Characterization of road runoff with regard to seasonal variations, particle size distribution and the correlation of fine particles and pollutants

R. Hilliges, M. Endres, A. Tiffert, E. Brenner and T. Marks

ABSTRACT

Urban runoff is known to transport a significant pollutant load consisting of e.g. heavy metals, salts and hydrocarbons. Interactions between solid and dissolved compounds, proper understanding of particle size distribution, dissolved pollutant fractions and seasonal variations is crucial for the selection and development of appropriate road runoff treatment devices. Road runoff at an arterial road in Augsburg, Germany, has been studied for 3.5 years. A strong seasonal variation was observed, with increased heavy metal concentrations with doubled and tripled median concentrations for heavy metals during the cold season. Correlation analysis showed that de-icing salt is not the only factor responsible for increased pollutant concentrations in winter. During the cold period, the fraction of dissolved metals was lower compared to the warm season. In road dust, the highest metal concentrations were measured for fine particles. Metals in road runoff were found to show a significant correlation to fine particles SS63 (<63 μm). Therefore, it is debatable whether treatment devices only implementing sedimentation processes provide sufficient removal rates.

INTRODUCTION

A number of research studies have shown that urban stormwater runoff can be a major source of diffuse pollutants to receiving water bodies (Valtanen et al. 2015; Djukic et al. 2016; Huber et al. 2016). A large variety of pollutants such as heavy metals, hydrocarbons and oils are transported via runoff to natural environments. Therefore, management of stormwater pollutant loads has gained importance, especially with regard to the chemical and ecological quality objectives for surface waters in the European Water Framework Directive WFD 2000/60/CE (Becouze-Lareure et al. 2016). Becouze-Lareure et al. (2016) have shown that catchment surface runoff can be the main contribution to urban wet weather discharges, but only a limited number of investigations have focused on the major sources of pollutants in the urban water cycle. Without doubt, one significant source of priority pollutants is traffic related activities, including vehicle and tire wear and tear and fluid leakages.

Pollutants in road runoff are known to appear both in dissolved as well as in particulate form. Many treatment devices focus on the reduction of sediment and sediment-associated contaminants (Selbig 2015). The characterization of particles in road runoff is therefore crucial for the selection and development of treatment devices and best management practices (BMP). The determination of particle characteristics – and therefore particle-associated contaminants – is of significance in order to assess their impact and understand their behaviour (Ruban et al. 2015).

In cold climates, pollutant input and transport mechanisms are strongly affected by accumulation of snow, pollutant built-up in snow and snowmelt (Westerlund & Viklander 2006; Valtanen et al. 2015) during the cold season. Furthermore, it has been observed that de-icing salt has an impact on runoff quality and metal mobility (Bäckström et al. 2005). De-icing salts are widely applied in cold climates for winter road maintenance. The most common de-icing salt is sodium chloride (NaCl), which can effectively be used at temperatures between 0 and −9 °C (Mahrosh et al. 2014). De-icing salt transported by road runoff into rivers and lakes has proved to have a negative effect, for example on lakes recovering from acidification.
(Jensen et al. 2014) and fish development (Mahrosh et al. 2014).

Besides seasonal effects, the particle size distribution is also crucial for sedimentation properties and therefore the efficiency of many treatment processes (Charters et al. 2015). The composition of urban runoff is heterogeneous as it consists of indirect sources such as atmospheric deposition (Murphy et al. 2014) as well as direct sources such as wear and tear of tires, brake linings and surface materials (roads and traffic signs etc.). Knowledge of particle composition and sizes is important, since particles in road runoff often operate as a carrier of other pollutants, depending on size and composition (Aryal et al. 2015). Studies indicate that there is no single distribution of particles in road runoff, but road runoff is known to have low median particle diameters between 8 and 95 μm for different traffic areas (Selbig 2015).

Therefore, the parameter SS63 is discussed in Germany for the evaluation of surface runoff. It presents ‘Fine Suspended Solids’ between 0.45 and 63 μm (Dierschke & Welker 2015); with 63 μm corresponding to a mesh size of 2.5/1,000 inch. Fine particles (<63 μm) represent the divide according to ISO 14688 International Soil Classification between clay/silt particles and sand/gravel particles, and therefore are often considered as between settleable and non-settleable particles. It has been shown that heavy metals, polycyclic aromatic hydrocarbons and other organic pollutants can be bound especially to the small particles in road runoff (Zhao et al. 2010; Dierschke & Welker 2015). Therefore, the amount of solids is sometimes used for the evaluation of road runoff concerning pollutant concentrations (Dierschke 2014). Typical SS63 concentrations in runoff from roofs are in the range of 20 mg L⁻¹ and are significantly higher in road runoff, usually with concentrations up to 200 mg L⁻¹ (Dierschke & Welker 2015).

The aim of this study is (i) to determine the effects of cold periods on pollutant concentrations and forms as well as (ii) to investigate the correlation of fine particles and pollutants in order to gain knowledge for the development and evaluation of treatment devices and BMPs.

**MATERIAL AND METHODS**

**Study site**

The study site is situated at an arterial road (Derchinger Straße) in the city of Augsburg, Germany, connecting the city with the A8 highway. The site is located within an industrial area with one road lane in each direction; the speed limit is 60 km h⁻¹. Both road lanes drain in the direction of the sampling unit. The average annual daily traffic (AADT) was measured to 9,690 vehicles d⁻¹ in 2014 (Endres et al. 2015).

Since 2010, a full-scale lysimeter facility has been operated, consisting of eight basins where four different geohydraulic safety measures and two different soil types in comparison to conventionally produced slopes have been investigated. Road runoff has been sampled as well as the leachate from each of the eight lysimeter basins. Samples have been collected and analysed as two-week composite samples. Samples were analysed regarding volume and the contained pollutants (Endres et al. 2016). De-icing salt (mainly NaCl) is applied in the cold months in Augsburg; no information on the applied amounts is available.

**Analyses**

For this publication, 61 samples from the period of fall 2012 until March 2016 have been used. Total metals and dissolved metals have been analysed. The fraction of dissolved heavy metals was obtained by filtration (0.45 μm, membrane filtration) prior to analysis. For measurement of the total metals, samples were treated with a saltpeter digestion using nitric acid according to DIN EN ISO 15587-2 prior to analysis. All analyses were carried out according to standard methods. Concentrations of copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), cadmium (Cd) and iron (Fe) were analysed by inductively-coupled-plasma mass-spectrometry (ICP-MS), according to DIN EN ISO 17294-2 (E 29). Samples were conserved prior to analysis by adding 0.5 ml concentrated nitric acid (suprapur). The instrument detection limits (DL) were 1 μg L⁻¹ for Cu, 1 μg L⁻¹ for Zn, 1 μg L⁻¹ for Pb, 1 μg L⁻¹ for Ni, 0.1 μg L⁻¹ for Ca and 10 μg L⁻¹ for Fe. Sulphate and chloride (Cl) were analyzed according to DIN EN ISO 10304-1:1995 by ion chromatography with a DL of 0.5 mg L⁻¹ for both elements. Dissolved organic carbon (DOC) was measured after filtration (0.45 μm, membrane filtration); the DL was 0.5 mg L⁻¹.

Measurements of pH values were done with a glass electrode and electric conductivity (EC) by a combined pH and conductivity meter (WTW Multi 3420 Set C). Particles in the road runoff have been analyzed since March 2015 in the form of ‘Fine Suspended Solids’ (0.45 μm-63 μm, (SS63)) according to Dierschke & Welker (2015). Furthermore, road dust samples were collected and analysed after partitioning and digestion. Analysis was carried out at the Federal Highway Research Institute (BASt) by atomic absorption spectrometry (Graphite-AAS) after hydrofluoric acid digestion using 10 mL nitric acid and...
4 mL hydrofluoric acid. The instrument DL were 1 µg L⁻¹ for Cd, Co, Cr, Cu, Mo, Ni, Pb and V.

Data analyses

Spearman rank order correlations and box-and whisker plots were calculated to determine the seasonal variations, the effect of de-icing salt and the relationships between heavy metals and fine particles SS63. Due to the non-normal distribution of most parameters, the non-parametric Spearman rank-order correlation was subsequently used following the example of Mosely & Peake (2001). Only correlations significant at p < 0.05 are reported in this study.

RESULTS AND DISCUSSION

Characterization of road runoff

Table 1 summarizes the results of 61 analysed composite samples taken at the study site during the period of fall 2012 until March 2016. In the last column, the threshold values according to the German regulation for infiltration into groundwater are given (BBSchV 1999).

Runoff constituents are subject to fluctuations with a considerable number of outliers due to a multitude of influencing parameters such as seasonal variations, atmospheric deposition, varying traffic activities and street sweeping (Westerlund & Viklander 2006; Valtanen et al. 2015; Huber et al. 2016).

Pollutant concentrations were found to be varying in orders of magnitude. In this investigation, Zn was the most abundant metal, followed by Cu, Pb, Ni and Cd. Similar results have been reported by Becouze-Lareure et al. (2016) for urban wet weather discharges. Cd could only be detected in some of the samples. Cd is very toxic, and is present as a trace metal in brake and tire wear (Mangani et al. 2005). In this study, the maximum Cd concentration was 14 µg L⁻¹. Similar findings have been reported in other studies (Hallberg et al. 2007; Zhao et al. 2010; Hilliges et al. 2013). Due to site specific and climatic conditions, differences in AADT and in sample taking, the results of different studies cannot be directly compared.

Maximum values for all heavy metals exceeded the threshold values according to the German regulation BBšSchV (see Table 1). Also, the limit values (as annual values) were crossed for the Environmental Quality Standards (EQS) in surface water for the priority substances Pb (7.2 µg L⁻¹), Ni (20 µg L⁻¹) and Cd (<0.25 µg L⁻¹ depending on water hardness) (EU EQS 2007). Treatment of road runoff prior to infiltration into groundwater or discharge into water bodies is therefore required. Even higher pollutant concentrations were found under similar climatic conditions by Helmreich et al. (2010) at a road with much higher AADT. Cu concentrations in this study varied between 10 and 273 µg L⁻¹; the mean concentration of 67.1 µg L⁻¹ exceeded the threshold value of 50 µg L⁻¹ significantly. Cu most likely originates from moving engine parts and brake linings (Mangani et al. 2005). Zn concentrations were measured at between 49 and 1,300 µg L⁻¹. According to Huber et al. (2016), Zn concentrations in road runoff have not changed over the past decades in Europe. The main sources of Zn in runoff are galvanized structures, traffic signs and car tires (Becouze-Lareure et al. 2016). Pb concentrations have decreased

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Median</th>
<th>BBSchV (1999)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, total</td>
<td>µg L⁻¹</td>
<td>&lt;1.0</td>
<td>92</td>
<td>21.4</td>
<td>17</td>
<td>25</td>
</tr>
<tr>
<td>Cd, total</td>
<td>µg L⁻¹</td>
<td>&lt;0.1</td>
<td>14</td>
<td>0.36</td>
<td>&lt;0.1</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu, total</td>
<td>µg L⁻¹</td>
<td>10</td>
<td>273</td>
<td>67.1</td>
<td>48.0</td>
<td>50</td>
</tr>
<tr>
<td>Ni, total</td>
<td>µg L⁻¹</td>
<td>1.0</td>
<td>67</td>
<td>12.1</td>
<td>7.0</td>
<td>50</td>
</tr>
<tr>
<td>Zn, total</td>
<td>µg L⁻¹</td>
<td>49</td>
<td>1,300</td>
<td>311</td>
<td>240</td>
<td>500</td>
</tr>
<tr>
<td>Cl</td>
<td>mg L⁻¹</td>
<td>0.93</td>
<td>7,400</td>
<td>_</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>SS63)a</td>
<td>mg L⁻¹</td>
<td>26</td>
<td>186</td>
<td>86.12</td>
<td>96.0</td>
<td>_</td>
</tr>
<tr>
<td>DOC</td>
<td>mg L⁻¹</td>
<td>2.1</td>
<td>21</td>
<td>6.87</td>
<td>5.60</td>
<td>_</td>
</tr>
<tr>
<td>pH value</td>
<td>–</td>
<td>7.11</td>
<td>8.15</td>
<td>7.83</td>
<td>7.84</td>
<td>_</td>
</tr>
<tr>
<td>EC</td>
<td>mS cm⁻¹</td>
<td>0.068</td>
<td>21.5</td>
<td>_</td>
<td>_</td>
<td>_</td>
</tr>
</tbody>
</table>

aValues not representative due to seasonal changes.

bSS63: data based on 17 samples analysed in the period March 2015–March 2016.
during recent decades due to lead-free antiknock gasoline. The remaining sources for Pb are lubrication oil and grease, vehicular component wear, tire and brake linings and Pb-containing paint (Helmreich et al. 2013). Huber et al. (2013) give a typical median value for total Pb in Europe of 15 μg L⁻¹. In this study, total Pb concentrations of up to 92 μg L⁻¹ were measured with a mean concentration of 17 μg L⁻¹. Ni and DOC were detected only in relatively low concentrations. As described in other studies, the pH value remained stable with a median value of 7.84.

Due to de-icing salt application, substantial variations were observed for electric conductivity (EC) and Cl. In the warm season, without de-icing salt application, the conductivity remained below 600 μS cm⁻¹ with Cl concentrations below 150 mg L⁻¹. De-icing salt application led to a sharp increase reaching EC of up to 21,500 μS cm⁻¹ and Cl concentrations of up to 7,400 mg L⁻¹. Composite samples were investigated; therefore even higher de-icing salt concentrations have to be expected in specific events.

Seasonal influences

Seasonal influences on road runoff are typical for cold climates. Westerlund & Viklander (2006) and Valtanen et al. (2015) investigated seasonal influences on road runoff quality in northern Europe, distinguishing between rainfall events, snowfall events and snowmelt. In northern Europe, snow can accumulate during winter, releasing snow storage during spring snowmelt, leading to momentarily very high pollutant loads if snowmelt occurs during a short period in spring. In northern Sweden, eight times higher concentrations and five times higher loads of particles were measured during the snowmelt period compared to warmer periods (Westerlund & Viklander 2006). Temperatures in Augsburg during the cold season lead to a rather short lifespan for snow and therefore many small snow melts during the cold period. Especially on roads with high traffic loads, it is rather uncommon that compact snow layers remain over long periods – also due to intensive de-icing salt application. Therefore, the cold season in this study was defined for events with EC above 1,000 μS cm⁻¹. A strong linear correlation between Cl and EC with $R^2 = 0.9954$ proves the strong influence of de-icing salt on the EC for this study (see Figure 1).

Figure 2 displays total Zn concentrations and EC in road runoff over the sampling period of 3.5 years. Obvious seasonal changes can be observed with significant increases of total Zn concentrations correlating with conductivity values. Winter 2015/16 was very mild, resulting in only minor elevated EC values and total Zn concentrations.

![Figure 1](image-url) Correlation between Cl concentration and electric conductivity (EC) in the road runoff (sampling period November 2012 until March 2016).

![Figure 2](image-url) Total Zn concentrations [mg L⁻¹] and electric conductivity [μS cm⁻¹] in road runoff.
Similar behaviour with increased heavy metal concentrations was also observed for Pb, Ni and Cu as well as for fine particles SS63. In Figure 3, box-and-whisker plots show a significant increase for these parameters in the cold season.

Mean values for total Zn concentrations in the warm season were calculated to 200 μg L⁻¹, whereas mean concentrations during the cold season were with 375 μg L⁻¹ almost twice as high. For total Pb concentrations, the mean values almost tripled from 11 μg L⁻¹ during the warm season to 30 μg L⁻¹ during the cold season. For Ni and Cu, an increase of 1.5 times was observed. Fine particles SS63 also showed a significant increase between the seasons from 69 to 108 mg L⁻¹ in the cold season.

Remobilization effects of already immobilized pollutants caused by intensive application of de-icing salts have already been proved (Bauske & Goetz 1995; Bäckström et al. 2003). In this study, only for total Zn a moderate Spearman correlation of 0.7406 was obtained with Cl. It can be estimated that especially Zn partly originating from galvanizes surfaces is much more effected by de-icing salt (Cl) induced corrosion compared to other parameters. Only weak correlations were obtained between Cl and the other metals. Therefore, the concentration increase during the cold season can not only be attributed to high de-icing application, exceeding the pollutant concentrations by orders of magnitude. Cold and wet weather conditions as such enhance corrosion, as well as the use of winter tires, snow handling and application of sand/ gritting material seem to be responsible for increased road and tire wear. Valtanen et al. (2015) also suggest that high emissions of gaseous impurities by traffic and heating as well as increased human and vehicular traction during the cold season lead to higher pollutant concentrations.

**Speciation of heavy metals**

Proper understanding of particle size distribution and distribution between dissolved and particulate pollutants is of great interest for the development and evaluation of stormwater treatment devices. Charters et al. (2015) suggest that short-retention treatment devices carry a high performance risk concerning fine particles.

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![Figure 3](https://iwaponline.com/wst/article-pdf/75/5/1173/454185/wst075051173.pdf)

*Figure 3 | Box-and-whisker plots for total Zn, Cu, Pb and fine particles SS63 for cold and warm seasons. Upper and lower bounds of box denote the 75th and 25th percentiles.*
In this present study, the median values for the dissolved fraction of the total metal concentrations were 57.1% for Ni, 23.5% for Zn, 5.0% for Pb and 28.5% for Cu (see Figure 4).

But, for all metals, high proportions of dissolved metals reaching close to 100% were measured in some of the samples, during all seasons. During the warm period, the dissolved fraction of metals increased. Especially for Zn and Cu, the dissolved fraction increased from 19.4% in the cold season to 33.9% in the warm season for Zn and from 21.9% to 34.7% for Cu. Higher particulate metals in the cold season to 33.9% in the warm season for Zn and from 19.4% in the cold season to 25.2% in the warm season respectively; minimum and maximum are displayed exemplarily for the warm season (not shown for all seasons and cold season due to readability).

Figure 4 | Median dissolved fractions of Ni, Zn, Pb and Cu during all seasons, the cold and the warm season respectively; minimum and maximum are displayed exemplarily for the warm season (not shown for all seasons and cold season due to readability).

In addition, particulate heavy metals are often bound to fine particles that cannot be settled easily. Zhao et al. (2010) measured that particles with a grain size <44 μm had the highest metal concentrations compared to larger particles. In this study, road dust was collected at the sampling site and fractionated into particles 0.45–63 μm, 63–200 μm, 200–630 μm, 630–2,000 μm and >2,000 μm. For Cd (1.08 mg kg⁻¹), Zn (1.269 mg kg⁻¹), Co and V, by far the highest metal concentrations were measured in the finest fraction (<63 μm). For all other metals (Ni, Pb, Cu, Fe), heavy metal concentrations were similar in different particle fractions, but the largest fraction >2,000 μm was the fraction with the smallest metal concentrations for all metals. Similar findings have also been made by Djukic et al. (2016) and Charters et al. (2015). This indicates that the removal of large particles does not necessarily contribute significantly to reducing pollutant concentrations. The mere use of sedimentation rates might therefore not be relevant for evaluation of treatment effectiveness, especially concerning removal of dissolved metals and fine particles.

Correlation between heavy metals and fine particles SS63

Due to the importance of fine particles the parameter SS63 was analyzed, presenting ‘Fine Suspended Solids’ between 0.45 and 63 μm (Dierschke & Welker 2015). In this study, the SS63 concentrations were between 26 and 186 mg L⁻¹ with a median concentration of 96 mg L⁻¹ (see Table 1) and comparable to findings in other studies (Dierschke & Welker 2015). Charters et al. (2015) have found that particle size distribution in asphalt road runoff showed consistent peaks centered around 6–10 μm and 70–100 μm, suggesting that the particle size peak around 6–10 μm could be derived from vehicle components such as tires and brake linings. The percentage of particles that are fine particles (<63 μm) ranged from 17–100% for road runoff. At a collector road, a median value of 82% for particles finer than 63 μm was reported by Selbig (2015). Similar findings were obtained in this study with SS63 portions of total particles being mainly above 85%.

Figure 5 shows the metals analyzed in relation to SS63 concentrations. In particular, Zn and Ni exhibited rather strong correlation to fine particles, with Spearman rank order coefficients of 0.8137 for Zn and 0.8615 for Ni. For these parameters, the evaluation of fine particles leads to a rather good estimation of Zn and Ni concentrations in the runoff. The level of significance was below 0.05 for all parameters. As expected, no correlation was observed between dissolved metals and SS63.

Cu and Pb showed weaker correlations to SS63 of 0.6838 and only 0.5417, respectively. Especially for Pb, this is a little surprising since Pb showed a relatively low ratio of dissolved fraction, usually below 10%. The weaker correlations for Cu and Pb might result from outliers measured during the cold season 2015. Street sweeping might also have a distorting effect on particles. Further measurements are needed to confirm these findings. According to Ball et al. (1998), street sweeping only eliminates 15% of the particle fraction <45 μm, but particles up to 240 μm can be re-suspended from road surfaces by air turbulences induced by vehicular traffic and winds. Strong correlations between heavy metals and solids have also been observed by Djukic et al. (2016)
who are suggesting that heavy metals are most likely precipitated rather than adsorbed to the particles.

**CONCLUSIONS**

Road runoff can have a deteriorating effect on the environment. Proper understanding of runoff composition and influencing factors is important for treatment devices. In this study, strong fluctuations were observed and heavy metals exceeding the threshold values in German regulation in untreated runoff.

Strong seasonal variation was observed, with significant concentration increases during the cold season for metals and fine solids. Apparently, de-icing salt is only one factor for increased concentrations in wintry conditions and effects. In addition to higher pollutant concentrations in winter, the distribution between dissolved and particulate fraction of metals also changed. Median values of dissolved fractions were between 19.4 and 37.1% for Zn, Cu and Ni. Pb is found primarily in undissolved from.

But high particulate metal concentrations do not lead automatically to simple removal by sedimentation. Analysed road dust samples showed the highest metals concentrations in the fraction <63 μm for Cd and Zn and the lowest metals concentrations for all metals in the largest particle size fraction >2 mm.

The relatively new runoff parameter SS63 showed significant correlation to total Zn and Ni and lower correlations for Cu and Pb. For Zn and Ni, a good estimation of metals in road runoff can be expected based on SS63 concentrations. SS63 median concentrations were 96 mg L$^{-1}$ reaching up to almost 200 mg L$^{-1}$, representing on average above 85% of total SS. The correlation between metals and fine particles SS63 emphasises that heavy metals in road runoff appear in dissolved form or are most likely attached to very fine particles – that are difficult to eliminate by pure sedimentation processes in treatment devices. Therefore, BMPs only implementing sedimentation have to be investigated closely concerning their effectiveness for treatment of polluted urban road runoff. Possibly subsequent steps are necessary in order to achieve effective pollutant removal.

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