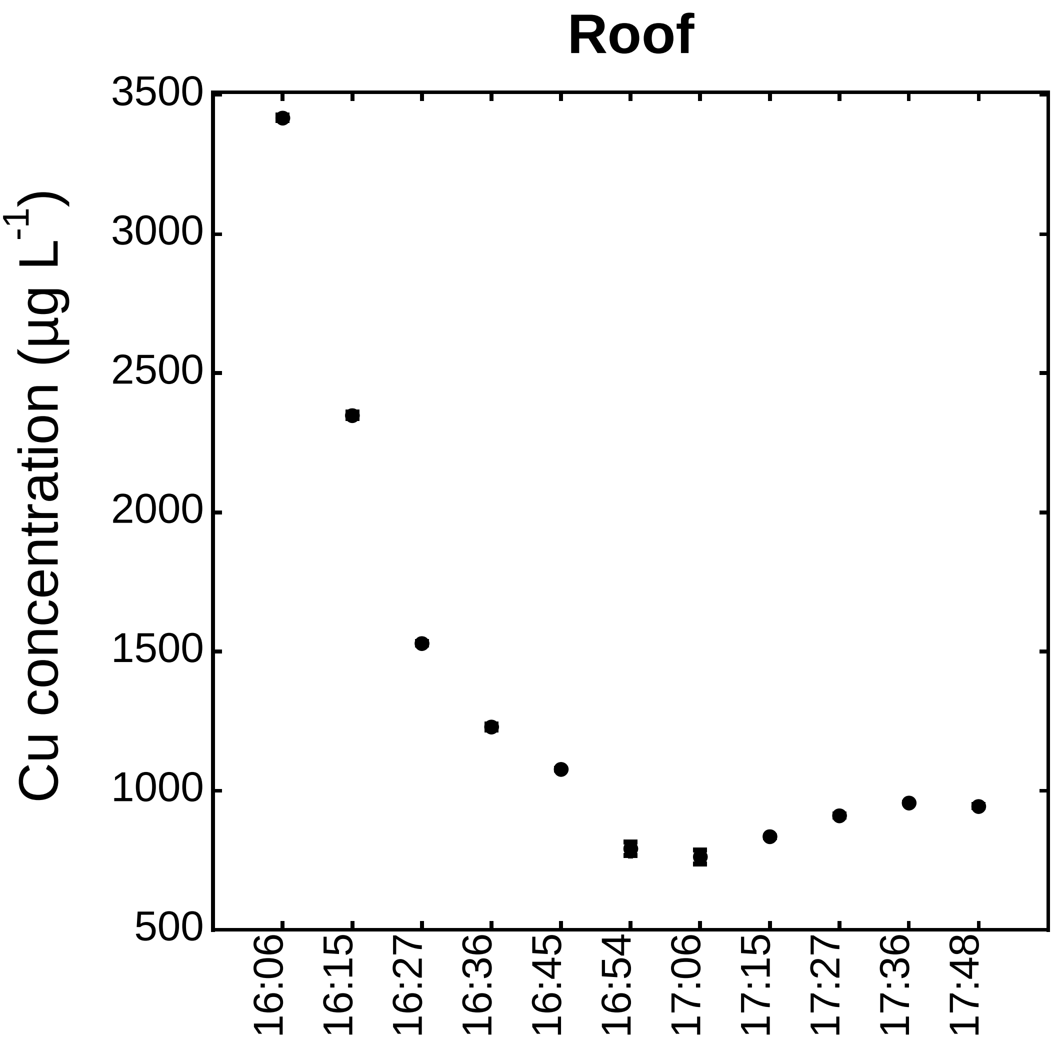

Figure 13. Total concentrations of copper in storm water collected from the roof during a the rainfall on December 3, 2011 measured after acidification by means of AAS.

3.2.2 Determination of total Cu – measured by means of stripping voltammetry and AAS

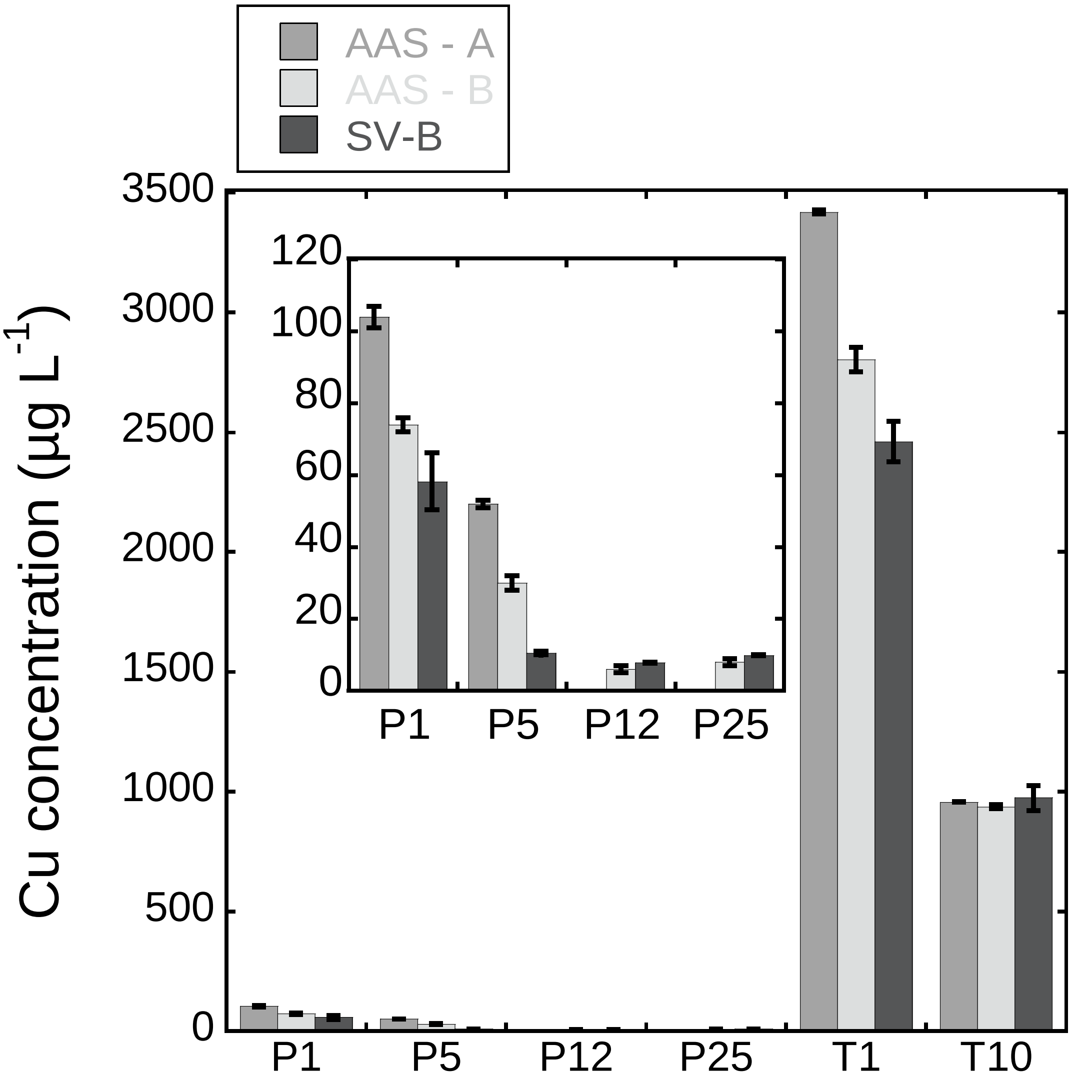

Figure 14. Comparison of total Cu concentrations of A and B samples, measured by AAS (note: A samples were acidified and B samples in addition digested; : B samples were sampled after A samples!), AAS-A and AAS-B, and B samples (digested) measured by stripping voltammetry (SV-B). Note that the accuracy of AAS-flame is reduced below 100 ppb since no blank sample was available that could be subtracted. AAS-A <LOD for P12 and P25. Corresponding exposure times for the samples: P1 – 16:09; P5 – 16:51; P12 – 17:47; P25 – last sample from following rainfall on December 9, 2011 ; T1 – 16:06; T10 – 17:36.

From Figure 14, it can be concluded that there was for most samples no significant difference between the two different analysing methods employed (AAS and SV). B samples (which were sampled directly after the A samples during the rainfall showed lower concentrations than initial samples, due to rapidly decreasing runoff rates of Cu with time (He et al., 2001, Zhang et al., 2002).

3.3 Complexation capacity measurements

It was not possible to determine the complexation capacity in samples with larger Cu concentrations than 50 µg/L since all available complexing ligands were occupied by copper. Two successful complexation capacity measurements were performed for samples P12B and P25B collected at the parking space (no acidification or digestion, natural sample, frozen prior to analysis) after 2 hours and 50 minutes, respectively, of sampling at the parking space site.

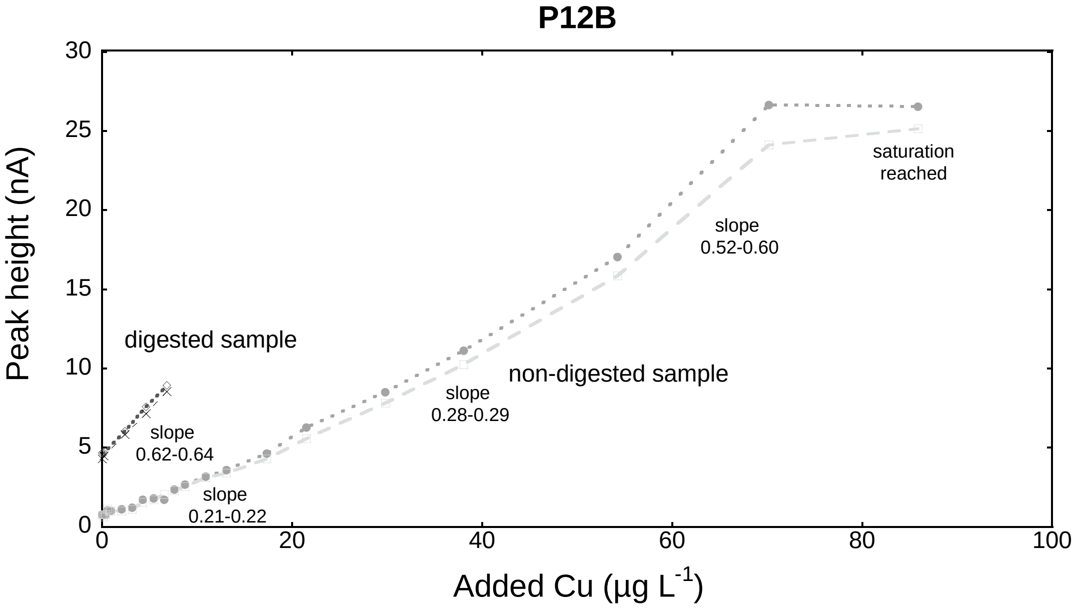

Figure 15. Complexation capacity measurements of sample P12B collected from the parking space – comparison of non-digested and digested sample. Two replicates are shown for each measurement. Note that the second replicate measurement in the case of the non-digested sample was always lower, due to a longer reaction time of ligands and copper. P12B corresponds to the exposure time slightly later than 17:57.

The calculated complexation capacity for sample 12B gave the following results; strongly bound Cu: 6.22 ± 0.16 µg L^{-1} (97.9 nM), weakly (L1) bound Cu: 19.9 µg L^{-1} (313 nM), weakly (L2) bound Cu: 19.1 µg L^{-1} (300 nM). Thus, in total (strong and weakly bound Cu), the complexation capacity is 45.2 µg L^{-1} (711 nM).

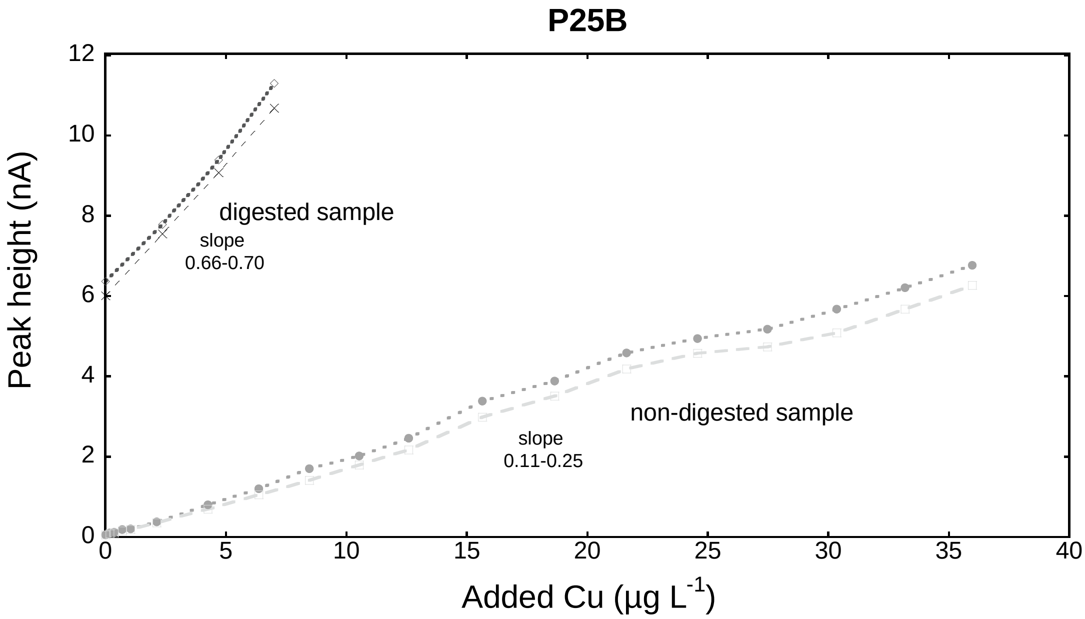

Figure 16. Complexation capacity measurements of sample P25B collected from the parking space by comparing a digested and non-digested sample. Two replicates are shown for each measurement. P25B is the last sample from the following rainfall on Dec 9.

From the calculated complexation capacity for sample P25B follows: strong bound Cu: 9.76 ± 0.10 µg L^{-1} (154 nM) and weakly bound Cu: > 36.12 µg L^{-1} (570 nM). In total, bound Cu (strong and weak) is estimated to be > 46 µg L^{-1} (722 nM).

Figures 15 and 16 show that a substantial part of the copper in the storm water from the parking space was complexed to ligands, compared to the total concentrations of copper in the samples (Figure 13). The amount is varying dependent on the flow rate and hence the presence and concentration of organic and inorganic matter (e.g., particles) in the samples. The presence of particles in these samples was visually observed.

For the roof samples, the total copper concentration was too high for any complexation capacity measurement using DPASV. However, previous measurements of roof samples at the same test site (Odnevall Wallinder et al., 2009) of low total copper concentrations (< 10 µg L^{-1}) showed complexation capacities of 3.5 µg L^{-1} (strongly bound) and additional 1.0 µg L^{-1} (weakly bound).

4 Discussion

4.1 Hydrology and hydraulics

The measured precipitation during the rainfall sums up to 10mm, which is close to the interpolated value of 8.4mm using data from the closest meteorological station, about 10 km away (SMHI station Tullinge A). The relative large difference (19%) between the gridded (interpolated) value and the measured value might be explained by local effects at the site e.g. from higher buildings surrounding the sampling site (Shaw, 1994; Wood et al., 2000). Precipitation estimates from one rain gauge only can have a standard error of 33 % for a 2 km square (Wood et al., 2000). Thus, an estimate of the rainfall quantity on the parking space based on data from the rain-gauge on the roof can have a relative large error. Especially considering that the parking space is surrounded by rather high buildings 15m + on three sides. Assuming a two minute lag between precipitation and runoff (Shaw, 1994) from the impervious surfaces of the copper roof (2 330 m^2) and parking space (14 000 m^2), the accumulated runoff (Tables A2 and A3) sums up to 132 and 154 % of the accumulated precipitation (Table A3). These runoff coefficients of 1.3 and 1.5 are higher than 0.95 which is the expected value for an urban impervious surface (Shaw, 1994). It is possible to explain the differences between estimated and expected runoff coefficients in several ways. One obvious explanation is the error in the measurement of the precipitation. The manufacturer (Rain wise Inc.) of the rain gauge states an accuracy of 1.5% at a 0.5mm per hour.). Since total precipitation is estimated for a period of several hours during a low-intensity rainfall, the sampling error for this type of instrument is believed to be around 1 % (Habib et al., 2001; Lanza and Stagi, 2008). Another obvious explanation is that the computational method overestimates the storm water flow, e.g. due to incorrect assumptions regarding equivalent sand-roughness size, k_S, or pipe gradient, S_0. In the case of the parking space there might be storage in the storm water pipes which will be added to the flow generated by the rainfall.

Thus, the estimate of 10 mm of rain on the roof is believed to be correct. For the copper roof the discrepancy between the measured storm water flow and the precipitation is believed to be due to the computational method. In particular the assumptions regarding the pipe gradient could generate errors of this magnitude. For the parking space, where the discrepancy is greater, the additional factor of incorrect rainfall data has to be considered.

In addition, the present study highlights the importance of a correct hydrograph, i.e discharge as a function of time. It is possible to estimate a total flow during the rainfall only from correct precipitation data and the correct area of the impervious surface. However, the temporal variability in copper concentrations in the runoff makes it necessary to correctly estimate the temporal variability in discharge as well. This is evident by looking at Figures 9 to 11. As can be seen in the case of the runoff of Cu from the parking space (Figures 9 and 10), a sharp decrease can be caused by both lower concentrations and a sudden decrease in the storm water flow due to surcharging. Similarly, by looking at the runoff of Cu from the roof as a function of time (Figure 11), the importance of the so called 'first flush' (He et al., 2001; Zhang et al., 2002) is evident. More than 50% of the accumulated runoff of Cu during the rain event occurred during the first 9 minutes. By combining the data of the flow and total Cu concentrations as function of time for the storm water from the roof (Figures 7 and 9), it is evident that the initial concentrations of released copper in the runoff water substantially decreases during the duration of the rainfall . The influence of environmental, rain and surface characteristics on the first flush process is described in detail elsewhere (e.g. He et al., 2001). A very important aspect that governs the magnitude of the first flush released copper portion is related to the rainfall intensity and prevailing environmental conditions prior to the rainfall, e.g. long dry periods without any runoff. Both these factors, in particular the effect of dry period preceding the rain event largely explains the relatively high extent of released copper from the roof during the single rainfall of this study.

In the present study, the temporal distribution of Cu concentrations are rather well constrained together with rather high resolution in storm water depth in the pipe, which allows for precise estimations of the storm water flow. Taken together these two data sets constrain the range of estimated values for the Cu runoff, see below.

4.2 Variability in emissions of copper from copper roofs during and between rainfalls

The range of Cu concentrations measured in the runoff from the roof in this study 3418 - 945 $\mu g\ L^{-1}$ (Table A5) is higher than in the previous measurements at the same site by Odnevall Wallinder et al. (2009). The latter study involved measurements of copper in runoff water from the copper roof that was sampled during six different, in time separated rainfall events, all preceded by relatively wet conditions that influenced the portion of first flush and the characteristics of the storm water pipe surfaces. A median Cu concentration of 18 (2 – 175μg/L) $\mu g\ L^{-1}$ was reported based on data from these six rainfall events. However, the copper concentration in the runoff from the parking space (see below) was similar in the present study as in findings by Odnevall Wallinder et al. (2009). Copper concentrations in storm water runoff are dependent on material specific properties and site specific application both in the case of parking spaces (wear of brake linings) and copper roofs (age and inclination). However, in the case of copper roofs there are in addition factors related to climate (temperature and precipitation) and the intensity of the rainfall itself (He et al., 2001). Therefore, it is natural to speculate on these factors as the explanation for the difference in measured Cu concentrations in the runoff from the copper roof between the present study and that of Odnevall Wallinder et al. (2009), especially since the site and points for storm water sampling and analyses were the same in both studies. A striking and essential difference between the studies though is that five out of six measurements in the study by Odnevall Wallinder et al. (2009) were carried out consecutively in a period of two weeks. The total rainfall quantity recorded for these five rainfall events was 88 mm ranging from 4 to 38 mm. This can be compared to the present study where the total rain fall quantity, including the rainfall the actual study was conducted, was 21.5 mm in 38 days. The rainfall quantity of different rainfall events recorded during this period had the highest value of 8.4 mm (actual study), second highest of 4.5 mm and third highest of 3.0 mm. Expressed as mm/day the period covering five out of six measurements in the study by Odnevall Wallinder et al. (2009) corresponded to 6 mm/day. The average daily rainfall quantity preceding and including the day of sampling in the present study corresponds of 0.56 mm/day, i.e. a substantially dryer period. It is therefore proposed that the predominating reason for the relatively large difference in measured concentrations between the present study and that of Odnevall Wallinder et al. (2009) is attributed to a lower intensity and substantially longer dry period prior to the rainfall measurements and hence a substantially larger first flush contribution in this study compared with the study reported in Odnevall Wallinder et al. (2009). A similar effect is also evident for the storm water pipe of concrete prior to site B. These observations are in agreement with findings by He et al. (2000), showing rainfalls of low intensity to result in higher amount of released copper from a copper roof compared with rainfalls of high rain intensity. Another important difference is the season (Odnevall Wallinder et al., 2009: summer/autumn; this study: winter) resulting in different deposited species, patina properties and dry/wet conditions on the copper roof that influence the dissolution properties of constituents within the copper patina and hence the release of copper. This is very important in this study due to a relatively long way between the copper roof and the sampling site. The study of Odnevall Wallinder et al. (2009) found that more than 90% of the copper was retained by surfaces within the downspouts and therefore not measured. This retention could have been significantly lower in this study due to different factors (rain acidity, organic matter in storm water, moisture content)

The average Cu concentration found in the present study, 1346 $\mu g\ L^{-1}$ is about half the Cu concentration (2600 $\mu g\ L^{-1}$) observed in urban storm water assumed to primarily originate from copper roofs in a literature review by Göbel et al., (2008). Unfortunately no information is given related to the inclination, age etc. of the copper roofs. Observed concentrations are further clearly lower than the average concentrations of 3233 (s.d. = 980) and 3575 (s.d. = 1425) $\mu g\ L^{-1}$ based on monthly measurements by Persson and Kucera (2001) from two copper roof panels during 12 months of exposure. However, as the inclinations of the exposed copper surfaces in the different studies are very different (relatively horizontal compared with 45°), direct comparisons cannot be made. However, as the copper runoff process from the roofs really depends on prevailing environmental-, rain and surface characteristics (e.g. inclination), any comparison between concentrations based on different exposure conditions may result in erroneous conclusions.

Using the estimated emission values for copper based on the rainfall from the copper roof in this study, 2.4 mg $mm^{-1}\ m^{-2}$, multiplied by the annual precipitation in Stockholm, 585mm (SMHI), an annual emission of 1.4 g m^{-2} was obtained and relevant for a copper surface inclined approximately 5° from the horizontal. This value is significantly higher than the estimated annual emission for Cu (inclined 45° from the horizontal) of 0.85 g $m^{-2}yr^{-1}$ extrapolated from a relatively short exposure study at a site in Stockholm by Persson and Kucera (2001). However, this extrapolated figure was by Odnevall Wallinder et al., 2004 believed to be too low due to experimental drawbacks including a too short exposure period. When applying a predictive model to calculate the release of copper for the given exposure period of Persson and Kucera (2001), an annual emission of 1.1 g m^{-2} was derived (Odnevall Wallinder et al., 2004). Again, these measurements were based on surfaces inclined 45° from the horizontal and cannot be compared directly. Bi-weekly measurements during 48 weeks of exposure of copper in Stockholm by He et al., (2001) resulted in a Cu runoff rate of 1.3 g m^{-2} y^{-1} (45°, facing south) for the first year. However, long-term findings by Odnevall Wallinder et al., (2009) have shown that the release of copper from naturally aged copper (inclined 45°, facing south) is gradually reduced with time and significantly lower than measurements made after the first year. Reported 12-year findings (1996 – 2008) by Odnevall Wallinder et al., (2009) of continuous runoff rate measurements in Stockholm for surfaces inclined 45° from the horizontal, facing south and annual rainfall quantities between 340 and 630mmyr^{-1} (median 487mm yr^{-1}) revealed annual runoff rates between 0.74 – 1.6 (median 1.0) g $m^{-2}yr^{-1}$, with the lowest rates observed after the longest exposure period.

When recalculating the observed runoff rate of Cu in this study to a surface inclined 45° from the horizontal, without considering the influence of different exposure conditions and surface interactions between the copper surface of different inclination both during the rain event, differences in deposition rates of pollutants and particles and retention of copper in the downpipes, the rate is approximately 30% lower, i.e. 0.98 g $m^{-2}yr^{-1}$, according to Odnevall Wallinder et al. (2004). This figure is in the lower range of observed long-term findings of Odnevall Wallinder et al., (2009).

The sensitivity of the exact time distribution of the copper roof concentration data is higher compared to the parking space data when estimating the accumulated flux of Cu during the rain event, since there is a peak (first flush) in Cu concentrations with a simultaneous high variability in the storm water flow in the initial phase of the rain. The runoff from the parking space also has a peak in Cu concentrations during the initial phase, but the storm water flow has a smaller variability. This becomes evident when comparing the time dependence of the Cu fluxes from the copper roof with that from the parking space (Figures 9 to 11).

4.3 Variability in emissions of copper from roads and parking spaces during rain events and between rainfalls

The concentrations of Cu in the storm water from the parking space in this study, 4 – 104 (average 33) μg L^{-1} (Table A4) are in the same range as the previous study by Odnevall Wallinder et al. (2009) at the same site. Their measured concentrations were in the range of 9.3 - 124 μg L^{-1} with a median value of 35 μg L^{-1}. Thus the concentrations of copper in the storm water runoff from the parking space at the site of the present study are in agreement with the earlier study. They are also similar to the range of average values measured at four other parking spaces, 5.5–20 μg L^{-1}, by Junesjö et al., (2007). The time dependence of Cu concentrations is similar to that found by Wicke et al., (2012) when they studied the runoff from a parking space with 650 lots. After an initial concentration of 80 μg L^{-1}, the concentration was below 10 μg L^{-1} after 20 minutes (Wicke et al., 2012). The average Cu concentration in runoff from the parking space in this study, 33 μg L^{-1} is close to the default value of 40 μg L^{-1} for parking spaces used by the Stormtac model and about half what Göbel et al., (2007) suggested being a representative value (80 $\mu g L^{-1}$). About 50% of the total copper storm water flux from the parking space occurs during the first 39 minutes of the rain event (Figure 10), indicating a considerably less pronounced 'first flush' compared to the runoff from the roof. Hence, using the default value 40 $\mu g L^{-1}$ for parking spaces from the Stormtac model will give a higher runoff of copper of 8.7 g, which is 124% of estimated based on the measured values in the present study. Using the representative value of 80 $\mu g L^{-1}$ suggested by Göbel et al., (2007) will give an even higher estimate, 17 g (252%).

Assuming the estimated emission figures for copper from the parking space in this study, 48 $\mu g\ mm^{-1} m^{-2}$ and multiply it by the annual precipitation in Stockholm, 585 mm (SMHI), a yearly Cu flux of 29 mg m^{-2} will be obtained. This figure is higher than that used by Cui et al. (2010), 16 mg $m^{-2}yr^{-1}$ to estimate the copper runoff rate for parking spaces. Their figure was based on a standard concentration of Cu in runoff of 30$\mu g L^{-1}$ from the software StormTac 2000-11(Larm, 2000). However, the ratio between Cu fluxes from copper roofs and parking spaces will be much higher using the values of Cui et al. (2010) compared to the present study: 2100/16 = 131 and 48 (see above), respectively. Similarly, Boulanger and Nikolaidis, (2003) used a much higher ratio between the two fluxes 2.14/0.01=214, based on measured data expressed as mass per time and precipitation (mg h^{-1} mm^{-1}).

In the studies by Sörme and Lagekvist (2002) and Cui et al. (2010) an indirect method based on the wear of brake pads (Westerlund, 1998 and 2001) was used to derive the contribution of Cu from traffic on roads. The derived emission, which is expressed as mass per vehicle work, e.g. μg Cu per km, depends on the Cu content of the pads which varies within a very large range (4 orders of magnitude) depending on manufacturer. This indirect method also depends on two other factors which can vary to rather large degree: the wear rate of the pad and the proportion of the worn of material which is lost to storm water and lost as airborne particles. Both these factors depend on driving patterns of the traffic: speed and braking. Sörme and Lagerkvist (2002) did not specifically estimate the contribution of Cu in runoff from parking spaces, while Cui et al., (2010) used the value of 16 mg m^{-2} yr^{-1} as described above.

4.4 Comparison of two sources of copper to the storm water in the City of Stockholm: copper roofs and roads.

The annual Cu runoff value based on findings from a single rainfall from a copper roof derived in this study, 1.4 gm^{-2} (representing data for a roof inclined 5° from the horizontal) corroborates with literature findings for Stockholm when recalculating generated data to a surface of equal inclination (i.e. 0.98 g m^{-2} when inclined 45° from the horizontal). Literature findings for surfaces inclined 45° from the horizontal report annual runoff rates of 1.3 g m^{-2} in He et al. (2001), 1.1 g m^{-2} in Odnevall Wallinder et al. (2004), and 1.6-0.76 g m^{-2} (median 1.0 g m^{-2}) during a 12 year exposure in Odnevall Wallinder et al. (2009). By also considering the estimate of 1.3 gm^{-2} based on an extensive literature study by the voluntary risk assessment of copper (2008) it is possible to constrain a default annual Cu runoff from copper roofs in Stockholm with one significant figure to 1 g m^{-2}. Multiplying this rate with the total area of new and naturally aged copper roofs in Stockholm of 176 845 m^2 and 447 745 m^2, respectively, (Ekstrand et al., 2001) a total annual emission of 0.6 ton Cu will be obtained.

Sörme and Lagerkvist (2002) have assumed that all of copper released from copper roofs will reach the storm water system and estimates the total contribution of copper from copper roofs to be 1200 kg for the city of Stockholm. However, these estimates are based on short term runoff data for copper reported in He et al., (2001) without neither considering the now available long-term findings nor the fact that solid surfaces in the near vicinity of buildings have a high capacity to act as sinks for released copper as e.g. reported in Odnevall Wallinder et al. (2009), Bertling et al. (2006), Bahar et al. (2008), Boulanger and Nikolaidis, (2003). Hence, by using the long-term emission factors reported in the literature in e.g. Odnevall Wallinder et al. (2009) supported by findings of the present study, the total annual contribution of Cu from copper roofs to storm water would be 50% of that estimated by Sörme and Lagerkvist (2002).

For Stockholm city, Sörme and Lagerqvist (2002) estimated that the main source of Cu from traffic, the wear of brake linings, would contribute 3820 kg of copper annually. Sörme and Lagerkvist (2002) estimate that only 20% of these emissions will be transported by the storm water since the rest will be lost as airborne particles. Thus the contribution of Cu from roads and parking spaces in the city of Stockholm will be 764 kg according to Sörme and Lagerkvist (2002).

In the city of Stockholm there is a total of 32 000 parking spaces on the street and 20 000 in parking lots and houses (EasyPark, 2013). If we use the same parking lot/area ratio as in the present study area (415/14000), the total parking space area in Stockholm is 1.75 km^2. From the annual Cu emission determined in the present study, 29 mg m^{-2} (similar findings as in Odnevall Wallinder et al. (2009)) follows an annual flux of 51 kg Cu.

According to Göbel et al., (2007), there are slightly higher Cu runoff concentrations from service roads and main roads, 86 μg/L and 97 μg/L, respectively, compared to parking spaces, 80 μg L^{-1}. In the city of Stockholm the area of roads with a daily traffic of more than 15 000 cars is 2 591 km^2. Applying the ratio of major roads/parking space (97/80) in Cu runoff concentrations to the yearly emission of 29 mg m^{-2} from this study and multiplying this number with the area of major roads in Stockholm, 2 591 km^2, an annual load of 91 kg will be obtained. The total area of impervious surfaces and buildings in the city of Stockholm is 99 km^2 (Stockholm Stad, 2013). Assume that 25% of this area consists of parking spaces, major roads and service roads. Applying then the copper runoff ratio between service roads and parking spaces (86/80), the estimated area of service roads in Stockholm (20.4 km^2) will contribute with 639 kg of Cu. Thus, in total, an annual load from roads and parking spaces would be 781 kg of Cu. This number is about the same as estimated by Sörme and Lagerkvist (2002).

That is, in the city of Stockholm the contribution of Cu from copper roofs is about 75% compared to that from roads and parking spaces. In the study by Sörme and Lagerkvist (2002) the contribution of Cu from copper roofs was 157% of that from roads and parking spaces in the city of Stockholm.

4.4.1 Aspects of temporal resolution

In the derivation of the runoff value of Cu from a copper roof, the temporal aspect is of crucial importance, as espoused above and evident from Figures 9 and 11. In the study by Odnevall Wallinder et al. (2009) at the same building and roof, their storm water samples had Cu median concentrations of 18 μg/L. This concentration will result in an annual Cu flux value of 0.018 mg $m^{-2}mm^{-1}$, assuming a runoff coefficient of 1. This value is clearly lower than the one of 2.4 g $m^{-2}mm^{-1}$ derived in this study. Direct measurements of the release of copper at the immediate release situation (no retention) in long-term studies report the annual runoff rates of Cu between 1.6 and 0.76 g $m^{-2}yr^{-1}$ for copper panels in Stockholm and with rates that decrease with time. Similar findings were obtained in this study. Similar experimental approaches were used in both studies. In the study by Odnevall Wallinder et al. (2009), runoff water was continuously collected on a weekly or monthly basis into polycarbonate containers followed by the consecutive analysis of acidified samples to determine the Cu concentration from which the total runoff rate was calculated on an annual basis. The total runoff quantity was calculated by summing up the contribution of released Cu during each sampling period. In principle, the present study had the same objective by integrating over rather short time intervals, 10 minutes for Cu concentrations and 3 minutes for water flow. If the interval would have been infinitesimally small, integration over the whole period would be equivalent to the method employed by Odnevall Wallinder et al. (2009), Odnevall Wallinder et al. (2004), He et al., (2001) and Persson and Kucera (2001). The lower measured Cu runoff concentrations from copper roofs in the present study compared to measurements made by e.g. He et al., (2001) and Persson and Kucera (2001) is the retention of copper in the down-spouts made of cast iron and sewers of concrete. Copper in the runoff water interacts with the surfaces forming the relatively stable mineral malachite, $Cu_3(CO_3)_2(OH)_6$ (Odnevall Wallinder et al., 2009). The retention capacity has shown to be strongly influenced by the differences in runoff water characteristics and flow rates (Bahar et al. (2008)) The capacity of different solid surfaces to act as sinks for released copper has been thoroughly discussed and elucidated for soil systems, limestone and concrete (e.g. pavement) in Bertling et al. (2006), Bahar et al. (2008).

To conclude, the Cu runoff from the copper roof measured in the present study is in line with findings of previous studies in Stockholm by Odnevall Wallinder et al., (2009), Odnevall Wallinder et al. (2004), He et al., (2001), Persson and Kucera (2001) and observed differences are explained by the different extent of retention of copper with down-pipe surfaces, flow rates of runoff water, sampling, differences between rainfall intensities, length of dry periods preceding the rainfall, and seasonal effects. The reason that studies like Sörme and Lagerkvist (2002), Cui (2009) and Cui et al., (2010) present considerably higher annual Cu runoff fluxes from copper roofs is that they consistently use an annual Cu runoff flux of 2.0 or 2.1 gm^{-2} and refer to the 48-week study by He et al., (2001). However, a more careful reading of He et al., (2001) does not support the use of Cu runoff fluxes of 2.0 or 2.1 gm^{-2}, since they are believed by the authors to be experimental artefacts. Instead, He et al., (2001), state that the annual Cu flux from copper roofs should be considered to be 1.3 gm^{-2}, regardless of the age of the copper panels.

4.4.2 Vehicle emission data

Regarding the estimations of annual Cu runoff fluxes from roads and parking spaces in the city of Stockholm, the choice of type of data can influence the results. As described above, this estimation is based either on vehicle work or on area of roads and parking spaces. An estimation based on vehicle work assumes a constant emission to ground and eventually storm water of Cu expressed as mass per vehicle work. This constant emission which in turn depends on wear rate of brake linings and brake lining manufacture (Cu content) is then multiplied by vehicle work. Vehicle work is defined as the total length driven by all cars during one year within the area of interest. By employing this method, one assumes that a representative sample is used to estimate the average Cu content of the brake linings used. However, both Sörme and Lagerkvist and Cui et al., (2010) refer to the study by Westerlund (1998 and 2001) which based his average Cu content on 69.5 % of the models of passenger cars which were in use in 1997. These models have to a large extent been replaced by others and hence it is unknown to what extent the average Cu content in brake linings derived by Westerlund (1998 and 2001) is still valid. The assumptions by Westerlund (1998 and 2001) on total the traffic work in the city of Stockholm and wear rate of the brake linings are considered to be constrained to a higher degree. The same methodology was applied by Westerlund (1998 and 2001) for the emissions from trucks and busses, but their combined contribution of Cu was considered to be small, around 5%. The fraction of particles emitted from the brake linings which become airborne in contrast to the fraction which are deposited to the ground, is another factor which is rather poorly constrained. This is dependent on the size distribution of the particles and the turbulence of the flow, which both can be dependent on the speed and density of traffic.

That is, by employing the method of estimating emissions of Cu from traffic using traffic work and wear of brake linings, there are two factors which are considered to be poorly constrained: the Cu content of the brake linings and the fraction which is emitted as airborne particles. These two factors can explain the much lower estimates of Cu emitted as particles to air based on measurements, an average of 160 μg per vehicle kilometre (vkm), compared to the estimate based on employing the method of traffic work and brake lining wear, 1.3 mg vkm^{-1} (Sternbeck et al., 2001 and 2002). However, in the case of Zn, there is a much smaller difference between the estimates based on the two methods, 222 μg vkm^{-1} and 0.3 mg vkm^{-1}, respectively: Thus, one conclusion is that the large difference between observations on Cu emitted as particles to air and estimates based on vehicle work and wear rate of brake linings in the study by Sternbeck et al., (2001 and 2002) is that the average Cu content in brake linings derived by Westerlund (1998 and 2001) were not representative. Since the time lag between the estimate derived by Westerlund (1998 and 2001) and the measurements done by Sternbeck et al., (2001, 2002) is rather short, 1997 to 1999/2000, the poor representativeness of the average Cu in brake linings derived by Westerlund (1998 and 2001) is probably not due to a change in the vehicle model fleet during the two to three year period between the derivation of the average value and the measurements by Sternbeck et al., (2001 and 2002). Instead, the explanation can be found in how the average Cu concentration in the brake linings was derived. In the study by Westerlund (1998, 2001) a random observation on passenger car on a major road in Stockholm resulted in a sample of 987 cars. From this sample of 987 cars, a sub-sample consisting of cars of a model which represents at least 1% (10 cars) of the total sample (987) was drawn. This sub-sample made up 63.5% of the total sample, in other words 627 cars. These 627 cars belong to 24 different car models and Westerlund (1998, 2001) derived his estimate of an average Cu content in brake linings on passenger cars by assuming a normal distribution of Cu in sample of 48 brake linings, one front and one rear for each car model. This approach can be problematic from a statistical point of view for two reasons. Firstly, the Cu content of the brake linings in about 1/3 of the sample is unknown. Considering that the range of Cu concentrations in 48 brake linings which were analysed span from 12.7 to 234 000 ppm, these missing data introduce a significant uncertainty. Secondly, the data from the 2/3 of the sample which are presented in Westerlund (1998, 2001) is highly skewed with a long tail to the right, like a Gamma or Lognormal distribution. This implies that by estimating a sample mean from a Normal distribution using these data can lead to a biased estimate.

To conclude, although the number derived for the annual emission of copper from traffic by Sörme and Lagerqvist (2002) is similar to that of the present study, the former is considered to be less constrained or well defined.

4.4.3 Comparison between the results of different data sets for the emissions of copper from roofs and vehicles

It is interesting to compare the estimated annual emissions of copper from copper roofs and traffic to storm water derived in the present study with the estimated fluxes of copper into the recipient Saltsjön in Stockholm from the two major waste water treatment plants and untreated storm water into Saltjsön and Lake Mälaren derived by Jönsson (2011). In the study by Jönsson (2011) the annual copper fluxes from untreated storm water into Saltsjön and Lake Mälaren was estimated to be 0.25 tons. The annual copper fluxes into Saltsjön in the treated waste water effluents from the two major WTPs in Stockholm was estimated to be 0.5 tons. Considering that the area of roads where storm water runs off untreated directly into Lake Mälaren and Saltsjön, make up only a minor part in Stockholm, the annual estimate of 0.25 tons seem to be on the high end since 0.25/0.8 is 25%. In the drainage areas with no treatment of storm water, there are also a very limited number of buildings with copper roofs (Ekstrand et al., 2001). On the other hand considering the number of approximations used to derive the estimates, the agreement between the two numbers can be considered to be fair. The fluxes of copper from treated sewage water that enters the recipients Saltsjön make up only a minor portion of the total load that enters the WTPs, since most of the copper is removed with the sludge. Since the load of copper with runoff from copper roofs and roads make up only a minor portion of

the total load of copper to the WTPs (Sörme and Lagerqvist, 2002), it is not possible to assess whether the estimated numbers for the runoff fluxes derived in the present study complies with the estimated loads of copper from the WTPs to the recipient Saltsjön in the study by Jönsson (2011).

It is also interesting to compare the yearly Cu fluxes from copper roof and roads and parking spaces to the corresponding estimates by Cui et al., (2010) for four local areas in Stockholm. In the study by Cui et al., (2010) the fluxes of Cu from roads and parking spaces were estimated by the vehicle work method described previously using the data from Westerlund (1998, 2001) while the Cu fluxes from copper roofs were estimated by using the annual Cu runoff of 2.1g m^{-2-} citing Persson and Kucera (2001). A comparison between the estimates of Cui et al., (2010) and estimates based on the corresponding Cu fluxes derived in the present study is presented in Table 1 below.

Table 1. Estimates of annual fluxes of Cu from traffic areas (parking spaces and roads) and copper roofs for five local areas in Stockholm based on run off values derived in this study and Cui et al. (2010)

Area	Cu flux (kg/yr) copper roofs		Cu flux (kg/yr) traffic	
	This study	Cui et al. 2010	This study	Cui et al. 2010
Laduviken	1.E-01	2.E-01	4.E+00	5.E+00
Råcksta Träsk	4.E+00	8.E+00	1.E+01	1.E+01
Judarn	5.E-01	1.E+00	4.E+00	4.E+00
Trekanten	2.E+00	5.E+00	4.E+00	6.E+00
Långsjön	2.E+00	4.E+00	2.E+01	1.E+01

As seen in Table 1, the annual flux of Cu from copper roofs based on the number derived in the present study about 50%, or less in the case of Trekanten, compared with data used by Cui et al., (2010). When the runoff is based on the figure derived in the present study, there are only small differences for the traffic areas, whereas Trekanten and Långsjön have clearly lower and higher annual Cu fluxes, respectively. Additionally, by using the annual Cu runoff values derived in the present study, traffic is clearly estimated to be a largest source of Cu to storm water in all areas. The difference in the relative importance of copper roofs and traffic as sources of Cu to storm water compared to the study by Cui et al., (2010) is clearly seen in the case of the area Trekanten. In the study by Cui et al., (2010), copper roofs are estimated to generate 60, 36 and 42 % of the annual Cu runoff generated by traffic for the areas Råcksta Träsk, Judarn and Långsjön respectively (Table 1). By using the annual Cu runoff values to storm water derived in this study, the corresponding contribution from copper roofs are 32, 12 and 10%. The difference is less dramatic in the area of Trekanten.

4.5 Copper complexation capacity of water samples

Both strong and weak ligands (Fig. 17) are normally present in runoff water samples (rain water that has interacted with a copper surface), as previously observed for samples from both the parking space and copper roof in the study by Odnevall Wallinder et al. (2009).

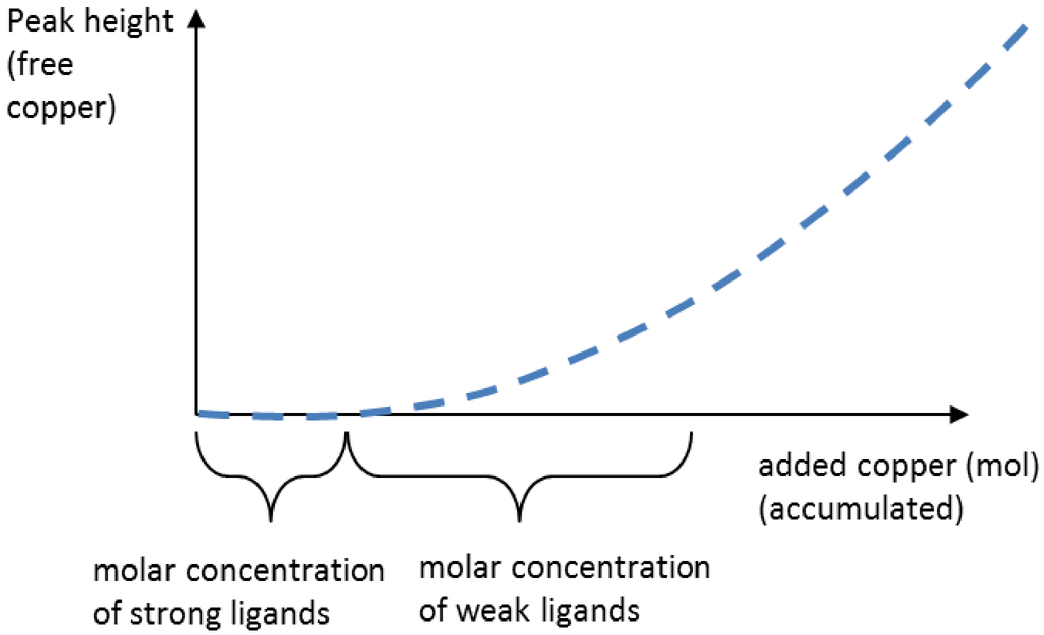

Figure 17. A complexation model with both strong and weak ligands (figure prepared by. Y. Hedberg, KTH).

Due to the higher concentrations of Cu in samples P1, P5, T1, T10 compared with the samples in the study by Odnevall Wallinder et al. (2009), the complexation capacity could not be determined by DPASV. However, if assuming a complexation model with both strong and weak ligands (Fig. 17), the complexation capacity will be lower than the total Cu concentrations measured in the samples (Figure 14): 104 (P1), 52 (P5), 3418 (T1) and 957 (T10) µg L^{-1}. This is also true for a complexation model with only strong ligands.

For the storm water samples collected from the roof, the comparison between the Cu concentrations before and after digestion (Fig. 18) indicates the lack of significant or systematic difference. This implies that the complexation capacity has to be lower than the difference between the samples, i.e. < 60 µg L^{-1}.

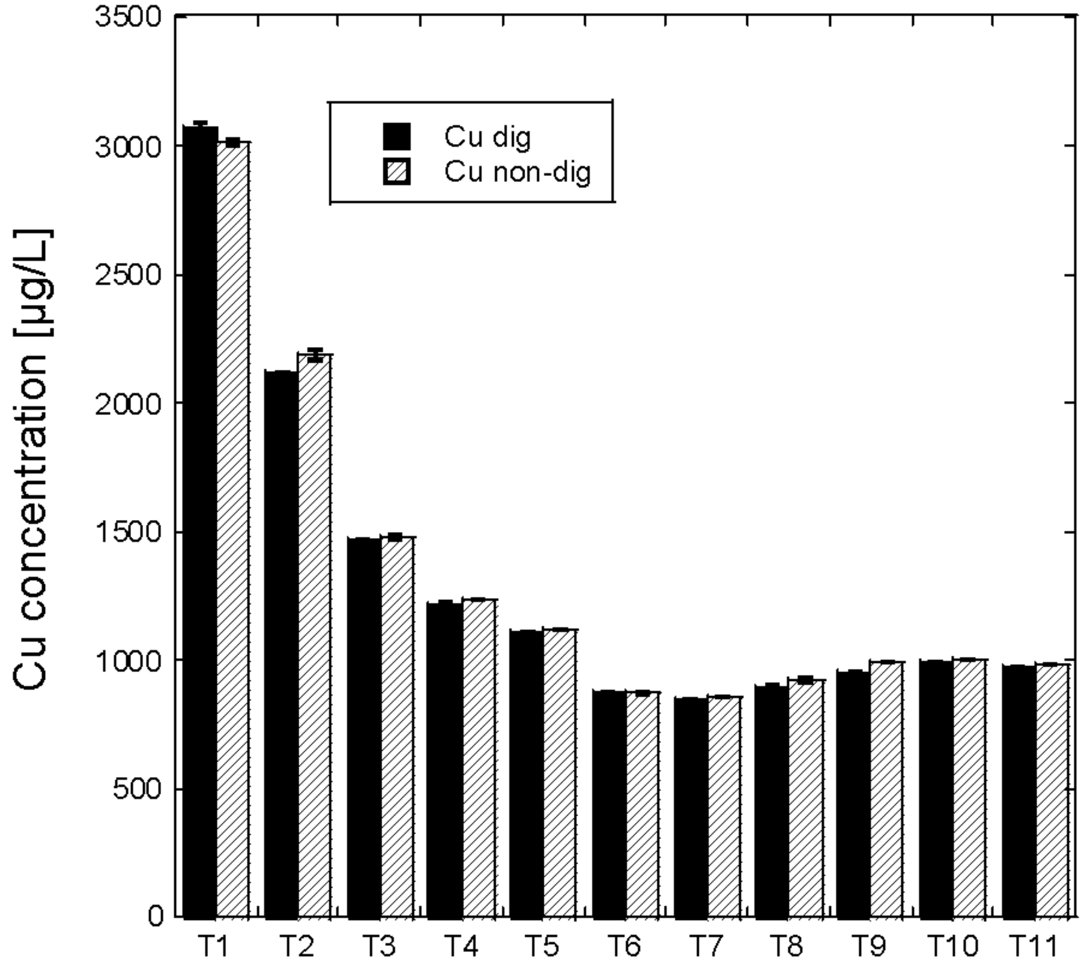

Figure 18. Total Cu concentrations determined by AAS for digested and non-digested samples.

It can be concluded that both the parking space and roof samples most probably contain both weak and strong ligands. In this study, the complexation capacity of the parking space storm water samples was estimated to approx. 40 µg L^{-1} which is a substantial percentage of the total Cu concentrations (< limit of detection – 104 µg L^{-1}), while it could not exactly be determined in the roof samples due to too high total copper concentrations. Based on the previous study (Odnevall Wallinder et al., 2009) and the comparison of digested and non-digested samples (Fig. 18), it can however be strongly assumed that the complexation capacity of the roof samples is a few µg L^{-1}. Strongly or weakly bound copper is not bioavailable (Odnevall Wallinder et al., 2009).

Related to the chemical speciation, but even more important for estimation of copper fluxes, is the retention of copper on surfaces such as concrete. The retention of copper on e.g. concrete or other solid surfaces is strongly related to the flow rate and composition (e.g. pH, organic matter etc.) and the total Cu concentration of the storm water and its changes, and is hence related to the complexation capacity of the storm water sample which depends on similar factors (Bertling et al., 2006; Bahar et al., 2008).

5 Conclusions

- A Cu runoff value has been derived based on findings during a single rainfall (10 mm) for a parking space: 48 μg $mm^{-1}m^{-2}$. This number corresponds to an annual Cu runoff value from parking spaces of 29 mg m^{-2} by multiplying with the annual precipitation in Stockholm, 585mm.
- The Cu runoff value for parking spaces could be applied also for service and major roads by multiplying it by coefficients to take into account differences in driving patterns.
- A copper runoff value has been derived for a copper roof during a rainfall of 2.4 mg $mm^{-1}m^{-2}$ after expected retention in downpipes of cast iron and concrete. This value corresponds to an annual Cu runoff value from copper roofs (representative for a surface inclined 5° from the horizontal) of 1.4 g m^{-2}. For a surface inclined 45° from the horizontal, which is representative for Stockholm, this number equals 1 g m^{-2}.
- Both runoff values are in line with other estimates based on long-term annual runoff rate studies of copper in Stockholm using comparable/compatible methods.
- Applying the derived Cu runoff values found in this study to the whole city of Stockholm leads to a halving of the contribution of Cu from copper roofs (600 compared to 1200 kg) and a similar estimation concerning traffic compared to the study by Sörme and Lagerkvist (2002). Traffic is estimated to be a 30% larger source of copper than copper roofs to storm water.
- Applying the derived Cu runoff values found in this study to five areas of Stockholm results in about 50% lower estimates of released copper from copper roofs in all five areas compared with the study by Cui et al., (2010). Traffic is estimated to be a significantly larger source of copper to storm water in all areas compared to copper roofs.
- The reasons for the difference in the estimates is explained by difficulties with estimating the contribution from traffic using the method by Westerlund (1998, 2001) which is based on traffic work and wear rate of brake linings, and incorrect estimates of the contribution from copper roofs.

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7 Appendix

Table A1. Precipitation data (in mm) from the rain gauge on the copper roof.

Time 12-3-11	Precipitation record (mm)	Time 12-7-11	Precipitation record (mm)	Time 12-9-11	Precipitation record (mm)
16:01	0.25	7:00	0.25	5:39	0.25
16:06	0.25	7:09	0.25	5:44	0.25
16:09	0.25	7:32	0.25	5:47	0.25
16:12	0.25	7:44	0.25	5:50	0.25
16:17	0.25	8:29	0.25	5:53	0.25
16:22	0.25	8:58	0.25	5:56	0.25
16:26	0.25	14:52	0.25	5:57	0.25
16:28	0.25	Time 12-8-11		6:00	0.25
16:34	0.25	0:08	0.25	6:02	0.25
16:37	0.25	Time 12-9-11		6:06	0.25
16:40	0.25	2:30	0.25	6:08	0.25
16:42	0.25	2:34	0.25	6:12	0.25
16:45	0.25	2:48	0.25	6:15	0.25
16:47	0.25	3:00	0.25	6:19	0.25
16:49	0.25	3:10	0.25	6:23	0.25
16:51	0.25	3:19	0.25	6:27	0.25
16:54	0.25	3:30	0.25	6:31	0.25
16:57	0.25	3:44	0.25	6:37	0.25
17:01	0.25	3:51	0.25	6:43	0.25
17:05	0.25	3:55	0.25	6:49	0.25
17:10	0.25	3:58	0.25	6:53	0.25
17:15	0.25	4:04	0.25	6:59	0.25
17:22	0.25	4:10	0.25	7:05	0.25
17:26	0.25	4:16	0.25	7:18	0.25
17:32	0.25	4:23	0.25	7:23	0.25
17:38	0.25	4:28	0.25	7:30	0.25
17:44	0.25	4:34	0.25	7:34	0.25
17:47	0.25	4:38	0.25	7:38	0.25
17:59	0.25	4:43	0.25	7:41	0.25
18:14	0.25	4:47	0.25	7:48	0.25
18:21	0.25	4:54	0.25		
18:26	0.25	5:01	0.25		
18:33	0.25	5:07	0.25		
18:38	0.25	5:11	0.25		
18:43	0.25	5:17	0.25		
18:49	0.25	5:22	0.25		
18:54	0.25	5:26	0.25		
18:59	0.25	5:30	0.25		
19:09	0.25	5:35	0.25		

Table A2. Data on storm water flow depth and speed from parking space. The flow (Q) is estimated by multiplying the cross sectional flow area (A_d) of the storm water with the estimated uniform flow speed using Darcy-Weisbach equation 6 assuming rough turbulence and equivalent sand-roughness size, k_S = 6,0mm.

Time Hour:min:sec	**Level, H (m)**	**Speed, v (m/s)**	**Flow, Q (m^3/s)**
16:00:00	0	0	0
16:03:00	0.001	0	0
16:06:00	0.001	0	0
16:09:00	0.007	0.033	4.5E-05
16:12:00	0.038	0.214	3.4E-03
16:15:00	0.063	0.069	1.1E-02
16:18:00	0.072	0.098	1.5E-02
16:21:00	0.076	0.048	1.6E-02
16:24:00	0.079	0.04	1.8E-02
16:27:00	0.082	0.03	1.9E-02
16:30:00	0.085	0.018	2.1E-02
16:33:00	0.088	0.006	2.3E-02
16:36:00	0.089	0.009	2.3E-02
16:39:00	0.09	0.007	2.4E-02
16:42:00	0.092	0.008	2.5E-02
16:45:00	0.099	0.018	2.9E-02
16:48:00	0.114	0.037	4.0E-02
16:51:00	0.128	0	5.1E-02
16:54:00	0.137	0	5.9E-02
16:57:00	0.143	0	6.5E-02
17:00:00	0.138	0	6.0E-02
17:03:00	0.131	0	5.4E-02
17:06:00	0.124	0	4.8E-02
17:09:00	0.116	0	4.1E-02
17:12:00	0.112	0	3.8E-02
17:15:00	0.108	0	3.6E-02
17:18:00	0.104	0	3.3E-02
17:21:00	0.098	0	2.9E-02
17:24:00	0.095	0	2.7E-02
17:27:00	0.094	0	2.6E-02
17:30:00	0.094	0	2.6E-02
17:33:00	0.092	0	2.5E-02
17:36:00	0.091	0	2.4E-02
17:39:00	0.09	0	2.4E-02
17:42:00	0.091	0	2.4E-02
17:45:00	0.091	0	2.4E-02
17:48:00	0.094	0	2.6E-02
17:51:00	0.096	0	2.7E-02
17:54:00	0.095	0	2.7E-02
17:57:00	0.09	0	2.4E-02
18:00:00	0.084	0	2.0E-02
18:03:00	0.076	0	1.6E-02
18:06:00	0.069	0	1.3E-02
18:09:00	0.062	0	1.0E-02
18:12:00	0.057	0	8.6E-03
18:15:00	0.052	0	7.0E-03
18:18:00	0.05	0	6.4E-03
18:21:00	0.053	0	7.3E-03
18:24:00	0.063	0	1.1E-02
18:27:00	0.074	0	1.5E-02

Table A3. Data on storm water flow depth and speed from copper roof. The flow (Q) is estimated by multiplying the cross sectional flow area (A_d) of the storm water with the estimated uniform flow speed using Darcy-Weisbach equation 6 assuming rough turbulence and equivalent sand-roughness size, k_S = 6,0mm.

Time Hour:min:sec	Depth, y (m)	Speed, V (m/s)	Flow, Q (m^3/s)
15:45:00	0.015	0	1.8E-03
15:48:00	0.015	0	1.8E-03
15:51:00	0.016	0	2.1E-03
15:54:00	0.024	0.006	5.2E-03
15:57:00	0.039	0.203	1.5E-02
16:00:00	0.041	0.256	1.7E-02
16:03:00	0.006	0.191	2.1E-04
16:06:00	0.046	0.253	2.2E-02
16:09:00	0.017	0.382	2.4E-03
16:12:00	0.017	0.418	2.4E-03
16:15:00	0.014	0.395	1.6E-03
16:18:00	0.013	0.393	1.3E-03
16:21:00	0.012	0.369	1.1E-03
16:24:00	0.01	0.355	7.1E-04
16:27:00	0.015	0.381	1.8E-03
16:30:00	0.016	0.393	2.1E-03
16:33:00	0.015	0.382	1.8E-03
16:36:00	0.013	0.369	1.3E-03
16:39:00	0.018	0.39	2.8E-03
16:42:00	0.02	0.414	3.5E-03
16:45:00	0.028	0.534	7.4E-03
16:48:00	0.031	0.521	9.2E-03
16:51:00	0.035	0.506	1.2E-02
16:54:00	0.035	0.52	1.2E-02
16:57:00	0.029	0.529	8.0E-03
17:00:00	0.025	0.495	5.7E-03
17:03:00	0.021	0.419	3.9E-03
17:06:00	0.018	0.373	2.8E-03
17:09:00	0.018	0.384	2.8E-03
17:12:00	0.016	0.348	2.1E-03
17:15:00	0.015	0.348	1.8E-03
17:18:00	0.013	0.349	1.3E-03
17:21:00	0.011	0.337	8.9E-04
17:24:00	0.013	0.353	1.3E-03
17:27:00	0.013	0.345	1.3E-03
17:30:00	0.011	0.34	8.9E-04
17:33:00	0.012	0.349	1.1E-03
17:36:00	0.011	0.354	8.9E-04
17:39:00	0.01	0.345	7.1E-04
17:42:00	0.011	0.345	8.9E-04
17:45:00	0.013	0.354	1.3E-03
17:48:00	0.016	0.351	2.1E-03
17:51:00	0.014	0.357	1.6E-03
17:54:00	0.01	0.328	7.1E-04
17:57:00	0.008	0.315	4.2E-04
18:00:00	0.007	0.317	3.1E-04
18:03:00	0.007	0.317	3.1E-04
18:06:00	0.006	0	0
18:09:00	0.011	0	0
18:12:00	0.013	0	0
18:15:00	0.009	0	0

Table A4. Total concentrations of copper and standard deviations (SD) in storm water samples from parking space. The limit of detection (LOD) is in the range 5-10 µg/L,

Sample ID	**Cu [µg/L]**	**SD [µg/L]**	**Time**
P1	104	3	16:09:00
P2	85	10	16:18:00
P3	73	1	16:30:00
P4	55	8	16:39:00
P5	52	1	16:51:00
P6	30	2	17:00:00
P7	15	1	17:09:00
P8	8	2	17:21:00
P9	9	1	17:30:00
P10	4	1	17:39:00
P11	<LOD		17:48:00
P12	<LOD		17:57:00
P13	<LOD		18:09:00
P14	<LOD		18:18:00

Table A5. Total concentrations of copper and standard deviations (SD) in storm water samples collected from roof. The limit of detection (LOD) is in the range 5-10 µg/L,

Sample ID	**Cu [µg/L]**	**SD [µg/L]**	**Time**
T1	3418	9	16:06:00
T2	2349	11	16:15:00
T3	1530	7	16:27:00
T4	1229	10	16:36:00
T5	1077	2	16:45:00
T6	793	25	16:54:00
T7	763	25	17:06:00
T8	835	3	17:15:00
T9	912	6	17:27:00
T10	957	1	17:36:00
T11	945	5	17:48:00