Science of the Total Environment 407 (2009) 4665–4672

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Phthalates and nonylphenols in urban runoff: Occurrence, distribution and area emission factors

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ARTICLE INFO

Article history:
Received 8 December 2008
Received in revised form 6 April 2009
Accepted 23 April 2009
Available online 19 May 2009

Keywords:
Catchment area emission factors (CAEFs)
Fate modeling
Nonylphenol
Phthalate
Sediment
Stormwater

ABSTRACT

The urban water system is believed to be an important sink for the nonpoint-source pollutants nonylphenols and phthalates. The presence of nonylphenols (NPs), nonylphenol ethoxylates (NPEOs), and eight phthalates was analyzed in urban stormwater and sediment from three catchment areas in Sweden. Emission loads for these substances were then calculated for a specific urban catchment area. In addition, substance distribution in road runoff passing through a sedimentation facility was modeled using a modified QWASI-model for chemical fate. High concentrations of DEHP, DIDP and DINP (≤48, 66 and 200 µg/g dw, respectively) as well as nonylphenol mono- and di-ethoxylate (6.6 and 20 µg/g dw, respectively) were found in the sediment. Aqueous concentrations of the pollutants varied considerably; branched NP was detected in concentrations up to 1.2 µg/L, whereas di(2-ethylhexyl) phthalate (DEHP), diisodecyl phthalate (DIDP), and diisononyl phthalate (DINP) were the most frequently detected phthalates in concentrations up to 5.0, 17 and 85 µg/L, respectively. The fate modeling demonstrated that predicted substance levels in water agreed well with measured levels, whereas the modeled sediment levels were underestimated. Calculation of catchment area emission factors from an urban highway environment revealed that as much as 2.1 kg of total phthalates and 200 g of NP and NPEOs may be emitted per hectare and year. The results indicate that all monitored phthalates, branched NPs and lower NPEOs are present in Swedish urban water systems. The long-chain phthalates DIDP and DINP are believed to occur at higher concentrations than other phthalates because of their higher environmental persistence and their increasing use in Sweden.

1. Introduction

Nonylphenols (NPs) and phthalates such as di(2-ethylhexyl) phthalate (DEHP) and dibutyl phthalate (DnBP) have evoked interest in the past decade because of their toxicity to aquatic organisms and endocrine disrupting effects (Jobling et al., 1996; Heudorf et al., 2007). These compounds are additives used in for example plastics and detergents, with a global production of approximately 4 million tons per year for phthalates (Lin et al., 2003) and 500 000 tons per year for nonylphenol ethoxylates (NPEOs) (Ying et al., 2002).

The occurrence of NP/EOs (NP and NPEOs) (Ying et al., 2002; Mayer et al., 2007) and specific phthalates (Lin et al., 2003; Vethaak et al., 2005) in natural water environments has been observed worldwide. The distribution and fate in aquatic environments have been reported for both NP/EOs (Ferguson et al., 2001; Huang et al., 2007) and phthalates (Staples et al., 1997; Cousins et al., 2003). Degradation of NPEOs involves a stepwise loss of ethoxy groups, generating shorter-chain NPEOs, nonylphenol ethoxycarboxylic acids and NP (Jonkers et al., 2001; Mayer et al., 2007). Shorter-chain NPEOs and NP show high affinity to suspended material in aquatic systems, and sediment is an important sink for these substances in natural waters (Isobe et al., 2001; Ying et al., 2002). In the case of the phthalates, the log octanol–water partitioning coefficient (K_{ow}) increases with molecular weight (MW), leading to the predominant partitioning to soils, suspended solids and sediments (Staples et al., 1997; Cousins et al., 2003). Due to effective microbial degradation, phthalates are not expected to persist in the environment, especially not short-chain phthalates under aerobic conditions (Peterson and Staples, 2003).

Stormwater is a major pathway for the spreading of nonpoint-source pollutants from urban environments. Previous stormwater research has focused mainly on nutrients, heavy metals, organic and particulate matter, and polycyclic aromatic hydrocarbons (PAHs) (see e.g. Brown and Peake, 2006; Kayhanian et al., 2007). Knowledge concerning the emission, occurrence and fate of other specific organic contaminants in urban runoff is poor (Rule et al., 2006; Eriksson et al., 2007). Compared to for example metals and nutrients, for which extensive series of data can be found, the costly and time consuming analysis of many organic pollutants has led to the fact that only a limited number of samples are usually analyzed and reported. Reports

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doi:10.1016/j.scitotenv.2009.04.040

on the occurrence of nonylphenols and phthalates in stormwater are no exceptions (Makepeace et al., 1995; Rule et al., 2006). To the authors' knowledge, the presence of diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP), which are currently used in large quantities as plasticizers, has not previously been examined in urban matrixes.

Because many water pollutants are associated with particulate matter, sedimentation practices have become important measures to reduce runoff pollution. The behavior of metals and nutrients in sedimentation facilities such as basins and ponds has been studied (German and Svensson, 2005; Marsalek et al., 2006), whereas the fate and distribution of phthalates and NPs have not been previously reported.

The objectives of this study were: (i) to determine the occurrence of nonylphenol, nonylphenol ethoxylates and eight phthalates in urban stormwater and stormwater sediment, (ii) to calculate the catchment area emission loads of the substances to stormwater, and (iii) to clarify the pollutants' fate and distribution in different compartments, for example sediment and air, in relation to runoff water using an environmental fate model. Stormwater from two residential areas and a high-density traffic area, and sediments from a facility treating road runoff, were sampled and analyzed regarding NP/EOs and phthalates. The emission factors of the compounds were estimated for the traffic area on the basis of measured sediment mass and analyzed pollutant concentrations. To further investigate the fate of the above-mentioned substances in the stormwater system, a simulation was performed using a modified QWASI-model (Quantitative Water Air Sediment Interaction) (Mackay et al., 1983). The results reported here contribute to an understanding of how these contaminants are distributed in different urban matrixes as well as forming a basis for further modeling, risk assessment and selection of treatment technology.

2. Materials and methods

2.1. Study sites

Stormwater sampling was performed in two urban residential areas in Stockholm, Nybohov and Skarpnäck, and one catchment area dominated by the E6 highway in Gårda, Göteborg (all in Sweden). In all catchments, storm runoff is separated from sanitary sewers. General properties of the study sites can be found in Table 1.

The sediment samples were collected in the Gårda sedimentation facility, where stormwater passes a series of seven underground chambers with a total volume of 122 m^3. After 40 h of detention, the stormwater is pumped into the nearby Mölndal stream. If the sedimentation chambers are full and precipitation continues, excess stormwater is directly discharged into the stream.

Table 1
Properties of the catchments where stormwater was sampled.

Catchment	Nybohov (Stockholm)	Skarpnäck (Stockholm)	Gårda (Göteborg)
Characteristic	Urban residential (2000 residents). Built in the 1960s, newly renovated roofs and exterior details.	Suburban residential (3000 residents). Built in the 1980s.	E6 Highway, sedimentation facility for treating runoff.
Area (ha)	3.9	7.7	5.1
Impervious area (ha)	2.6	6.2	2.1
Land use (% of impervious area)			
Roads	5	13	82
Roofs	30	43	6
Other imp. areas[a]	65	44	12
Average daily traffic[b]	960	2000	85 700
Sampling equipment used			
Flow meter	Mainstream	Swedmeter LFT 3000	ADS 3600
Automatic sampler	Xian 1000	Level Control WS 3000	ISCO 6700

[a] For example footpaths and parking spaces.
[b] Number of vehicles. Includes passenger cars, motorbikes and heavy vehicles.

2.2. Stormwater and sediment sampling

A total of 13 storm events were sampled in the three catchment areas during June and October 2006. June was exceptionally dry with few, but rather heavy showers, as opposed to October with longer storm events. The intention was to sample water during the entire period from June to October, but the unusually dry summer did not allow samples to be collected from July to September. To allow accumulation of pollutants on the urban surfaces, stormwater samples were collected if the antecedent dry period exceeded 24 h. Area–velocity flow meters and automatic water samplers were installed in all catchments, allowing flow-weighted samples to be collected for the duration of the storm. Samples were pooled to represent event mean concentrations (EMCs) of the pollutants in water from a given storm event.

Water was also collected at the outlet of the Gårda sedimentation facility. Outgoing water was sampled at non-uniform time intervals adjusted to the emptying time of the facility, thus providing volume-representative subsamples.

The Gårda facility was emptied of water prior to sediment collection from chambers number 1, 3, 5 and 7. The sediment age at the time of sampling was 32 months. From each of the four chambers, three subsamples, which were thoroughly mixed, were collected manually using a metal core sampler.

No materials or products known or suspected to contain NP/EOs or phthalates were used during sampling and sample treatment. Teflon tubing was employed and samples were collected in thoroughly washed glass bottles. Samples were sent in coolers to the analyzing laboratory the same day as sediment sampling and at the end of the storm events.

2.3. Chemical analysis

All chemical analyses of stormwater and sediment were carried out by certified laboratories. In order to ensure quality, stormwater and sediment were sampled at three catchments in Stockholm (different from the areas used in the current study) and analyzed for DEHP and NP/EOs at four certified laboratories (Wahlberg and Wistrand, 2006). The results varied between the laboratories, and the variances in concentrations were explained by the different extraction and clean-up methods used. The laboratory with the most uniform results from the interlaboratory study, and the lowest detection limits (d.l.) for the compounds to study, was selected for this project.

The phthalates were extracted from unfiltered water samples by liquid–liquid extraction with a mixture of ethyl acetate/cyclohexane (1:1) and from sediment samples shaken with acetone and hexane/acetone (1:3). The evaporated extracts were analyzed for the eight phthalates: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), butyl benzyl phthalate (BBP), dioctyl phthalate (DOP), di(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP); following a standardized procedure with GC-MS.

Nonylphenol and ethoxylates (mono–hexa; NP1EO–NP6EO) were extracted from the unfiltered stormwater samples by liquid–liquid extraction with dichloromethane; derivatized by MSTFA (N-methyl-N-(trimethylsilyl)trifluoroacetamide), followed by a GC-MS standardized analysis of the evaporated extracts. Nonylphenol and ethoxylates in sediments were extracted using acetone and hexane, and dried with sodium sulfate prior to GC-MS analysis. As a quality control, 4-NP (branched) and NP1EO–NP6EO in water and sediment were also analyzed by another certified laboratory. Water was analysed

Table 2
Physical–chemical property data[a], and reference water and sediment concentrations of phthalates and NP/EOs used for the QWASI-modeling.

Chemical compound	DBP	DEHP	DINP	DIDP	4-NP, branched	NP1EO
MW (g/mol)	278.4	390.6	418.6	446.7	220.4[b]	264.4[b]
Melting point (°C)	−35	−46	−48	−46	−8[c]	−6[c]
Water solubility (mg/L)	9.9	2.5×10^{-3}	3.8×10^{-4}	2.0×10^{-4}	5.4[d]	3.0[d]
Vapor pressure (Pa)	4.7×10^{-3}	2.5×10^{-5}	6.8×10^{-5}	1.8×10^{-6}	0.02[c]	5.5×10^{-5}[c]
Log K_{ow}	4.3	7.7	8.6	9.5	4.5[b]	4.2[b]
$T_{1/2}$ water (h)	60	530	1200	1200	960[e]	960[e]
$T_{1/2}$ sediment (h)	5500	5500	5500[f]	5500[f]	1440[e]	1800[e]
Concentrations used for comparison of QWASI-model results and measured data (standard deviations in parenthesis)[g]						
Incoming water ($n=5$, μg/L)	0.11 (0.10)	1.6 (1.8)	19 (33)	4.0 (6.5)	0.11 (0.070)	0.36 (0.45)
Outgoing water ($n=2$, μg/L)	0.68	<d.l.	1.1	0.78	0.26	<d.l.
Sediment ($n=4$, μg/g dw)	0.35 (0.050)	42 (9.7)	160 (43)	53 (13)	1.2 (0.24)	5.4 (2.0)

[a] Unless otherwise stated, the reference to the property data is Staples, 2003.

[b] Ying et al., 2002.

[c] ECB, 2002.

[d] Ahel and Giger, 1993.

[e] Chang et al., 2004; Yuan et al., 2004.

[f] No reference found, data estimated.

[g] Based on measurements of stormwater and sediment from the Gårda sedimentation facility. Mean value of incoming and outgoing water concentrations, and sediment concentrations. In the case of NP1EO and DEHP, the compounds were not detected in outgoing water from the sedimentation facility, thus half the d.l. was used for further calculations.

according to the method described by Wahlberg et al. (1990). The sediment samples were homogenized and extracted with methyl tert-butyl ether. Prior to GC-MS analysis, silica gel was used for extract clean-up and MSTFA for derivatization.

2.4. Calculation of emission factors for the Gårda catchment area

The specific catchment area emission factors (CAEFs) describe the annual load of phthalates and nonylphenols emitted per hectare impervious area (g/(ha yr)) to the stormwater system in the Gårda catchment. The CAEFs are based on pollutant loads in the sedimentation facility, and calculations of pollutant masses assumed to reach the receiving waters with outgoing water from the facility.

The sediment loads were calculated from the analyzed dry weight pollutant concentrations and measured sediment masses in the Gårda facility (see Table S1 of Appendix A, for full details). Mass balances for the entire system, that is both treated and overflow water, have earlier been presented by Pettersson et al. (2005). Treated water was sampled at the outlet of the facility; non-settled particles and material resuspended from the sediment is therefore accounted for in the mass balance. Pettersson's study reveals that the average removal efficiency (RE) was approximately 20% for parameters of varying character, including total suspended solids (TSS), volatile suspended solids (VSS), PAHs and several metals. The REs are dependent on the substances' ability to adsorb to suspended solids, which is controlled by physical–chemical properties such as the K_{ow}, and the characteristics of the particles (Ying et al., 2002; Cousins et al., 2003; Pettersson et al., 2005). The low MW phthalates DEP and DMP have K_{ow} values indicating low partitioning to suspended solids, but all analyzed compounds do, to some extent, have the ability to adsorb to suspended solids, and sediment is an important sink for these elements in the aquatic environment (Isobe et al., 2001; Cousins et al., 2003; Mayer et al., 2007; Wang et al., 2008; Zeng et al., 2008). An RE of 20%, implying that 80% of the pollutant load will be transported out of the facility, was therefore used for estimating the loads of phthalates and nonylphenols entering the receiving water.

2.5. Chemical fate modeling of the Gårda sedimentation facility

To give a rough idea of the fate of the substances once they have entered the treatment system in Gårda, a fate modeling exercise was performed, using the QWASI-model (Mackay et al., 1983). The model has mainly been applied to describe chemical fate in rivers and lakes (see e.g. Woodfine et al., 2000; Warren et al., 2002) and has not previously been used for the current purpose. The model describes chemical fate in an air–water–sediment system at steady state. The steady state assumption is questionable in the Gårda case since the sewer is regularly emptied and water flows thus vary over time. The model was, however, regarded as a useful tool for a first screening simulation to indicate whether it would be of interest to develop a more sophisticated model for the stormwater system.

4-nonylphenol, DnBP and DEHP were selected as model substances; the latter two representing low MW and high MW phthalates, respectively. Due to the increasing use of DINP and DIDP, these substances were also considered interesting to model.

The QWASI-model requires input data in the form of the physical–chemical properties of the compounds (Table 2) and characteristics of the water system. Calculations of sedimentation rates, and characteristics adapted to dimension the system can be found in Appendix A.

To evaluate the performance of the model and its applicability, simulations were initially run using measured concentrations of selected compounds in ingoing water to the sedimentation facility as input data (Table 2). Model outputs, in the form of bulk aqueous concentration and concentration in sediment solids, were then compared with measured data. Ideally, site mean concentrations of the substances in water should have been used in the modeling to reflect the performance of the system during a longer period of time. The collection of stormwater during long time periods was, however, not technically possible, therefore averaged concentrations were used for the modeling.

A second simulation was carried out using identical, hypothetical ingoing concentrations for the different compounds, for the purpose of investigating the system's relative ability to remove the various substances from the water phase.

3. Results and discussion

3.1. Water samples

The aqueous concentration of detected phthalates and NP/EOs can be found in Fig. 1A and B, respectively (more details in Appendix A, Table S3). The detection limit (d.l.) for each phthalate was 0.10 μg/L, except for DEHP, for which d.l. was 1.0 μg/L. For all nonylphenolic compounds d.l. was 0.20 μg/L, except for 4-NP, for which d.l. was 0.1 μg/L. The number of samples from Nybohov was three, and five each from Skarpnäck and Gårda. All concentrations refer to the water

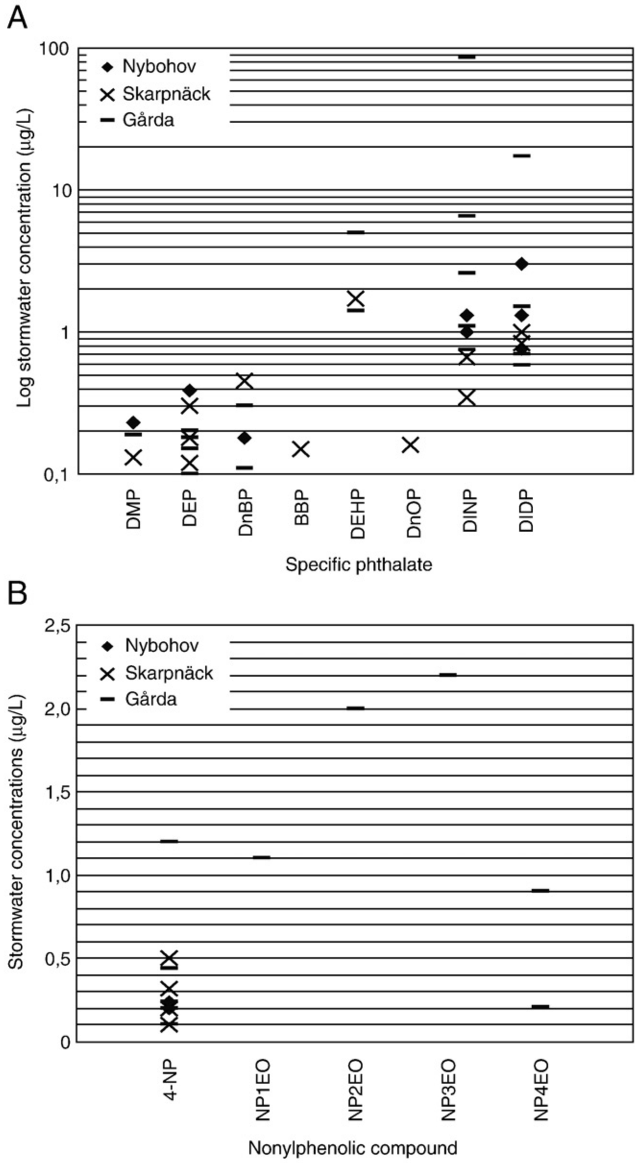

Fig. 1. Concentrations of detected phthalates (A) and nonylphenolic compounds (B) in stormwater from Nybohov, Skarpnäck and Gårda.

phase with particles included. No further summary statistics are presented due to the many sample concentrations below d.l.

3.1.1. Phthalates

Observed concentrations of phthalates were in many water samples close to, or below d.l. All examined phthalates occurred, however, in detectable levels in one or more stormwater samples. The concentrations of phthalates varied significantly (Fig. 1A); one storm event in Gårda had high levels of DINP (85 µg/L), DIDP (17 µg/L) and DEHP (5.0 µg/L), compared to the lower MW phthalates, DMP, DEP, DnBP and BBP (all ≤0.3 µg/L). The detection frequencies for the phthalates were highest for DIDP and DINP (69%), followed by DEP (62%), DnBP (31%), DMP and DEHP (23%), and BBP and DnOP (8%). Measured DnBP and DEHP concentrations, ranging from <0.10 to 0.45 and from <1.0 to 5.0 µg/L, respectively, were considerably lower than the Canadian freshwater quality guidelines for the protection of aquatic life (no Swedish guidelines exist) of 19 and 16 µg/L, respectively (CCME, 2008). DINP and DIDP showed the highest EMCs during the same storm event and the highest relative composition of total phthalate concentration in all samples, in the following order: DINP (72%) > DIDP (19%) > DEHP (5.9%) > DEP (1.2%) > DnBP (0.76%) > DMP (0.40%) > DnOP (0.12%) > BBP (0.11%).

The small series of sampled storms did not allow testing for any significant difference between the three catchment areas. However, the highest phthalate detection frequency, EMCs as well as the highest sum-concentrations for all storm events were detected in the high-density traffic area Gårda. These findings suggest that the pollutants may occur in higher amounts in the vicinity of a traffic route compared to in residential areas. Phthalates are mainly used as plasticizers in PVC-products such as coated panels and cables (Heudorf et al., 2007). Vehicle components and reclaimed asphalt (Norin and Strömvall, 2004) have also been identified as potential sources, which implies that the phthalates found in the highway area are likely to have a traffic-related origin.

There are very few published results on the concentrations of phthalates in stormwater for comparison, and no study presenting the occurrence of DINP and DIDP in urban matrixes has been found. Screenings performed in the early 1990s revealed higher concentrations of several phthalates in stormwater compared to results from the current study; from less than ten times greater for DnOP and DEHP (Makepeace et al., 1995) up to 140 times greater for BBP (Pitt et al., 1995). More recent results from Rule et al. (2006) showed DEHP concentrations up to 1.5 µg/L, i.e. the same magnitude as concentrations found in the current study. The higher concentrations found in older studies may be explained by the difference in used amounts of phthalates a decade ago and the current situation.

3.1.2. Nonylphenols and nonylphenol ethoxylates

Branched 4-nonylphenol was detected at concentrations up to 1.2 µg/L (Fig. 1B) in more than half of the stormwater samples (detection frequency 57%), whereas the straight-chain 4-n-NPs were below d.l. in all samples. NP1EO (1.1 µg/L), NP2EO (2.0 µg/L), NP3EO (2.2 µg/L) and NP4EO (0.90 µg/L) were detected in the same single sample from Gårda, whereas NP5EO and NP6EO were below d.l. in all samples. The concentrations of nonylphenol and its ethoxylates in the sample from Gårda exceeded the Canadian water quality guideline for the protection of aquatic life (no Swedish guidelines exist) of 1.0 µg/L (CCME, 2008). It can be concluded that, in the samples where the NP/EOs could be detected, they occurred in low concentrations close to the d.l. However, in most stormwater samples, the nonylphenolic compounds could not be detected.

From the Stockholm interlaboratory study, NP, NP1EO and NP2EO were found in higher concentrations; ≤0.57 µg/L, ≤1.9 µg/L and ≤5 µg/L, respectively (Wahlberg and Wistrand, 2006). Rule et al. (2006) reported NPEO concentrations ranging from <20 µg/L to >400 µg/L in stormwater from an industrialized area. Car washes using detergents which contain NP/EOs were believed to be the major source in this industrial area. NP/EOs are also used in applications such as air entraining agents in concrete (Togerö, 2006) and for lubricant, paint and sealant production (ECB, 2002). In the current study, the highest NP/EO detection frequency and the highest water concentrations were reported for the high-density traffic catchment. However, no specific reason for the slightly higher concentrations of NP/EOs in this area could be identified.

The results from Stockholm and Göteborg indicate highly variable phthalate and NP/EO concentrations in urban stormwater. The highest concentrations in each catchment were observed in June, thus it can be assumed that the heavy rainfall during the fall washed out much of the accumulated pollutants, leading to lower EMCs in October. Other studies have stressed the difficulty in predicting runoff quality with respect to rain characteristics (Egodawatta et al., 2007; Kayhanian et al., 2007), and in the current study, the data set was too small to analyze any relationship between precipitation patterns and aqueous pollutant concentrations.

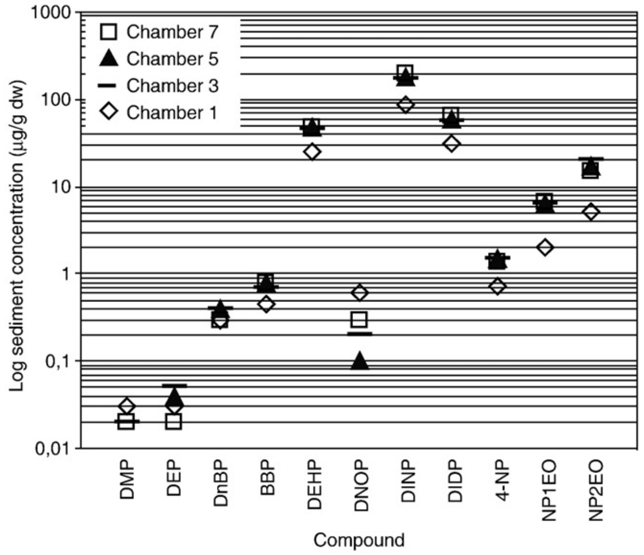

Fig. 2. Concentrations of specific phthalates, branched 4-NP, NP1EO and NP2EO in sediments from the Gårda stormwater treatment facility.

3.2. Sediment samples

3.2.1. Phthalates

As shown in Fig. 2, DINP and DIDP were found in concentrations at least one order of magnitude higher than the low MW phthalates in the sediment; up to 200 and 66 µg/g dw, respectively for DINP and DIDP. The relative composition of phthalates in sediment was highest for DINP with 62%, followed by DIDP 21% and DEHP 17%. The observed low concentrations of short-chain phthalates in water and sediment indicate low total environmental levels in the studied areas.

The higher molecular weight phthalates DINP, DIDP and DEHP showed increasing concentrations in the Gårda sedimentation chambers, with the highest concentrations in chamber 7. The phthalate concentrations were positively correlated with organic content ($0.49 \leq r \leq 0.99$) due to high log K_{ow} values. Earlier studies have shown that the sediment particle size is negatively correlated with the organic content in the Gårda facility (Jakobsson et al., 2006).

Very few published studies on phthalate occurrence in stormwater sediments have been found. In sediments from a stormwater pond in Järnbrott, Göteborg, studied by Strömvall et al. (2006), the DEHP concentration was 23 µg/g dw. In the Stockholm interlaboratory study, the maximum DEHP concentration analyzed was 98 µg/g dw (Wahlberg and Wistrand, 2006). Reported concentrations are in the same magnitude as those detected in Gårda (25–48 µg/g dw), indicating that the Gårda catchment does not exhibit extreme DEHP concentrations.

Previous studies have identified DEHP as the most frequently detected phthalate found at the highest concentrations in urban environments (Makepeace et al., 1995; Vethaak et al., 2005). Results from the current study indicate that DEHP is still present at high concentrations in stormwater and sediments, but it appears not to be the predominant emitted phthalate at the present time in urban areas in Sweden. The high levels and common occurrence of DINP and DIDP, compared to the other analyzed phthalates, correspond well with their increasing use in Sweden during the past decade (Keml, 1992–2006). Since the beginning of the year 2000, DINP comprises approximately 50% of the Swedish plasticizer market volume, DIDP close to 30%, while DEHP has decreased from over 60% to 20% over the last ten years. The relative phthalate distribution in the sediment (sediment age ~3 years) correlates strongly ($r > 0.97$) with the last five to six years' distribution of phthalate usage in Sweden. These findings indicate that the phthalates found in the current study are mainly emitted from fairly new products.

3.2.2. Nonylphenols and nonylphenol ethoxylates

In the Gårda sediment, branched nonylphenols were detected in concentrations of 0.72–1.5 µg/g dw (Fig. 2), whereas straight-chain 4-n-NP was below d.l. in all samples. Of the ethoxylates, only NP1EO and NP2EO concentrations, 2.0–6.7 and 5.1–20 µg/g dw respectively, were above d.l. The concentrations of NP/EOs in sediments exceed the Canadian sediment quality guideline for the protection of aquatic life (no existing Swedish guidelines) of 1.4 µg/g dw for nonylphenol and its ethoxylates (CCME, 2008).

Strömvall et al. (2006) reported values in sediment from a stormwater pond of 4-NP, NP1EO and NP2EO at 3.1, 5.3 and 1.5 µg/g dw respectively. Similar NP/EO concentrations, NP ≤ 3.5 µg/g dw, NP1EO ≤ 2.8 µg/g dw and NP2EO ≤ 0.99 µg/g dw, were measured in sediments in the Stockholm interlaboratory study (Wahlberg and Wistrand, 2006).

The branched NPs are used in commercial mixtures of additives (ECB, 2002) and this fact explains why straight-chain NPs are not found in detectable concentrations in this study. NP/EOs containing between six and 12 ethoxylate groups (EO) are commercially the most significant, but only NPEOs with six or fewer EO groups can be analyzed at many laboratories today. Reports on the analysis of long-chain ethoxylates are starting to appear (see e.g. Loyo-Rosales et al., 2007; Céspedes et al., 2008), still, most reports are on ethoxylates with less than 6 EOs. This implies that only a fraction of all NPEOs present in the environment are detected; a shortcoming that has also been elucidated by Shang et al. (1999). Their study on the occurrence of NP/EOs in marine sediments revealed that the most frequently reported NP, NP1EO and NP2EO made up less than half of the sediment sum-concentrations of total nonylphenols, whereas NP3EO–NP20EO made up the remaining half, suggesting that the total concentration is often underestimated by a factor of 2. Ferguson et al. (2001), however, found that NP4–15EOs made up only a smaller fraction (8.5%) of the total measured NPEO concentration in marine sediments. The predominant occurrence of NP and shorter NPEOs was suggested to be a result of degradation of long-chain NPEOs prior to deposition in the marine environment.

In the current study, NP, NP1EO and NP2EO were detected in sediments whereas higher oligomers (3–6 EOs) were all below d.l. These observations are most likely a result of the stronger adsorption to particulate matter for the more hydrophobic lower oligomers, whereas the long-chain ethoxylates are either present in the water phase or degraded during the transport from the source to the sediment (Ferguson et al., 2001; Mayer et al., 2007; Céspedes et al., 2008). The analyzed concentrations in water may not reveal all the ethoxylates present since water solubility of the NPEOs increases with the number of ethoxylate groups, and ethoxylates with EO > 6 are considered water soluble (Ying et al., 2002). In the current study, only NP1EO–NP6EO analyzed in water, which means that the most water soluble NPEOs were not analyzed and detected.

3.3. Emission factors for the Gårda catchment area

The CAEFs of phthalates and nonylphenols varies from less than a gram per ha for low MW phthalates, to over a hundred grams for NP2EO and up to over a kilogram for DINP (Fig. 3). From the entire Gårda area (2.1 ha impervious area), a total of 340 g of total NP/EOs and as much as 3.4 kg of total phthalates have the potential to reach the recipient Mölndal stream every year. The CAEFs for DMP and DEP are assumed to be underestimated since the CAEFs are based on sediment concentrations and removal efficiencies due to sedimentation, whereas these substances are more likely to remain dissolved and enter the receiving waters with outgoing water (Cousins et al., 2003).

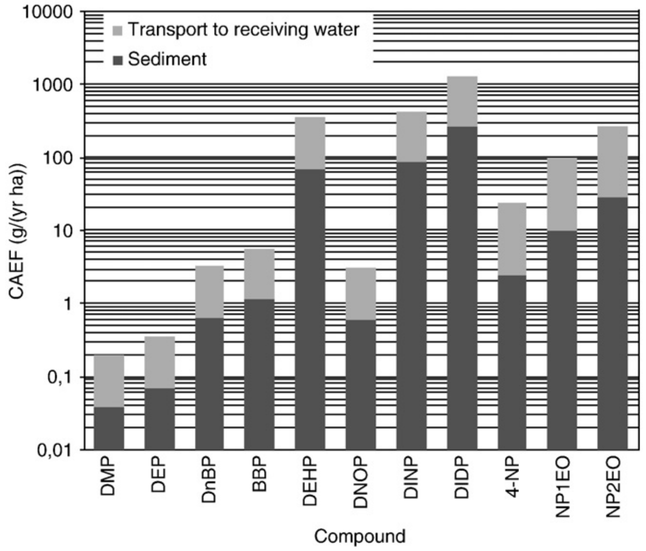

Fig. 3. Total catchment area emission factors (CAEFs) for specific phthalates, 4-NP and NPEOs in the Gårda catchment, expressed as loads accumulated in sediment and loads transported to the receiving water.

The load of NP3EO and higher NPEOs could not be determined, as these oligomers were not detected in sediment, and no average concentration in water or stormwater volumes could be used for this calculation. Therefore, the reported load of nonylphenolic compounds is not complete and total NP-loads are likely to be underestimated.

The calculated CAEFs can be seen as loads expected to occur in an urban highway area similar to Gårda and may be used for predicting flows and fluxes of contaminants in urban environments.

3.4. Chemical fate modeling of the Gårda sedimentation facility

3.4.1. Model applicability

The average ratios between measured/modeled concentrations varied from 0.2 for DINP in water, to 3.9 for NP1EO in sediment (Table 3). The predicted levels in water generally agreed well with measured levels, whereas the sediment levels were underestimated by the model. However, these ratios can be considered satisfactory for this screening modeling, and are in the same order of magnitude as found in other QWASI-application studies (Warren et al., 2002; Dalla Valle et al., 2003). It was observed that sedimentation rates, see Appendix A, did not have a significant influence on the model output and that other factors such as physical–chemical property data were more important.

3.4.2. Predicting chemical fate

Simulations with ingoing aqueous concentrations set to 1.0 μg/L for all the substances were carried out. The highest sedimentation rate of 1600 g/(m^2 day) was chosen for this assessment.

According to the simulation results (Table 3), 4-NP and NP1EO are expected to occur in the highest concentrations in water at steady state; about 5 to 20 times higher than the concentration of individual phthalates. Among the phthalates, DnBP is expected to exhibit the highest concentrations in water. The predicted residence time in water was highest for NP1EO (2.7 days) followed by NP and DnBP (both 1.4 days). The residence time for the remaining phthalates was predicted to be <2 h. Considering the hydraulic residence time in the basin (40 h), it can be concluded that NP1EO poses the highest risk for further spreading into the environment, whereas in particular the high MW phthalates will have deposited in the sediment or degraded before the system is emptied. This phenomenon is directly related to the distribution to particles, which was predicted to be highest for DEHP, DINP and DIDP (between 99 and 100%), and only 3–5% for the remaining substances. At steady state, the modeling shows that resuspension is nearly as fast as sedimentation. The resuspension will, however, vary with time and principally occur when water is flowing in to the facility, and slow down when the flow ceases. The 40 h water detention time in the facility allows re-sedimentation of the disturbed sediment. To evaluate the accuracy of the predictions of partitioning, a larger data set of outgoing concentrations would be needed. In this study, only four samples of outgoing water were analyzed and many samples showed pollutant concentrations below the detection limit.

Biodegradation is believed to be the dominant removal mechanism for phthalates in the natural environment (Staples et al., 1997; Peterson and Staples, 2003). Several studies demonstrate that low MW phthalates are more degradable than their high MW counterparts (Yuan et al., 2002; Peterson and Staples, 2003). This is in agreement with the model results, which indicated that degradation in combination with chemical transformation was the principal removal mechanism for DnBP in the treatment system, whereas the removal of DEHP, DINP and DIDP from the water column is governed by sediment burial.

This modeling exercise should be regarded as an initial investigation of the applicability of chemical fate models to stormwater. The present study indicates that tools such as the QWASI-model may be used, but to optimize the model, an adaptation to the dynamic characteristics of the stormwater treatment system would be required. Considering the large variation in water flows and ingoing

Table 3
Results from steady state QWASI-modeling of the selected phthalates, 4-NP (branched) and NP1EO with a sedimentation rate of 1600 g/(m^2 day).

	DnBP	DEHP	DINP	DIDP	4-NP	NP1EO
Conc. in water: measured/modeled	0.6	n.a[a]	0.2	0.8	0.9	n.a[a]
Conc. in sediment: measured/modeled	3.4	3.8	1.2	1.9	2.4	3.9
Total inflow[b] (g/h)	1.6×10^{-3}	1.6×10^{-3}	1.6×10^{-3}	1.6×10^{-3}	1.6×10^{-3}	1.6×10^{-3}
Concentration in water at steady state (μg/L)	0.99	0.25	0.25	0.25	3.2	5.2
Total amount in water at steady state (g)	0.12	0.030	0.030	0.030	0.39	0.64
Partitioning to particles (%)	3.0	99	100	100	5.0	3.0
Sediment burial (g/h)	1.9×10^{-4}	1.4×10^{-3}	1.5×10^{-3}	1.5×10^{-3}	9.5×10^{-4}	7.9×10^{-4}
Degradation/chemical transformation (g/h)	1.4×10^{-3}	1.7×10^{-4}	1.5×10^{-4}	1.5×10^{-4}	6.2×10^{-4}	6.9×10^{-4}
Transport water–air (g/h)	1.8×10^{-6}	1.3×10^{-7}	1.2×10^{-7}	2.3×10^{-9}	3.3×10^{-5}	1.2×10^{-4}
Sedimentation (g/h)	2.2×10^{-3}	1.6×10^{-2}	1.7×10^{-2}	1.7×10^{-2}	1.1×10^{-2}	9.5×10^{-3}
Resuspension (g/h)	2.0×10^{-3}	1.5×10^{-2}	1.5×10^{-2}	1.5×10^{-2}	1×10^{-2}	8.4×10^{-3}
Residence time in water phase (days)	1.4	0.080	0.080	0.080	1.4	2.7
In comparison to the inflow (%)						
Sediment burial	12	89	91	91	59	50
Degradation/chemical transformation	88	11	9.6	9.6	39	43
Transport to air	0.1	0.0	0.0	0.0	2.1	7.4

[a] Measured concentration below d.l.
[b] Assuming an inflow concentration of 1.0 μg/L for each compound.

concentrations, the steady state assumption is questionable for the Gårda case, and a time-resolved model similar to those that have been developed for sewage treatment plants (Seth et al., 2008) would be desirable.

Results from the fate modeling, as well as chemical analyses, showed that phthalates and NP/EOs are efficiently removed from stormwater when sedimentation is present. Pettersson et al. (2005) revealed that facilities like the Gårda chambers must be carefully designed to optimize the pollutant removal efficiency. The water detention time needs to be adjusted to minimize overflow volumes during large storms, at the same time as the settling of particles is maximized. Shorter detention times may disable the settling of more water soluble compounds such as NP, NP1EO, and DnBP, which have longer residence times in water.

4. Conclusions

Results from the current study show that branched nonylphenol, NP1EO–NP4EO and the analyzed phthalates are present in Swedish stormwater and sediment, but at varying concentrations. The lower MW phthalates and the nonylphenolic compounds often occur at aqueous concentrations close to the detection limit. The high MW phthalates DIDP and DINP were detected at highest concentrations in both stormwater and sediment, which is suggested to be a reflection of the substances' increasing use in Sweden, and their higher environmental persistence compared to other studied phthalates. Most of the analyzed compounds have a high tendency to adsorb to suspended solids in water and stormwater sediment is therefore an important sink for these substances in urban areas. It was estimated that as much as 2.1 kg of total phthalates and 200 g of NP/EOs may be emitted per hectare and year in the Gårda catchment area. The current study indicates that fate models can be useful tools for planning and designing stormwater treatment systems, as these models illustrate the ability of substance deposition, degradation and transportation into and out of the system. To optimize the fate model, an adaptation to the dynamic characteristics of the stormwater treatment system would be required.

Acknowledgements

The research was funded by The Swedish Research Council Formas and the Environment and Health Administration of Stockholm. Klas Öster, Stockholm Vatten AB, and Lars-Ove Sörman, Chalmers, are gratefully acknowledged for their assistance with sampling.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2009.04.040.

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Leaching of additives from construction materials to urban storm water runoff

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ABSTRACT

Urban water management requires further clarification about pollutants in storm water. Little is known about the release of organic additives used in construction materials and the impact of these compounds to storm water runoff. We investigated sources and pathways of additives used in construction materials, i.e., biocides in facades' render as well as root protection products in bitumen membranes for rooftops. Under wet-weather conditions, the concentrations of diuron, terbutryn, carbendazim, irgarol®1051 (all from facades) and mecoprop in storm water and receiving water exceeded the predicted no-effect concentrations values and the Swiss water quality standard of 0.1 µg/L. Under laboratory conditions maximum concentrations of additives were in the range of a few milligrams and a few hundred micrograms per litre in runoff of facades and bitumen membranes. Runoff from aged materials shows approximately one to two orders of magnitude lower concentrations. Concentrations decreased also during individual runoff events. In storm water and receiving water the occurrence of additives did not follow the typical first flush model. This can be explained by the release lasting over the time of rainfall and the complexity of the drainage network. Beside the amounts used, the impact of construction materials containing hazardous additives on water quality is related clearly to the age of the buildings and the separated sewer network. The development of improved products regarding release of hazardous additives is the most efficient way of reducing the pollutant load from construction materials in storm water runoff.

Key words | additives, biocides, construction materials, leaching, storm water pollution, terbutryn

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INTRODUCTION

In urban areas, different pollutants are released from various sources to storm water runoff. Accountable are abrasion processes of road and railway traffic and detached inorganic substances from metal surfaces (Clark *et al.* 2005; Burkhardt *et al.* 2008). Both are leading to the occurrence of heavy metals in runoff in terms of particles and dissolved fractions (Mikkelsen *et al.* 1997). In addition, dust from incineration processes and exhaust emissions deposited during dry weather pollute storm water runoff. Well-known substance groups of organic pollutants in storm water are petroleum-derived hydrocarbons from industrial applications and traffic, and herbicides from maintained lawns, pathways and terraces or insecticides from pests' control (Skark *et al.* 2002). Several organic substances such as diuron, carbendazim, mecoprop, irgarol®1051 and phthalates are found in runoff. Blanchoud *et al.* (2004) reported the highest measured diuron concentration in water due to its use on impervious surfaces. Further substances expected in urban runoff are listed by Eriksson *et al.* (2007) and for surface water by Götz *et al.* (2009).

doi: 10.2166/wst.2011.128

Recently, irgarol®1051 and diuron were detected in small rivers showing no seasonal variation (AWEL 2008). Terbutryn, which is no longer registered as a herbicide for agricultural application in the EU since 2003, has been found in receiving waters of urban water catchments until 2006 (Quednow & Puttman 2007). A mass balance of polychlorinated biphenyls (PCB) in waste water treatment plants illustrates that the major part of the xenobiotics load originates from urban storm water (Rossi *et al.* 2004).

The sources of substances measured in remarkable concentrations are often unknown or uncertain; however, more than a few substances found are used in construction materials. Additives like flame retardants, UV-filters, stabilizers, corrosion inhibitors or plasticisers are on the market and have widespread applications, for example, in paints, plastics and concrete. To date, a limited number of studies has been published on leaching behaviour under laboratory conditions so far (e.g. Cadmus & Brophy 1982; Schoknecht *et al.* 2003; Togerö 2006) and less on field scale (e.g. Bucheli *et al.* 1998). Recently, Schoknecht *et al.* (2009) demonstrated the leachability of several biocides under different test conditions.

Biocides are per se functional additives to control growth of unwanted microorganisms and reduce deterioration of the construction material by microbial activity. The placing of biocidal products on the market is regulated in Europe under the Biocidal Products Directive 98/8/EC (BPD 2000). The application of biocides such as fungicides and algaecides in resin-based paints and renders of facades is state-of-the-art in material protection of organic coatings (Table 1) (Paulus 2005). These products have more than 95% market share on thermal insulated facades and are popular for refurbishments of facades. For a single biocide, typical contents in paints, renders or both layers in combination are in the range of 0.1 to 2.0 g/kg and 0.3 to 4.0 g/m^2, respectively. The different species of fungi and algae require mixtures of 3 to 5 biocides in combination, leading to a total content of nearly 0.5% in renders and exterior paints. Taking additionally into account the typical application practice of facade materials (0.4 kg/m^2 paint, 3.0 kg/m^2 render) and the annual installation of about 8 mio m^2 painted and rendered coatings each in Switzerland, about 50 to 100 tons of biocides are used per year in Switzerland; half in paints and half in renders.

Table 1 | Characteristics of biocides typically used in exterior resin based paints and renders. The concentration ranges have been reported by manufacturers as upper and lower reference values

Active ingredient	In paint, render (mg/kg)	Target organisms	PNEC[a] (ng/L)	Use in agriculture
Diuron	400–2,000	Algae	20	Yes
Terbutryn	300–1,000	Algae	34	No[b]
Irgarol®1051 (Cybutryn)	250–500	Algae	1	No
Carbendazim	300–1,000	Fungi	34	Yes
OIT (Octhilinone)	150–500	Algae/Fungi	13	Yes
DCOIT (SeaNine)	<1,000	Algae/Fungi	8	No

[a] PNEC: predicted no-effect concentration; referred in Burkhardt *et al.* (2009).

[b] Since 2003 not registered as pesticide anymore in EU and since 2008 in Switzerland.

Leachable biocides potentially enter the natural environment (Lindner 1997; Jungnickel *et al.* 2008; Kahle & Nöh 2009). Calculated predicted no-effect concentrations (PNEC) of biocides used as film-preservatives in facades highlight their ecotoxicological effects (Table 1). Additives which are demonstrably leachable as well as persistent and bioaccumulative in the environment are of considerable concern (WFD 2000). In Switzerland about half of the biocides applied in facades are persistent. Some plant protection products used in urban and rural areas may have the same active ingredients (Table 1).

The Swiss Water Protection Directive defines storm water runoff from buildings as generally non-polluted (Swiss Water Protection Directive 1998). In the exceptional cases of pollution storm water runoff has to be treated. For example, treatment of runoff from metal coatings is mandatory, for larger surfaces with suited adsorber systems (VSA 2002). The infiltration of roof runoff from bitumen membranes containing the herbicide mecoprop is restricted. In those cases, runoff has to be discharged to waste water collection systems. However, the hazardous substances may not reach the treatment plant under wet-weather conditions, but directly enter surface waters through storm water overflows. Regarding separate storm water systems, diffuse pollution is of increasing concern since runoff may enter natural water bodies without sufficient treatment in a strongly decentralized way. Treatment is either not feasible or realised with lower efficiency off-site, e.g., by swales or basins.

We investigated the occurrence of organic additives in storm water of a separate sewer system and the leaching behaviour from buildings. Emphasis has been placed on terbutryn used in facades and mecoprop in bitumen membranes. These investigations are completed by leaching studies under defined laboratory conditions.

MATERIAL AND METHODS

Field study

The separate sewer network in an urban catchment nearby the city of Zürich has been characterised regarding potential pollutant sources and sewer nodes (Figure 1). Based on mapping it is supposed that 90% of runoff drain directly to the storm water system from impermeable car parks, flat roofs and facades of residential and commercial buildings. Additives used in architectural coatings and roofing materials were reviewed and initial stock concentrations estimated. Sampling site 1 is connected to four buildings and an underground parking draining an area of about 0.5 ha with a new housing development. The storm water channel is 30 cm in diameter. At site 2, the sub-catchment encloses an area of about 11 ha by a sewer with 1.6 m height and 2.4 m width. All buildings are not older than eight years.

Leaching of terbutryn has been investigated at a recently constructed buildings' facade and of diuron at a facade of a 4 year old building (Figure 1: new and old). Both are west oriented facades showing stronger exposition to weather conditions than the other ones. Alloy gutters were installed at the bottom of each facade to collect runoff in 5 L PTFE-and glass bottles. Water samples were taken during selected rain events over a period of eight months.

Samples from the separate sewer were taken under wet-weather conditions. The occurrence of seven biocides used in material protection products: iodopropynyl butylcarbamate (IPBC), carbendazim, terbutryn, irgarol$^{®}$1051, diuron, octyl-isothiazolinone (OIT), and the root protection agent mecoprop were tracked in the storm water and at the discharge to receiving water (sampling 3). At site 1 and 2 storm water flow was monitored continuously and time proportional samples were taken (Sigma 900 Max, HACH, Loveland, CO). Precipitation was monitored at the field site (OTT Pluvio, Ott GmbH, Kempten).

Laboratory study

The leaching at real facades has been completed by a semi-technical study in a weathering chamber. As typical for building practice, a biocide-free mineral sub-render followed by a resin-based top-render (2 mm grain size, styrene-acrylate binder) containing biocides was applied on a thermal insulation panel (height 2.0 m, width 0.75 m, 0.16 m thick; material: expanded polystyrene foam, EPS). The

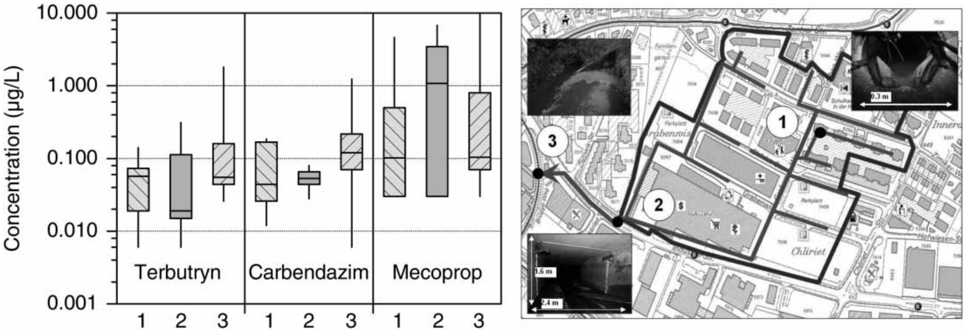

Figure 1 | Concentrations of organic additives determined in water samples (at each site $n = 20$) taken at three sampling sites (left). The results are given as box-plots with median values (horizontal line in the box) and 25%-percentiles (upper and lower boundary of the box) and minima und maxima concentrations represented by the vertical bars. Map of the urban catchment with corresponding sampling sites (right): (1) Area of 0.5 ha with four buildings; (2) about 11 ha catchment; (3) Sampling of discharge to the receiving water.

focus was set on the most persistent biocides diuron, terbutryn, irgarol®1051 and carbendazim. The biocides were spiked to the render each at 0.5 g/kg using formulated market products. Considering an application of 3.0 kg/m^2 render, the final application amount was 1.5 g/m^2 for each biocide. The render obtained from a manufacturer did not contain any biocide as previously arranged. The leaching of the biocides was investigated over the course of 80 sprinkling intervals using tap water. After 20 intervals in five days, two sprinkling-free days followed. Within each interval of 6 h 85 mm were sprinkled in one hour. The temperature was increased twice after 20 and 60 intervals from +50 °C to +60 °C. The hygrothermal cycles have been performed according to ETAG 004 testing procedure for external thermal insulation composite systems (ETAG004 2000). The cumulated sprinkling of 6,800 mm is corresponding to the rainfall of six years in the area of Zurich. During the sprinkling course, 16 runoff events have been sampled. In order to gain information on the leaching within the sprinkling period, 20 time-proportional samples were additionally taken within 5 sprinkling events.

The leaching of mecoprop from flexible bitumen membranes labelled as 'root-resistant' was tested on semi-technical scale (length 2.5 m, width 1.0 m) likewise. Two marketed sealants containing the protection products Preventol®B2 (B2; polyglycolester of mecoprop) and Herbitect® (HE; ethylhexylester of mecoprop) were installed on flat roofs covered with coarse gravel. The contents were normalized to the thickness of the sealants (without shale-coating 4.8 mm), one millimetre of HE-membrane contains about 3.0 g/m^2 and of B2-membrane 6.0 g/m^2 mecoprop as esters. Sprinkling with deionised water has been performed 11 times each of 5 h duration. Eight runoff events were sampled consisting of five time-proportional water samples. The total amount of 1,100 mm in 70 days corresponds with the annual rainfall in Zurich.

Chemical analysis of water samples was performed using solid phase extraction (SPE). Samples from storm water and facades were analysed using high pressure liquid chromatography-tandem mass spectrometry LC-MS/MS. Isotope-labelled internal standards were added for each biocide except IPBC to account for matrix suppression. Quantification limits are in the range of 5 to 30 ng/L. The water samples from bitumen membrane testing under laboratory conditions were analysed by HPLC-UV; the quantification limit was 100 ng/L.

RESULTS AND DISCUSSION

Field study

The collected storm water runoff samples showed substantial differences in biocides concentrations, but all persistent biocides were detected at every sampling site. In the investigated sub-catchment (site 1), four buildings, paved parking lots and roofs are connected to the storm water sewer. Measured concentrations of carbendazim and terbutryn in the storm water runoff reached up to a few hundred ng/L (Figure 1). The data for diuron are not shown because significant concentrations were only determined at sampling site 1. These biocides were applied in exterior paints and renders in this building block. The low concentrations are confirmed by the findings in facades runoff of the aged coatings. Significant contributions of mecoprop originated from sealing membranes in foundations and from green roofs of underground parking. The concentrations were nearly one order of magnitude higher (2 μg/L) compared to the biocides used in the paint and render (Figure 1). It is estimated that between 0.7 and 21 μg/m^2 mecoprop were delivered from root resistant bitumen membranes installed on 2,800 m^2 by every runoff event. The cumulated load varied between 2 and 60 mg mecoprop for a single runoff event.

At the new facade with an initial Terbutryn content of 1.7 g/m^2, concentrations between 100 and 800 μg/L terbutryn were measured in the facades' runoff. In all samples the metabolite desethyl-terbutryn occurred. The concentrations of 30 to 360 μg/L emphasize that terbutryn is degradable by UV-irradiation (Paulus 2005). Compared with PNEC values in aquatic systems, measured concentrations are at least three orders of magnitude higher. Under the same field conditions, runoff water concentrations of carbendazim, diuron and irgarol®1051 measured at the aged building were at least 1,000-times lower than at new building. In some samples biocides were not quantifiable.

The concentration pattern in storm water samples reflects the characteristics of buildings and the drainage network. Beside the amounts of additives used, the age of construction materials and the dilution factor influence the concentration level in storm water. Consequently pollution of storm water may increase along the water pathway down to the receiving water if the pollutants load from urban sources increase or *vice versa*. Diuron, for example, measured in remarkable concentrations at sampling site 1 (sub-catchment) has not been found in a comparable range in samples of site 2 and 3. The dilution with storm water not polluted with diuron reduced the concentration and load, respectively. On the other hand, the median concentrations of some additives tend to increase from the drains nearby buildings up to the receiving water. For instance, mecoprop and terbutryn were detected in higher concentrations at sampling site 3 compared to site 2 and 1 (Figure 1). Just before storm water is discharged into the brook, maxima concentrations of terbutryn, carbendazim and mecoprop of 1.8, 1.1 and 10 µg/L were measured (Figure 1, maxima values at site 3). The same has been observed for carbendazim. In the case of terbutryn the occurrence pattern in storm water gives further advice. This biocide is applied exclusively in exterior facades. Terbutryn can be used as an excellent tracer for coatings.

Quite a number of substances in urban areas are transported with a first-flush phenomenon. According to the definition of Bertrand-Krajewski *et al.* (1998), at least 80% of the total substance load has to be transported in the first 30% of the volume discharged during rainfall events. Surprisingly, the studied additives did not occur with a first flush in storm water, neither at the sub-catchment site nor at the larger catchment (Figure 2). The concentrations indicate a highly diffuse transport mechanism. The occurrence seems to be triggered by a continuous release during rainfall on the one hand, and the complexity of the drainage network on the other hand. In the case of the drainage network: firstly, runoff from the source has to enter the drains and secondly, the runoff from drains installed around buildings has to enter the larger storm water system. This complex pathway is accountable for the delayed transport of additives regarding measured rainfall and runoff (Figure 2). Consequently, the main drivers are rainfall intensity and duration. Orientation of the facade, roof overhang, wind direction and wind speed are additional factors influencing runoff at facades. Under the conditions relevant for mecoprop, the sub-soil installations react even more slowly than top-roof installations covered with gravel. Thus the two different applications release mecoprop in quite different dynamic behaviour to the storm water.

The natural brook reflects the storm water quality of the urban catchment to some extent. In the receiving water, concentrations were recorded in the same order of magnitude during several rainfall events. Under wet-weather conditions the brooks seem to be dominated by storm water discharge form separate sewers. These measured concentrations in receiving water were higher than the PNEC-values and frequently higher than the Swiss value claimed for surface

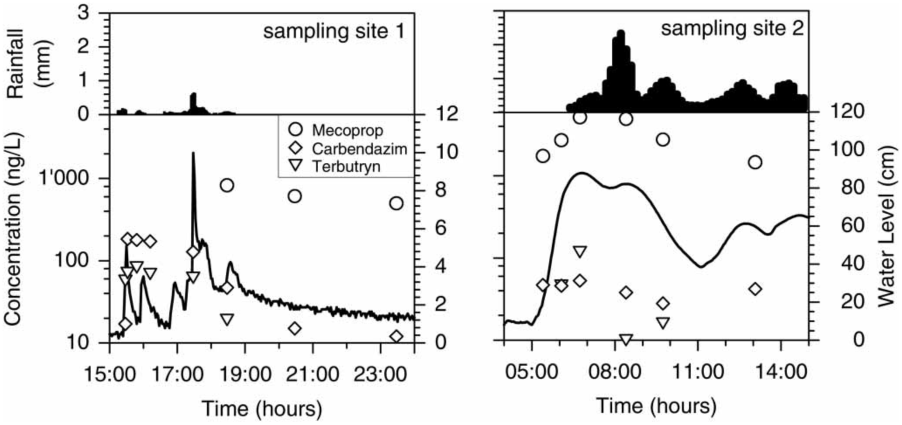

Figure 2 | Concentrations of additives detected in storm water sample taken from the sub-catchment (sampling site 1: 0.5 ha) and the larger catchment (sampling sites 2: 11 ha). The rainfall amounts, water level of runoff and measured concentrations for two different runoff events are shown.

water (0.1 µg/L per biocide). Only the additives IBPC and OIT were not detected in any sample taken from storm water and the natural brook. Both biocides are known as fast degradable substances and do not persist.

Laboratory study

In over 80 runoff events, the biocide concentrations in facade runoff decreased between one and two orders of magnitude (Figure 3). Under the studied conditions maximum concentrations were between 7,000 µg/L for diuron and 700 µg/L for carbendazim measured in the first litre of the initial sprinkling interval and about 70 µg/L diuron and 40 µg/L carbendazim in the first litre of the last interval (Figure 3). The concentrations after the 5th runoff event are in the range as observed on field scale for new facades material. Figure 3 shows that higher temperatures enhance the diffusion to the surface of the coating. A temperature increase from +50 °C to +60 °C increases the concentrations in runoff substantially.

Diuron with 42 mg/L water solubility is washed out with the highest concentrations. The concentrations of the triazines, terbutryn and irgarol®1051 as well as of carbendazim are consistently lower demonstrating that water solubility is an important parameter for leaching. However, the leaching of both triazines is very similar despite their different water solubility of 7 mg/L for irgarol®1051 and 25 mg/L for terbutryn. On the other hand the water solubility of carbendazim (8 mg/L) and irgarol®1051 is the same, but leached concentrations are about 1.5 to 2 times lower over the entire experimental period. The transport processes seem to be additionally influenced by further parameters like partitioning between solids and water phase in facades, substance specific diffusion and enrichment at the coatings surface. Recently, Schoknecht *et al.* (2009) have shown for these biocides the same ranking of leachability and explained the losses by physicochemical properties. Additionally, they concluded that release of biocides is diffusion-controlled.

The losses in runoff reached about 29% diuron, 21% terbutryn, 19% irgarol®1051, and 7% carbendazim, all calculated relatively to the amount of each biocide (1.5 g/m^2) added to the render. The mass balance has been completed by the extraction of the weathered render. Consequently, under real weathering conditions diuron is likely to be leached five times more quickly than carbendazim. During the first sprinkling interval totalling 85 mm, the load reached already 1.5% of the entire losses. After 5,100 mm sprinkling over 60 intervals, the load in the 61st interval was only 0.1% and the same thereafter. The results of fast release fit well our field observations. However, losses at facades in the field with a limited amount of runoff are about one order of magnitude smaller than under the laboratory conditions established.

Biocide concentrations do not only decrease over the 80 intervals, but also during individual runoff events. For terbutryn, as an example, a difference of one order of magnitude between the concentration measured in the first and the last of totally 85 L/m^2 runoff was found (Figure 4). Within the first ten minutes already 50 to 60% of the 60 min event-based loads occur in runoff. According to driving rain under real weather conditions, it seems reasonable that even short rain events stimulate significant loads in runoff.

The installation of root-resistant bitumen membranes on flat roofs is the main source of mecoprop in storm water

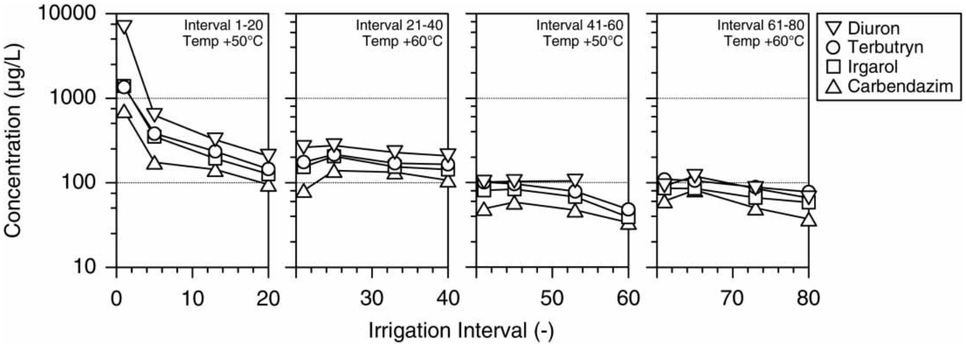

Figure 3 | Leaching of biocides used in renders over 80 sprinkling intervals. The temperature was increased from +50 °C to +60 °C before the 21st and the 61st interval. The concentrations are plotted logarithmically.

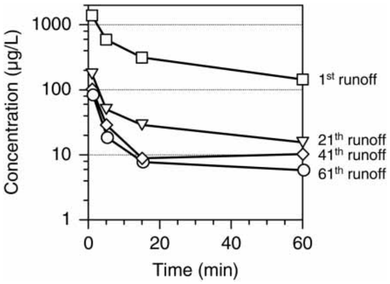

Figure 4 | Concentrations of terbutryn in facades runoff within the 1st, 21st, 41st and 61st irrigation interval each of 60 min period. The concentrations are plotted logarithmically.

runoff in the studied catchment. Bucheli *et al.* (1998) identified hydrolysis as the main process of mecoprop release for B2. Thus the release of mecoprop from the root protection products B2 and HE used in bitumen membranes has been investigated on semi-technical scale.

The results demonstrated that the root protection product B2 caused significant higher leaching rates than the product HE (Figure 5). Concentrations of mecoprop leached from B2 membranes were in the range of a few hundred micrograms at the beginning and decreased by two orders of magnitude to about 1 to 10 µg/L over the entire irrigation course. The concentrations in runoff samples from HE-membranes were by a factor of 10 to 20 times consistently lower, although the amounts in the membranes differed only by a factor of 2.

The mecoprop load was derived from runoff volume and measured concentrations. The B2-membrane released 12.4 mg/m^2 mecoprop and HE-membrane 1.1 mg/m^2 (Figure 6). These losses are corresponding to 0.2% B2 and to 0.04% HE of the amounts added into the upper millimetre of the membranes. The cumulated losses after 1,100 mm sprinkling within 11 intervals confirm a difference of a factor of 10 between both products. For the first two samples the difference is even larger. Obviously the ethylhexylester of mecoprop in HE is less susceptible to hydrolysis than the polyethylene glycolester present in B2. These results demonstrate that changing the material from B2 to HE as a typical measure of source control is a very successful approach to limit storm water pollution from organic additives.

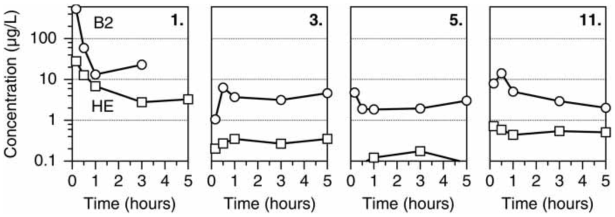

Figure 5 | Concentrations of mecoprop leached from bitumen membranes containing Preventol®B2 (B2) and Herbitect® (HE). The results of the 1st, 3rd, 5th, and 11th runoff event are shown. Both membranes were installed on a semi-technical gravel-covered flat roof and irrigated. The input-concentrations were a factor of 2 higher in the B2- compared to the HE-membrane. The concentrations are plotted logarithmically.

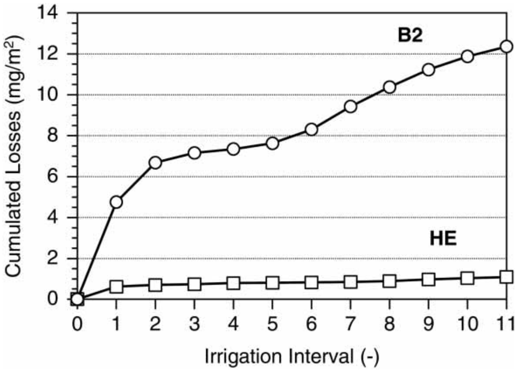

Figure 6 | Cumulated mecoprop losses calculated on the basis of the 5 h composite concentration and the runoff amount for 11 events. The bitumen membranes contain Preventol®B2 (B2) and Herbitect® (HE). Initial concentrations in membranes differed by a factor of 2.

CONCLUSIONS AND OUTLOOK

Our results clearly show that large amounts of additives used in building envelopes and applied on land, enter storm water and receiving waters by separate storm water discharge. All persistent additives were detected in the separate sewer network. The storm water quality is affected by age, surface area and composition of the building material, concentration and substance properties, the hydrologic weather conditions, and the hydraulics of the drainage system. The age profile of the buildings in the catchment has a considerable influence on biocide concentrations and load. New and refurbished facades primarily contribute to the sewer loads especially at higher facades temperatures. Even short rain events contribute to the pollutant loads in runoff. From facades, the release of diuron is about factor two faster than terbutryn and irgarol®1051 followed by carbendazim. Only OIT and IPBC release from facades do not lead to surface water pollution due to the rapid transformation of both biocides.

At new buildings the concentrations in runoff are several orders of magnitude above the ecotoxicological effect values derived by the PNEC versus measured environmental concentrations (MEC) and temporary in receiving waters. However, at the present time it is hard to assess temporary ecotoxic effects of organic pollutants to aquatic organisms attributed to the rainfall pattern due to knowledge gaps regarding fluctuating pollutant loads. Thus PNEC/MEC ratios give not more than a rough estimate.

The pollutant load at the discharge point of urban storm water systems into receiving water gives limited information on the pollutant sources as long as the water catchment is not well characterised regarding type, amount and location of applied xenobiotics. Thus, the identification of urban sources is of particular importance for sustainable storm water management and a prerequisite for on-site treatment measures and source control. Proper treatment technologies are requested in the context of efficient soil and water protection and represent the forthcoming challenge of storm water management.

Source control measures are of particular importance for economically and environmentally sustainable water protection. On the basis of our laboratory and field study results, the three most important manufacturers of bitumen membranes in Switzerland have revised their formulations and switched either to HE or to Preventol®B5 (ocytlester) – a root protection product newly developed with leaching characteristics like HE. B2 is no longer being used. This example demonstrates the possible support of applied research studies and the necessary willingness of the producers to develop more sustainable products in favour of the water environment.

ACKNOWLEDGEMENTS

We thank our Eawag colleagues from the Department for Environmental Chemistry for their support in the analysis of field samples and from the Department of Process Engineering for their assistance in laboratory and field work. The project is funded by grants from the Swiss Federal Office for the Environment (FOEN) and the Zurich Cantonal Office for Waste, Water, Energy and Air (AWEL). We thank for the excellent support from manufacturers of biocides and construction materials.

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Science of the Total Environment 541 (2016) 895–919

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Critical review of heavy metal pollution of traffic area runoff: Occurrence, influencing factors, and partitioning

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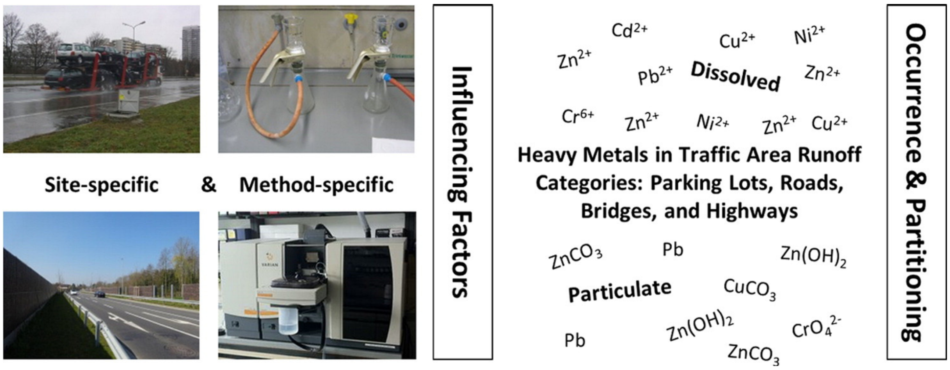
HIGHLIGHTS

- Heavy metal runoff concentrations in parking lots, bridges, and roads
- Large dataset of dissolved and total metal concentrations in traffic area runoff
- Description of site-specific and monitoring method-specific factors
- Summary of traffic-related and anthropogenic heavy metals in road runoff
- Reduction in Pb concentrations over time is one of the robust chemical results.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 June 2015
Received in revised form 7 September 2015
Accepted 7 September 2015
Available online xxxx

Editor: F.M. Tack

Keywords:
Bridge
Dissolved heavy metals
Highway
Parking lot
Road
Site-specific factor

ABSTRACT

A dataset of 294 monitored sites from six continents (Africa, Asia, Australia, Europe, North and South America) was compiled and evaluated to characterize the occurrence and fate of heavy metals in eight traffic area categories (parking lots, bridges, and three types each of both roads and highways). In addition, site-specific (fixed and climatic) and method-specific (related to sample collection, preparation, and analysis) factors that influence the results of the studies are summarized. These factors should be considered in site descriptions, conducting monitoring programs, and implementing a database for further research. Historical trends for Pb show a sharp decrease during recent decades, and the median total Pb concentrations of the 21st century for North America and Europe are approximately 15 μg/L. No historical trend is detected for Zn. Zn concentrations are very variable in traffic area runoff compared with other heavy metals because of its presence in galvanized structures and crumbs of car tire rubber. Heavy metal runoff concentrations of parking lots differ widely according to their use (e.g., employee, supermarket, rest areas for trucks). Bridge deck runoff can contain high Zn concentrations from safety fences and galvanizing elements. Roads with more than 5000 vehicles per day are often more polluted than highways because of other site-specific factors such as traffic signals. Four relevant heavy metals (Zn, Cu,

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Abbreviations: AADT, average annual daily traffic; BR, bridge; d, dissolve; HL, highway with low AADT (>30,000) and non-urban land use; HU, highway with high AADT (>30,000) and urban land use; HWY, highway; p, particulate; Pb_21, dataset including only Pb concentrations measured in the 21st century; PL, parking lot; RL, road with low AADT (<5000); RM, road with medium AADT (5000 < AADT < 15,000); RU, road with high AADT (>15,000); t, total.

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http://dx.doi.org/10.1016/j.scitotenv.2015.09.033

Ni, and Cd) can occur in the dissolved phase. Knowledge of metal partitioning is important to optimize stormwater treatment strategies and prevent toxic effects to organisms in receiving waters.

Contents

1. Introduction

Traffic area runoff summarize precipitation- and snowmelt-related discharges of mostly impervious surfaces (sidewalks, parking lots (PL), feeder streets, major roads, and highways (HWY)). The main contamination sources of traffic area runoff are related to traffic, surrounding land use, atmospheric contamination, and other meteorological and environmental conditions (Muschack, 1990; Ball, 2002; Crabtree et al., 2009; Valtanen et al., 2014). It is difficult to determine the dominant sources of pollutants because most substances have more than one origin and the water quality data of runoff from different sites are extremely heterogeneous because of differing background levels, types of uses (Göbel et al., 2007), and method-specific factors.

The substance spectrum analyzed in traffic area runoff waters includes organic parameters such as polycyclic aromatic hydrocarbons, total petroleum hydrocarbons, chemical oxygen demand, biological oxygen demand, and total organic carbon; heavy metals such as Pb, Zn, and Cu; and materials from de-icing salts such as chloride (Smullen et al., 1999; Moy et al., 2003; Eriksson et al., 2007; Kayhanian et al., 2012).

As HWY account for a small percentage of urban land use, they contribute only a small portion of pollutant loads compared with other road surfaces (Shelley et al., 1987). In urban catchments, all road surfaces represent approximately 10%–15% of the total area (Bannerman et al., 1993; Ball, 2002), and in commercial and industrial areas, PL can constitute up to 46% of the total area (Bannerman et al., 1993). Therefore, it is essential to consider all types of traffic area runoff.

In most cases, runoff waters from PL and road surfaces contain higher levels of the heavy metals than other types of runoff in drainage systems such as conventional roof runoff (Schueler, 2000; Ball, 2002). Metals in roof and road runoff contribute up to 80% of the total mass flow in combined sewer systems (Ellis et al., 1987; Boller, 1997). The present review focuses on all heavy metals in traffic area runoff that have either traffic or anthropogenic sources. These metals are transported by stormwater runoff either attached to solids or in dissolved form depending on the prevailing redox and pH conditions (Ball, 2002). However, in most cases, only total metal concentrations are analyzed from runoff waters during measurement campaigns.

Some of these heavy metals can have acute or chronic impacts as a result of their accumulation in receiving waters in terms of aquatic habitats, drinking water resources, and recreational uses (Ellis and Revitt, 1982; Yousef et al., 1984). For potential toxic effects, the partitioning between the total and dissolved heavy metals is essential because the dissolved fractions are directly biologically available (Paulson and Amy, 1993; Crabtree et al., 2008). The toxicity of traffic area runoff has been investigated by various researchers (Gjessing et al., 1984; Pitt et al., 1995; McQueen et al., 2010). A particular link to the heavy metals was made by Tiefenthaler et al. (2001), who identified trace metals (particularly Zn) as important contributors to toxicity in PL runoff, and by Kayhanian et al. (2008), who identified dissolved Cu and Zn as the primary causes of toxicity in HWY runoff. In general, the toxicity of heavy metals is a function of several factors such as metal speciation and physical characteristics of receiving waters (Revitt and Morrison, 1987). If conditions change, particulate metals transported into receiving waters have the potential to repartition into the dissolved phase (Sansalone, 2002; Westerlund and Viklander, 2006). Metal partitioning is also important for designing appropriate stormwater treatment strategies (Hilliges et al., 2013; Maniquiz-Redillas and Kim, 2014).

The present review focuses on the objectives as follows:

- To describe site-specific factors (both fixed and climatic conditions) that influence the occurrence and partitioning of the heavy metals in traffic area runoff from different sites and that should be documented in investigation programs.
- To compile and evaluate the conditions of the monitoring methods, including sample collection, sample preparation, sample analysis, and calculation methods.
- To summarize the concentrations and fractionation of the heavy metals to produce a comprehensive dataset, to characterize different types of traffic areas, and to identify relevant heavy metals.

- To identify tendencies such as seasonal effects, phase-out measures, and land use influences that should be considered for planning stormwater treatment plants.

2. Material and methods

A dataset based on nearly 300 studies ($n = 294$) was analyzed. In addition to peer-reviewed journal papers, reports, books, and non-reviewed journal articles were considered after validation that presented heavy metal concentrations in traffic area runoff, including additional data concerning the monitoring program.

Several researchers evaluated street sweeping, the performance of grass swales, wetlands, detention ponds, biofiltration systems, porous asphalt surfaces, and artificial treatment plants. Only some characterized the quantity and quality of traffic area runoff containing heavy metal partitioning and influencing factors as their main objective. Therefore, the details of each monitoring program presented in publications differed and information regarding influencing factors such as those described in Section 3.1 are often missing.

To analyze historical trends and obtain a wide range of data, it is important to consider publications of the last decades. In North America and Europe, a large number of runoff data have been collected since the 1970s. Since the 1990s, data from Australia and New Zealand have been available, and since the 2000s, the number of publications from Asia, Africa, and South America has increased.

The date of the monitoring program was used instead of the publication date. If the date of the monitoring program was not available, the date of paper submission was used. All data are subdivided into eight categories: PL; bridges (BR); roads with an average annual daily traffic (AADT) of <5000 (RL), 5000 < AADT < 15,000 (RM), and >15,000 (RU); urban HWY with an AADT of >30,000 (HU); non-urban HWY with an AADT of >30,000 (HN); and HWY with an AADT of <30,000 (HL). If the AADT was not mentioned, the classification was performed from the description of the monitoring site, e.g., a feeder street was classified as category RL. Each site was linked to one category. The identification (ID) of each site consists of two capital letters according to the category and two consecutive numbers, e.g., PL01. These IDs are used in Tables 1, 2, and 3 and in Sections 4.3 and 4.4.

One important step was to ensure that each dataset from one site was only considered once, although it might have been published twice or more in different forms. All data of one site was recalculated to obtain one dataset per site, except where the investigation period was not continuous (e.g., a new monitoring program after several years) or site-specific factors varied because of construction work (e.g., new road surface). In these cases, one site provides two or three datasets (highlighted in Tables 1, 2, and 3 by adding a letter a, b, or c at the end of an ID).

At data collection, total (t), dissolved (d), and particulate (p) concentrations were distinguished, as were mean and median concentrations. If authors presented both mean and median values, both values were used in this review. For sites including all single-event concentrations, both mean and median concentrations were calculated. Some extreme measured concentrations were deleted for plotting the figures but all these concentrations are mentioned in Section 4.

For statistical analysis and plotting histograms and box plots, the software package SPSS 22 (IBM) was used. For box and whisker plots, the bottom and top of each box are the first and third quartiles and the band inside the box is the median. The whiskers represent 1.5 times the interquartile range (IQR). Outliers (>1.5 times IQR) are marked as small circles and extreme values (>3.0 times IQR) as stars.

3. Occurrence and influencing factors

Literature datasets have a wide variation due to site-specific and monitoring-method-specific factors (Fig. 1). Site-specific factors can be divided into fixed site-specific factors (spatial variance) and climatic site-specific factors (temporal variance); both affect the real pollution of surface runoff. Method-specific influences on the results, which should represent the real situation, are caused by the boundary conditions of a measurement program and occur during sample collection, sample preparation, sample analysis, and calculation.

3.1. Site-specific factors

3.1.1. Fixed site

Fixed site-specific factors can be divided into three categories: surrounding land use characteristics, traffic area site data, and operational characteristics (Shelley et al., 1987).

For the first factor, i.e., *surrounding land use characteristics*, several categories are used: non-urban, urban, ultra-urban, transportation, residential, open, agriculture, commercial, mixed, and industrial categories (Kayhanian et al., 2003; Flint and Davis, 2007). Driscoll et al. (1990) specified urban (undefined, commercial/residential, residential, and suburban) and non-urban (undefined rural, forest, undeveloped, agricultural, and desert) land use categories. Because the term residential land use could include a mixture of streets, driveways, rooftops, and lawns (Schueler, 2000), its use for analysis is restrictive and only comparisons of land use categories analyzed in one research program can provide an indication of their influence. E.g., the results of Dannecker et al. (1990) showed similar runoff pollution levels of an industrial road and a main street of an inner urban city.

The second factor, i.e., the *traffic area site data*, contains information about vegetation, topography, and road design. Only some data are available for surrounding *vegetation*, street surface covered with trees, and *topography*, which describes the slope and the configuration of the traffic area (cut, at grade, or elevated (Driscoll et al., 1990)). Jenewein and Schinner (1982) did not find a correlation of the slope with runoff concentrations. Most fixed site-specific data are available about *road design*, including information about cross-sections, pavement surfaces, and drainage areas. The cross-section describes the number of lanes per direction and the existence of curbs, median strips, hard shoulders, drainage systems, crash/noise barriers, and safety fences. The absence of curbs has a positive effect on reducing runoff concentrations (Driscoll et al., 1990), and further influences are described by Irish et al. (1998) and Li et al. (2008). Hard shoulders have an influence on water quality because they act as a sink for suspended solids and particle-associated metals (Berbee et al., 1999). Detailed information about the types of surfaces drained and sampled in monitoring programs is available in literature (62.9% of the datasets). Most surfaces are conventional asphalt surfaces ($n = 122$), followed by concrete ($n = 33$), asphalt and concrete ($n = 15$; mostly HWY with new lanes), porous asphalt ($n = 9$), asphalt and paver ($n = 3$; PL), paver ($n = 2$; PL), and crushed stone ($n = 1$; feeder street). Drapper et al. (2000) concluded that a concrete surface does not have a significant impact on pollutant runoff concentrations compared with asphalt surfaces. The surface condition has an effect on concentrations by either increasing runoff loads from decomposition products or reducing them during filtration into cracks and pot-holes (Driscoll et al., 1990). The size of the drainage area in the dataset of this study varies widely (3–429,000 m^2) and has an effect on the first flush (Lau et al., 2009) and metal concentration, when the ratio of the drainage area to traffic volume is considered (CH2MHILL, 1998). The same applies to the imperviousness of the surface. Noise barriers lead to an increase in runoff concentrations (Dierkes, 1999; Kocher et al., 2010a,b), and concrete barriers can retain more solids on road surfaces (Barrett et al., 1998). Speed limits and traffic signals have an influence on runoff concentrations because braking and acceleration activities lead to increased abrasion of tires, higher use of brake linings, and increased automotive exhaust gas emissions (Muschak, 1990; Langbein et al., 2006). Drapper et al. (2000) measured higher concentrations of Cu and Zn at locations with exit lanes due to sharp braking by exiting vehicles and road signs release metals as a result of rain and splashing water (Van Bohemen and Van de Laak, 2003).

Table 1

Register of studies investigating parking lot runoff.

ID	Literature	Location	Sampling period	Special conditions[a]	Discharge area[m^2]	Type and characteristics of parking lots	Number of events sampled	Type of sample collection	Sampling strategy	Pore diameter for filtration	Partition[b]	Metals detected[c]
PL01	Grotehusmann and Kasting (2002)	DEU	2001-01–2001-12	D, M, S	10,000	Tank farm and rest area for 41 trucks and four busses	40	Active-automatic	Flow-prop.	0.45	d, t	Cd, Cr, Cu, Hg, Pb, Pd, Pt, Zn
PL02	Grotehusmann and Kasting (2002)	DEU	2001-01–2001-12	D, M, S	5000	Tank farm and rest area for 122 cars	43	Active-automatic	Flow-prop.	0.45	d, t	Cd, Cr, Cu, Hg, Pb, Pd, Pt, Zn
PL03	Grotehusmann and Kasting (2002)	DEU	2001-01–2001-12	D, M, S	17,700	Tank farm and rest area for 18 trucks, 16 busses and 78 cars	42	Active-automatic	Flow-prop.	0.45	d, t	Cd, Cr, Cu, Hg, Pb, Pd, Pt, Zn
PL04	Pick et al. (2002)	DEU	1999-03–2000-11	–	300	Campus parking lot	–	Active-automatic	Mixed	–	t	*Cd (<1.0)*, Cr, Cu, Ni, Pb, Zn
PL05	Engelhard et al. (2012)	AUT	2010-04-02–2011-02-21	D	–	Supermarket	–	Passive-automatic	Mixed	–	t	Cd, Cr, Cu, Ni, Pb, Zn
PL06	Gromaire-Mertz et al. (1999)	FRA	1996-07–1997-05	–	–	Courtyard, old residential district with small businesses	7	Active-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Pb, Zn
PL07	Gnecco et al. (2005)	ITA	2002-01-23–2003-09-28	–	1000	Campus parking lot, typical urban residential area	9	Active-automatic	Time-prop. (equally timed)	–	d	Cu, Pb, Zn
PL08	Gnecco et al. (2008)	ITA	2005-11-15–2006-07-12	–	14,000	Airport parking area with 100 vehicles per hour	4	Active-automatic	Time-prop. (equally timed)	0.45	d, p	Al, Cu, Fe, Mn, Pb, Zn
PL09	Nowakowska-Blaszczyk and Zakrzewski (1996)	POL	–	S	–	–	–	–	–	–	t	Pb
PL10	Hogland et al. (1987)	SWE	1985	–	470	Research center	2	Active-automatic	Time-prop. (equally timed)	–	t	Al, Cd, Cr, Cu, Pb, Zn
PL11	Wei and Morrison (1994)	SWE	1992-05-26	–	–	Park and ride	1	–	–	0.45	d, t	Pt
PL12	Pitt et al. (1995)	USA	–	–	–	Park and ride	1	Manual	Random	0.45	d, t	Al, Cd, Cr, Cu, Ni, Pb, Zn
PL13	Caltrans (2003)	USA	2002-11-07–2003-04-24	–	–	Park and ride, commercial site within the foothills	8	Active-automatic	Flow-prop.	–	d, t	As, *Cd (<0.2)*, Cr, Cu, Ni, Pb, Zn
PL14	Caltrans (2003)	USA	2002-12-09–2003-02-12	–	–	Park and ride	8	Active-automatic	Flow-prop.	–	d, t	As, Cd, Cr, Cu, Hg, Ni, Pb, Zn
PL15	Caltrans (2003)	USA	2002-11-07–2003-02-15	–	–	Park and ride	8	Active-automatic	Flow-prop.	–	d, t	As, Cd, Cr, Cu, Hg, Ni, Pb, Zn
PL16a	Caltrans (2003)	USA	2002-11-29–2003-05-02	–	–	Park and ride, campus parking lot	8	Active-automatic	Flow-prop.	–	d, t	As, Cd, Cr, Cu, Ni, Pb, Zn
PL16b	Tiefenthaler et al. (2001)	USA	2000-07-15–2000-10-07	S	608	Park and ride, campus parking lot	5	Active-automatic	Time-prop. (equally timed)	0.45	d, t	Al, Cd, Cr, Cu, Fe, Ni, Pb, Zn
PL17	Caltrans (2003)	USA	2002-11-07–2003-04-14	–	–	Park and ride	8	Active-automatic	Flow-prop.	–	d, t	As, Cd, Cr, Cu, Ni, Pb, Zn
PL18	Caltrans (2003)	USA	2002-12-20–2003-04-14	–	–	Park and ride, rural area near foothills	4	Active-automatic	Flow-prop.	–	d, t	Cd, Cr, Cu, Ni, Pb, Zn
PL19	Caltrans (2003)	USA	2002-11-07–2003-04-12	–	–	Park and ride, flat business/retail area	8	Active-automatic	Flow-prop.	–	d, t	As, Cr, Cu, Ni, Pb, Zn

PL20	Caltrans (2003)	USA	2002-11-08–2003-04-14	–	–	Park and ride	8	Active-automatic	Flow-prop.	–	d, t	As, Cd, Cr, Cu, Ni, Pb, Zn
PL21	Caltrans (2003)	USA	2002-12-12–2003-03-14	–	–	Rest area with planter boxes and restrooms	8	Active-automatic	Flow-prop.	–	d, t	As, Cd, Cr, Cu, Ni, Pb, Zn
PL22	Caltrans (2003)	USA	2003-02-12–2003-04-12	–	–	Rest area, rolling grassy hills	3	Active-automatic	Flow-prop.	–	d, t	As, Cd, Cr, Cu, Ni, Pb, Zn
PL23	Caltrans (2003)	USA	2002-12-16–2003-04-17	–	–	Rest area, flat agricultural land	3	Active-automatic	Flow-prop.	–	d, t	As, Cd, Cr, Cu, Ni, Pb, Zn
PL24	Rushton (2001)	USA	1998-11–1999-11	–	1050	Florida Aquarium	30	Active-automatic	Flow-prop.	–	t	Cu, Fe, Mn, Pb, Zn
PL25	Rushton (2001)	USA	1998-11–1999-11	–	1050	Florida Aquarium	30	Active-automatic	Flow-prop.	–	t	Cu, Fe, Mn, Pb, Zn
PL26	Steuer et al. (1997)	USA	1993-10, 1994-05–1994-08	–	54,000	Commercial	12	Passive-automatic	Flow-prop.	0.45	d, t	Cu, Cd, Pb, Zn
PL27	McQueen et al., 2010	USA	2006-10-16–2007-07-17	nD, M	1254	Campus parking lot for 23 of 231 cars, residential/commuter	19	Active-automatic	First flush (2.54 mm)	–	t	Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn
PL28	McQueen et al., 2010	USA	2007-01-05–2007-07-30	nD, M	6398	Campus parking lot for 189 of 1089 cars, residential/commuter	12	Active-automatic	First flush (2.54 mm)	–	t	Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn
PL29	Line et al. (1997)	USA	1993-11-05	–	16,000	Vehicle maintenance	1	Active-automatic	First flush (5 min)	–	t	*As (<10)*, *Cd (<2)*, *Cr (<5)*, Cu, *Hg (<0.2)*, *Ni (<10)*, *Pb (<5)*, *Sb (<50)*, Zn
PL30	Line et al. (1997)	USA	1993-11-27	–	24,000	Vehicle maintenance	1	Active-automatic	First flush (5 min)	–	t	*As (<10)*, *Cd* (<2), Cr, Cu, *Hg (<0.2)*, *Ni (<10)*, Pb, *Sb (<50)*, Zn
PL31a	Booth and Leavitt (1999)	USA	1996-11–1996-12-25	–	18	Employee parking lot with once-in, once-out daily usage	3	Passive-automatic	Flow-prop.	–	d, t	Ba, Cu, Fe, Mn, Pb, Zn
PL31b	Brattebo and Booth (2003)	USA	2001-11–2002-03	–	18	Employee parking lot with once-in, once-out daily usage	9	Passive-automatic	Flow-prop.	–	d, t	Cu, *Pb (<1)*, Zn
PL32	Bannerman et al. (1993)	USA	1991-05-05–1991-07-07	–	–	Commercial	5	Passive-automatic	Flow-prop.	0.7; 0.45	d, t	Cd, Cr, Cu, Pb, Zn
PL33	Bannerman et al. (1993)	USA	1991-05-05–1991-07-07	–	–	Industrial	9	Passive-automatic	Flow-prop.	0.7; 0.45	d, t	Cd, Cr, Cu, Pb, Zn
PL34	Hatt et al. (2009)	AUS	2007-01–2007-11	–	4500	Campus parking lot, top level of a multi-level carpark	17	Active-automatic	Flow-prop.	–	t	Cu, Mn, Pb, Zn
PL35	Maniquiz et al. (2010)	KOR	2006-06–2008-10	–	10,700	Vehicle registration office, commercial and light industrial	45	Manual	Time-prop. (first flush-enhanced)	–	t	Pb, Zn

[a] D = De-icing salt application, nD = no de-icing salt application, M = Maintenance, S = Sweeping.

[b] d = dissolved, p = particulate, t = total.

[c] Metals measured below study-specific detection limits are highlighted in this table with italics and the detection limits are presented in brackets behind these elements.

Table 2
Register of studies investigating road runoff.

ID	Literature	Location	Sampling period	Special conditions[a]	Discharge area[m^2]	AADT [Vehicles per day]	Number of events sampled	Type of sample collection	Sampling strategy	Pore diameter for filtration	Partition[b]	Metals detected[c]
RL01	Xanthopoulos and Hahn (1995)	DEU	–	–	–	3200	87	–	–	–	t	Cd, Cu, Ni, Pb, Zn
RL02	Dannecker et al. (1990)	DEU	1987	–	210	500	17	Active-automatic	Mixed	250, 0.45	t	Al, As, Ba, *Be (<0.2)*, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn
RL03a	Dannecker et al. (1990)	DEU	1986	–	290	2300	16	Active-automatic	Mixed	250, 0.45	p, t	Al, As, *Be (<0.2)*, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn
RL03b	Dannecker et al. (1990)	DEU	1987	–	290	2300	16	Active-automatic	Mixed	250, 0.45	p, t	Al, As, Ba, *Be (<0.2)*, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn
RL04	Daub and Striebel (1995)	DEU	1994	–	–	<1000	3	Active-automatic	–	0.45, 0.1	d, p	Cu, Pb
RL05	Legret et al. (1996)	FRA	1991–1994	M	2800	2000	39	Passive-automatic	First flush	0.45	d, t	Cd, Cu, Pb, Zn
RL06	Van Dam et al. (1986)	NDL	1982-07–1985-12	M, S	176	3200	11	–	–	–	t	Cd, Cr, Cu, Pb, Zn
RL07	MacKay et al. (2011)	USA	2006-08-29	M	549	3000	1	Active-automatic	Time-prop. (equally timed)	0.45	d, t	Cu, Pb, Zn
RL08	MacKay et al. (2011)	USA	2006-08-29	M	1161	3000	1	Active-automatic	Time-prop. (equally timed)	0.45	d, t	Cu, Pb, Zn
RL09	MacKay et al. (2011)	USA	2008-08-15	M	1302	4000	1	Active-automatic	Time-prop. (equally timed)	0.45	d, t	Cu, *Pb (<5)*, Zn
RL10	MacKay et al. (2011)	USA	2008-09-06	M	279	2000	1	Active-automatic	Time-prop. (equally timed)	0.45	d, t	Cu, Pb, Zn
RL11	Gilbert and Clausen (2006)	USA	2002-06–2003-05	–	199	–	12	Passive-automatic	Mixed	–	t	Cu, Pb, Zn
RL12	Gilbert and Clausen (2006)	USA	2002-06–2003-05	–	405	–	12	Passive-automatic	Mixed	–	t	Cu, Pb, Zn
RL13	Gilbert and Clausen (2006)	USA	2002-06–2003-05	–	225	–	12	Passive-automatic	Mixed	–	t	Cu, Pb, Zn
RL14	Steuer et al. (1997)	USA	1993-10, 1994-05–1994-08	S	104,000	<3100	12	Passive-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Pb, Zn
RL15	Driscoll et al. (1990)	USA	1970s and early 1980s	–	5059	2000	–	–	–	–	t	Cu, Pb, Zn
RL16	Driscoll et al. (1990)	USA	1970s and early 1980s	–	1012	2500	–	–	–	–	t	Cu, Pb, Zn
RL17	Bannerman et al. (1993)	USA	1991-05-05–1991-07-07	S	–	100–400	10	Passive-automatic	Flow-prop.	0.7, 0.45	d, t	Cd, Cr, Cu, Pb, Zn
RL18	Bannerman et al. (1993)	USA	1991-05-05–1991-07-07	S	–	500–2150	9	Passive-automatic	Flow-prop.	0.7, 0.45	d, t	Cd, Cr, Cu, Pb, Zn
RL19	Waschbusch (1996)	USA	1994–1995	–	–	378	–	–	–	–	d, t	Cd, Cu, Pb, Zn
RL20	Davis and Birch (2010)	AUS	2007-08-19–2008-04-06	–	860	2000	4	Active-automatic	Time-prop. (first flush-enhanced)	250, 0.45	d, p	Cu, Pb, Zn
RL21	Maniquiz-Redillas and Kim (2014)	KOR	2010-05–2012-11	–	520	–	24	Manual	Time-prop. (first flush-enhanced)	0.45	d, t	Cd, Cr, Cu, Fe, Ni, Pb, Zn
RM01	Robien et al. (1997)	DEU	1990–1991	D, S	600	6000	4	Active-automatic	–	0.45, 0.1	d, p	Cd, Cu, Fe, Ni, Pb, Zn
RM02	Nadler and Meißner (2007)	DEU	1996-10-01–2005-09-08	D	17.3	6800	36	Passive-automatic	Mixed	–	t	Cd, Cr, Cu, Fe, Mo, Ni, Pb, Pt, Sb, V, Zn
RM02x	Nadler and Meißner (1999)	DEU	1997-10-01–1997-12-31	D	17.3	6100	1	Passive-automatic	Mixed	0.45	d, t	Cd, Cu, Pb, Zn
RM03	Muschack (1990)	DEU	1984-09–1985-08	–	–	14,200	31	–	–	–	t	Cd, Cr, Cu, Fe, Hg, Ni, Pb, Zn
RM04	Holthuis et al. (2012)	DEU	2008-09–2010-07	D	41,200	15,000	8	–	–	–	t	Cu, Fe, Zn
RM05	SEH (2010)	DEU	2008-08-20–2010-02-08	D	250	5500	18	Passive-automatic	Flow-prop.	–	t	*Cd (<50)*, *Cu (<100)*, *Pb (<100)*, Zn
RM06	SEH (2010)	DEU	2008-08-20–2010-02-08	D	250	5500	17	Passive-automatic	Flow-prop.	–	t	*Cd (<50)*, *Cu (<100)*, *Pb (<100)*, Zn
RM07	SEH (2010)	DEU	2008-08-20–2010-02-08	D	400	12,800	17	Passive-automatic	Flow-prop.	–	t	*Cd (<50)*, *Cu (<100)*, *Pb (<100)*, Zn
RM08	Krauth and Stotz (1993)	DEU	1991-12-17–1993-04-30	D	15,300	9870	111	–	–	–	t	Cd, Cr, Cu, Fe, Ni, Pb, Zn
RM09	Jenewein and Schinner (1982)	AUT	–	–	–	–	–	–	First flush	–	t	Cu, Pb, Zn
RM10	Rutz (2009)	CHE	2008-01-16, 2008-04-14, 2008-07-03	–	23,000	12,000	3	Manual	Random	–	d, t	Cd, Cr, Cu, Pb, Zn

RM11	von Ballmoos (2007)	CHE	2006-04-11, 2006-08-09	–	–	–	2	Manual	Random	–	t	*Cd (<1)*, *Cr (<5)*, Cu, *Pb (<5)*, Zn
RM12	Gromaire-Mertz et al. (1999)	FRA	1996-07–1997-05	M, S	602	–	7	Active-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Pb, Zn
RM13	Barbosa and Hvitved-Jacobsen (1999)	PRT	–	–	5970	6000	10	Active-automatic	Time-prop. (first flush-enhanced)	0.45	t	*Cd (<1)*, *Cr (<1)*, Cu, Pb, Zn
RM14a	Westerlund et al. (2003)	SWE	2000-03-25–2000-04-25	–	660	7400	4	Active-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Ni, Pb, Zn
RM14b	Westerlund et al. (2003)	SWE	2000-05-25–2000-06-26	–	660	7400	3	Active-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Ni, Pb, Zn
RM15	Pitt et al. (1995)	USA	–	–	–	–	1	Manual	Random	0.45	d, t	Al, Cd, Cr, Cu, Ni, Pb, Zn
RM16	MacKay et al. (2011)	USA	2007-08-09, 2008-04-28, 2008-05-02	M, S	1079	8000	3	Active-automatic	Time-prop. (equally timed)	0.45	d, t	Cu, Pb, Zn
RM17	MacKay et al. (2011)	USA	2006-09-03	M, S	1898	–	1	Active-automatic	Time-prop. (equally timed)	0.45	d, t	Cu, Pb, Zn
RM18	MacKay et al. (2011)	USA	2006-09-03	M, S	866	–	1	Active-automatic	Time-prop. (equally timed)	0.45	d, t	Cu, *Pb (<5)*, Zn
RM19	Fulkerson et al. (2007)	USA	2005-03-03–2005-07-30	nS	8100	5000	14	Manual	Time-prop. (equally timed)	0.7	d, p	MeHg, THg
RM20	Steuer et al. (1997)	USA	1993-10, 1994-05–1994-08	S	16,000	10,600	12	Passive-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Pb, Zn
RM21	Steuer et al. (1997)	USA	1993-10, 1994-05–1994-08	S	21,000	3100–5100	12	Passive-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Pb, Zn
RM22	Steuer et al. (1997)	USA	1993-10, 1994-05–1994-08	–	49,000	–	12	Passive-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Pb, Zn
RM23	Driscoll et al. (1990)	USA	1970s and early 1980s	–	1133	7300	–	–	–	–	t	Cu, Pb, Zn
RM24	Bannerman et al. (1993)	USA	1991-05-05–1991-07-07	S	–	2850–7300	10	Passive-automatic	Flow-prop.	0.7; 0.45	d, t	Cd, Cr, Cu, Pb, Zn
RM25	Bannerman et al. (1993)	USA	1991-05-05–1991-07-07	–	–	–	10	Passive-automatic	Flow-prop.	0.7; 0.45	d, t	Cd, Cr, Cu, Pb, Zn
RM26	Novotny et al. (1998)	USA	–	D	–	–	–	–	–	–	d, t	Cu, Pb, Zn
RM27	Novotny et al. (1998)	USA	–	D	–	–	–	–	–	–	d, t	Cu, Pb, Zn
RM28	Waschbusch, 1996	USA	1994–1995	D	–	6157	–	–	–	–	d, t	Cd, Cu, Pb, Zn
RM29	Novotny et al. (1998)	CAN	–	D	–	–	–	–	–	–	d, t	Cu, Pb, Zn
RM30	Novotny et al. (1998)	CAN	–	D	–	–	–	–	–	–	d, t	Cu, Pb, Zn
RM31	Brockbank et al. (1999)	AUS	–	–	–	–	–	–	–	–	d, p	Cu, Fe, Mn, Pb, Zn
RM32	Prestes et al. (2006)	BRA	2002-09–2004-03	S	1300	9000	21	Manual	Flow-prop.	0.45	d, t	Cd, Cu, Pb
RM33	Zhang et al. (2013)	CHN	2010-06-06–2011-08-04	nD	540	10,000	9	–	Time-prop. (first flush-enhanced)	–	d	Cu, Pb, Zn
RU01	Wüst et al. (1994)	DEU	1990-03-28, 1990-05-08, 1990-06-02	D, S	133	25,000	3	Manual	–	0.45, 0.1	d, p	Cd, Cu, Pb, Zn
RU02	Herrmann et al. (1992)	DEU	1991-07-14, 1991-08-15, 1991-08-17	nD, S	30	16,000	3	Active-automatic	–	0.45, 0.1	d, p	Cd, Cu, Fe, Ni, Pb, Zn
RU02x	Laschka et al. (1996)	DEU	1991	D, S	30	16,000	6	Active-automatic	–	–	t	Pt
RU03a	Helmreich et al. (2010)	DEU	2003-11–2005-11	D, S	400	57,000	63	Passive-automatic	First flush (1 mm rain)	0.45	d, t	*Cd (<0.5)*, Cu, Ni, Pb, Zn
RU03b	Hilliges et al. (2013)	DEU	2006-07-01–2007-06-30	D, S	100	57,000	24	Active-automatic	Flow-prop.	–	t	Cu, Pb, Zn
RU04	Dannecker et al. (1990)	DEU	1987	–	250	16,200	12	Active-automatic	Mixed	250, 0.45	t	Al, As, Ba, *Be* (<0.2), Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn
RU05	Dierkes (2010)	DEU	2009-01-12–2009-11-27	D	2300	18,000	11	Manual	Random	–	t	Cd, Cu, Pb, Zn
RU06	Gäth et al. (1990)	DEU	1988-12-01–1989-01-13	–	162.2	18,129	8	Active-automatic	Time-prop. (equally timed)	–	t	Cd, Cu, Pb, Zn
RU07a	Kasting et al. (2003)	DEU	2000-10–2001-09	D	15,000	45,000	–	Manual	Random	–	d, t	Cu, Pb, Zn
RU07b	Kasting and Grotehusmann (2007)	DEU	–	D	15,000	45,000	–	Manual	Random	–	d, t	Cu, Pb, Pt, Zn
RU07c	Grotehusmann and Kasting (2009)	DEU	2007-02-09–2008-01-07	D	15,000	45,000	10	Manual	Random	–	d, t	*As (<5)*, Cd, Co, Cr, Cu, Fe, *Hg (<0.2)*, *Mo (<5)*, Ni, Pb, Sb, V, Zn
RU08	Dierkes (1999)	DEU	1997-06–1999-02	D	–	26,000	28	Passive-automatic	Mixed	0.45	d, t	Cd, Cu, Pb, Zn
RU09	Daub and Striebel (1995)	DEU	1994	–	100	22,000	3	Active-automatic	–	0.45, 0.1	d, p	Cu, Pb
RU10	Schütte (1997)	DEU	1996-09–1996-12	–	–	15,000–20,000	10	–	–	–	t	Cd, Cu, Fe, *Hg (<0.5)*, Ni, Pb, Zn
RU11	Steiner et al. (2010)	AUT	–	–	–	–	–	–	–	–	t	Cr, Cu, Ni, Pb, Zn
RU12	Windhofer et al. (2012)	AUT	2011-10-21–2011-12-10	D	3300	26,000	4	–	Flow-prop.	–	t	Cu, Rh, Pt, Zn
RU13	Langbein et al. (2006)	CHE	2002-10-23–2004-07-08	–	1500	17,000	7	Active-automatic	Time-prop. (first flush-enhanced)	0.45	d, t	Cd, Cr, Cu, Fe, Ni, Pb, Zn

(continued on next page)

Table 2 (*continued*)

ID	Literature	Location	Sampling period	Special conditions[a]	Discharge area[m^2]	AADT [Vehicles per day]	Number of events sampled	Type of sample collection	Sampling strategy	Pore diameter for filtration	Partition[b]	Metals detected[c]
RU14	Steiner et al. (2006)	CHE	2002–2004	–	14.1	17,000	–	Passive-automatic	Mixed	–	t	Cd, Cr, Cu, Fe, Pb, Sn, Zn
RU15	Klimaszewska et al. (2007)	POL	2003-01–2003-05	S	–	59,000	13	Passive-automatic	Flow-prop.	–	t	Cd, Pb, Zn
RU16	Klimaszewska et al. (2007)	POL	2003-01–2003-05	S	–	39,400	8	Passive-automatic	Flow-prop.	–	t	Cd, Pb, Zn
RU17	Nowakowska-Blaszczyk and Zakrzewski (1996)	POL	–	S	–	–	–	–	–	–	t	Pb
RU18	Wei and Morrison (1994)	SWE	1992-05-26	–	–	–	1	–	–	0.45	d, t	Pt
RU19a	Bannerman et al. (1993)	USA	1991-05-05–1991-07-07	S	–	20,000	10	Passive-automatic	Flow-prop.	0.7, 0.45	d, t	Cd, Cr, Cu, Pb, Zn
RU19b	Waschbusch (1996)	USA	1994–1995	–	–	18,600	–	–	–	–	d, t	Cd, Cu, Pb, Zn
RU20	Bannerman et al. (1993)	USA	1991-05-05–1991-07-07	S	–	19,800	9	Passive-automatic	Flow-prop.	0.7, 0.45	d, t	Cd, Cr, Cu, Pb, Zn
RU21	Davis and Birch (2010)	AUS	2007-08-19–2008-04-06	–	1095	84,500	6	Active-automatic	Time-prop. (first flush-enhanced)	250, 0.45	d, p	Cu, Pb, Zn
RU22	Lloyd and Wong (1999)	AUS	1999-01-22, 1999-01-29	nS	1500	32,000	2	Manual	Time-prop. (equally timed)	–	t	Cd, Cu, Pb, Zn
RU23	Timperley et al. (2005)	NZL	2002-08-24–2002-09-18	–	–	17,000	4	Active-automatic	Flow-prop.	–	d, p	Cu, Pb, Zn
RU24	Chang et al. (2009)	CHN	2005-06-28, 2005-09-21	–	–	–	2	–	Time-prop. (equally timed)	0.45	d, t	Cd, Cr, Cu, Ni, Pb, Zn
RU25	Huang et al. (2007)	CHN	2005-06–2006-09	–	3875	30,000	5	Active-automatic	Time-prop. (first flush-enhanced)	–	t	Cu, Pb, Zn
RU26	Maniquiz et al. (2010)	KOR	2006-06–2008-10	–	5000	–	45	Manual	Time-prop. (first flush-enhanced)	–	t	Pb, Zn

[a] D = De-icing salt application, nD = no de-icing salt application, M = Maintenance, S = Sweeping, nS = no sweeping.

[b] d = dissolved, p = particulate, t = total.

[c] Metals measured below study-specific detection limits are highlighted in this table with italics and the detection limits are presented in brackets behind these elements.

Table 3
Register of studies investigating bridge runoff.

ID	Literature	Location	Sampling period	Special conditions[a]	Discharge area [m^2]	AADT [vehicles per day]	Number of events sampled	Type of sample collection	Sampling strategy	Pore diameter for filtration	Partition[b]	Metals detected[c]
BR01a	Legret and Pagotto (1999)	FRA	1995-03-28–1996-02-26	D, S	3200	12,000	49	Active-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Pb, Zn
BR01b	Pagotto et al. (2000)	FRA	1997-06-09–1997-11-09	D	3200	12,000	25	Active-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Pb, Zn
BR02a	Hallberg et al. (2007)	SWE	2005-05-03–2005-08-26	D	13,700	108,300	4	Active-automatic	Flow-prop.	0.45	d, t	Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn
BR02b	Hallberg et al. (2007)	SWE	2005-12-14–2006-02-14	D	13,700	108,300	5	Active-automatic	Flow-prop.	0.45	d, t	Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn
BR03	Driscoll et al. (1990)	USA	1970s and early 1980s	–	6070	42,000	–	–	–	–	t	Cu, Fe, Pb, Zn
BR04	Yousef et al. (1984)	USA	–	–	6825	55,000	11	–	–	–	d, t	Cd, Cr, Cu, Fe, Ni, Pb, Zn
BR05	Yousef et al. (1984)	USA	1982-08–1983-05	–	19,800	11,500	15	–	–	–	d, t	Cd, Cr, Cu, Fe, Ni, Pb, Zn
BR06	Driscoll et al. (1990)	USA	1970s and early 1980s	–	5787	70,000	–	–	–	–	t	Cd, Cr, Cu, Pb, Zn
BR07	Dean et al. (2005)	USA	2002-04-11–2002-06-16	–	544	–	4	Manual	Time-prop. (equally timed)	0.45	d, p	Cd, Cu, Pb, Zn
BR08	Wu et al. (1998)	USA	1995-09-22–1996-07-01	D, M	1497	25,000	10	Active-automatic	Time-prop. (pre-set time)	–	t	*Cd* (<0.5), Cr, Cu, Ni, Pb
BR09	Barrett et al. (1998)	USA	1994-04-29–1995-05-18	–	526	8780	26	Active-automatic	Flow-prop.	–	t	Cu, Fe, Pb, Zn
BR10	Barrett et al. (1998)	USA	1994-10-17–1995-05-08	–	1060	47,000	8	Active-automatic	Flow-prop.	–	t	Cu, Fe, Pb, Zn
BR11	Bourcier and Hindin (1979); Bourcier et al. (1980)	USA	1976-10-14–1977-03-23	M, S	2323	–	3	–	–	–[d]	d, t	Cr, Fe, Pb, Ti, W, Zn
BR12	Driscoll et al. (1990)	USA	1970s and early 1980s	–	401	42,000	–	–	–	–	t	Cu, Pb, Zn
BR13	Driscoll et al. (1990)	USA	1970s and early 1980s	–	890	17,000	–	–	–	–	t	Cu, Pb, Zn
BR14	Wilson (2006)	USA	2003-04-08, 2003-10-06, 2004-01-14	–	250	100,000–180,000	3	Active-automatic	Flow-prop.	–	d, t	As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, V, Zn
BR15	Driscoll et al. (1990)	USA	late 1970s and early 1980	–	8498	53,000	35	–	–	–	t	Cd, Cr, Cu, Fe, Hg, Pb, Zn
BR16a	Frazer, 1990	CAN	–	–	–	–	29	–	–	–	t	Cd, Cu, Ni, Pb, Zn
BR16b	Marsalek et al. (1997)	CAN	16 months	–	–	83,700–102,100	53	Passive-automatic	Flow-prop.	0.45	d, t	Cd, Cu, Ni, Pb, Zn
BR17	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	5200	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR18	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	3548	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR19	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	15,524	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
RB20	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	23,672	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR21	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	15,766	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR22	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	27,000	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR23	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	12,156	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR24	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	13,302	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR25	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	14,312	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR26	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	33,000	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR27	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	33,000	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR28	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	35,248	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR29	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	33,191	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR30	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	26,950	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR31	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	26,826	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR32	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	50,304	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR33	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	46,235	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR34	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	32,000	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR35	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	32,000	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR36	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	45,000	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR37	Drapper et al. (2000)	AUS	1997-07–1999-01	–	–	5900	12	Passive-automatic	First flush (20 l)	–	t	Cu, Pb, Zn
BR38	Gan et al. (2008)	CHN	2006-04-06–2006-06-12	M	110	31,000	7	Active-automatic	Time-prop. (first flush-enhanced)	–	t	Cd, Cr, Cu, Ni, Pb, Zn
BR39	Yu and Zhao (2012)	CHN	2007-04-22–2007-09-01	–	–	–	3	–	Time-prop. (equally timed)	–	t	Cd, Cr, Ni, Pb, Zn

[a] D = De-icing salt application, M = Maintenance, S = Sweeping.

[b] d = dissolved, p = particulate, t = total.

[c] Metals measured below study-specific detection limits are highlighted in this table with italics and the detection limits are presented in brackets behind these elements.

[d] Centrifuging 50 ml of sample for 5 min at 681 g.

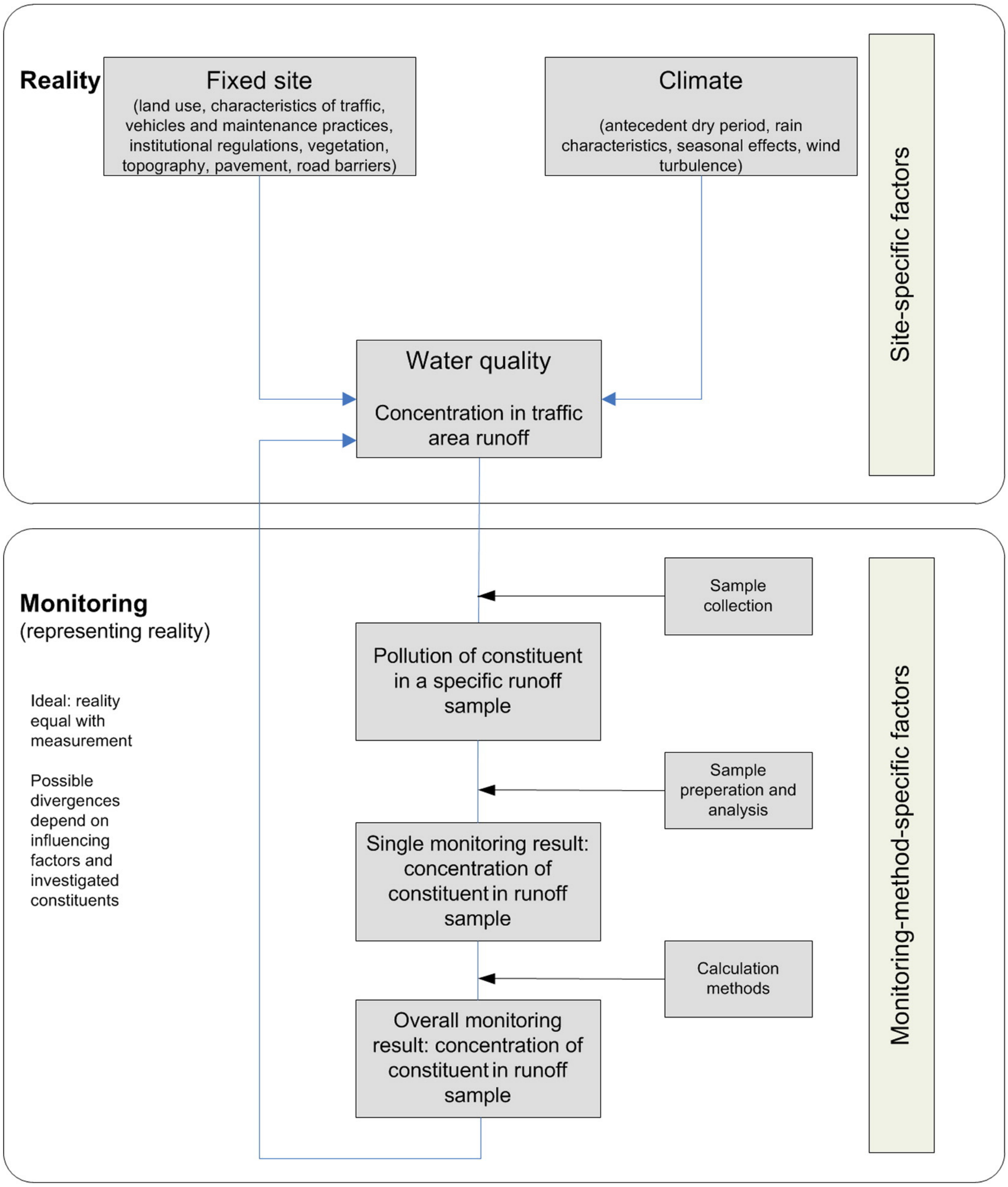

Fig. 1. Factors influencing monitoring programs and general flow schema for analysis of runoff characteristics and concentrations.

The final part of site-specific factors describes *operational characteristics* concerning traffic, types of vehicles, maintenance, and institutional regulations. Traffic volume is mostly characterized by *AADT* and varies in this review between 100 and 328,000 vehicles per day. Although some authors have concluded that AADT has the greatest influence on runoff concentrations of metals (Mangani et al., 2005; Crabtree et al., 2008), it might not be the best indicator for traffic area runoff concentrations and should not be used as a sole predictor because it only explains approximately 30% of the variation in these concentrations (Driscoll et al., 1990; Drapper et al., 2000; Kayhanian et al., 2003). Special cases of AADT are the traffic flow volume during sampling and between two sampling periods (Shinya et al., 2003; Hallberg et al., 2007; Li and Barret, 2008). CH2MHILL (1998) concluded that splashing and washing of pollutants from vehicles is more important than the wash-off of pollutants accumulated on road surface during dry periods and splashing corresponds with average vehicle speed during storms (Hallberg et al., 2007). It has not been specified whether the stated AADT is only valid for the monitored lanes or for all lanes in both directions; this makes it difficult to compare different studies, e.g., the site described by Aryal and Lee (2009), and to evaluate the impact of AADT on runoff concentrations. Another traffic-related aspect is that the *percentage of trucks* can be very high in industrial zones (approximately 37%) (Dannecker et al., 1990) and can be as much as 60% of the AADT (Gan et al., 2008). Further factors influencing runoff quality are construction works, car accidents, firefighting foams, and leakages (Hogland et al., 1987; Barrett et al., 1998; Holthuis et al., 2012). *Maintenance* factors, which differ widely among countries (Gan et al., 2008), are mowing of the roadside shoulders (Barrett, 2008), street sweeping (Gromaire-Mertz et al., 1999; Waschbusch, 2003; Horwatich and Bannerman, 2009; Helmreich et al., 2010), and winter services (Sansalone and Glenn, 2002; Bäckström et al., 2003; Crabtree et al., 2006; Hallberg et al., 2007; Klimaszewska et al., 2007; Tromp et al., 2012). The most important *institutional regulation* was the phase-out of Pb (cf. Section 4.1).

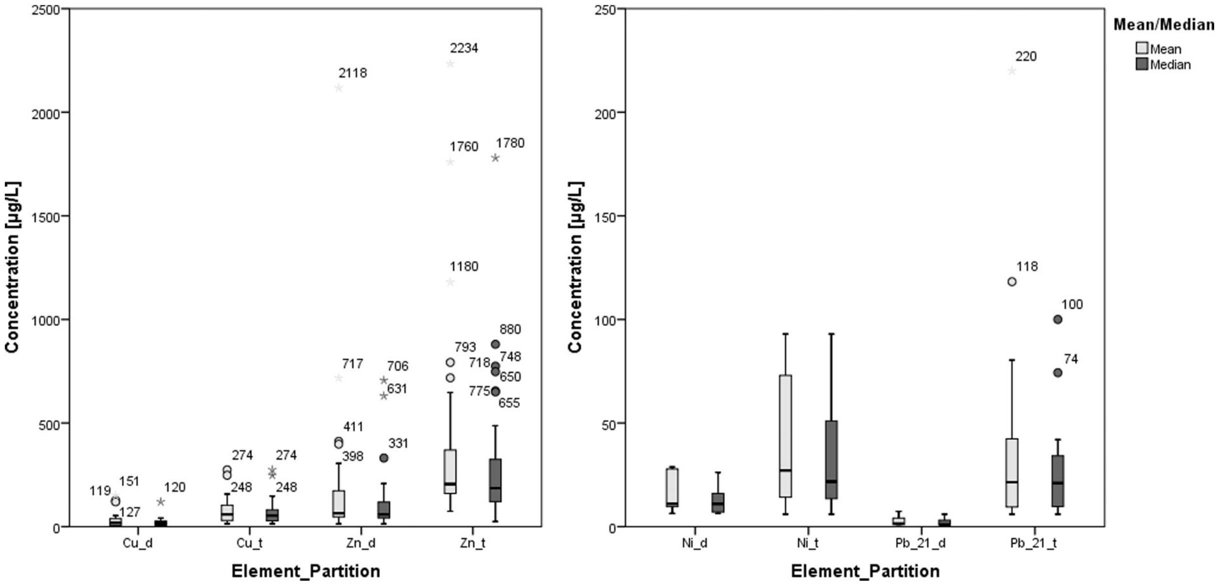

Fig. 2. Differences between mean and median values (d and t) for Cu, Zn (both left), Ni and Pb (both right) for highway runoff data (n = 41). Data were obtained from monitoring programs with more than two observed rain events, and both mean and median data were calculated for each site.

3.1.2. Climate

Climatic site-specific factors are dry deposition rates, antecedent dry periods (ADP), rain characteristics (volume, intensity, and duration), seasonal effects, and wind turbulence. Significant non-traffic-related sources are *dustfalls and dry deposition* during periods without rain, which entrains contaminants and removes them from the atmosphere (Hamilton et al., 1987; Ball, 2002). *ADP* were found to be a statistically significant factor for runoff concentrations due to the accumulation of substances on the traffic area surface (Harrison and Wilson, 1985; Hewitt and Rashed, 1992; Pitt et al., 1995; Irish et al., 1998; Drapper et al., 2000; Shinya et al., 2003; Westerlund et al., 2003; Mangani et al., 2005; Han et al., 2006a; Prestes et al., 2006; Wilson, 2006; Alo et al., 2007; Gan et al., 2008; Li and Barrett, 2008; Moores et al., 2010; Lee et al., 2011). However, Moy and Crabtree (2003), Shinya et al. (2003), Langbein et al. (2006), and Nason et al. (2012) found no relation between ADP and metal concentrations. This is most probably because of street sweeping, wind turbulence, and air turbulence caused by traffic (Bourcier et al., 1980; Helmreich et al., 2010). However, not all storm events completely clean the road surface and this effect prolongs the actual ADP (Cristina and Sansalone, 2003). A special case in (semi)arid regions is the first storm of each season characterized by higher runoff concentrations (Stenstrom and Kayhanian, 2005; Terzakis et al., 2008).

For *rain characteristics*, mostly poor correlations were obtained (Moy et al., 2003; Han et al., 2006a; Desta et al., 2007; MacKay et al., 2011; Nason et al., 2012; Zhang et al., 2013) and only rain history appears to have an effect on the washed-off substances (Steiner and Goosse, 2007). In contrast, some researchers found a correlation between runoff concentrations and storm intensities (Pitt et al., 1995; Tiefenthaler et al., 2001; Crabtree et al., 2006).

Moy et al. (2003) have observed an influence of *seasonal effects* on runoff concentrations; however, the conclusions are heterogeneous. Several studies have indicated that metal concentrations are higher in snowmelt runoff than in rainfall runoff because of the snow accumulation period, and the following melting period appears to be a critical

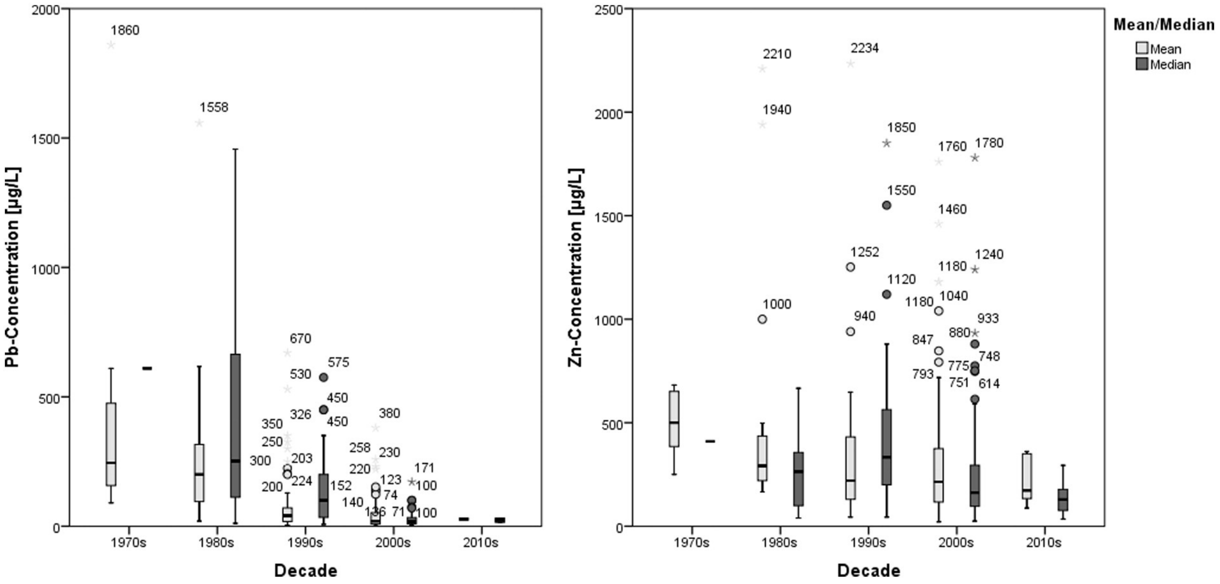

Fig. 3. Historical trends of Pb (n = 194 for mean; n = 146 for median) and Zn (n = 206 for mean; n = 148 for median) in traffic area runoff from the 1970s to date.

Table 4
Statistics of Fig. 3 — historical trends of lead (n = 194 for mean; n = 146 for median) and zinc (n = 206 for mean; n = 148 for median) in traffic area runoff from the 1970s to date.

Element	Decade	Calculation for all mean values from the literature										Calculation for all median values from the literature									
		Min	Median	Geometric mean	Mean	75th	90th	95th	Max	SD	95%[a]	Min	Median	Geometric mean	Mean	75th	90th	95th	Max	SD	95%[a]
Pb	1970s	90,0	293	346	558	923	[b]	[b]	1860	662	694	610	610	610	610	[b]	[b]	[b]	610	[b]	[b]
Pb	1980s	20,0	200	162	277	328	617	[b]	1558	346	167	11,0	252	230	393	685	995	1281	1457	377	146
Pb	1990s	4,0	41,0	40,7	79,6	71,5	227	339	670	119	28,8	7,0	100	73,3	133	200	350	450	575	133	38,2
Pb	2000s	1,4	19,2	20,7	42,2	56,0	118	152	380	59,9	12,0	2,3	18,0	17,2	26,1	34,2	59,0	92,3	171	28,2	7,0
Pb	2010s	24,0	27,5	27,3	27,5	[b]	[b]	[b]	31,0	4,9	44,5	15,0	31,0	37,3	52,7	[b]	[b]	[b]	112	52,0	129
Zn	1970s	250	455	776	3540	5240	[b]	[b]	19,100	7624	8000	410	410	410	410	[b]	[b]	[b]	410	[b]	[b]
Zn	1980s	166	292	366	535	467	1994	[b]	2210	614	316	40,0	264	217	366	364	655	2336	2892	565	238
Zn	1990s	43,8	220	230	329	450	620	940	2234	342	89,1	44,0	333	332	445	564	846	1486	1850	372	116
Zn	2000s	21,0	215	201	295	375	652	857	1760	287	52,4	25,0	162	170	264	304	667	891	1780	296	68,0
Zn	2010s	88,0	173	188	213	353	[b]	[b]	361	115	121	35,0	154	189	545	861	[b]	[b]	2560	991	1040

[a] 95% confidence errors on the means.
[b] No values because of small universe.

one for metal runoff concentrations (Lygren et al., 1984; Sansalone and Buchberger, 1996; Westerlund et al., 2003). A general increase of metals in traffic area runoff in winter was detected due to higher wear and tear as well as to an increased corrosion enhanced by de-icing salts and lower rain intensities (Legret and Pagotto, 1999; Hallberg et al., 2007; Helmreich et al., 2010). In contrast, Mungur et al. (1995) and Brezonik and Stadelmann (2002) detected the highest runoff loads in spring and summer, and Langbein et al. (2006) did not observe any seasonal dependency.

The final climatic factor, i.e., *wind and car-induced turbulence*, leads to a decrease in atmospheric deposition and reduces metal runoff concentrations (Stotz, 1987; Ball et al., 1998; Barbosa and Hvitved-Jacobsen, 1999; Preciado and Li, 2005). Wind turbulence increases with increasing vehicle speeds and decreases with the existence of hard shoulders and road barriers (Scheiwiller, 2008). In special cases such as in Auckland, New Zealand, frequent rain does not allow contaminants to be blown off the road surface (Timperley et al., 2005).

Further description of several site-specific factors for HWY can be found in Opher and Friedler (2010).

3.2. Monitoring-method-specific factors

In most studies, mean or median metal concentrations from runoff of a particular surface type are analyzed; other studies used pollutographs of single events. Further differences occur in sample preparation and analysis. The largest possible deviations arise during sampling and sample preparation, while the actual sample analysis causes less variation, if appropriate analytical methods are used.

3.2.1. Sample collection

The *type of sampling* (automatic or manual) depends on the research objective. For short-term sampling, *manual* (*grab*) *samples* are regularly used because they are a sampling requirement for stormwater permit applications (Line et al., 1997) and are easily manageable for an evaluation of the effectiveness of decentralized stormwater treatment plants (van Ballmoos, 2007; Dierkes, 2010; Rutz, 2012). *Automatic composite samplers* are used for a convenient collection of representative samples with up to several hundred subsamples of entire storm events (Ma et al., 2009; Steiner and Goosse, 2011b). Within the literature study, 13% of the datasets containing information about the sampling type were based on manual sampling, whereas 38% conducted passive-automatic sampling and 49% conducted active-automatic sampling. Active-automatic sampling can lead to the loss of particulate metals (Pagotto et al., 2000). This depends on the runoff composition, the mixture of the flowing water, the sampler intake orientation, and the tube and suction pump used. To minimize the fractionation effect during sampling, highest flow rates and shortest sampling tubes possible should be used; the loss of metals by adsorption can be avoided using polytetrafluoroethylene sampling tubes (Hewitt and Rashed, 1992). For the determination of pH and temperature, automatic samplers should not be used and manual sampling is recommended (Minervini, 2008). This recommendation is applicable to all rapidly degradable compounds and to substances that can adhere on container surfaces. To avoid cross-contamination of runoff samples, bottles must be changed for each rain event to prevent the mixing of samples from two events. Therefore, criteria for detecting a runoff are essential, as well as the event definition, which is directly linked to the sampling strategy and considers both the beginning and end of each event, to prevent a sampling of overlapping events. An appropriate cleaning of tubes, bottles, and the parts of the sampling device in contact with the runoff is necessary. For manual sampling, only bottle cleaning must be considered. Detailed examples of passive-automatic sampling devices have been given by Bannerman et al. (1993) and Li et al. (2008); an active-automatic sampling device has been described by Striebel et al. (1994). A comparison of grab and composite sampling techniques by Ma et al. (2009) concluded that a large number of grab samples (>30)

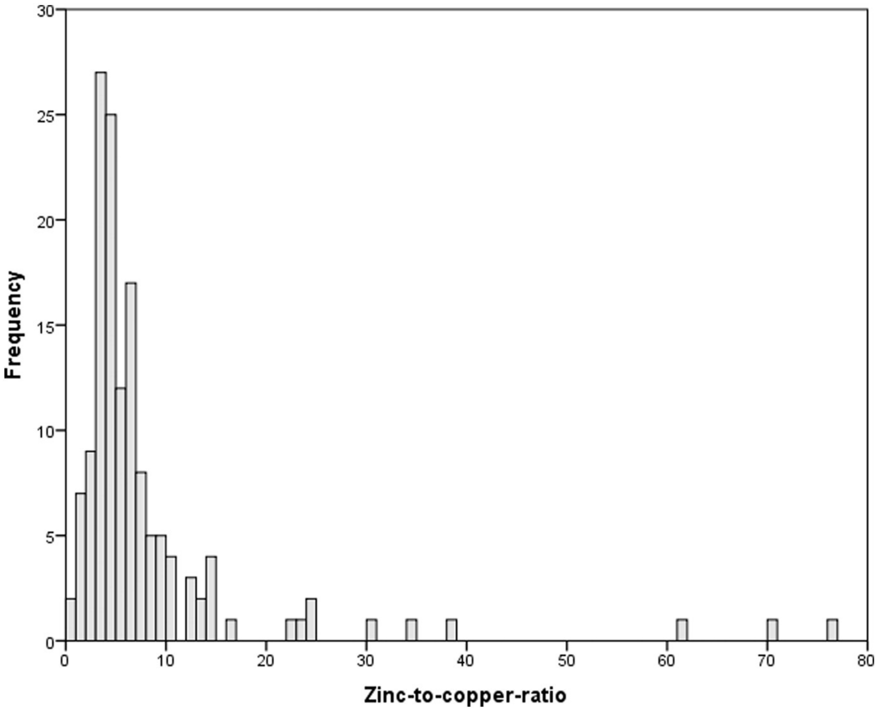

Fig. 4. Frequencies of Zn-to-Cu-ratios for all datasets containing median values (n = 141; mean = 8.1, SD = 10.9).

is required to approach the precision and accuracy of flow-proportional automatic sampling and for detecting a first flush effect, even more grab samples must be obtained. For manual sampling, the best strategy is to collect grab samples flow-proportionally (Stenstrom and Kayhanian, 2005). A storing of samples at 3 °C–6 °C is preferred (Hallberg et al., 2007; Hilliges et al., 2013; Scheiwiller, 2014).

The *sampling strategy* differs between flow-proportional (38% of datasets with information about the sampling strategy), time-proportional (24%), first flush (21%), mixed (12%), and random (5%) sampling.

In *flow-proportional sampling*, combined samples are mostly collected but discrete sampling is used for producing pollutographs (Legret and Pagotto, 1999) and a second device is required to trigger the sampling device. The second device can be, e.g., a magnetic inductive flow meter (Hilliges et al., 2013), a V-shaped overflow with an immersed ultrasonic flow meter (Legret and Pagotto, 1999; Hatt et al., 2009), a weir with a pressure probe (Hallberg et al., 2007), or a bubbler flow meter (Barrett et al., 1998; Nason et al., 2012). Criteria for sampling are very site-specific and can be 20 mL of sample for every 100 L of a runoff (Tromp et al., 2012). This strategy is limited by the detection limit of the second device sensor (Lau et al., 2009).

Time-proportional sampling can be subdivided into first flush-enhanced and equally timed sample collection. Han et al. (2006b) performed first flush-enhanced sampling, in which five grab samples were collected every 15 min in the first hour after the start of a detectable runoff. Subsequently, one sample was obtained every hour for the following 7 h and one or two additional grab samples were collected for events lasting longer than 8 h. Equally timed samples were obtained at specific time intervals by considering the sampling type and site-specific factors such as rain intensity, the slope of the catchment area and the season (Stotz, 1987). In most cases, the time interval is 5 min but it varies between a few minutes (2 min (Tiefenthaler et al., 2001) or 3 min (Chang et al., 2009)) up to 45 min (Golwer and Schneider, 1983) and 60 min (Gäth et al., 1990). Discrete time-proportional samples can be handled similar to mixed/combined flow-proportional samples by considering the data for simultaneous and continuous flow measurements.

For *first flush sampling*, which is a special case of time-proportional sampling, three types of triggering signals are used: time, volume, or rain depth. Line et al. (1997) sampled water of the first 5 min per rain event, Mangani et al. (2005) collected the first 10 L, Drapper et al. (2000) collected the first 20 L, Helmreich et al. (2010) collected the first 400 L (equaling a rain depth of 1 mm for this monitored site), and McQueen (2008) collected the first 2.5 mm runoff of a storm event. For an evaluation of the first flush effect, which might occur in the first 30 to 60 min, a sampling of the entire rain event is necessary (Han et al., 2006a). Definitions of the first flush effect are given by Wanielista and Yousef (1993), Saget et al. (1996), and Bertrand-Krajewski et al. (1998).

Mixed sampling by collecting the complete runoff volume of one event is an ideal method to obtain representative concentrations of a storm event. However, this strategy is only practical for small catchment areas (<20 m^2) and a settling of particles in a storage tank must be avoided (Kasting et al., 2003). Some mixed samples are taken over a time period containing several rain events (Nadler and Meißner, 2007; Engelhard et al., 2012).

All *randomly collected samples* were taken manually during storm events to evaluate the effectiveness of best management practices.

The type and strategy of sampling have an influence on metal concentration, as does the *location*, from which runoff samples are taken. E.g., sediments can be retained by the overflow of a measurement channel and are not sampled by the suction pump of an automatic sampler (Legret and Pagotto, 1999). Further aspects are related to the characteristics of the channel. A concrete channel has an influence on pH and long distances between the runoff edge, and the sampling device might allow the settling of solids in the channel during rain events with low intensities. Coatings and tube materials (e.g., stainless steel) can increase Ni concentrations in the samples (Nadler and Meißner, 1999).

Overall, as a result of rain events without runoff, equipment failure, and operational reasons such as holidays, not all rain events can be sampled: Grotehusmann and Kasting (2009) sampled and analyzed about half of all events during a one-year investigation period, Lee et al. (2011) monitored 50 out of more than 100 storm events during a

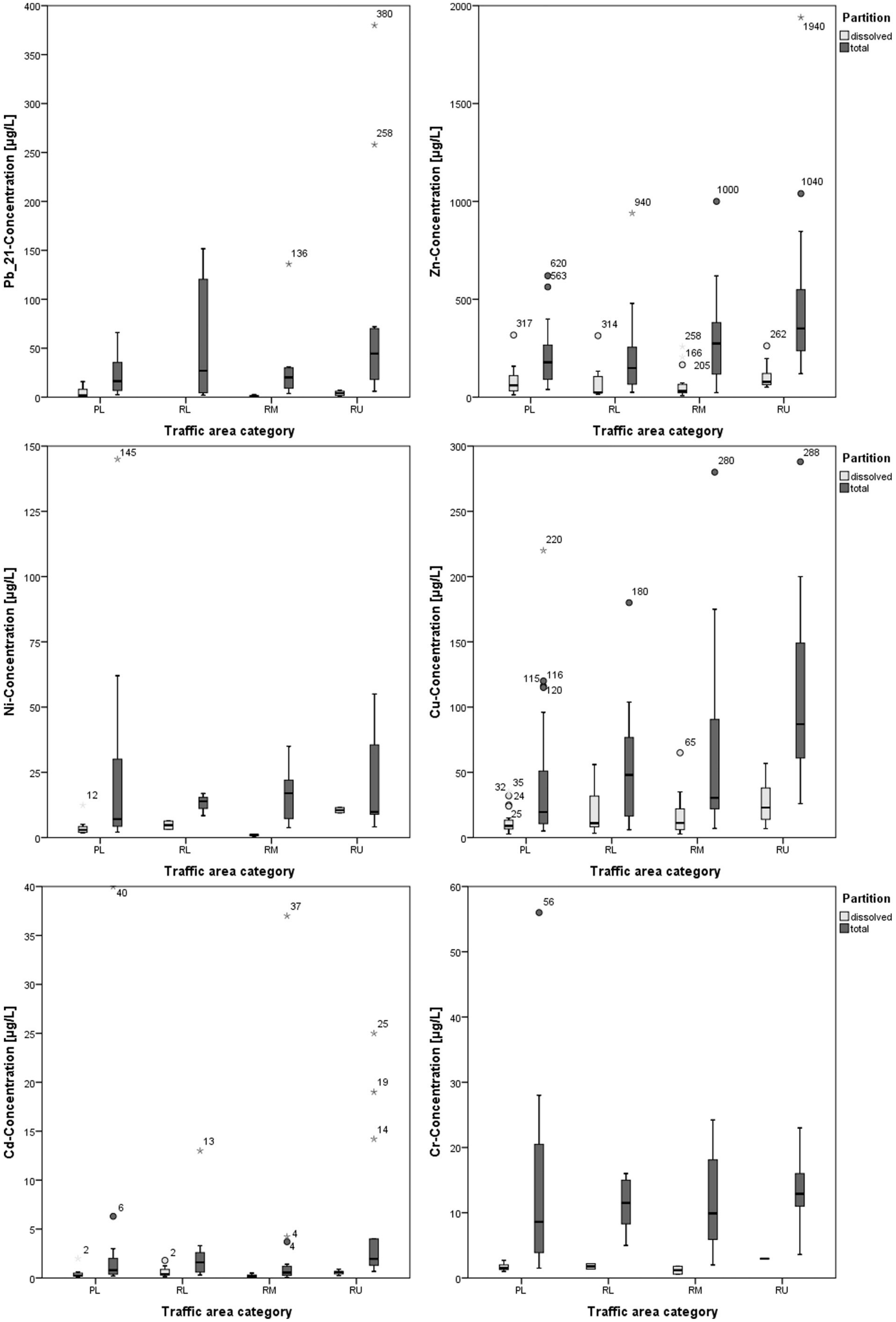

Fig. 5. Mean metal concentrations (d and t) in parking lot (PL) and road (RL, RM, and RU) runoff.

three-year period, and Terzakis et al. (2008) sampled 41 out of 58 rain events during a one-year period.

In conclusion, sampling programs had different objectives and constraints, and the sampling types and strategies used varied widely. Further influencing factors arise from equipment and operators.

3.2.2. Sample preparation and analysis

Prior to analysis, samples must be prepared according to the objectives. Only 36% of the datasets contain information about *preparation methods* (e.g., homogenization, subsampling, and filtration) and only 55 sets describe the holding time. For all metal analyses except those for total concentrations, the *holding time* is essential by having a critical effect on pH and on the fractionation of metals. Runoff samples were held for less than 1 h (Dean et al., 2005; Fulkerson et al., 2007), for 2–3 h (Barbosa and Hvitved-Jacobsen, 1999), for 7 h (Lau et al., 2009) or for a maximum of 24 h (Stotz, 1987; Stotz and Krauth, 1994; Booth and Leavitt, 1999; Brattebo and Booth, 2003; Flint and Davis, 2007; Moores et al., 2010; Lee et al., 2011; Nason et al., 2012; Borne et al., 2013) before delivery to a laboratory and beginning of preparation. Other studies stated the holding time as “immediately” or did not specify it properly. As Minervini (2008) discussed, the description of the sample collection and analysis often does not state how the pH analysis was performed, especially considering the maximum recommended holding time of 15 min (APHA, 2005). Only pH measurements in the field can comply with this requirement (Sansalone et al., 2005). As on-site filtration is risky owing to possible contamination of aqueous samples, samples should be fractionized as soon as practically possible within hours after collection in a laboratory to preserve the partitioning at the time of interest (Gnecco et al., 2008). For the *fractionation process*, a 0.45-μm-pore-diameter membrane filter is used (APHA, 2005) and the metals passing through the filter are the *dissolved part*. Filters with smaller pores (0.1 μm (Herrmann et al., 1992), 0.2 μm (Kluge et al., 2014), and 0.22 μm (Mangani et al., 2005)) and larger pores of up to 0.8 μm (Golwer and Schneider, 1983; Fulkerson et al., 2007) have also been applied. In addition, centrifuging (Bourcier and Hindin, 1979) and decanting before filtration (Bäckström et al., 2003) have been conducted. After filtration, the samples are mostly conserved with nitric acid to a pH of less than 2. The *soluble part* is determined as the dissolved part but from an acid preserved solution. Further factors associated with the filtration process are the diameter of the filter, the manufacturer, the volume of sample processed, and the amount of suspended solids in the sample, from which an inclusion/exclusion of colloidally-associated trace metals can occur (Horowitz et al., 1996). Measurements by Langbein et al. (2006) detected that the filtrate might contain fine colloids and particulate material in the nanometer range. An example of contamination during preparation and analysis of aqueous samples that was detected using blanks is described by Bannerman et al. (1993), in which the samples were contaminated with Zn during filtering procedure.

Preciado and Li (2005) described a procedure of using a chelex resin in a glass column to obtain the *resin-exchangeable part* of heavy metals, which is highly bioavailable.

To determine the potentially bioavailable part of a sample that can be *mobile* in different environmental conditions (i.e., for most metals at a lower pH), one part of a sample can be decanted and acidified followed by filtration after 24 h (Bäckström et al., 2003).

The *acid-exchangeable part* of metals is also called the total recoverable or pseudo-total concentration and is determined by adding a strong acid to the sample. Depending on the oxidizing potential of the acid and other equipment used (i.e., autoclave, microwave), a different part of all metals (i.e., all dissolved/soluble and a varying part of the particulate bound metals) is analyzed.

For the determination of *total concentration* of metals, aqua regia digestion (Nadler and Meißner, 1999; Hilliges et al., 2013), aqua regia digestion with a microwave (Shinya et al., 2000; Shinya et al., 2003), or lithium metaborate digestion must be used to destruct any particulate matter. The difference between the results of total and acid-exchangeable concentrations depends on the element, fixed site-specific factors, and climatic factors.

The particulate content is measured by separating and weighing the particulates gravimetrically. The metal concentration in *particulates*, i.e., the particulate bound metals, is usually taken as the difference of total or acid-exchangeable and dissolved or soluble concentrations but can also be determined in the filter residue by acid digestion, autoclaves, microwave digestion, or a combination of these digestion methods.

After sample preparation, the concentrations were determined in most cases using *atomic absorption spectroscopy* (AAS, 62 times), *inductively coupled plasma optical emission spectrometry/inductively coupled plasma mass spectrometry* (ICP-OES/ICP-MS, 108 times), or both techniques consecutively to reduce the detection limits of several elements (25 times), and to improve the differentiation of solid and liquid phases (Sansalone and Buchberger, 1997b).

To obtain precise and accurate data, it is essential to conduct several *quality assurance/quality control* (QA/QC) procedures. First, field replicate samples should be collected and analyzed. Second, field and method blanks, certified reference materials, matrix spikes, and duplicates or triplicates must be considered and analyzed to prevent failures during sample preparation/analysis (Line et al., 1997; Wilson, 2006). Line et al. (1997) used standard and spiked samples for a minimum of 10% of their field samples. A further QA/QC procedure is the use of materials from two manufacturers for every elemental standard used in the analysis (Westerlund and Viklander, 2006).

3.2.3. Calculation methods

Thomson et al. (1997) and Drapper et al. (2000) concluded that a minimum of 17 runoff events provides a statistically representative sample database. In the dataset of this review, the number of events sampled varied between 1 and 211 (Moxness, 1986), with a mean of 18.

The most influential factor for the calculation of mean or median values concerns the analyzed concentrations of samples below the *detection limits*. There are several methods of dealing with this type of result: they could be discarded and only observed concentrations could be used for the calculation (Pitt et al., 1995), or they could be set as the detection values (Barrett et al., 1998; Dierkes, 1999; Lange et al., 2003; Borne et al., 2013), or as numerical values of one-half the detection level (Herrmann et al., 1992; Bannerman et al., 1993; Laschka et al., 1996; CH2MHILL, 1998; Brattebo and Booth, 2003; Flint and Davis, 2007; Grotehusmann and Kasting, 2009; Lau et al., 2009). None of the studies included in the dataset specified, when a mean or median value is stated as “not detected” or when it is calculated using either the full or one-half the detection values and it is often not specified, how many of the analyses were below the detection limit. This has a crucial effect on the concentrations of elements near the detection limit such as Cd or dissolved Cr concentrations and might lead to an overestimation of the dissolved fraction. A comparison of the mean and median concentrations of a HWY runoff shows that the median Cd concentration was as high as the detection limit (1.0 μg/L) and only the mean concentration was slightly higher (1.6 μg/L) (Lange et al., 2003).

Some researchers selected the storm events used for analysis. The *main criterion for the selection* is associated with ADP to distinguish between different events or to discard several rain events. In the first case, different lengths of time between 30 min (Steiner et al., 2008) and 10 h (Barett et al., 1998) of dry weather are used to separate two events and the concentration of each event is used for the calculation of mean/median values. In the second case, an ADP between 24 h (Moy et al., 2003; Wilson, 2006) and up to five days was maintained before stormwater sampling was deployed (Hares and Ward, 1999). This approach, together with the influence of the ADP on runoff concentrations (longer ADP leads to higher concentrations, cf. Section 3.1), might lead to higher metal concentrations in a runoff in comparison with measurements obtained without a selection. A minimum rain depth, which varied between 1.5 mm (Steiner et al., 2008), 3.8 mm

(Nason et al., 2012), 5.1 mm (Horwatich and Bannerman, 2009), 6.4 mm (Wilson, 2006), and 13 mm (Brattebo and Booth, 2003), is considered to ensure that sufficient and representative sample volumes could be collected. Nason et al. (2012) considered a minimum rain duration of 1 h.

Further influencing factors involve data processing and plausibility tests for all relevant data such as flow measurements, clock time adjustments, and communication among sampling devices.

The most important criterion for representative datasets must be a sampling of a full range of seasonal conditions for a complete range of rainfall intensities, depths, and durations (Thomson et al., 1997; Moy et al., 2003; Stagge et al., 2012; Tromp et al., 2012) and all sources of critical pollutants should be considered (Sansalone and Buchberger, 1997b). However, most studies have been performed within a single year or a part of a year and their conclusions often do not reflect the seasonality and environmental variability of the site (Uhl and Kasting, 2002; Steiner and Goosse, 2011a).

Overall mean and median values presented in previous studies, which were calculated using different methods and should describe the real water quality (Fig. 1), are not assumed to be comparable. To prove the correctness of this hypothesis, mean and median concentrations that are both available for each HWY site and contain a minimum of three events are presented in Fig. 2. For the mean datasets, more extreme values and outliers are computed (for all four elements and for the dissolved and total fractions) in comparison with the median values. Therefore, for this review, mean and median datasets are not combined and are used separately to characterize the central tendency and variability of runoff concentrations among sites or site categories.

4. Occurrence and partitioning

4.1. Historical trends

Historical trends of Pb and Zn in traffic area runoff published in literature were analyzed from the 1970s to date. As described by Kayhanian (2012), for HWY runoff, Pb concentrations have been decreasing continuously in the last few decades. The decrease of Pb use as an anti-knocking agent started in the USA in the mid-1980s and was completed in 1996 (FHWA, 1999). In Europe, the situation was not as homogenous as in the USA. In Germany, the beginning of the phase-out of leaded gasoline began in 1976, when the permitted concentration of Pb in gasoline decreased sharply to 150 mg/L (Golwer and Schneider, 1983). The phase-out in other countries of Western Europe started at the latest in 1986 (Berbee et al., 1999) and ended with the elimination of leaded gasoline in Italy in January 2002 (Mangani et al., 2005). At the same time, leaded gasoline was banned in China (Gan et al., 2008). Further reductions in Pb runoff concentrations are related to the substitution of Pb in other sources such as tires and brake linings (Sansalone et al., 1996; Legret and Pagotto, 1999; Davis et al., 2001), lubricating oil and grease (Ball et al., 1998), weights added to vehicles for tire balance (Root, 2000; Bleiwas, 2006), and Pb-based paints on roads and HWY (Mosley and Peake, 2001; Preciado and Li, 2005; Masanao et al., 2006). However, tires still contain Pb (Shinya et al., 2006; McKenzie et al., 2009).

A decline in Pb concentrations can be observed in the dataset of this review. Because of different numbers of measurements per year, the collected data were aggregated into decades to ensure that there were sufficient data for statistical analysis. Less data is available for the 1970s and 2010s compared to the other three decades (Fig. 3). The decline of Pb starting in the 1980s correlates with the statements mentioned above and is comparable to the one presented by Kayhanian (2012) for HWY runoff. Overall median concentrations of Pb in the 1980s are 252 μg/L (for all median values) and 200 μg/L (for all mean values). In the 2000s, overall median concentrations are one order of magnitude lower at 18.0 μg/L (for all median values) and 19.2 μg/L (for all mean values). All data is summarized in Table 4. The highest concentrations in the 21st century illustrated in Fig. 3 were measured in Poland by Klimaszewska et al. (2007), South Korea by Maniquiz-Redillas and Kim (2014), and China by Zhao et al. (2001). To increase the benefit of all other data analysis, only Pb data for the 21st century were used. These Pb concentration datasets shown in Figs. 5 and 6 are highlighted by the use of the index "21". However, in this selected dataset, artifacts caused by the wash-off of Pb deposited on the upper part of road soils cannot be excluded completely.

For Zn, the trend is different. Neither a significant decline nor an increase in measured concentrations can be identified for the last few decades (Fig. 3). For the medians, overall concentrations of Zn in the 1980s are 264 μg/L (for all median values) and 292 μg/L (for all mean values). In the 2000s, overall median concentrations are 162 μg/L (for all median values) and 215 μg/L (for all mean values). All data is summarized in Table 4. Kayhanian et al. (2007) compared different Zn datasets obtained in California and concluded that there was a decrease in measured concentrations. In contrast, an increase in runoff concentrations is proposed as a result of an increasing use of Zn for safety fences (Dierkes and Geiger, 1998) and of galvanized car parts containing a Zn plating that should prevent corrosion (Sansalone and Buchberger, 1997a). In addition to these increasingly common applications, Zn has been used for decades in several structural elements, batteries (Davis et al., 2001), tires (Van Bohemen and Van de Laak, 2003; McKenzie et al., 2009), brake linings (Legret and Pagotto, 1999), motor oils and grease (Ball et al., 1998). Consequently, Legret and Pagotto (1999) indicated that Zn concentrations remain highly variable depending on the use of safety barriers made from galvanized steel and site-specific factors that have an influence on tire and brake wear. This is confirmed by the occurrence of several outliers and extreme values shown in Fig. 3. The highest values in the 21st century are affected by the corrosion of galvanized elements (Wilson, 2006; Gan et al., 2008) or by highly trafficked and congested roads (Helmreich et al., 2010; Moores et al., 2010) and HWY (Lau et al., 2009; Kluge et al., 2014). Preciado and Li (2005) identified Zn as a metal of future potential concern because it was second in concentration to Fe in most dust, air, and water samples.

4.2. Variability of Zn

Zn concentrations are very variable in traffic area runoff compared with other heavy metals as shown in Section 4.1. In recent years, most monitoring programs measured Zn and Cu, and frequencies of Zn-to-Cu-ratios are calculated for all datasets containing median values ($n = 141$, Fig. 4) to show the variability of Zn compared to Cu.

Calculation of Zn-to-Cu-ratios was first performed by Moores et al. (2010) for total median concentrations of HWY runoff in New Zealand. The calculated ratios in untreated runoff waters were within the range of 4–5 at all four sites (6–8 rain events per site; active-automatic and flow-proportional sampling) except at one site with porous asphalt that had a lower median concentration ratio of 2.4.

The most frequent ratios of Fig. 4 are between 3 and 5 with a larger deviation ($\text{mean} = 8.1$, $\text{SD} = 10.9$). For the highest ratios, either sample contamination or special site conditions are responsible. The highest value of 76.5 was calculated for a PL runoff that received water from a slate roof with Zn gutters (Gnecco et al., 2005). The ratio of 70.5 could be explained by the presence of a nearby Zn smelter (Driscoll et al., 1990), the ratio of 30.8 by vehicle maintenance (Line et al., 1997), and the ratio of 24.5 by the surrounding old residential district (Gromaire-Mertz et al., 1999). The ratio of 23.4 is correlated with a failure of galvanizing material of a BR (Wilson, 2006). Mangani et al. (2005) described the presence of safety fences at a construction site with a nearby agricultural land use, where metal-containing pesticides are used, that might have led to the high Zn-to-Cu-ratio of 22.7. Further ratios might be influenced by the presence of guardrails (ratios 14.0 and 16.5) (Gäth et al., 1990; Nadler and Meißner, 1999), and the erosion of galvanized utilities and noise barrier walls (ratio 14.8) (Gan et al., 2008). The Zn-to-Cu-ratios of 24.9, 34.2, 38.0, and 61.0 are caused by a temporal contamination of samples by a Zn-containing anti-corrosive paint have (Dierkes, 1999).

Table 5

Statistics of Figs. 5 and 6 — mean metal concentrations (dissolved and total) in parking lot (PL), road (RL, RM, and RU), bridge (BR), and highway (HL, HN, and HU) runoff.

Element	Traffic area category	Dissolved concentrations										Total concentrations									
		Min	Median	Geometric Mean	Mean	75th	90th	95th	Max	SD	95%[a]	Min	Median	Geometric Mean	Mean	75th	90th	95th	Max	SD	95%[a]
Pb_21	PL	1,0	1,7	2,5	4,3	8,0	12,0	[b]	15,9	4,6	2,6	2,5	16,3	15,5	23,1	36,3	59,8	65,8	66,0	19,5	9,1
Pb_21	RL	–	–	–	–	–	–	–	–	–	–	2,0	27,0	21,5	61,5	123	[b]	[b]	152	66,2	61,3
Pb_21	RM	0,13	0,4	0,4	0,9	2,3	[b]	[b]	2,8	1,3	2,0	3,7	20,3	18,3	32,3	30,5	[b]	[b]	136	43,1	36,0
Pb_21	RU	0,5	4,0	2,7	3,9	6,5	[b]	[b]	7,0	2,8	4,4	6,0	44,5	38,8	79,3	71,0	331	[b]	380	112	67,4
Pb_21	BR	0,13	0,14	0,4	1,4	[b]	[b]	[b]	3,8	2,1	5,3	24,0	41,7	42,5	49,9	83,7	[b]	[b]	92,3	32,3	51,4
Pb_21	HL	0,01	1,0	0,3	1,3	2,6	[b]	[b]	3,1	1,3	1,3	2,5	25,0	32,1	64,4	118	212	[b]	230	73,1	49,1
Pb_21	HN	12,8	12,8	12,8	12,8	[b]	[b]	[b]	12,8	[b]	[b]	4,4	16,0	18,7	31,7	64,5	[b]	[b]	90,0	34,1	35,8
Pb_21	HU	0,8	2,1	2,3	3,0	4,9	[b]	[b]	7,4	2,4	2,6	1,4	12,6	16,8	33,1	39,7	81,7	155	220	44,9	16,5
Zn	PL	12,0	60,4	56,1	77,2	113	157	293	317	69,1	30,6	39,0	178	155	201	295	397	586	620	147	53,7
Zn	RL	15,0	24,0	42,6	76,2	119	[b]	[b]	314	98,8	76,0	25,0	149	141	212	272	525	[b]	940	219	109
Zn	RM	7,9	31,0	41,4	68,0	73,0	226	[b]	258	77,2	42,8	23,0	274	203	285	384	533	886	1000	217	89,6
Zn	RU	51,0	78,3	97,7	113	159	[b]	[b]	262	71,6	55,1	120	351	379	474	556	982	1805	1940	397	176
Zn	BR	50,0	148	191	354	646	[b]	[b]	1226	432	332	77,0	498	611	2231	700	15,572	[b]	19,100	5607	3766
Zn	HL	5,0	66,5	54,3	76,9	108	177	[b]	191	53,0	30,6	32,3	217	207	306	371	642	1540	1760	359	155
Zn	HN	8,6	66,8	90	204	453	[b]	[b]	577	231	177	52,5	216	248	385	388	1202	1875	2210	477	193
Zn	HU	11,0	50,0	77,1	217	166	595	1838	2118	449	194	21,0	213	237	338	414	682	986	2234	358	103
Ni	PL	1,8	3,0	3,2	3,8	4,4	10,2	[b]	12,4	3,0	1,9	2,1	7,1	10,5	23,7	35,0	86,9	[b]	145	37,0	19,7
Ni	RL	3,1	4,7	4,5	4,7	[b]	[b]	[b]	6,3	2,2	20,2	8,4	13,9	12,5	13,1	[b]	[b]	[b]	16,9	4,3	10,7
Ni	RM	0,5	1,0	0,9	0,9	[b]	[b]	[b]	1,3	0,4	1,0	3,8	17,0	12,7	16,3	23,0	[b]	[b]	35,0	11,2	11,3
Ni	RU	9,5	10,5	10,5	10,5	[b]	[b]	[b]	11,5	1,4	12,7	4,1	9,8	13,8	20,5	40,4	[b]	[b]	55,0	20,2	21,2
Ni	BR	3,0	4,8	8,3	15,9	35,5	[b]	[b]	49,0	19,5	20,5	6,0	26,7	28,0	82,0	65,0	[b]	[b]	458	154	129
Ni	HL	–	–	–	–	–	–	–	–	–	–	6,0	12,0	15,6	22,6	35,2	[b]	[b]	73,0	25,3	26,5
Ni	HN	4,0	11,0	10,6	14,0	[b]	[b]	[b]	27,0	11,8	29,3	4,0	20,0	16,1	29,3	57,0	[b]	[b]	83,0	30,8	23,7
Ni	HU	1,9	9,6	9,9	14,9	28,3	[b]	[b]	28,8	12,5	15,6	2,0	8,7	9,5	19,2	31,5	68,8	[b]	93,0	25,1	12,1
Cu	PL	2,7	9,0	9,4	11,8	13,5	28,5	34,3	35,0	8,7	3,7	5,0	19,6	23,4	40,7	56,0	116	165	220	49,2	15,4
Cu	RL	3,3	11,0	14,5	20,3	37,8	53,2	[b]	56,0	17,9	11,4	6,0	48,0	37,5	53,7	77,4	104	[b]	180	43,9	21,2
Cu	RM	2,7	11,2	11,2	16,0	23,0	35,0	[b]	65,0	14,9	7,2	7,0	30,5	38,6	64,6	100	175	264	280	71,3	31,6
Cu	RU	6,8	23,0	22,2	26,4	39,0	55,0	[b]	56,8	15,9	9,6	26,0	86,9	86,9	105	149	197	275	288	66,6	29,5
Cu	BR	16,0	23,5	24,7	26,1	31,1	[b]	[b]	47,0	9,9	8,3	20,0	54,0	54,9	63,9	93,2	133	[b]	136	36,1	25,8
Cu	HL	5,7	18,0	18,9	23,3	31,1	56,9	[b]	64,0	16,4	9,9	13,3	48,0	49,4	60,7	91,7	124	138	140	38,8	17,2
Cu	HN	4,0	28,7	25,8	34,6	51,5	88,0	[b]	100	26,9	17,1	23,0	53,0	61,8	84,4	97,0	205	394	430	90,4	39,1
Cu	HU	4,1	15,4	18,8	35,5	49,1	122	144	151	42,0	17,3	13,0	56,4	51,4	63,5	74,7	118	145	274	45,5	13,2
Cd	PL	0,05	0,3	0,3	0,4	0,6	1,6	[b]	2,0	0,5	0,3	0,2	0,8	0,9	3,0	2,0	5,6	36,6	40,0	8,6	3,9
Cd	RL	0,14	0,4	0,5	0,7	1,2	[b]	[b]	1,8	0,6	0,6	0,3	1,6	1,5	2,7	2,8	12,0	[b]	13,0	3,8	2,7
Cd	RM	0,01	0,2	0,1	0,2	0,3	0,4	[b]	0,5	0,1	0,1	0,06	0,6	0,7	3,2	1,3	14,1	[b]	37,0	9,1	4,8
Cd	RU	0,25	0,6	0,5	0,6	0,7	[b]	[b]	0,9	0,2	0,2	0,67	2,0	2,7	5,6	6,5	22,0	[b]	25,0	7,8	4,5
Cd	BR	0,04	0,5	0,3	0,5	1,0	1,0	1,0	1,0	0,4	0,4	0,28	3,5	3,9	10,3	15,0	43,8	[b]	47,0	14,4	10,3
Cd	HL	0,02	0,1	0,1	0,5	0,8	[b]	[b]	2,6	1,0	1,1	0,05	0,9	0,7	1,8	1,9	7,6	[b]	9,0	2,6	1,6
Cd	HN	0,50	1,1	1,2	1,4	1,8	[b]	[b]	3,0	0,8	0,8	0,14	1,3	1,2	2,6	4,6	6,2	11,6	11,9	3,0	1,4
Cd	HU	0,10	0,9	0,8	1,3	1,7	[b]	[b]	3,8	1,2	1,1	0,06	1,7	1,6	4,1	2,4	12,5	31,3	35,0	7,9	2,9
Cr	PL	1,0	1,5	1,6	1,7	2,2	2,7	[b]	2,7	0,6	0,4	1,5	8,6	8,6	13,1	21,0	26,4	50,4	56,0	12,5	5,4
Cr	RL	1,4	1,8	1,7	1,8	[b]	[b]	[b]	2,2	0,6	5,3	5,0	11,5	10,4	11,2	15,3	[b]	[b]	16,0	4,3	4,5
Cr	RM	0,6	1,2	1,0	1,2	[b]	[b]	[b]	1,8	0,8	7,6	2,0	9,9	9,0	12,0	24,2	[b]	[b]	24,2	8,9	8,3
Cr	RU	3,0	3,0	3,0	3,0	[b]	[b]	[b]	3,0	[b]	[b]	3,6	12,9	11,6	13,2	17,8	[b]	[b]	23,0	6,4	6,7
Cr	BR	1,3	3,2	3,3	4,0	7,1	[b]	[b]	7,5	2,6	2,7	7,5	11,0	26,7	83,5	140	[b]	[b]	381	140	129
Cr	HL	–	–	–	–	–	–	–	–	–	–	4,9	12,5	14,4	18,6	38,0	[b]	[b]	40,4	14,4	13,3
Cr	HN	0,5	11,3	3,3	11,3	[b]	[b]	[b]	22,1	15,3	137	2,7	9,3	12,7	25,0	36,8	88,7	[b]	89,0	33,4	23,9
Cr	HU	1,5	3,2	3,3	4,5	8,0	[b]	[b]	11,9	4,3	5,3	1,0	7,3	8,6	17,9	13,8	69,3	103	105	26,8	12,5

[a] 95% confidence errors on the means.

[b] No values because of small universe.

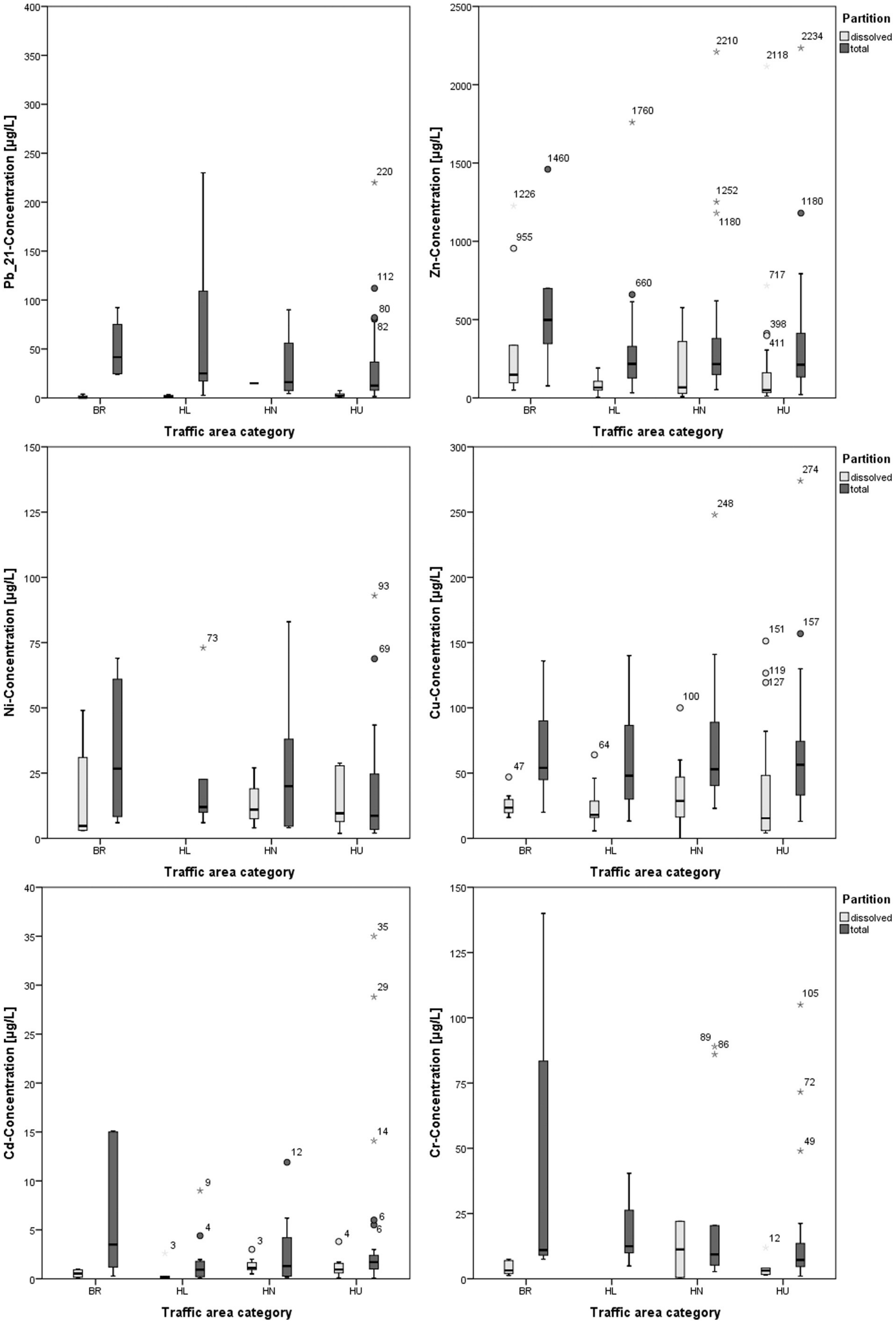

Fig. 6. Mean metal concentrations (d and t) in bridge (BR) and highway (HL, HN, and HU) runoff.

Table 6
Elements that are detected in sampling programs and that are related to traffic or might be used as a tracer for anthropogenic sources.

Element	Literature (partition)
Co	Dannecker et al. (1990) (p, t); Hares and Ward (1999)(t); Bäckström et al. (2003) (d, t); Wilson (2006) (d, t); Hallberg et al. (2007) (d); Herrera (2007) ([a]; d, t); Steiner and Goosse (2007) (t); von Ballmoos (2007) (t); Grotehusmann and Kasting (2009) (t)
Mn	Ellis and Revitt (1982) ([a]; d, t); Golwer and Schneider (1983) (t); Harrison and Wilson (1985) (d, t); Dannecker et al. (1990) (p, t); Sansalone and Buchberger (1997a) (d, t); Booth and Leavitt (1999) (d); Brockbank et al. (1999) (d, t); Hares and Ward (1999) (t); Shinya et al. (2000) (t); Rushton (2001) (t); Bäckström et al. (2003) (p); Shinya et al. (2003) (t); Preciado and Li (2005) (d, t); Hallberg et al. (2007) (d); Gnecco et al. (2008) (t); Hatt et al. (2009) (t); McQueen (2010) (t)
PGE	Wei and Morrison (1994) (Pt; d, t); Laschka et al. (1996) (Pt; t); Grotehusmann and Kasting (2002) (Pd; d, t; Pt; d, t); Moy et al. (2003) (Pd; t); Moy and Crabtree (2003) (Pt; t); Hilliges (2007) (Rh; t); Kasting and Grotehusmann (2007) (Pt; d, t); Nadler and Meißner (2007) (Pt; t); Windhofer et al. (2012) (Pt, Rh; t)
Sb	Dannecker et al. (1990) (p, t); CH2MHILL (1998) (t); Hares and Ward (1999) (t); Wilson (2006) (d, t); Herrera (2007) ([a]; t, d); Nadler and Meißner (2007) (t); Stachel et al. (2007) ([a]; t); Scheiwiller (2008) (t); Grotehusmann and Kasting (2009) (t); Steiner and Goosse (2009) (t)
Ti	Bourcier et al. (1980) (t); Golwer and Schneider (1983) (d, t); Fürhacker et al. (2013) (t)
W	Bourcier et al. (1980) (t); Bäckström et al. (2003) (d, t)

[a] Literature study.

The explanation for low Zn-to-Cu-ratios related to porous asphalt could only be confirmed by one Zn-to-Cu-ratio with a value of 1.2 (Berbee et al., 1999). For comparison, mean ratios of porous asphalt vary between 1.0 and 3.9 with one exception of a ratio of 8.5 (Stotz and Krauth, 1994), which strengthens the conclusion of Moores et al. (2010). Examples of low median ratios resulting from higher Cu concentrations could not be identified.

In conclusion, the calculation of median Zn-to-Cu-ratios can be used to evaluate datasets to detect possible sample contamination and to emphasize the importance of detailed site descriptions.

4.3. Characteristics of traffic area categories

The data for all traffic areas are subdivided into eight categories, as described in Section 2. The data for five categories, including PL, different roads without HWY, and BR, which are presented for the first time, are shown in detail in Tables 1, 2, and 3.

In Table 1, 35 PL are included, of which two were investigated in two monitoring programs (PL16a + b and PL31a + b). Most PL samples were collected in the USA; some samples were obtained in Europe (Germany, Austria, France, Italy, Poland, and Sweden). Only one PL runoff was collected in each of Australia and South Korea.

Generally, PL have low traffic densities. Thus, even in high-use parking areas such as at supermarkets, vehicle changes only occur up to four times per hour and might not exceed 50 vehicles per day per parking slot (Göbel et al., 2007). However, drip losses, tire and brake wear due to braking and steering activities, and exhaust gas emissions because of acceleration are higher compared with non-congested roads. Therefore, most of the Cu loads in runoff waters from industrial land uses originate from PL (Bannerman et al., 1993; Steuer et al., 1997) and PL runoff are a dominant contributor of total Zn and Cd loads in urban runoff (Steuer et al., 1997). Another factor is the contamination of parked vehicles (Pick et al., 2002). PL maintenance includes regular sweeping and cleaning of drains about three times a year (Grotehusmann and Kasting, 2002).

All types of road categories with an AADT of <5000 (RL, 21 sites), 5000 < AADT < 15,000 (RM, 33 sites), and >15,000 (RU, 26 sites) are presented in Table 2.

For RL, most published data are for US sites, with four sites in Germany and one site each in France, the Netherlands, Australia, and South Korea. The land uses are mostly urban and residential but also rural (RL07–RL10), industrial (RL03 + RL18), non-urban desert (RL15), and non-urban agricultural (RL16). RL mostly includes residential, feeder, and smaller collector streets, often with sidewalks and sometimes with side parking zones and curbs. Urban sites have single-family houses and two- to six-story buildings nearby. For RM, 14 datasets have been published for US sites, eight for German sites, and a total of twelve for sites in eight other countries. The land uses are mostly urban and residential but also include rural (RM11, RM13, RM16–18) and non-urban agricultural (RM23) uses. RM include collector roads, residential driveways, and other medium-traffic major roads with mostly two lanes, curbs, and limited on-street parking. RL and RM can be maintained by daily sweeping of street gutters and pressurized washing of sidewalks and gutters several times a week (Gromaire-Mertz et al., 1999). For porous asphalts pressurized water spraying and suction to prevent clogging is used (Legret et al., 1996; Dierkes et al., 1999). For RU, ten sites are located in Germany, three in Poland, three in the USA, and a total of ten sites in six other countries. All sites are highly trafficked arterial roads with almost no hard shoulders. The number of lanes varies between two and five for urban sites, which sometimes have medians, and only RU08 is a two-lane rural road with hard shoulders.

All BR are summarized in Table 3. 21 of the 39 sites are from a huge Australian study by Drapper et al. (2000), and 13 sites are located in the USA. One site in France was monitored with original asphalt surface and after renovation with porous asphalt (BR01a + b), one site in Sweden was selected to evaluate seasonal variations (summer/winter; BR02a + b), one site in Canada was monitored in two different decades (BR16a + b), and two sites are located in China. BR are monitored because contaminant sources are assumed to be exclusively traffic-related (Wilson, 2006), minimal infrastructure modifications are required for sampling (Drapper et al., 2000), and sites are better protected against vandalism (Marsalek et al., 1997). BR decks are intensively maintained (Wu et al., 1998).

All HWY sites are classified depending on the AADT according to Strecker et al. (1990). For HWY with an AADT of >30,000, all sites are distinguished between urban (HU, 64 sites) and non-urban (HN, 33 sites) land uses, which have been proposed to be the only factor having a statistically significant influence on pollutant concentrations for US datasets (Strecker et al., 1990; Kayhanian et al., 2007; Nason et al., 2012). The dataset also includes 35 HL sites. Data are available for five of six continents (no data for South America); 47 of the 132 sites are located in the USA, 24 in Germany, and eleven in each of Switzerland and the United Kingdom. The main difference between RU and HWY in European countries is that the latter mostly have hard shoulders and roads may have traffic signals in contrast to HWY.

4.4. Runoff concentrations of traffic area categories

All published mean metal concentrations (d and t) in PL, RL, RM, and RU runoff for Pb (n = 74), Zn (n = 154), Ni (n = 55), Cu (n = 164), Cd (n = 103), and Cr (n = 64) are plotted in Fig. 5 (Table 5). As datasets are not plotted because of fewer available data (n = 24 with 18 for PL). In most cases, the overall median concentrations for PL are lower than those for roads. Differences in pollution are related to the type of PL use: Employee PL (mostly once-in and once-out per day usage, PL31) are less polluted than highly frequented car PL (supermarket, PL05) and PL for trucks are higher loaded for almost all parameters in comparison to car PL (Grotehusmann and Kasting, 2002). RU is the road category with the highest runoff concentrations for all metals except Ni. Zn has the highest total runoff concentration, followed by Cu, Pb, Ni, Cr, and Cd. The highest dissolved concentrations have Zn and Cu, followed by Ni, Pb, Cr, and Cd. Thus, Pb and Cr are mostly in the particulate phase, whereas Ni and Cd are almost dissolved. For PL, median values for As (2.1 μg/L t; 1.1 μg/L d) are higher than those for Cd (0.8 μg/L t; 0.3 μg/L d). The total concentrations of PL08 (only one event analyzed in contrast to the dissolved values) and the very high values of RL21 are not plotted in Fig. 5.

In Fig. 6, all published mean metal concentrations (d and t) in BR, HL, HN, and HU runoff are plotted separately (Table 5). For BR, the number of datasets varies between seven for Pb and 20 for Zn. For HWY runoff, much more data are available for Pb (n = 61), Zn (n = 144), Ni (n = 42), Cu (n = 142), Cd (n = 83), and Cr (n = 44). For BR, the order of total and dissolved concentrations is equal to the ones presented in Fig. 5 but the Zn concentrations of BR runoff are higher compared with all other categories (cf. Sections 3.1, 4.2, and 4.3). Median values of total Cr concentrations (n = 13) are very high compared with all other datasets. This might be related to the generally very high total concentrations of BR11 (19,100 μg/L Zn, 1860 μg/L Pb, 140 μg/L Cr) and to specific conditions in China (BR38, BR39; 26.8–381 μg/L Cr). From a comparison of two monitoring programs of a French BR with asphalt and after renovation using porous asphalt (BR01a + b), it can be concluded that heavy metal runoff concentrations of porous asphalt are markedly lower and the type of BR deck surface does not affect heavy metal partitioning. A comparison of the effects of winter and summer on the runoff concentrations of a BR in Sweden (BR02a + b) showed higher mean concentrations during winter, and a comparison of two Canadian BR runoff (BR16a + b) indicated a sharp historical decrease in Zn and Pb concentrations and an increase in Cu and Ni concentrations during the 1990s.

For HWY, no significant difference among the three categories HL, HN, and HU could be detected. This contrasts with the conclusions obtained using US datasets that HL and HN have lower runoff concentrations compared with HU (Strecker et al., 1990). For comparison with this dataset, note that in this evaluation, all HN of US sites are in category HL. Thus, in HN, only European and two New Zealand sites are included. According to Strecker et al. (1990), the concentrations of HL should be lower than those of HN and HU. However, by considering worldwide data, the correlation among HWY runoff concentrations, AADT, and land use could not be verified. Thus, other site-specific aspects such as hard shoulders, median strips, noise barriers, and grade of congestion might be better indicators to characterize HWY runoff concentrations. This is confirmed by a comparison of RU data with HWY datasets. For RU, nearly all overall heavy metal median concentrations are higher in comparison to each of the three HWY categories. For special site conditions such as for RM03, the runoff concentrations of an urban road can be higher than most measurements of HWY because of braking and acceleration activities at traffic signals. The results of an evaluation of runoff concentrations of a HWY construction site not yet in use with two other sites on the same HWY showed that Zn runoff concentrations of the construction site are sometimes higher compared with the other two sites and that Cu and Pb concentrations of the construction site are lower (Mangani et al., 2005). This demonstrates the importance of site-specific factors for HWY runoff.

An analysis was performed to examine the hypothesis that a lower pH of the runoff corresponds to a higher proportion of dissolved metals (Mikkelsen et al., 1994; Sansalone and Buchberger, 1997b; Genç-Fuhrman et al., 2007). The dissolved concentrations in runoff samples are influenced by the capacity for rainwater and pH-modified runoff (cf. Section 4.6) to dissolve metals from a surface, which is influenced by kinetic factors, and by the rate of dissolution, which increases as pH decreases. An acidic pH of one entire event confirms the ionic form for Cu as most relevant (Gnecco et al., 2008). However, an evaluation of datasets for the percentages of Cu and Zn dissolved at the prevailing runoff pH could not confirm the speciation proposed by Genç-Fuhrman et al. (2007). The dissolved fraction of Cu in runoff from different sites was analyzed as 52% at a pH of 6.2 (Caltrans, 2003), 81% at a pH of 6.7 (Lau et al., 2009), and 72% at a pH of 8.0 (Mangani et al., 2005). The dissolved Cu fraction varies between 1% at a pH of 7.6 (Pitt et al., 1995) and 93% at a pH of 7.2 (Golwer and Schneider, 1983). For Zn, the dissolved fraction varies between 2% at a pH of 8.1 (Mangani et al., 2005), 11% at a pH of 7.1 (Lange et al., 2003), and 91% at a pH of 6.7 (Lau et al., 2009). Thus, nearly no decrease of the dissolved fraction of Zn and Cu can be found in the pH range between 6.2 and 8.1, and the hypothesis could not be confirmed. Potential reasons include the likelihood that dissolution is kinetically limited, the relative independence of dissolved and particulate sources, or differences in the sample preparation and analysis.

The results from all datasets show that Cu and Zn mostly exhibited intermediate behavior (Harrison and Wilson, 1985; Dean et al., 2005; Herrera, 2007; Kayhanian et al., 2007) but sometimes, they were more dissolved (Timperley et al., 2005; Wilson, 2006; Hilliges et al., 2013). The concentrations of Pb and Cr are mostly in the particulate phase; this was confirmed in several individual monitoring programs (Harrison and Wilson, 1985; Shinya et al., 2000; Timperley et al., 2005; Herrera, 2007; Kayhanian et al., 2007; Kayhanian, 2012; Hilliges et al., 2013). Ni (Shinya et al., 2000) and Cd (Wilson, 2006) are mainly in the dissolved form, although they are sometimes equally partitioned between the two phases (Harrison and Wilson, 1985; Dean et al., 2005; Kayhanian et al., 2007). The particulate fraction of heavy metals might be higher for snowmelt events than rain events (Westerlund et al., 2003). Bäckström et al. (2003) confirmed this for Pb and Zn, although other metals remained at a constant fraction during winter, and Hallberg et al. (2007) determined higher dissolved fractions of Cd, Cr, and Ni in winter compared to summer, whereas no significant differences occurred for Cu, Pb, and Zn. Helmreich et al. (2010) concluded that the fractionation of the heavy metals was not affected by seasonal variations but remarkable fluctuations were observed between different rain events with dissolved fractions greater than 90%. Similar results were confirmed by Dauber et al. (1979). However, Dean et al. (2005) stated that the partitioning of Pb was unaffected by flow rate.

4.5. Other elements

Other elements that are detected in sampling programs and that are related to traffic or might be used as a tracer for anthropogenic sources are listed in Table 6. As tracers, Co and W are potentially suitable for roads and traffic because of their low natural concentrations in environmental waters (Bäckström et al., 2003). Nadler and Meißner (1999) and Huang et al. (1994) suggest that Sb should be used as a marker, too.

Co is mainly used in steel and paints (Makepeace et al., 1995) and in diesel (Roeva et al., 1996). Steiner et al. (2006) concluded that traffic is not the main source for Co in soils, whereas Ward (1990) observed increased levels of Co in soils because of traffic activities. Bäckström et al. (2003) clearly demonstrated that roads act as a source for Co. Total mean concentration of Co varies between 1.5 μg/L (Grotehusmann and Kasting, 2009) and 13.3 μg/L (Bäckström et al., 2003) and dissolved mean concentrations are between 0.1 μg/L (Dannecker et al., 1990) and 15.1 μg/L (Hallberg et al., 2007); dissolved fractions vary between 4.1% (Dannecker et al., 1990) and 67% (Bäckström et al., 2003). The highest mass of Co (around 94%) in runoff was transported during winter at one site in Sweden (Bäckström et al., 2003).

Bourcier et al. (1980) measured W, which is used in tire studs, in concentrations between non-detectable (2.5 mg/L) and 25 mg/L in road runoff (completely in the particulate phase) and did not detect it in precipitation and dust samples. Bäckström et al. (2003) measured W at two sites in summer and winter and found that the particulate fraction is low and the concentrations increased by a factor of ten during winter (5.8–9.2 μg/L).

Sb is a very toxic element, and the main traffic-related sources are brake pads (Von Uexküll et al., 2005). Concentrations of Sb have been presented in ten publications (cf. Table 6). Total mean Sb concentrations are between 0.8 μg/L (Dannecker et al., 1990) and 10.7 μg/L (CH2MHILL, 1998). Dissolved concentrations were analyzed at three sites and vary between 1.2 μg/L (Dannecker et al., 1990) and 5.05 μg/L (Wilson, 2006).

Anthropogenic sources of Mn are moving engine parts (Ball et al., 1998; Drapper et al., 2000), gasoline additives such as methylcyclopentadienyl manganese tricarbonyl (MMT) (Young et al., 1996; Preciado and Li, 2005), brake wear (Ward, 1990; Sansalone et al., 1996), and tire wear (Hares and Ward, 1999). Values of Mn concentrations in runoff from different sites have been presented in 17 publications (cf. Table 6). Shinya et al. (2000) reported that Mn is mainly particle-bound, whereas Sansalone and Buchberger (1997a) and Harrison and Wilson (1985) reported that it is mainly dissolved. Total mean concentrations of Mn vary between 11.1 μg/L (Rushton, 2001) and 659 μg/L (Gnecco et al., 2008) (both PL), and dissolved mean concentrations are between 9 μg/L (Booth and Leavitt, 1999) and 255 μg/L (Sansalone and Buchberger, 1997a). Ward (1990) measured elevated levels of Mn in soils with increased traffic density.

Of the PGE only Rh, Pd, and Pt are related to traffic sources. Since the end of the 1980s, these three elements have been primarily used as catalytic converters and the number of automobiles equipped with these converters has increased sharply (Wei and Morrison, 1994). A three-way catalytic converter contains a total of 2–3 g of Rh, Pd, and Pt (Geiger-Kaiser and Jäger, 2005). Fritsche and Meisel (2004) determined the distribution of PGE in soils along major Austrian HWY and concluded that Rh, Pd, and Pt significantly exceeded natural background values. In road runoff, Rh was only detected by Hilliges (2007) at a concentration of 1.14 μg/L and by Windhofer et al. (2012) at a concentration of 0.08 μg/L. Pt concentrations vary between 0.0065 μg/L (Wei and Morrison, 1994) and 24 μg/L (Moy and Crabtree, 2003), and Pd concentrations are between 0.34 μg/L (Moy et al., 2003) and 8 μg/L (Grotehusmann and Kasting, 2002). The dissolved phases of Pd and Pt are high (65%–81%, Grotehusmann and Kasting, 2002). According to Laschka et al. (1996), Pt runoff concentrations depend on ADP, rain intensity, and rain duration.

Ti was only measured in three studies, and its main source is the wear of white road marking paint containing titanium dioxide as pigment (Makepeace et al., 1995), which is often renewed once a year (Golwer and Schneider, 1983). Another source is tire studs (Bourcier et al., 1980). Ti was not measured in precipitation samples by Bourcier et al. (1980) but was measured in road runoff with a mean concentration of 12.7 mg/L. Golwer and Schneider (1983) detected that Ti was mostly particulate and only 26 μg/L was dissolved. Fürhacker et al. (2013) measured Ti in one HU runoff sample with a total concentration of 630 μg/L.

4.6. Correlation between pH and type of surface

The partitioning of metals in runoff is strongly influenced by the pH of the rainfall, the solids present, the solubility of all substances, the pavement residence time, and the type of surface (Prestes et al., 2006). For asphalt, no significant level of alkalinity is provided to neutralize the pH of rainfall (Sansalone and Buchberger, 1997a), whereas a concrete pavement provides alkalinity to raise the runoff pH more than that of an asphalt pavement (Dierkes, 1999). Therefore, concrete surfaces should have a stronger influence on metal partitioning to the particulate phase than asphalt surfaces.

The evaluation of pH for 63 asphalt, 13 asphalt and concrete, 21 concrete, and four porous asphalt surfaces cannot provide significant differences. The median pH of asphalt surfaces was the lowest (6.8) and varied between 5.4 (Driscoll et al., 1990) and 8.2 (Zhang et al., 2013). A combination of asphalt and concrete surfaces had a median pH of 6.9 and varied between 6.4 (Lau et al., 2009) and 7.5 (Grotehusmann and Kasting, 2009). For concrete surfaces, a mean value of 7.2 was calculated, which is 0.4 units higher than the value for asphalt. The values varied between 5.6 (Driscoll et al., 1990) and 7.9 (Geiger-Kaiser and Jäger, 2005). For porous asphalts, the median value is 7.5.

The non-significant evaluation results of all datasets can be explained by two factors. First, the pavement residence times vary between each monitored site and samples were sometimes collected from a concrete channel that would have had an influence on the pH (Dierkes, 1999). Second, the pH of the rain itself can be different. Two-thirds of the measurements with concrete surfaces were conducted in the 1980s, when rain was more acidic. Conversely, the pH of the runoff of a concrete BR deck increased slightly with increasing flow rates (Dean et al., 2005). Drapper et al. (2000) compared asphalt and concrete BR decks and did not observe any variance in the pH or runoff concentrations. Aspects that might have an effect on porous asphalts have been described by Muschack (1990), and a literature review was provided by Barrett et al. (2006).

4.7. Continental trends

The runoff concentrations of Pb, Zn, and Cu that occur in the highest concentrations compared with other heavy metals were evaluated separately for each continent for which more than five datasets were available (i.e., Asia, Australia, Europe, and North America). For Pb, the recent concentrations are very low and the older, higher concentrations correlate well with the phase-out of leaded gasoline for all continents (cf. Section 4.1). The overall median Pb values for Europe and North America are approximately 30 μg/L and 15 μg/L for the 21st century. For Asia, both Pb values are approximately 50 μg/L, which correlates with the later Pb-phase out in Asia compared with Europe and North America (cf. Section 4.1). The Australian overall median Pb concentration is approximately five times higher than those of Europe and North America for the complete dataset and approximately three times for the dataset of the 21st century. The same results were obtained by Kayhanian et al. (2012) for HWY runoff, whereas the Asian HWY values consist out of one extreme value (Maniquiz et al., 2010). For Cu, the overall median concentrations are approximately 30 μg/L for North America and approximately twice as much for Asia, Australia, and Europe. For Zn, the overall median concentrations are approximately 170 μg/L for North America, 250 μg/L for Europe, 300 μg/L for Australia, and 620 μg/L for Asia. For Asia, it must be considered that fewer data are available compared with the other three continents and the data are mostly for heavily loaded traffic areas. In conclusion, the median values in North America are the lowest for Pb, Zn, and Cu, and the variance of Pb and Zn runoff concentrations among the continents is higher than the variance of Cu.

4.8. Planning stormwater treatment plants

Several factors concerning the occurrence and partitioning of heavy metals must be considered when planning stormwater treatment plants because the differentiation between the dissolved and particulate phases is of great concern for a successful treatment of stormwater to prevent negative effects on groundwater and surface water. As not all metals are present predominantly in the particulate phase (Cd, Ni, Zn, and Cu; cf. Section 4.4), an additional priority should be set for the reduction of dissolved metal concentrations in runoff treatment programs (Tiefenthaler et al., 2001). Because dissolved metals cannot be removed mechanically with solids (e.g., by sedimentation and filtration), a second treatment step (e.g., filter media) is necessary to reduce higher metal runoff concentrations (Hilliges et al., 2007; Steiner and Goosse, 2008; Minervini, 2010; Kayhanian et al., 2012). Maniquiz-Redillas and Kim (2014) investigated the partitioning of heavy metals in runoff and in the effluent of a stormwater treatment plant (manufactured eco-biofilter) and concluded that the fractionation of heavy metals plays an important role on the performance of the system and a reduction of dissolved metal concentrations is necessary. It is recommended that not only the initial runoff or the first 25% of the total runoff should be treated but the entire water volume (Flint and Davis, 2007; Maniquiz-Redillas and Kim, 2014). In addition, the individual site and climatic influencing factors (cf. Section 3.1) are relevant for the construction and operation of treatment plants to prevent negative toxic effects on ecosystems (Schueler, 2000; Nason et al., 2012; Dierkes et al., 2015). As discussed in Section 4.3, the treatment of runoff from large PL should be considered for an effective control of heavy metal loads. Furthermore, a proper control of BR runoff, runoff of congested streets, and arterial roads with traffic signals becomes a concern. A better knowledge of the historical trends (cf. Section 4.1) and seasonal variations of heavy metal runoff concentrations (cf. Section 4.4) can be used for optimization of treatment processes (Hallberg et al., 2007).

5. Conclusions

The conclusions of this review are summarized as follows:

- Trace element pollutant loads determined at a given site depend on the unique subset of site-specific (surrounding land use characteristics, traffic area site data, operational characteristics, and climatic factors) and method-specific factors (sample collection, preparation, analysis, and calculation). In literature, inconsistent conclusions have been obtained regarding how specific variables affect traffic area runoff. Thus, a combination of several interacting factors results in heavy metal runoff pollution, and these factors should be described in detail for each monitoring site. These factors should also be implemented in databases to allow further specifications in future.
- The calculation of median Zn-to-Cu-ratios can be used to detect possible sample contamination and relevant site-specific factors.
- Historical trends for Pb show a sharp decrease during the last decades, consistent with the phase-out of leaded gasoline; no historical trends were detected for Zn.
- The heavy metal runoff concentrations of PL differ widely according to their use (e.g., employee, supermarket, rest areas for trucks). BR deck runoff can contain high Zn concentrations from safety fences and galvanizing elements. Roads with more than 5000 vehicles per day are often more polluted than HWY because of other site-specific factors such as braking and acceleration at traffic signals. Worldwide HWY runoff concentrations are not significantly influenced by AADT and urban/non-urban land uses.
- Pb and Cr are mostly particle-bound, while Zn, Cu, Ni, and Cd occur at a higher fraction in the dissolved phase. Therefore, the treatment of runoff waters containing dissolved heavy metal pollutants by stormwater treatment strategies is important.
- Further traffic-related elements are Mn, Rh, Pd, Pt, and Ti. As tracers, Co, W, and Sb, which have anthropogenic sources, are potentially suitable for traffic areas.

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