DOCTORAL THESIS

An evaluation of sources contributing to urban runoff pollution

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Urban Water Engineering

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To Edith and August,

identified as the *major sources* of joy and meaning in my life.

Preface

This doctoral thesis presents a summary of my research work in the Urban Water Engineering research group at the Department of Civil, Environmental, and Natural Resources Engineering at Luleå University of Technology (LTU). The work was carried out as part of the research cluster Stormwater&Sewers, a collaboration between the Urban Water Engineering research group at LTU, the municipal water utilities Lumire, Vakin, MittSverige Vatten&Avfall, Nodra, and VA SYD, Boden, Skellefteå, and Östersund municipalities, RISE Urban Water Management, NTNU Trondheim and the Swedish Water & Wastewater Association (Svenskt Vatten). The research was given financial support by the Swedish Governmental Agency for Innovation Systems, Vinnova (Grant no. 2014-00804), the Swedish Research Council Formas (Grant no. 942-2016-73), Åke och Greta Lissheds stiftelse (Grant no. 2016-00045), and Vinnova, as part of DRIZZLE Centre for Stormwater Management (Grant no. 2016-05176).

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Alexandra Müller
Luleå, October 2022

Abstract

Urban runoff is a significant pathway for the transport of diverse substances from the urban environment to receiving water bodies. Many of these substances are pollutants of environmental concern with potentially harmful effects on aquatic life. Detailed knowledge of the sources of pollutants entering stormwater runoff is needed to mitigate these effects. The overall aim of this doctoral thesis is therefore to provide new knowledge on the sources contributing to urban runoff pollution and to evaluate the specific contributions of micropollutants from two known major sources: building and structure surface materials, and vehicular activities. The work presented herein also (i) identifies pollutants that are expected to occur in runoff from buildings and other structure surfaces in the urban environment as well as in runoff from the road environment, (ii) estimates the concentrations of these pollutants released into runoff, and (iii) evaluates methods for identifying sources contributing to the pollution of urban stormwater runoff.

The novel work presented in the thesis includes a critical review of the literature on sources contributing to urban runoff pollution, laboratory leaching tests and open-air sampling of pilot panels of building and structure surface materials, and field sampling of urban roadside snow. The literature review was not restricted in terms of type of pollution, while the experiments focused on selected metals and organic micropollutants including phthalates, alkylphenols, bisphenol A, and polycyclic aromatic hydrocarbons (PAHs).

According to the literature review, atmospheric deposition, vehicular activities, and metallic building envelopes are the major pollution sources in the urban environment and have been studied far more extensively than other sources. Moreover, their dominance is likely to continue given their central roles in urban environments. The experimental results confirmed that vehicular activities were sources of octylphenols, bisphenol A, and phthalates as well as the metal(loid)s Sb and W, both of which were rarely determined in previous studies on urban runoff. Building and structure surface materials such as copper sheets, zinc sheets, and polyvinyl chloride (PVC) roofing membranes were found to release Cu, Zn, nonylphenols, and phthalates. Among alkylphenols, nonylphenols were predominantly found in building surface runoff while octylphenols occurred predominantly in roadside snow. Metals occurred more commonly in dissolved (<0.45 μm) form in building surface runoff than in roadside snow, where metals were mainly attached to particles.

A comparison of methods for identifying building surface materials contributing to runoff pollution showed that laboratory leaching tests were generally effective for source identification but not for estimating concentrations in actual runoff, whereas open-air pilot studies were resource-intensive but give results that agree well with analyses of real runoff. In addition, the release of pollutants from building surface materials subjected to in-situ ageing was investigated and the water quality of rainwater-induced runoff was compared to that of snowmelt-induced runoff; neither of these issues were adequately addressed in the previous literature. These studies showed that pollutant concentrations were generally higher in rain runoff than in snowmelt runoff and that pollutant releases from most materials and substances exhibited no decreasing or increasing trend over time. However, the release of nonylphenols from one of the PVCs did decrease over time, possibly because of washing out and material ageing.

Sammanfattning

Dagvatten är en viktig transportväg för en mängd olika ämnen från den urbana miljön till recipienter såsom sjöar och vattendrag. Många av dessa ämnen är föroreningar med potentiellt skadliga effekter på vattenlevande organismer. Detaljerad kunskap om de källor som bidrar med de föroreningar som hamnar i dagvatten behövs för att kunna motverka dessa negativa effekter. Det övergripande målet med denna doktorsavhandling är därför att bidra med ny kunskap om källor till föroreningar i dagvatten och att utvärdera bidraget av föroreningar från två av de största kända källorna: byggnadsmaterial och trafik. Arbetet som presenteras i denna avhandling syftar också till att (i) identifiera föroreningar som kan väntas förekomma i avrinning från byggnader och andra urbana ytor samt i avrinning från vägmiljön, (ii) uppskatta koncentrationerna av dessa föroreningar i avrinning och (iii) utvärdera metoder för att identifiera källor som bidrar till förorening av dagvatten.

Arbetet som presenteras i denna avhandling omfattar en kritisk litteraturstudie av kunskapen om de källor som bidrar till förorening av dagvatten, lakförsök i laboratorium och provtagning i utomhusmiljö från pilotskalepaneler av byggnadsmaterial, samt provtagning av snö från plogvallar vid trafikerade vägar. Litteraturstudien var inte begränsad gällande typ av förorening, medan de utförda experimenten fokuserade på utvalda metaller och organiska föroreningar inklusive ftalater, alkylfenoler, bisfenol A och polycykliska aromatiska kolväten (PAH).

Litteraturstudien visade att atmosfäriskt nedfall, trafik och metalliska byggnadsmaterial är de största källorna till föroreningar i den urbana miljön och har studerats i mycket större detalj än andra källor. Dessutom verkar denna bedömning kvarstå givet deras centrala funktioner i den urbana miljön. De experimentella resultaten visade att trafik är en viktig källa till oktylfenol, bisfenol A och ftalater samt metalloiderna Sb och W, som sällan rapporterats i tidigare dagvattenstudier. Byggnadsmaterial såsom kopparplåt, zinkplåt och takmembran av polyvinylklorid (PVC) visade sig bidra med Cu, Zn, nonylfenoler och ftalater till avrinningen. Bland alkylfenoler visade sig nonylfenoler förekomma i avrinning från byggnadsmaterial, medan oktylfenoler förekom i vägnära snö. Metaller var i större utsträckning i löst form (<0.45 μm) i avrinning från byggnadsmaterial jämfört med i vägnära snö, där övervägande delen av metallkoncentrationerna var partikelbundna.

En jämförelse av metoder för att identifiera bidraget av föroreningar från byggnadsmaterial till avrinning visade att lakförsök i laboratorium generellt var effektiva för att identifiera källor, men inte för att uppskatta koncentrationer i verklig avrinning, medan pilotskaleförsöken utomhus var resurskrävande men gav resultat som överensstämmer med verklig avrinning. Dessutom undersöktes bidraget av föroreningar över tid från byggnadsmaterialen som utsatts för naturlig åldring på plats och avrinning från regn jämfördes med avrinning från snösmältning, vilket inte har studerats tidigare. Resultaten visade att föroreningskoncentrationerna generellt var högre i avrinning från regn än från snösmältning och att de flesta material och ämnen inte uppvisade några tydliga förändringar i koncentrationer över tid. Ett undantag var nonylfenoler i avrinning från ett PVC-material som minskade över tid, möjligtvis till följd av urlakning och materialåldring.

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List of papers

I. Müller, A., Österlund, H., Marsalek, J., & Viklander, M. 2020. *The pollution conveyed by urban runoff: A review of sources.* Science of the Total Environment, 709, 136125.

II. Müller, A., Österlund, H., Marsalek, J., & Viklander, M. 2021. *Comparison of three explorative methods for identifying building surface materials contributing pollutants to stormwater.* Journal of Environmental Management, 299, 113574.

III. Müller, A., Österlund, H., Nordqvist, K., Marsalek, J., & Viklander, M. 2019. *Building surface materials as sources of micropollutants in building runoff: A pilot study.* Science of the Total Environment, 680, 190-197.

IV. Müller, A., Österlund, H., Nordqvist, K., Marsalek, J., & Viklander, M. *Releases of micropollutants from building surface materials into rainwater and snowmelt induced runoff.* Submitted to Water Research, October 2022.

V. Müller, A., Österlund, H., Marsalek, J., & Viklander, M. 2022. *Exploiting urban roadside snowbanks as passive samplers of organic micropollutants and metals generated by traffic.* Environmental Pollution, 308, 119723.

Assessment of contribution to the above papers:

Paper no.	**Development of idea**	**Research study design**	**Data collection**	**Data processing and analysis**	**Data interpretation**	**Publication process**	
						Manuscript preparation for submission	***Responding to reviewers***
I	Shared responsibility	Shared responsibility	Shared responsibility	Shared responsibility	Shared responsibility	Responsible	Responsible
II	Shared responsibility	Shared responsibility	Shared responsibility	Responsible	Responsible	Responsible	Responsible
III	Contributed	Shared responsibility	Contributed	Responsible	Responsible	Responsible	Responsible
IV	Contributed	Shared responsibility	Shared responsibility	Responsible	Shared responsibility	Responsible	N/A
V	Responsible	Responsible	Responsible	Responsible	Responsible	Responsible	Responsible

Responsible – developed, consulted (where needed) and implemented a plan for completion of the task.
Shared responsibility – made essential contributions towards the task completion in collaboration with other members in the research team
Contributed – worked on some aspects of the task completion
No contribution – for valid reason, has not contributed to completing the task (e.g., joining the research project after the task completion)
N/A – not applicable

Publications written within the degree, but not included in this thesis:

Müller, A., Österlund, H., Marsalek, J., & Viklander, M. 2021. *Comparison of three methods for identification of building surface materials as sources of stormwater pollution.* Presented at the 15th International Conference on Urban Drainage, 2021 (ICUD2021).

Milovanovic, I., Herrmann, I., Hedström, A., Nordqvist, K., **Müller, A.,** & Viklander, M. 2021. *Synthetic stormwater for laboratory testing of filter materials.* Environmental Technology, 1-13.

Viklander, M., Österlund, H., **Müller, A.,** Marsalek, J., & Borris, M. 2019. *Kunskapssammanställning: Dagvattenkvalitet. (In Swedish). (State of knowledge: Stormwater quality).* Svenskt Vatten Utveckling. Report 2019-2.

Andersson-Wikström, A., Österlund, H., & Viklander, M. 2016. *Size fractionation of dissolved metals in stormwater in Umeå, Sweden.* In NOVATECH 2016: International conference NovaTech, Urban Water–Planning and technologies for sustainable management, Lyon, France.

Andersson Wikström, A., Österlund, H., Hedström, A. & Viklander, M. 2015. *The release of pollutants from roofing materials in laboratory experiments.* Presented at the 17th IWA International Conference on Diffuse Pollution and Eutrophication, Berlin, Germany.

1 Introduction

Urban stormwater and snowmelt runoff is a major transport vector of pollutants released in the urban environment and therefore contributes significantly to the deterioration of urban receiving waters' quality (e.g., Masoner et al., 2019). The European Water Framework Directive (2000) states that mitigating diffuse pollution is essential for achieving good surface water quality and its amending priority pollutant directive (Directive 2013/39/EU) lists several critical pollutants that should be monitored when assessing water quality. Reliable knowledge about the sources of these pollutants is required to effectively mitigate the adverse effects of stormwater pollution. It is widely recognised that runoff quality is profoundly affected by the properties of the surfaces within a catchment (Charters et al., 2021). Accordingly, building surface materials are a major source of stormwater pollution (De Buyck et al., 2021a) along with atmospheric deposition (Liu et al., 2018) and vehicular activities (Huber et al., 2016).

Moreover, the main aim of the urban water management has traditionally been to protect urban areas from flooding by rapidly removing runoff waters, most commonly through underground pipes that convey runoff to nearby surface water bodies (Butler et al., 2018). However, conventional urban drainage systems now often include stormwater control measures (SCMs) that are designed to reduce flow peaks and volumes and/or to treat runoff, for example by removing particles. The effective implementation of source controls and other SCMs requires detailed knowledge about the sources of pollution (Loganathan et al., 2013). Previous efforts to identify sources contributing to urban runoff pollution have mainly focused on conventional pollutant groups such as solids, metals, and hydrocarbons. However, relatively little is known about releases of organic micropollutants from sources such as building surface materials (De Buyck et al., 2021a) and vehicular activities (Awonaike et al., 2022) in the urban environment. Furthermore, new substances, products, and materials are continuously introduced into urban environments as a result of technological development and the phasing-out of harmful substances, meaning that the set of potentially important pollution sources and pollutants that may be present in urban runoff is constantly changing. For example, the phasing-out of leaded gasoline markedly reduced levels of Pb in road runoff (Kayhanian, 2012). Identifying sources of pollutants in urban runoff will therefore continue to be an important task in stormwater quality research.

1.1 Aim and research objectives

The primary aim of the thesis is to provide new knowledge on the sources contributing to urban runoff pollution and to evaluate the specific contributions of micropollutants from two known major pollution sources: building and structure surface materials, and vehicular activities. The following research objectives were therefore defined:

1. Identify pollutants that are expected to occur in runoff from buildings and other structure surfaces in the urban environment and in runoff from the road environment, and estimate the magnitude of the released concentrations.

2. Characterise the differences between the pollution in rain and snowmelt induced building runoff, and roadside snow.
3. Evaluate methods for identifying sources contributing to the pollution of urban runoff.

1.2 Thesis structure

The thesis is based on five appended papers, referred to as Papers I-V. The relationships between these papers are illustrated in Figure 1. Paper I presents a critical review of the literature and the current state of knowledge concerning sources contributing to urban runoff pollution, covering a wide range of pollution sources affecting stormwater quality. The findings of this review may provide helpful guidance in efforts to plan and implement runoff pollution control measures. Papers II-IV focus on the release of pollutants from building and structure surface materials. Paper II reports a screening of substances that can potentially be released from different building and structure materials and then transported with rainwater runoff, while papers III and IV report measured concentrations of pollutants in runoff from pilot panels of the same materials. Paper II also compares and evaluates different methods used for source identification and offers recommendations for the planning of future stormwater quality studies. Paper III includes a discussion of factors influencing the release of substances from building surface materials in open-air environments, which is further elaborated in Paper IV. Moreover, Paper IV investigates the effect of material ageing and surface temperature on micropollutant releases from building surface materials and presents measurements of snowmelt runoff quality, which is a topic not previously addressed in the published literature. Finally, Paper V investigates the contributions of traffic to the burden of micropollutants (metal(loid)s, PAHs, phthalates, alkylphenols, and bisphenol A) in runoff by analysing roadside snow from Stockholm and Luleå.

Collectively, papers I-V provide insights into the relative importance of building surface materials and traffic as sources of pollution when compared to one-another, to the other source types discussed in Paper I, and to relevant guideline values. In addition, the results presented in these papers are used to identify some important implications for future stormwater quality studies and provide a basis for guidance on the selection of mitigation options and a discussion of the effects of factors influencing the runoff pollution burden as well as suitable methods for source identification. This integrative discussion is facilitated by the fact that the pollutant groups studied in Papers II-V are very similar (Paper I was a literature review, not restricted in terms of type of pollution), including conventional pollutants such as suspended solids and metals as well as pollutants of emerging concern such as phthalates and alkylphenols.

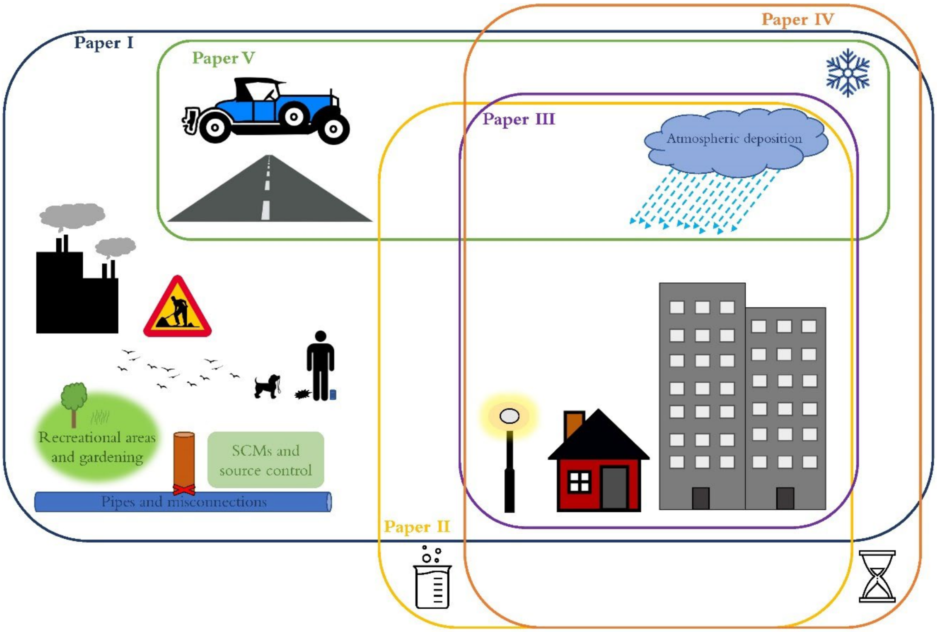


Figure 1 Synthesis of the research topics studied within this thesis, including the appended papers (indicated by roman numerals I-V), as well as an overview of the sources of urban stormwater runoff pollution.

2 Background

Urban stream syndrome, i.e., the ecological degradation of streams draining urban land, is characterised by changes in water chemistry with respect to pollutant concentrations and temperature as well as larger fluctuations in stream hydrology (Walsh et al., 2005). These changes are mainly caused by inputs of runoff water from impermeable surfaces in urban areas (Walsh et al., 2005). Stormwater quality has been studied actively since the mid-20th century and even the earliest studies in this area showed that the composition of stormwater runoff can be highly variable (Åkerlindh, 1950). Vehicular traffic (Laxen & Harrison, 1977) and metallic building surfaces (Malmqvist, 1983) were early identified as some of the most important sources of stormwater pollution. More recent studies have confirmed that these are the major sources of pollutants in stormwater runoff but have also identified additional important sources including atmospheric deposition (Brinkmann, 1985) and the application of road salts (Marsalek, 2003), gravel, and grit (Westerlund & Viklander, 2006) during winter road maintenance.

Stormwater runoff can contain a wide variety of substances originating from diverse anthropogenic activities and drainage surfaces. Many of these substances are of environmental concern and are therefore subject to regulations concerning their use and releases into the environment. For example, the European Union has listed 45 priority substances in a directive on priority substances (Directive 2013/39/EU (2013) that was incorporated into the Water Framework Directive (WFD). This directive also includes environmental quality standards that specify the maximum concentrations and annual average concentrations of these substances that are permitted in surface waters. Similarly, the U.S. Environmental Protection Agency (U.S. EPA) established a priority pollutant list of 126 pollutants that was incorporated into the Clean Water Act (CWA) in 1977. In addition, the National Pollutant Discharge Elimination System (NPDES) permit program was formed under the CWA, addressing stormwater discharges from municipal storm sewers, as well as drainage from areas subject to construction or industrial activities. Permit applications may require collecting and reporting stormwater quality data. Moreover, because there are no regulations dealing with the quality of stormwater discharges on a national level in Sweden, some municipalities and cities have introduced their own regulations for this purpose. For example, in 2008 the Swedish city of Gothenburg introduced guideline stormwater effluent concentrations for substances including metals, nutrients, organic pollutants such as oil and benzo[a]pyrene, total organic carbon (TOC), suspended solids, and pH. The guideline document was updated in 2020. Instead of regulating discharge concentrations, the city of Stockholm (2016) has implemented a requirement of local treatment of the first 20 mm of runoff from impervious surfaces in new constructions and major reconstruction projects. The value of 20 mm was chosen based on estimates indicating that it would imply treatment of 90% of the annual runoff (City of Stockholm, 2016).

The aim of this chapter is to describe the scientific state-of-the-art of the pollutants commonly studied from a stormwater quality perspective (Section 2.1) and the sources of pollutants in stormwater (Section 2.2), before summarising the methods that have been used for source identification in stormwater quality research (Section 2.3), as well as the factors known to affect pollutant releases (Section 2.4).

2.1 Pollutants found in urban runoff and their environmental effects

Many different substances may be present in urban stormwater runoff, and their occurrences and concentrations vary with numerous factors including the season and catchment type. Moreover, because paved surfaces in the urban environment are heated up by solar radiation, runoff may carry significant thermal pollution that can adversely affect heat-sensitive aquatic environments such as cold water fisheries (Van Buren et al., 2000; Thompson et al., 2008). This section describes the pollutants frequently detected and measured in stormwater quality studies.

2.1.1 Solids

Suspended solids are a widely recognised component of stormwater pollution and were therefore measured even in the earliest studies on this topic (Weibel et al., 1964; Leopold, 1968; Lisper, 1974). The solids in stormwater have highly variable characteristics and may include particles of both organic and inorganic origin; mineral and anthropogenic particles originating from tyre and road wear are particularly common (U.S. EPA, 1983). The pollution of water bodies with microplastic particles (MPs) is a global environmental problem that has attracted considerable attention in recent years (Horton et al., 2017a). MPs are a diverse group of particles originating from the anthroposphere and include tyre and road wear particles (TRWPs) originating from vehicular traffic. High concentrations of TRWPs have been measured in roadside snowbanks (Vijayan et al., 2022) and highway runoff (Lange et al., 2022).

Solids in water are often reported as total suspended solids (TSS), a term encompassing everything from larger particles such as sand (which are deposited in still or slowly flowing water but may be resuspended if the flow increases) to smaller particles (e.g., silt and clay) that are easily transported in flowing water. Moreover, a comparative study of five methods measuring suspended sediment concentrations and TSS indicated that depending on the method used, the results may vary widely and that standard TSS measurements risk underestimating particle concentrations, especially for the larger particles (Nordqvist et al., 2014). Particles in stormwater can cause a range of problems – for example, they can clog bioretention systems and other stormwater control measures (SCMs) (Blecken et al., 2017) as well as adversely affecting the health of aquatic organisms by clogging gravel substrates that provide habitats and spawning sites for fish, reducing light penetration in the water column, and clogging and abrading fish gills (Bilotta & Brazier, 2008). Particles can also be efficient carriers of other pollutants in street sediments, stormwater, and receiving waters (Marsalek et al., 2008). While smaller particles typically have higher pollutant concentrations (Viklander, 1998), coarser particles account for a greater proportion of the total sediment mass and may collect pollutant-carrying fine particles that are subsequently released during wet weather (Borris et al., 2016). Stormwater runoff may also contain dissolved solids such as chlorides, which originate mainly from the application of road de-icer during winter months and can cause toxic effects in the receiving waters (Marsalek, 2003) as well as increasing the solubility of metals (Reinosdotter & Viklander, 2007).

2.1.2 Metals

Metals are ubiquitous in the urban environment and therefore also in urban stormwater and snowmelt runoff. Accordingly, the U.S. Nationwide Urban Runoff Program (NURP) (1983) concluded that metals were the most prevalent priority pollutant in urban runoff. The metals studied most frequently in an urban stormwater quality context are Cu, Pb, Zn and Cd (Makepeace et al., 1995), often together with Cr and Ni. Metals occur in stormwater as freely dissolved ions, colloidal complexes (Luan & Vadas, 2015), and particle-bound species (Viklander, 1998). Particulate and dissolved metals are commonly distinguished by filtration through a 0.45 µm filter (Buffle et al., 1992) but further fractionation of the dissolved phase has been achieved by, e.g., ultrafiltration (Lindfors et al., 2020) and asymmetric flow-field flow fractionation (Luan & Vadas, 2015). Dissolved metal ions are generally considered to be more bioavailable and toxic than other metal species (Buffle et al., 1992; Makepeace et al., 1995; Luan & Vadas, 2015). An analysis of chemicals threatening the health of aquatic environments in the UK concluded that Cu, Al and Zn posed the highest risk (Johnson et al., 2017). However, many other metals found in stormwater runoff may also be toxic to aquatic life and humans if present in high enough concentrations (Makepeace et al., 1995). Because of their potential to damage aquatic environments, metals such as Pb, Cd and Ni are among the 45 priority substances of major concern for European waters (Directive, 2013/39/EU) and are included in the list of Toxic and Priority Pollutants of the U.S. Clean Water Act (U.S. EPA).

2.1.3 Polycyclic aromatic hydrocarbons (PAHs)

PAHs are organic compounds that occur naturally in e.g., crude oil and gasoline and are commonly spread in the environment through combustion of fossil fuels or wood. Many of them have documented carcinogenic and toxic effects on animals, aquatic organisms, and humans (Makepeace et al., 1995). Consequently, in 1976 the U.S. EPA selected the following 16 representative compounds as target analytes for monitoring PAH levels in environmental samples: naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, benzo[a]anthracene, chrysene, pyrene, fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and dibenzo[a,h]anthracene. The concentrations of these 16 PAHs are now determined routinely in water and other media (Keith, 2015). In addition, one of these compounds, benzo[a]pyrene (BaP), is sometimes used by itself as a marker of PAH levels, notably in environmental quality standards based on the priority substances of major concern for European waters (Directive 2013/39/EU). A substance flow analysis (SFA) and risk assessment found that PAHs were the highest priority organic pollutants emitted from traffic and roads (Markiewicz et al., 2017). Because PAHs are generally hydrophobic, they are often adsorbed on sediment particles or organic matter in stormwater runoff (Shaver et al., 2007). Other hydrocarbons that may be present in stormwater and whose concentrations may be considered when evaluating its quality include oil and grease, benzene, toluene, ethylbenzene, and xylenes (BTEX).

2.1.4 Phthalates

Phthalates are organic industrial chemicals used mainly as plasticisers in the production of plastics, particularly polyvinyl chloride (PVC). Historically, the most commonly used phthalate was di-(2-ethylhexyl)phthalate (DEHP), but it was recently banned for certain applications because of its documented toxic effects and is therefore increasingly being replaced by, e.g., diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) (Jamarani et al., 2018). Phthalates are generally hydrophobic and tend to adsorb onto suspended solids in water (Staples et al., 1997; Björklund et al., 2009). The potential presence of phthalates in stormwater runoff has been known for decades, as demonstrated by the fact that DEHP was monitored during the NURP in the late 1970s and early 1980s (but with severe blank contamination problems obstructing interpretation of the results) (U.S. EPA, 1983). However, it is only in recent years that stormwater quality studies have started regularly including measurements of phthalates, primarily DEHP (Björklund et al., 2009; Zgheib et al., 2012; Gasperi et al., 2022). Because of its documented toxicity and endocrine disrupting effects, DEHP is one of the 45 priority substances of major concern for European waters (Directive, 2013/39/EU). However, toxicological studies on female zebrafish have also demonstrated adverse effects on aquatic organisms after exposure to DINP (Forner-Piquer et al., 2017; Forner-Piquer et al., 2018).

2.1.5 Alkylphenols and alkylphenol ethoxylates

Alkylphenols (APs) are organic industrial chemicals that are mainly used to produce alkylphenol ethoxylates (APEOs), a group of non-ionic surfactants with diverse applications; among other things, they are used in cleaning agents, varnishes, paints, and as industrial process aids (Thiele et al., 1997). Accordingly, a SFA of APs in Stockholm, Sweden, showed that their main uses were in paints and varnishes, sealants, building materials, concrete additives, cleaning agents, and plastic materials (Andersson & Sörme, 2007). APEOs have both hydrophobic and hydrophilic properties, and are degraded into their parent compounds, APs, in the environment (Thiele et al., 1997). The most commonly used APs in industrial applications are nonylphenols (NPs) and octylphenols (OPs) (Björklund, 2011), both of which are among the priority substances of major concern for European waters (Directive, 2013/39/EU). NPs and OPs are acutely and chronically toxic to aquatic organisms and have estrogenic effects (Thiele et al., 1997; ECB, 2002). Several recent studies on urban stormwater runoff have therefore included measurements of their concentrations (Rule et al., 2006; Björklund et al., 2009; Bressy et al., 2011; Gasperi et al., 2014; Becouze-Lareure et al., 2019; Masoner et al., 2019; Gasperi et al., 2022). However, the main sources from which they are released into urban runoff have not been identified in the published literature.

2.1.6 Nutrients

The nutrients N and P are commonly found in stormwater runoff and may be considered a major concern because they can stimulate algal growth, potentially giving rise to algal blooms in receiving waters exposed to sunlight and high temperatures (Shaver et al., 2007; Collins et al., 2010). N occurs in stormwater in many forms, and can be analysed as, e.g., total nitrogen, organic/inorganic nitrogen, nitrate, nitrite, ammonia, and Total Kjeldahl Nitrogen (Makepeace et al., 1995). Similarly, P may be measured in stormwater, e.g., as total, soluble and/or particulate phosphorous, as well as phosphate (Makepeace et al., 1995; Miguntanna et al., 2013). Nutrients in urban runoff commonly originate from fertilisers, pet and wildlife droppings, fallen leaves in the autumn, and atmospheric deposition (Waschbusch et al., 1999; Selbig, 2016; Hobbie et al., 2017). Moreover, Hobbie et al. (2017) found that household fertiliser use was the most important input of N, whereas the main inputs of P were dog waste and transport from residential landscapes to streets.

2.1.7 Other pollutants

Another substance of emerging concern found in urban stormwater is Bisphenol A (BPA), which is an industrial additive used in plastic products such as epoxy resins and may have toxic effects in aquatic environments (Vermeirssen et al., 2017). BPA was previously measured in stormwater runoff (Gasperi et al., 2014; Flanagan et al., 2018) and sediments from a stormwater detention basin draining an industrial area (Wiest et al., 2018). Moreover, laboratory leaching experiment results have shown that it can be released from car bodies, tyres, and PVC (Lamprea et al., 2018; Deshayes et al., 2019).

Pesticides are another important group of pollutants in urban stormwater. In urban environments they are used in agriculture and gardens, and also to protect building structures from weeds, fungi, and algal growth. Many pesticides have been detected in stormwater runoff including atrazine, benzalkonium chloride, carbendazim, cybutryn, diuron, isoproturon, mecoprop, pentachlorophenol, and terbutryn (Burkhardt et al., 2007; Bollmann et al., 2014; Gromaire et al., 2015; Masoner et al., 2019). These chemicals may be harmful to aquatic organisms for obvious reasons, so their use has been restricted or banned in some countries. For the same reason, several pesticides are priority substances of major concern for European waters (Directive, 2013/39/EU) and are included in the list of Toxic and Priority Pollutants of the U.S. Clean Water Act (U.S. EPA).

Pathogenic bacteria may also be present in stormwater; their presence is often monitored by measuring the levels of faecal indicator bacteria (FIBs) as was done by Galfi (2020). Commonly monitored FIBs include Escherichia coli (E. coli) and enterococci, because of their high survival rates also in cold climate regions, and associations with other stormwater quality constituents (Galfi et al., 2016). Baral et al. (2018) estimated that stormwater runoff was the main input of microorganisms to an urban creek during wet weather. Major sources of FIBs in urban runoff include pet and wildlife droppings as well as wastewater contamination of stormwater resulting from misconnections (Ellis, 2004; Paule-Mercado et al., 2016; Baral et al., 2018).

As noted previously, a comprehensive list of all chemicals that may be present in urban runoff would be very long. In addition to the pollutant groups mentioned above, stormwater quality studies have detected polychlorinated biphenyls (PCBs) (Gilbreath & McKee, 2015), organotin compounds (Zgheib et al., 2012), per- and polyfluoroalkyl substances (PFAS) (Gasperi et al., 2022), and dissolved organic matter (DOM), which strongly affects the transport and fate of many other pollutants (McElmurry et al., 2014).

2.2 Sources contributing to stormwater pollution

Sources of pollution in urban stormwater have been studied for several decades and considerable efforts have been made to identify specific pollutant groups from many sources. Much of this work has focused on the known 'major' sources: vehicular traffic, atmospheric deposition, and metallic building envelopes. However, the current literature lacks a comprehensive overview of the sources contributing to the pollution of urban runoff. This section summarises the current state of knowledge concerning sources contributing pollution to urban runoff.

2.2.1 Vehicular traffic and roads

Vehicular traffic was among the first sources identified as contributing significantly to the pollution of stormwater runoff (e.g., Sylvester & DeWalle, 1972; Shaheen, 1975; Laxen & Harrison, 1977) and has therefore been studied extensively in this context. Early studies often evaluated road and highway runoff quality primarily on the basis of TSS, nutrients, and metals. The scale on which these studies have been conducted is illustrated by the work of Huber et al. (2016), whose review of the literature on metal pollution of traffic area runoff includes results from almost 300 monitored sites on six continents. Two major pollution sources associated with vehicular traffic and roads were identified: (i) vehicle operation, including exhausts, leaks, and wear; and (ii) road abrasion by vehicles and road maintenance work. Exhausts from petrol and diesel vehicles with internal combustion engines were identified as sources of solids, PAHs, nitrogen oxides (NO_x), carbon monoxide, sulphur dioxide, and Ni (Brinkmann, 1985; Duong & Lee, 2011; Markiewicz et al., 2017). In addition, vehicles powered by internal combustion engines are usually equipped with catalytic converters, which were identified as sources of Pt, Pd, and Rh (Rauch et al., 2005). Leaks of automotive fluids such as oils and fuels, were identified as the most important source of PAHs from traffic (Markiewicz et al., 2017). Vehicle wear can also add a wide array of chemicals to the road environment that may subsequently enter runoff, and tyre and brake wear were identified as primary sources of pollution (Muschack, 1990). Among the main pollutants associated with tyre wear are Zn (Councell et al., 2004) and microplastics (Horton et al., 2017b), while brake wear mainly releases Cu (McKenzie et al., 2009) and other metals including Zn, Ni, Sb and Pb (Hjortenkrans et al., 2007). Road abrasion is mainly caused by vehicle operations and is exacerbated by the use of studded tyres (Lindgren, 1996); it is an important source of TSS (Hvitved-Jacobson & Yousef, 1991), PAHs (Markiewicz et al., 2017), and microplastics originating from asphalt bitumen and road marking paints (Vijayan et al., 2022). Snow ploughing, which is commonly done for snow management purposes, may scrape particles off the road surface and thereby release road wear particles to the road environment (Westerlund et al., 2003). Other common snow management practices include the application of traction agents such as sand and grit together with road salts as de-icers, leading to the addition of TSS and chloride ions to the runoff (Marsalek, 2003; Westerlund & Viklander, 2006).

PAHs are not the only important organic micropollutants; Awonaike et al. (2022) highlighted that traffic is a major source of many different organic pollutants in road runoff and receiving waters. In particular, studies conducted over the last decade have established that pollutants such as DEHP, NPs, OPs, BPA and PFAS may be present in road and highway runoff (Zgheib et al., 2012; Gasperi et al., 2014; Flanagan et al., 2018; Becouze-Lareure et al., 2019; Gasperi et al., 2022). However, the specific sources of these pollutants have not been fully identified. Car washing, and car wash detergents were suggested as plausible sources of NPs and NPEOs in stormwater (Rule et al., 2006; Björklund, 2010). In addition, laboratory leaching experiments identified tyres as potential sources of OPs and BPA, and car body parts (e.g., plastic details) and automotive fluids as potential sources of NPs and BPA (Lamprea et al., 2018).

2.2.2 Building and structure surface materials

Like vehicular traffic, metallic building materials were early identified as major sources of metals (e.g., Cu and Zn) in urban stormwater runoff (Malmqvist, 1983). Gromaire et al. (2001) estimated that >80% of the Cd, Pb and Zn in wet-weather flows in a combined sewer system in central Paris, France, originated from corrosion of roof cover materials and was released with roof runoff. Similarly, Boller and Steiner (2002) estimated that >50% of the Cu load in urban drainage systems originated from copper used on roofs. Among metallic materials, galvanised steel is an important source of Zn because of its extensive use in urban environments; among other things, it is used in lamp poles, road barriers and fences, and building envelopes and gutters (Clark et al., 2008; Robert-Sainte et al., 2009). Moreover, the metal releases from metallic structures are mainly in the dissolved (<0.45 μm) form and tend to be fairly consistent (or even to increase) over time (Charters et al., 2021). Surface coatings of lacquer or paint were previously suggested to reduce the release of metals from metallic materials relative to that from raw metal sheets. However, even coated metal objects may release significant quantities of Zn and other metals (Robert-Sainte et al., 2009; Winters et al., 2015; Charters et al., 2021). Non-metallic building and structure surface materials are commonly regarded as minor sources but may release substantial amounts of metals to runoff. For instance, pressure-treated wood is an important source of Cu (Clark et al., 2008; Winters et al., 2015) and ethylene propylene diene monomer (EPDM) rubber roof covers released Zn (Winters et al., 2015).

Building surface materials have also been reported to be important sources of pesticides, which are added to products such as renders and paints, bituminous roofing materials, and roofing tiles to prevent weed, moss, and algae growth. Paijens et al. (2020) found that among the pesticides commonly found in stormwater, combined sewer overflows (CSOs), and wastewater, diuron, isoproturon and mecoprop were attributed to the releases from buildings. Other studies have found building surfaces to be sources of e.g., terbutryn and carbendazim (Bollmann et al., 2014) and benzalkonium chloride (Gromaire et al., 2015). Some building and structure surface materials may also release other organic micropollutants. For instance, a SFA identified roofing and façade materials as important sources of NPs and phthalates (Björklund, 2010). This was partly confirmed by Bressy et al. (2011), who found that building runoff was the main source of APs in runoff from a residential catchment in the outskirts of Paris. However, the specific building surface materials used in the catchment that could plausibly have released these APs were not described. One study was found in the literature that investigated the releases of phthalates in runoff from several building surface materials, by open-air pilot panel experiments. However, the levels of the detected phthalates were in that study generally low, and only the pressure treated wood exhibited detectable DEHP concentrations (Winters et al., 2014). In addition, laboratory leaching experiments have identified PVC and some concrete materials as likely sources of NPs (Lamprea et al., 2018). Overall, relatively little is known about the releases of organic micropollutants from building and structure surface materials (DeBuyck et al., 2021a) and the knowledge that does exist comes primarily from SFAs and laboratory experiments; in contrast, the current knowledge of metal releases from metallic building and structure surface materials is based largely on direct measurements.

Interestingly, although there has been extensive research on the quality of rainwater-induced runoff from building surfaces (e.g., roof runoff), a literature search revealed only one study that investigated the quality of snowmelt roof runoff (Daub et al., 1994). This work revealed that levels of dissolved organic carbon (DOC) in runoff from tar felt roofs were higher than those from other roof types.

2.2.3 Atmospheric deposition

Atmospheric deposition (AD) can transport pollutants generated in urban environments, leading to their deposition on drainage surfaces during precipitation events or by dry deposition. Thus, from a stormwater quality perspective, the atmosphere serves more as a pollutant transport pathway than an actual source of pollution (Petrucci et al., 2014), enabling the import of pollutants from local, regional, and remote sources. AD is thus unique among stormwater pollution sources in that it can introduce pollutants generated outside the runoff catchment. Because AD is influenced by an extremely wide variety of pollution sources including industrial activities and vehicular traffic as well as air transport and runoff processes, its impact on stormwater quality can be highly variable (Malmqvist, 1983; Brinkmann, 1985; Morselli et al., 2003; Sabin et al., 2005). Nevertheless, multiple studies have identified AD as an important source of pollutants in stormwater runoff (Brinkmann, 1985; Gunawardena et al., 2013; Petrucci et al., 2014; Liu et al., 2018). In particular, it can contribute significantly to the loads of the following pollutants in urban stormwater: TSS (Murphy et al., 2015); N and P (Hobbie et al., 2017); metals (Davis & Birch, 2011; Omrani et al., 2017; Al Ali et al., 2017; Liu et al., 2018); and PAHs (Boom & Marsalek, 1988; Ruban et al., 2010; Al Ali et al., 2017).

2.2.4 Industrial activities

Industrial activities may contribute pollution to stormwater by releasing pollutants into the atmosphere (with subsequent wet or dry atmospheric deposition) or through direct surface runoff from industrial catchments. Several stormwater quality studies have identified runoff from industrial catchments as 'pollutant hotspots' for metals such as Zn, Cu, and Pb (Pitt et al., 1995; Brown & Peake, 2006; Tiefenthaler et al., 2008; Liu et al., 2018), PAHs (Becouze-Lareure et al., 2019), and NPs/NPEOs (Rule et al., 2006). Additionally, industrial sites producing plastic pellets and other plastic products are potential sources of microplastics in stormwater (Cole et al., 2011). The types and quantities of pollutants that are released depend strongly on the nature of the industrial activities that are conducted, but industrial areas are generally characterised by heavy traffic and a high proportion of impermeable surfaces.

2.2.5 Construction activities

Construction sites and actives are major sources of solids in stormwater because of processes such as soil erosion when land cover is removed (Marsalek et al., 2008). Consequently, TSS is among the most commonly measured parameters in runoff quality studies focusing on construction sites (Wang et al., 2013; Sillanpää & Koivusalo, 2015; Sajjad et al., 2019). Sajjad et al. (2019) found that TSS levels in urban runoff during active construction work were higher than during periods following the completion of construction work. The main construction activities affecting water quality were reported to be earthworks, paving, house construction, and temporary wastewater discharges (Sillanpää & Koivusalo, 2015). In addition, the demolition of old buildings may cause releases of microplastics (Magnusson et al., 2016) and 'legacy pollutants' such as PCBs (Andersson et al., 2004).

2.2.6 Urban drainage systems

Urban drainage systems are generally designed to convey urban runoff in combined or separate sewers and incorporate SCMs designed to reduce runoff volumes, peak flows, and/or pollution levels in the runoff waters. In separate sewer systems, misconnections linking different elements of the wastewater system can be major sources of pollution in urban surface waters. Misconnections include both intentional and unintentional cross-connections between wastewater and stormwater sewers and can cause the entry of industrial and household wastewater into stormwater sewers. Such misconnections may occur in areas where combined sewers have been converted into separate sewers (Brown et al., 2004). In the U.K., toilets, kitchen sinks and washing machines were identified as major problems (Revitt & Ellis, 2016), contributing nutrients, organics, and household detergents to stormwater. Additionally, misconnections were found to be the main contributor of faecal coliforms to stormwater (Makepeace et al., 1995) and can introduce pharmaceuticals and personal care products (PPCPs) that are rarely found in stormwater runoff into stormwater sewers (Boyd et al., 2004).

The pipe materials in the sewer systems are another potential source of stormwater pollution and may cause the quality of stormwater to change during conveyance. For instance, concrete pipes were suggested to increase stormwater pH (Davies et al., 2010; Wright et al., 2011), and Borris et al. (2017) observed significant releases of Zn from galvanised corrugated steel pipes during laboratory experiments. Moreover, synthetic sewer relining materials installed in existing pipes may be sources of various chemicals including carcinogens and endocrine-disrupting compounds, especially shortly after their installation (Whelton et al., 2013; Tabor et al., 2014; Ra et al., 2018; Li et al., 2019).

SCMs and green infrastructure elements of urban drainage systems are generally installed to improve stormwater conveyance. However, factors such as deficient maintenance or poor planning of their installation may cause them to increase the pollutant content of the conveyed runoff. For instance, stormwater ponds or detention basins that were designed to trap particulate pollutants may act as sources of resuspended sediments during periods of high flow or in response to changes in the ambient chemistry (Marsalek & Marsalek, 1997; Wiest et al., 2018). Additionally, road salts can increase metal mobilisation and TSS levels in such systems and other SMCs (Winston et al., 2016; Søberg et al., 2017; Flanagan et al., 2019), and certain materials used in the construction of SCMs may release pollutants. For example, Flanagan et al. (2019) showed that phthalates, APs, and BPA were released from plastic drains, drain filter fabrics, and geomembranes installed in a bioretention system in Paris. Green roofs can also be sources of nutrients, both from their substrate materials (Cheng et al., 2022) and from applied fertilisers (Czemiel Berndtsson, 2010), especially when the roofs are saturated (Alim et al., 2022).

2.2.7 Other sources

Pets and wildlife are important sources of nutrients (Hobbie et al., 2017), and faecal bacteria in stormwater runoff (Baral et al., 2018). In urban areas, dog waste and bird droppings are major inputs of these pollutants (O'Keefe et al., 2005; Steele et al., 2018). For example, Hobbie et al. (2017) estimated that dog waste was the largest source of P and the third largest source of N (after residential fertilizers and atmospheric deposition) in an urban watershed in Minnesota, U.S.A. Fertilizers are commonly applied to gardens, parks, and grassed surfaces such as lawns, all of which usually have relatively permeable surfaces and thus generate little or no runoff unless the ground is saturated or in the case of heavy rainstorms. Nevertheless, lawns and their soils were found to be an important source of P in urban runoff (Waschbusch et al., 1999; Hobbie et al., 2017), along with fallen leaves (Selbig, 2016). Moreover, gardening activities in such areas and others may introduce pollutants originating from garden pesticides into urban runoff (Wittmer et al., 2010; Botta et al., 2012; Bollmann et al., 2014). In addition, artificial turf and recycled rubber mulch, both of which are commonly used in park areas and recreational facilities, are possible sources of microplastics in runoff (Magnusson et al., 2016), and several studies have reported the leaching of Zn, PAHs, and phthalates from rubber mulches into runoff (Kanematsu et al., 2009; Bocca et al., 2009; Llompart et al., 2013; Celeiro et al., 2021).

Littering on urban catchment surfaces can also contribute to the pollution of urban stormwater runoff: cigarette butts can release nano-scale particles, metals (Chevalier et al., 2018), and nicotine (Roder Green et al., 2014), while the degradation of plastic litter can release microplastic particles (Öborn et al., 2022). Intentional and unintentional spills of fluids such as household chemicals, paints, or oils onto catchment surfaces or directly into storm sewer inlets are another possible source of stormwater pollution (Butler et al., 2018). However, studies on such incidents in the scientific literature are scarce, likely because of the difficulty of predicting when littering or fluid spills will occur.

Finally, a possible source of stormwater pollution is the washing of structure surfaces, buildings and road elements, and cars. However, with the exception of detergents used in the cleaning process, the pollutants released by these processes usually originate from sources discussed above such as AD, building surface materials, and vehicular traffic. There have been relatively few published studies on the impact of washing on stormwater quality. However, an analysis of wash water from the washing of road tunnels revealed high levels of PAHs and metals (Meland et al., 2010), consistent with the pollutants commonly found in highway runoff. Car washing releases pollutants such as metals and particles that are attached to the vehicles as well as chemicals used in car-care products (Sörme et al., 2001). Moreover, the washing of plastic-covered surfaces (e.g., painted or coated roofs) may be a source of microplastics in runoff (Sundt et al., 2014).

2.3 Methods used for source identification

Several methods have been used to identify stormwater pollution sources in the scientific literature. This section summarises some of the most commonly used ones, which include field sampling, pilot-scale studies, laboratory experiments, and SFAs. However, the literature contains few comparative evaluations of the relative merits of different experimental methods for identifying sources contributing to urban runoff pollution.

2.3.1 Field measurements

Field measurements of stormwater quality usually have a relatively coarse spatial resolution, meaning that they are best used to detect sources at the catchment level. Studies based on field measurements include large-scale research programmes such as the NURP (U.S. EPA, 2018) and more recently the National Stormwater Quality Database (NSQD), which aims to map and compare stormwater runoff quality in different catchments with different land use types, including industrial, residential, and highway catchments (Pitt et al., 2018). A number of publications have presented field measurements of various pollutants (most commonly those discussed in Section 2.1) in diverse catchment types including highways and roads (e.g., Kuoppamäki et al., 2014; Huber et al., 2016; Lange et al., 2022; Gasperi et al., 2022), residential catchments (e.g., Bressy et al., 2011; Petrucci et al., 2014), and commercial and industrial catchments (e.g., Becouze-Lareure et al., 2019; Lindfors et al., 2020). The field measurements reported in these works include evaluations of stormwater runoff quality based on grab sampling or automatic sampling from storm sewers or sewer inlets (e.g., Lindfors et al., 2020), roadside snow samples collected in cold regions (e.g., Vijayan et al., 2022), pond sediments from detention pods in various catchments (Wiest et al., 2018; Flanagan et al., 2021), and runoff collected from specific sources in urban areas including road and roof runoff (Förster, 1999; Charters et al., 2016).

2.3.2 Pilot-scaled studies

Pilot-scale studies can provide information on runoff quality with a more fine-grained spatial resolution than field measurement campaigns. These studies typically focus on releases of chemicals from specific sources or materials. For example, pilot-scale set-ups have been used to quantify the release of pollutants from various roofing materials (Bertling et al., 2006; Clark et al., 2008; Robert-Sainte et al., 2009; Winters et al., 2015; Gromaire et al., 2015). Pilot-scale studies commonly include analyses of naturally induced runoff samples, normally from rain (as in the studies cited above) or snowmelt, although only one study examining snowmelt samples was found (Daub et al., 1994). Alternatively, they may examine water samples from a controlled source, such as simulated rain on pilot panels. The latter approach was used by authors including Egodawatta et al. (2009), Bielmyer et al. (2012), and Wicke et al. (2014).

2.3.3 Laboratory studies

Small-scale experiments in laboratory environments can be used to study specific sources in a way that cannot easily be replicated in field measurements. For instance, they can be used to investigate the pollutant burden due to specific car parts whose contributions would be impossible to separate from those of other vehicle components if measurements were conducted while the vehicle was in operation. Experiments of this sort have been used to study the leaching of particles from tyres (Davis et al., 2001) and brake pads (Legret & Pagotto, 1999) as well as the release of pollutants from car body parts, leakage of automotive fluids, and shredded pieces of tyres (Lamprea et al., 2018). Other studies have involved collecting dry debris from brakes (Adachi & Tainosho, 2004) and spraying fluid onto disc-brakes to collect the dripping leachant (McKenzie et al., 2009). Similar experiments have been performed on construction materials, including roofing materials, and asphalt and concrete surface materials, for example by Kayhanian et al. (2009). Specific standardised tests have also been used for this purpose, including the dynamic surface leaching test (DSLT) (Bandow et al., 2018), and a modified toxicity characteristic leaching procedure (TCLP) test to simulate acid rain, followed by a 'synthetic rainfall' applied with a spray bottle over the surface of the material (Clark et al., 2008). Other laboratory leaching studies have examined a set of 16 roofing materials (De Buyck et al., 2021b), pre-exposed copper and zinc panels that were sprayed with synthetic rainwater (He et al., 2001), and shredded pieces of construction materials such as PVC and concrete that were leached in methanol and water (Lamprea et al., 2018). Finally, Öborn et al. (2022) studied the releases of microplastics from the degradation of plastic litter, through accelerated weathering and subsequent leaching tests.

2.3.4 Substance flow analyses

Analyses of the sources and fluxes of pollutants are often referred to as substance flow analyses (SFAs) (Hansen, 2002). In stormwater quality research, SFAs have revealed building surface materials to be likely sources of phthalates and NPs (Björklund, 2010), clarified inputs of Cu into aquatic systems in Lausanne, Switzerland (Chèvre et al., 2011), and identified sources of organic pollutants in road runoff (Markiewicz et al., 2017). In addition, Petrucci et al. (2014) developed a SFA method for identifying sources of pollutants in urban catchments that incorporates a protocol for managing uncertainties and applied it to sources of Cu, Pb, Zn and PAHs in a residential catchment in the Paris region. A recent study by Revitt et al. (2022) developed a method to predict pollutant concentrations of Cd, Cu, Zn and PAHs in highway runoff based on pollutant emission factors and the SFA methodology, and presented future scenarios for pollutant concentrations. However, Björklund (2010) concluded that there is a lack of knowledge about the emission behaviours of many pollutants in open-air environments. Indeed, this is a limitation of the applicability of the SFA approach, but it is well suited for screening chemicals to target in future studies.

2.4 Factors influencing pollutant releases

Releases of pollutants from various sources are strongly influenced by the ambient environment. For instance, as mentioned previously, sources with highly permeable surfaces that would normally generate little runoff (e.g., parks and gardens) may become significant pollutant sources when the ground is saturated, or during heavy rainstorms. Moreover, some source categories such as winter road maintenance activities are seasonal. This section describes the current state of knowledge concerning factors influencing pollutant releases from two major sources of stormwater pollution: vehicular traffic and the road environment, and, building and structure surface materials. Different mechanisms play an important role for pollutant releases from these two source categories: while releases of pollutants from vehicular traffic and the road environment are largely governed by processes such as abrasion, wear, and tear; the releases from building and structure surface materials are influenced mainly by weathering and leaching. Both source categories have in common the process of build-up and wash-off of deposited pollutants, which is mainly associated to the preceding dry period.

2.4.1 Within the road environment

Pollution that is deposited in the road environment and may subsequently be transported with runoff originates mainly from vehicular traffic activities. The levels of such pollution and the extent of its transformation is sensitive to several factors relating to both the origin of the runoff (i.e., rain or snowmelt) and traffic patterns. For instance, several studies have found that the deposited sediments in braking, accelerating, and decelerating zones on roads generally have higher metal concentrations than other road locations (Loganathan et al., 2013). Vehicle speed and traffic density (ADT) were also reported to be important parameters that correlate positively with pollutant concentrations, mainly because of higher exhaust emissions and increased road wear (Duong & Lee, 2011; Burant et al., 2018). Another important factor affecting the amount and properties of particles from road wear is the road surface material: Duong and Lee (2011) found that road dust from concrete highways had higher metal concentrations than that from asphalt-concrete mixtures, mainly because the concrete was subject to more severe abrasion.

Rain characteristics such as rainfall intensity (Crabtree et al., 2006) and antecedent dry periods (ADD) (Kayhanian et al., 2003) may also influence pollutant loads in runoff. In cold climates with seasonal snow, the accumulation of pollutants in roadside snow over long periods of time may cause pollutant concentrations to peak during snowmelt (Westerlund & Viklander, 2006; Meyer & Wania, 2008). In the longer term, historical changes in the composition of car fuels have also influenced runoff quality – for example, Pb concentrations in road runoff have fallen significantly following the phasing-out of leaded gasoline (Kayhanian, 2012). Revitt et al. (2022) predicted that the progressive replacement of combustion engine vehicles by electric vehicles will similarly reduce PAH emissions, which are closely related to exhaust emissions.

2.4.2 Releases from buildings and structure surfaces

In addition to their effects on the pollutant content of road runoff, rainfall characteristics affect pollution levels in building runoff. For example, Yaziz et al. (1989) found that higher rainfall intensity led to more effective wash-off of pollutants and that ADD increased the accumulation of pollutants (from AD) in between wash-off events. Several studies have confirmed the influence of rain intensity and ADD on the wash-off of deposited pollutants (e.g., Egodawatta et al., 2009; Wicke et al., 2012; Liu et al., 2018), and rain intensity was also shown to influence the leaching of metals from metallic materials by increasing the removal of corrosion products from metal surfaces (He et al., 2001). Interestingly, however, the dissolution of Cu from copper sheets was higher during low-intensity rainfall than during periods of more intense precipitation (Winters et al., 2015; Charters et al., 2016; McIntyre et al., 2019). Metal leaching is also inversely correlated to rainfall pH (Quek & Förster, 1993; Wicke et al., 2014). It is not yet clear whether rainfall characteristics affect the releases of organic pollutants from buildings to runoff, although it has been suggested that the release of pesticides from façades is influenced by their orientation because the prevailing wind direction affects the amount of façade runoff (Wicke et al., 2022).

In addition to factors associated with rainfall characteristics and the ambient environment, material properties may influence pollutant releases. For example, the release of metals from metallic materials was shown to increase with material age. Specifically, two studies comparing new copper and zinc sheets to old used sheets (material age: 40-55 years) found that the older sheets released larger quantities of Cu and Zn to runoff than newer materials (Robert-Sainte et al., 2009; Wicke et al., 2014), possibly because corrosion led to the formation of a porous surface layer that enhanced metal dissolution (Wicke et al., 2014). McIntyre et al. (2019) also found that material age was positively correlated with Zn releases from painted galvanised steel over four years of measurements. In general, however, little is known about the effects of aging on the release of pollutants (especially organic pollutants) from non-metallic materials. Moreover, material surface characteristics may strongly influence pollutant build-up and wash-off: rough surfaces will probably retain deposited pollutants more effectively than smooth ones because less is transported away by wind and a greater force (i.e., rainfall intensity) is needed for effective wash-off (Quek & Förster, 1993; Egodawatta et al., 2009; Wicke et al., 2012).

3 Methods

Paper I presents a critical review of the previous literature on sources of urban runoff pollution. Paper II comparers three methods for identifying pollution releases from building surface materials: material composition screening, laboratory leaching experiments, and an open-air pilot study. Open-air sampling was conducted in three of the sub-studies presented in this thesis: Papers III and IV, which deal with pollutants found in runoff from pilot panels of commonly applied building and structure surface materials, and Paper V, which focuses on pollution in roadside snowbanks.

3.1 Literature review

The aim of the literature review presented in Paper I was to comprehensively summarise current knowledge concerning the various sources contributing to the pollution of urban stormwater. Because pollution was defined broadly to encompass a wide range of chemical pollutants and solids as well as thermal pollution, two limitations were imposed to ensure that the review's scope remained manageable. First, stormwater was defined as the urban runoff caused by rain and snowmelt that is normally conveyed in public separate storm sewers (thus, excluding combined sewers) and other conveyance elements commonly found in contemporary drainage systems. Second, runoff conveyed via private drainage or treatment systems (e.g., runoff from airports) was considered outside the review's scope. Moreover, detailed analyses of factors affecting pollution releases, the need for mitigation, and potential effects on receiving waters were excluded. Systematic literature searches were performed in scientific databases including Scopus and Google Scholar to find relevant peer-reviewed journal papers, conference proceedings, and books, which formed the basis of the review. The search terms consisted of keywords relevant to the study topic as well as alternate terms with similar meanings (e.g., 'urban runoff' and 'stormwater', or 'vehicle', 'car' and 'traffic') where appropriate. Additional relevant publications were found by reviewing the reference lists of the articles retrieved in the initial searches.

3.2 Laboratory based studies

Nine materials were examined in the laboratory leaching experiments and material composition screening studies presented in Paper II: metal sheets of zinc (ZNS), copper (CUS), galvanised steel (GAL), coated corrugated steel (CST) and stainless steel (STS); bitumen felt (BIF) roofing membranes and bitumen shingles (SHI); and PVC membranes from two manufacturers (PVA, PVB). These materials were chosen based on dialogues with retailers and a roofing company in Luleå, Sweden, and were also partly based on a report by the Swedish National Board of Housing and Planning (Boverket, 2010) on the technical status of Swedish buildings. The purpose of the screening experiments was to investigate whether and to what extent the studied pollutants were present in the materials, while the laboratory leaching experiments were conducted to evaluate the likelihood that the materials would release these substances when in contact with water.

3.2.1 Material composition screening

For the material composition screening experiments, appropriately sized samples of all materials except CST were cut using stainless steel scissors. For the CST sample, the coating was scraped off the underlying steel sheet using stainless steel tools and analysed separately because only the surface layer would come into contact with runoff water in roofing materials used under realistic conditions. To separate the top layer from the underlying layers was not possible for the other materials. The material samples were placed in glass jars and delivered to the accredited laboratory ALS Scandinavia AB, where chemical analyses were performed (for details, see Section 3.5). As shown in Table 3, the solid metal sheets (ZNS, CUS, GAL and STS) were only analysed with respect to metals because it was considered unlikely that they would contain any organic chemicals. The CST coating was analysed with respect to metals and NP/NPEOs, while the other materials (SHI, BIF, PVA and PVB) were analysed with respect to metals, NP/NPEOs, and phthalates.

3.2.2 Laboratory leaching experiments

Duplicate samples of each of the nine materials were cut to appropriate sizes using stainless steel tools. Separate leaching experiments were conducted to evaluate releases of metals and organic compounds to minimise adsorption of constituents to the beaker walls: metal leaching experiments were performed in 500 mL polypropylene (PP) beakers, while organic analyte leaching experiments were performed in 1000-3000 mL glass beakers (depending on the volume needed for analyses). PP beakers were acid-washed in 1 M HNO_3 and rinsed with deionised water, while the glass beakers were rinsed with hexane before each leaching round. For materials whose edges and back faces differed from the front (CST, SHI, BIF, PVA and PVB), the edges and back faces were covered with three layers of a metal-free lacquer for metal analysis. For organic analyses, two material samples were screwed together back-to-back or a single sample was used with its back pressed against the beaker's walls. To detect possible sources of contamination during the leaching process, pieces of plexiglass were used as control samples in the metal leaching experiments and were treated in the same way as the other material samples, including the application of lacquer. For the organic analyses, glass beakers with no added material samples were used as controls.

Synthetic rainwater was used as a leachant to mimic real leaching conditions as closely as possible. The synthetic rainwater was prepared in the Environmental Laboratory of the Luleå University of Technology and its composition was based on Swedish rainwater quality data (Granat, 1990; Kindbom et al., 2001; Karlsson et al., 2003). A stock solution was prepared using Sartorius ultrapure arium® pro water (0.055 µS/cm) mixed with 9.45 M hydrochloric acid (HCl) and six salts ($NaNO_3$, KNO_3, $(NH_4)_2SO_4$, $CaCl_2 \times 2H_2O$, $MgSO_4 \times 7H_2O$ and NaCl) and subsequently diluted 1:1000 with Sartorius ultrapure arium® pro water prior to the leaching experiments, yielding synthetic rainwater with the following concentrations: 3.0 mg/L Cl^-, 0.42 mg/L NH^{4+}-N, 0.49 mg/L NO^{3-}-N, 0.73 mg/L SO_4^{2-}-S, 0.20 mg/L Ca^{2+}, 0.21 mg/L Mg^{2+}, 0.10 mg/L K^+, 1.8 mg/L Na^+, and pH 4.4 ± 0.2. A similar leachant composition was shown to successfully simulate rainwater under field conditions in Sweden (Odnevall Wallinder et al., 2002). Synthetic rainwater with a relatively low pH was preferred in order to simulate a 'worst case scenario' rain, because it was hypothesised that its acidity would maximise the leaching of substances from the materials. The leachant was added to the glass and PP beakers in a volume corresponding to a 32 mm water column on the material surfaces, which corresponds to a 24-hour rain event with a one-year average return interval in Sweden (Wern & German, 2009). The material pieces were then placed in the beakers such that they were immersed in the synthetic rainwater, and covered with either PP lids (for PP beakers) or aluminium foil (for glass beakers), and agitated for 24 hours on an orbital shaking device operating at a low frequency (60 revolutions per minute). Upon completion of this process, the material pieces were left to dry for a minimum of 24 hours and the leaching procedure was repeated. The leachates from the first round of leaching were discarded to avoid bias resulting from high wash-off of chemicals from the brand-new materials. After the second leaching round, the material samples were evaluated visually to detect potential changes in their surface properties, the pH and electric conductivity of the leachate were determined, and leachate samples were submitted to ALS Scandinavia AB for chemical analysis. Total and dissolved metals were analysed in the leachates from all nine materials. In addition, NP/NPEOs were analysed in CST, SHI, BIF, PVA and PVB leachates while phthalates were analysed in SHI, BIF, PVA, and PVB leachates (see Table 3).

Figure 2 Experimental setup for leaching experiments: polypropylene beakers holding material samples and synthetic rainwater (left), and PVB pressed against the wall of a glass beaker before adding the synthetic rainwater (right).

3.3 Open-air pilot study

The open-air pilot study was presented in Papers II, III and IV. Triplicate panels of the nine materials mentioned in Section 3.2 were installed in an outdoor setting at campus of the Luleå University of Technology (LTU) during the winter season of 2016-2017 together with panels of two additional materials: Corten weathering steel (COR) and pre-patinated and lacquered zinc (CTZ) (the CTZ panels were installed at a later stage).

Between their installation and the start of sampling, the panels were exposed to winter and spring weather conditions, including approximately 145 mm of precipitation in the form of both snow and rain. The material panels had dimensions of 1 x 2 m (width x length) and were installed in a randomised order at a mild slope of approximately 10%. The tested materials were brand new (as received from their manufacturers) and were installed roughly six months before the start of sampling. For the purposes of the pilot study, STS was used as a control material to detect airborne sources of the studied pollutants. Moreover, each individual panel was equipped with stainless steel gutters and overlays to collect their runoff while preventing the entry of rainwater. All studied substances were analysed in runoff from STS because it was used as a control material. However, organic substances were not analysed in runoff from the other metal sheets because it was considered very unlikely that they would release organic pollutants. The other substances analysed in the collected runoff were chosen based on the laboratory experiments and screenings described in Section 3.2 as well as trial sampling experiments conducted at the pilot site using a simplified setup. For details on the substances analysed in each materials' runoff, see Table 3.

The study location was surrounded by green areas, office and residential buildings, parking lots, and a small road. Potential nearby sources of airborne pollution included a district heating plant and a steel production plant located approximately 8 km south-east of the LTU campus, although it should be noted that the most common prevailing wind direction at the site was southerly or south-westerly according to the Swedish Meteorological and Hydrological Institute. The measured rain pH at the site was in the range of 5.6±0.4. To facilitate sampling of metals and organic substances from the same sample vessel, runoff samples from the 33 individual panels were collected in perfluoroalkoxyalkane (PFA) bags of approximately 20 L volume. Those PFA bags were supported by plastic pails for stability. Moreover, the surface temperature of one replicate panel of each tested material was continuously recorded at 30-minute intervals using Tinytag Plus 2 loggers with surface thermistor probes (Tinytag PB-5003) mounted on one of the upper corners of the panel (so a total of 11 probes were used). Precipitation data were collected from a weather station approximately 700 m southwest of the experimental site. The configuration of a panel and the runoff collection bag in the open-air pilot experiments is depicted schematically in Figure 3 and photos of pilot panels during rain and snowmelt sampling are shown in Figure 4.

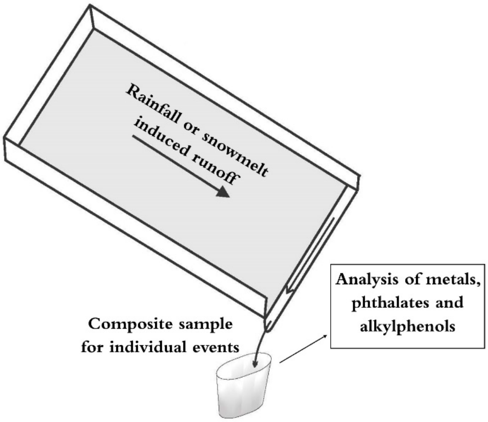


Figure 3 Schematic representation of the open-air pilot experiment setup.

Figure 4 Pilot panels with PFA bags installed before a rain event (left) and during snowmelt runoff collection (right).

3.3.1 Rainfall runoff sampling

Before forecasted rain events, the PFA bags were attached to the gutters using cable ties. The pilot panels were also inspected to ensure that no big leaves or other debris blocked the gutter outlet. The entire runoff volume from one rain event was collected in one PFA bag and treated as a single sample. The concentrations measured in the subsequent analyses can therefore be regarded as event mean concentrations (EMCs). The PFA bags were detached from the pilot panels within at most 15 hours of the end of the rainfall and brought to the Environmental Laboratory of Luleå University of Technology, where their volume was determined by weighing. Each sample was then mixed thoroughly and poured into bottles for determination of its physical and chemical parameters as described in Section 3.5.

Runoff was collected from 11 rain events (R1-R10) between June 2017 and July 2021, and the characteristics of each rain event (in terms of the season in which they occurred, the duration of the antecedent dry period, and the rain characteristics) varied. One of the rain events was interrupted by a brief dry period, during which the PFA bags were exchanged. The samples collected during this event before and after the interruption were processed separately because the bags were almost full and in order to investigate differences between the early and late parts of a rain event (R5.1 and 5.2). Details of the sampled events are presented in Table 1.

Table 1 Characteristics of the sampled rainfall (R) and snowmelt (SM) induced runoff events.

Event	Date	Precipitation (mm)	Average daily temperature[b] (°C)	Antecedent dry days
R1	12/6/2017	10[b]	12	6
R2	4/7/2017	3.5	11	7
R3	26/10/2017	3.2	1.0	0 (23 h)
R4	7/5/2018	3.3	5.2	2
R5.1	28/6/2018	4.6	11	4
R5.2	28/6/2018	5.3	11	0
R6	30/8/2019	9.7	16	5
R7[a]	2/11/2019	3.4	-0.5	2 (snow)
R8	20/8/2020	2.9	16	16
R9	9/6/2021	1.8	16	17
R10	15/7/2021	1.2	20	4
SM1	17/3/2022	0	-0.3	n/a
SM2	18/3/2022	0	2.7	n/a
SM3	21/3/2022	0	4.2	n/a

[a] Approximately 3 cm of snow cover was lying on the panels before the rain started.

[b] Data were collected from the SMHI station approximately 9 km south of the experimental site.

3.3.2 Snowmelt runoff sampling

Snowmelt runoff was collected three times in March 2022. Before the first sampling event, the snow depth on the pilot panels was between 0.4 and 0.5 m. The PFA bags used for sampling were installed in the same manner as for rain sampling, either late in the evening or early in the morning before the start of melting, which is induced by a combination of the temperature rising above 0°C and sunlight on the snow covers. The sampling event was considered complete when the runoff stopped. However, sampling had to be stopped before this occurred for SM2 and SM3 to prevent overfilling of the PFA bags. After sampling, the samples were collected and brought to the Environmental Laboratory of the Luleå University of Technology on the next morning, where they were treated and analysed in the same manner as the rain runoff samples (see Section 3.5).

3.4 Roadside snow sampling

The majority of the roadside snow collection campaign for Paper V was performed in Luleå, a town in northern Sweden (65.62° N, 22.12° E). Luleå has a subarctic climate

(Köppen climate classification code Dfc) and commonly has snow cover for several months in the winter season, allowing pollutants to accumulate in the snow over an extended period. Sampling was performed at seven roadside sites (LU1-LU7) with varying annual average daily traffic (AADT) counts and one reference site (REF) in an urban setting but not in direct proximity to the road environment. Samples were collected during two separate events in the winter season of 2021: February 17th (henceforth referred to as S1) and March 5th (S2), after 56 and 72 days of snow cover, respectively. Sampling at the REF site was performed to determine how much of the measured pollutants could be attributed to airborne transport. Additionally, to compare the roadside snow collected in Luleå to that from a road whose AADT substantially exceeds those of roads in or around Luleå, roadside snow was also collected on one occasion (February 10th, 2021, after 13 days of snow cover) from a highway in Stockholm (E4S) that has one of Sweden's highest AADT values. Stockholm is located approximately 900 km south of Luleå (59.33° N, 18.07° E) and has a humid continental climate (Köppen climate classification code Dfb) with occasional snow cover in the winter season. Details of the different sampling sites are presented in Table 2.

Table 2 Characteristics of the eight roadside sampling sites and the reference site, which was not located in direct proximity to a road environment. AADT data are given for one traffic direction and were collected from the Swedish Transport Administration website (https://vtf.trafikverket.se/SeTrafikinformation).

Sampling location name	Site characteristics	AADT (year of measurement)	No. of lanes per traffic direction	Speed limit, km/h
E4S	Highway north of Stockholm.	50 860 (2018)	4	110
LU1	Highway deceleration zone in Luleå	10 591 (2017)	2	90
LU2	Beginning of main road from central Luleå	9 623 (2018)	2	70
LU3	Road in central Luleå	9 693 (2018)	2	70
LU4	Road in central Luleå	6 318 (2015)	1	50
LU5	Road in central Luleå	4 917 (2020)	1	70
LU6	Road in Luleå city centre	4 806 (2020)	2	50
LU7	Residential main street in Luleå	2 031 (2020)	1	50
REF	Reference site near Luleå city centre, around 150 m from the nearest road.	n/a	n/a	n/a

The sampling locations were required to satisfy the following criteria: (i) the standard snow removal practice at the site was to leave the snow in a snowbank next to the road, (ii) the site did not have a bicycle and/or pedestrian path, bus lane, road fence, or other obstacle that prevented sampling, and (iii) it was not common practice to push the snow away from the road, or entirely remove it to maintain accessibility or visibility. Furthermore, the sampling sites in Luleå were chosen with the aim of maximising AADT. The sole exception was LU7 (a residential main street with a relatively low AADT), which was included for comparative purposes. Moreover, while road salt was used for de-icing at E4S (Stockholm), the most common method for preserving road traction during winter conditions in Luleå involves applying sand and grit; road salt is only applied sparsely at critical spots such as bus stops and road intersections.

3.4.1 Sampling strategy

Samples were collected from roadside snowbanks using an aluminium snow shovel. Where needed, a titanium ice drill was used to detach snow that had been trapped by ice formation. To maximise the likelihood of obtaining samples with detectable pollutant concentrations, samples were collected as close to the driving lane as possible; depending on the snowbank's location, the distance from the sampling location to the driving lane was between 0.5 and 4 m. Previous studies have shown that pollutants in road environments accumulate close to the road and their concentration decreases markedly with distance from the road (Reinosdotter et al., 2006; Kuoppamäki et al., 2014). At each site, triplicate samples were collected along the snowbanks at intervals of 1-2 m in the driving direction. For each replicate, snow from the full depth of the snowbank (from top to bottom) was collected in a single sample of 5-6 kg in total and stored in PFA bags of approximately 20 L supported by plastic pails. The snow samples collected in Stockholm (E4S) were transported to Luleå in a Styrofoam box with no evidence of melting during transportation and were treated in the same way as the other samples upon arrival. At the reference site with undisturbed snow, samples representing the full snow depth were collected approximately 10 m away from the nearest pedestrian path using the same aluminium shovel and PFA bags as for the other sites. After the sampling, the samples were left in the PFA bags in room temperature (approximately 19°C) to thaw until they were completely melted, after which they were mixed thoroughly and distributed into bottles for physical and chemical analysis as described in Section 3.5. All snow samples were analysed with respect to TSS, the metal(loid)s Cd, Cr, Cu, Ni, Pb, Pd, Sb, W and Zn, PAHs, NPs, OPs and –ethoxylates, phthalates, and BPA.

3.5 Physical and chemical analysis

Physical analyses of the water samples (i.e., leachates from laboratory experiments in Paper II, rainwater panel runoff in Paper III and IV, and snowmelt panel runoff in Paper IV, and melted roadside snow in Paper V), were performed in the Environmental Laboratory of Luleå University of Technology. The chemical analyses of both the water samples and the solid material samples for the material composition screening in Paper II were outsourced to an accredited laboratory, ALS Scandinavia AB. The accreditation of this laboratory certifies its compliance with international quality assurance and quality control (QA/QC) procedures and is regularly verified by a third party. All roadside snow samples were subjected to the same chemical analyses targeting metal(loid)s, PAHs, NPs, OPs and –ethoxylates, phthalates, and BPA. The substance groups analysed in the runoff samples from the different building surface materials examined in the material composition screening experiments and the leachates from the laboratory leaching experiments depended on the identity of the material. Basic water quality parameters and metal analyses were performed for all runoff and leachate samples, but organic micropollutants (phthalates and alkylphenols) were only analysed for the samples derived from materials considered likely to release such pollutants as well as those derived from the control material (STS) in order to evaluate the contribution of atmospheric deposition. The analytes targeted for each material were chosen based on knowledge of the materials' composition (from e.g., product descriptions) and previous screening studies. The substance groups analysed in the material composition screening, laboratory leaching experiments, and open-air pilot study are listed in Table 3.

Table 3 The studied building surface materials and the substance groups analysed in the samples derived from each one in the material composition screening, laboratory leaching experiments, and open-air pilot study.

Material	Description	Material screening	Laboratory leaching	Open-air pilot study
STS	Stainless steel sheet	Metals	Metals	Metals, AP/APEOs, phthalates
PVA	PVC membrane	Metals, AP/APEOs, phthalates	Metals, NP/NPEOs, phthalates	Metals, AP/APEOs, phthalates
PVB	PVC membrane	Metals, AP/APEOs, phthalates	Metals, NP/NPEOs, phthalates	Metals, AP/APEOs, phthalates
SHI	Bitumen shingle	Metals, AP/APEOs, phthalates	Metals, NP/NPEOs, phthalates	Metals, AP/APEOs
BIF	Bitumen felt	Metals, AP/APEOs, phthalates	Metals, NP/NPEOs, phthalates	Metals, AP/APEOs
CUS	Copper sheet	Metals	Metals	Metals
GAL	Galvanised steel	Metals	Metals	Metals
COR	Corten steel	n/a	n/a	Metals
CST	Coated, corrugated steel	Metals, AP/APEOs	Metals, NP/NPEOs	Metals
ZNS	Titanium-Zinc sheet	Metals	Metals	Metals
CTZ	Pre-patinated, lacquered zinc sheet	n/a	n/a	Metals

3.5.1 Solid material samples

Samples for the material composition screening, which is described in full in Paper II and briefly in Section 3.2.1, were submitted to ALS Scandinavia AB in glass jars. For the metal analyses, the material samples were homogenised by cutting and grinding if needed, digested with HNO_3/HCl/HF, and analysed using inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) in accordance with the SS EN ISO 17294-1, 2 standards and EPA method 200.8: 1994. The following metals were analysed: Cd, Cr, Cu, Ni, Pb, Ti, and Zn. Samples for phthalate analysis were extracted with ethyl acetate and analysed by gas chromatography-mass spectrometry (GC-MS) in accordance with the E DIN 19742:2014-08 standard. The following 13 phthalates were analysed: dimethylphthalate, diethylphthalate, di-n-propylphthalate, di-n-butylphthalate, diisobutylphthalate, di-n-pentylphthalate, di-n-octylphthalate, di-(2-ethylhexyl)phthalate (DEHP), butylbenzylphthalate, dicyclohexylphthalate, diisodecyl phthalate (DIDP), diisononyl phthalate (DINP), and di-n-hexylphthalate. Analyses of APs/APEOs were performed using liquid chromatography–tandem mass spectrometry (LC-MS-MS) and targeted the following compound classes: nonylphenols (NPs), nonylphenol ethoxylates (NPEOs), octylphenols (OPs), and octylphenol ethoxylates (OPEOs). The analytical reporting limits were 5 mg/kg for NPs and OPs and 10 mg/kg for all phthalates, NPEOs, and OPEOs.

3.5.2 Water samples

Electrical conductivity (EC), pH and total suspended solid (TSS) analyses were performed as soon as possible after sample collection, normally within 24 hours. EC was measured with a CDM 210 (Radiometer Copenhagen, Denmark) instrument that was regularly calibrated and tested using deionised water before performing measurements. All pH measurements were performed using a WTW pH 330 instrument with a WTW SenTix 41 pH electrode (WTW, Weilheim, Germany), calibrated with standard solutions of pH 4 and 7 before use. TSS analysis was performed in accordance with the Swedish standard EN 872:2005. Briefly, samples were vacuum filtered through glass fibre filters with pore size of 1.6 μm. The initial sample volume and filter mass were then recorded, and after filtration the filters were oven-dried at 105°C ± 2°C, after which the filter mass was recorded and the suspended solids concentration could be calculated. The lower limit of determination was 2 mg/L. Aliquots of samples selected for metals analysis were filtered through 0.45 μm membrane syringe filter units (Filtropur S, Sarstedt AG&Co KG, Nürmbrecht, Germany) to determine the dissolved metal concentrations.

Samples for total and dissolved metal analyses were submitted to the analytical laboratory (ALS Scandinavia AB) in controlled and acid-washed plastic containers. Metal analyses were performed according to the SS EN ISO 17294-2: 2016 standards and EPA method 200.8: 1994 using ICP-SFMS. Prior to total metal analysis, 12 mL of each sample was digested in an autoclave with 1.2 mL 14 M HNO_3 (supra-pure), while the filtered samples were acidified with 1% 14 M HNO_3 (supra-pure). Unlike the other metals analyses, those presented in Paper V included determination of Pt, Pd, Rh, Sb, and W, necessitating different sample pre-treatment processes. For determination of Pt, Pd and Rh, aqua regia was used instead of HNO_3, while for analysis of W, samples were digested with HF and HNO_3 in a hot block. Indium was added at a concentration of 25 μg/L to all samples, blanks, controls, and calibration standards before analysis to serve as an internal standard.

The measured concentrations of the studied organic substances (i.e., PAHs, APs/APEOs, BPA and phthalates) are reported as total concentrations for individual substance groups and were determined by GC-MS. The 16 PAHs were analysed using a method based on the following standards: US EPA 8270D, US EPA 8082 A, CSN EN ISO 6468, and US EPA 8000D. A method based on the ISO 18857–2 standard was used in the analysis of APs/APEOs; briefly, the samples were acidified (pH 2±0.2), loaded onto styrene-divinylbenzene columns, and extracted with dichloromethane. The extracts were then derivatised with 5% N-Methyl-N-(trimethylsilyl)trifluoroacetamide in isooctane, and a mixture of 4-n-Nonylphenol and 4-n-Nonylphenoldiethoxylate was added as an internal standard. The method for analysing BPA was based on the same standard as that for APs/APEOs. Phthalates were analysed in accordance with the DIN EN ISO 18856 method by loading the samples onto reversed phase C18 columns that were then dried with nitrogen and extracted with hexane. The internal standard in this case was a mixture of four deuterated phthalates: di(2-ethylhexyl)phthalate-d4, diisobutylphthalate-d4, butylbenzyl-phthalate-d4, and di-n-octylphthalate-d4.

3.6 Data analysis

All raw data from the experiments described above were stored in Excel files and processed using the following applications: Excel (Papers I-V), Minitab (Paper III), SIMCA (Paper IV), and RStudio (Papers IV and V). Simple statistical quantities such as means and standard deviations were calculated using Excel. Moreover, in Paper III, the individual event-specific material contributions of different substances were compared to those of the control material using a two-sample t-test assuming unequal variance with a significance threshold of $p<0.1$, and Pearson correlation tests were performed to investigate correlations between influential factors (ADD, air temperature, event-average rainfall intensity, and TSS concentrations in runoff) and the EMC in runoff from the studied materials, including the control. In Paper IV, the yearly contributions of pollution from the different materials were estimated as the products of the site mean concentrations (SMC) and seasonal average precipitation values for Luleå over the most recent 30-year period for which data were available (1991-2020, data collected from the Swedish Meteorological and Hydrological Institute, SMHI). Separate estimates were generated for rainy and snow seasons; for details, see Paper IV.

In some cases, the results of phthalate and AP analyses are reported in terms of elevated reporting limits (RLs) rather than actual concentrations because of matrix effects. Furthermore, all samples contained some substances whose concentrations were below the RL. In papers II and III, such results were replaced with half of the RL for the purpose of calculations. The Nondetects and Data Analysis for Environmental Data (NADA) R package was used to improve the statistical analysis of such left-censored data in Papers IV and V, where larger datasets were available. Means were calculated using the regression on order statistics (ROS) method, the significance of correlations was tested using the nonparametric Kendall's tau test, and substances quantified in at least 25% of samples were included in the analyses.

In Paper IV, a principal component analysis (PCA) was performed using the SIMCA 17 software package to visualise the dataset and analyse correlations between the studied parameters. For details of the PCA analysis, see Paper IV.

4 Results

This section summarises and synthesises the results presented in the five appended papers (Papers I-V). The stormwater pollution sources identified in the literature review are discussed in Section 4.1, while Section 4.2 outlines the results of the material composition screening and laboratory leaching experiments. Section 4.3 presents the results of the open-air sampling studies, first by discussing the pilot study and the roadside snow sampling study separately and then by analysing their results in an integrated fashion. Finally, Section 4.4 presents the results for the considerations for planning source identification studies, and Section 4.5 presents a summary of the sources of various pollutant groups as found by the appended papers (I-V).

4.1 Pollution sources identified in the literature review

The sources contributing pollution to urban runoff may vary considerably depending on factors including the season, catchment type, and rainfall characteristics. The literature review (Paper I) indicated that the contributions from different sources are not all understood equally well: there is a relatively well-established knowledge base concerning pollution from vehicle traffic and metallic building structures, but much less is known about pollutant contributions from gardens, parks, and other green areas, or releases of organic micropollutants from non-metallic building surfaces. Despite the gradual phasing out of vehicular sources known to release large quantities of specific pollutants (as exemplified by the declining use of leaded gasoline), vehicle traffic and metallic building structures are likely to remain major sources of pollution, because of their intensity and wide use in urban areas. The literature review presented in Paper I also indicated that atmospheric deposition is a major source of pollution, contributing up to 100% of the stormwater export loads of certain pollutant groups. Finally, it became clear that there is a need for further research on emerging pollutants and their sources, especially given the constant introduction of new products and materials into the urban environment. Together with the steady development of emission-reducing interventions and the phasing-out of pollutants of high environmental concern, this means that there is an ongoing need for work on identifying important stormwater pollutants and their sources.

Figure 5 shows the main sources known to contribute pollution to urban runoff as well as the major pollutant transport pathways in urban environments (which are represented by arrows). Anthropogenic activities release pollutants that are either deposited directly on drainage surfaces or released into the atmosphere and subsequently deposited on drainage surfaces, which may also independently contribute pollution to runoff. The urban drainage systems that convey the runoff to the receiving waters may also introduce new pollutants, for example as a result of misconnections, releases of pollutants from the materials used in the construction of the infrastructure, or resuspension of settled particles from runoff that passed through the system at an earlier point.

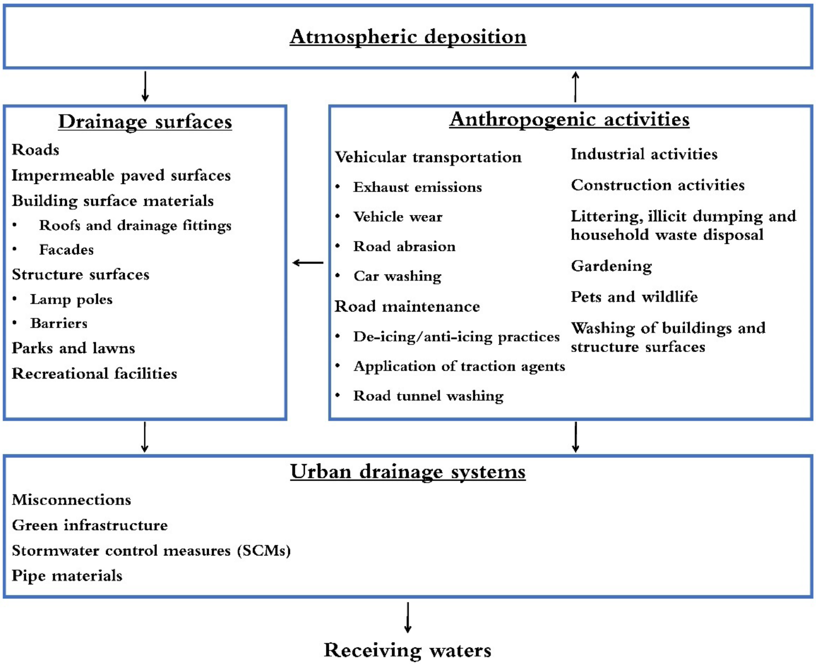


Figure 5 Grouping of urban runoff pollution sources identified in Paper I and pollution transport pathways (indicated by arrows). Figure adapted from Paper I.

4.2 Sources identified by laboratory leaching and screening experiments

The results of the material composition screening and laboratory leaching experiments are presented in Table 4. The stainless steel sheets (STS) had high concentrations of the metals Cu, Cr and Ni (up to 149 g/kg in the case of Cr). However, these metals were not released from STS in the laboratory leaching experiments. The zinc sheets (ZNS) and galvanised steel (GAL) both had substantial Zn contents and released high concentrations of Zn (up to 12 mg/L for ZNS) in the leaching experiments. Similarly, both the leaching experiments and the screening studies showed that copper sheets (CUS) contained and released high concentrations of Cu. Coated steel (CST) had a higher Zn concentration than GAL (60 g/kg compared to 23g/kg) but the release of Zn from CST in the leaching experiments was over an order of magnitude lower than that from GAL or ZNS. Both the screening studies and the leaching experiments indicated that bitumen shingle (SHI) was a source of Cu and Ni. The material composition screening studies showed that Pb was present in several of the materials (with the highest concentrations occurring in ZNS, GAL and SHI) but was not readily released in the leaching experiments. NPs were not detected at concentrations above their RL in any material included in the material composition screening study, and NPEOs were only detected at concentrations above their RL in one PVC material (PVB). In contrast, no NPEOs were found in any of the material leachates but NPs were detected in the leachates from the bitumen felt (BIF), SHI, and both PVC materials (PVA and PVB). The screening study also revealed high concentrations of phthalates in PVA and PVB, with the most abundant being DINP (its concentration in PVA was 190 g/kg). However, phthalates were not detected at concentrations exceeding their RLs in the leaching experiments.

Table 4 Total concentrations of the studied substances found in the tested materials and their leachates. The figures represent results for a single sample in the material composition screening and the average for duplicate samples ± the difference from the average for the laboratory leaching experiments. Table modified from Paper II.

	STS	ZNS	CUS	GAL	CST	BIF	SHI	PVA	PVB	Blank
Material composition screening (mg/kg)										
Cd	0.54	1.3	0.045	0.046	0.14	0.16	0.2	0.085	<0.02	n/a
Cr	149000	1.9	<0.8	89	89	19	460	0.61	0.2	
Cu	960	1410	920000	23	399	3.3	826	1.5	<0.5	
Ni	1070	0.66	3.7	28	38	37	1140	0.45	<0.2	
Pb	0.15	22	6.7	19	2.9	3	17	4.7	3.7	
Zn	22	941000	85	22800	60000	36	211	403	285	
NPs	n/a	n/a	n/a	n/a	<5.0	<5.0	<5.0	<5.0	<5.0	
NPEOs	n/a	n/a	n/a	n/a	<10	<10	<10	<10	34	
DINP	n/a	n/a	n/a	n/a	<1000	*<150*	*<100*	190000	140000	
DIDP	n/a	n/a	n/a	n/a	<1000	*<150*	*<100*	*<30000*	41000	
DNOP	n/a	n/a	n/a	n/a	<1000	<10	<10	2700	*<2000*	
DEHP	n/a	n/a	n/a	n/a	<1000	<10	<10	770	*<100*	
Laboratory leaching experiments (µg/L)										
Cd	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.15 ± 0.062	<0.05	<0.05	<0.05
Cr	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9
Cu	1.7 ± 0.15	<1	1530 ± 85	<1	<1	<1	43 ± 0.80	2.0 ± 0.01	3.0 ± 1.4	5.1 ± 2.5
Ni	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	45 ± 2.1	<0.6	<0.6	<0.6
Pb	<0.5	<0.5	<0.5	1.2 ± 0.47	0.74 ± 0.16	<0.5	<0.5	<0.5	0.59 ± 0.076	0.69 ± 0.080
Zn	12 ± 4.7	12 000 ± 1400	26 ± 1.9	9120 ± 3380	380 ± 98	<4	21 ± 10	17 ± 0.05	11 ± 3.1	6.7 ± 1.8
NPs	n/a	n/a	n/a	n/a	<0.100	2.0 ± 0.085	0.41 ± 0.007	1.9 ± 0.93	8.9 ± 0.69	<0.100
NPEOs	n/a	n/a	n/a	n/a	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100
DINP	n/a	n/a	n/a	n/a	n/a	n/a	n/a	*<10*	*<10*	*<10*
DIDP	n/a	n/a	n/a	n/a	n/a	n/a	n/a	*<10*	*<10*	*<10*
DNOP	n/a	n/a	n/a	n/a	n/a	<1.0	<1.0	<1.0	<1.0	<1.0
DEHP	n/a	n/a	n/a	n/a	n/a	<1.0	<1.0	<1.0	<1.0	<1.0

4.3 Pollutant releases from building surface materials and vehicular traffic

4.3.1 Pollutants found in rain and snowmelt induced pilot panel runoff

Table 5 shows the mean values and standard deviations of selected water quality parameters in 42 samples of runoff (33 representing rain-induced runoff and 9 representing snowmelt-induced runoff) derived from 11 materials. Because of complications resulting from matrix effects, the results of the chemical analyses of APs and phthalates were often given as heavily elevated RLs rather than actual concentrations, which hindered further analysis. These matrix effects were likely due to the presence of other substances (e.g., similar phthalates and/or APs) that interfere with the analysis.

Table 5 Mean values ($\bar{x}$) and standard deviations (σ) of the pH, electric conductivity (EC), total suspended solids (TSS), concentrations of Al, Cr, Cu, Ni, Pb and Zn, 4-Nonylphenols (4-NP), 4-nonylphenol monoethoxylate, diethoxylate and triethoxylate (NP-1E, NP-2E, NP-3E), and the phthalates Di-(2-ethylhexyl)phthalate (DEHP), Diisodecyl phthalate (DIDP), diisononyl phthalate (DINP) in μg/L, and proportions of censored values (% cens.) for organic pollutants. $\bar{x}$ and σ calculated with R are shown in italics. The highest reported RL (r) is presented instead of the mean for substances with >75% censored values. Adapted from Paper IV.

		STS	**PVA**	**PVB**	**SHI**	**BIF**	**CUS**	**GAL**	**COR**	**CST**	**ZNS**	**CTZ**
		n=41	n=42	n=42	n=42	n=41	n=42	n=42	n=42	n=42	n=42	n=33
pH	x̄	5.9	5.9	6.0	6.0	6.2	6.0	6.3	6.0	6.0	6.4	5.9
	σ	0.47	0.33	0.33	0.48	0.35	0.21	0.22	0.33	0.36	0.22	0.29
EC	x̄	8.7	16	12	18	21	11	15	8.5	9.7	20	9.5
μS/cm	σ	4.5	17	10	15	20	5.3	12	4.8	6.5	9.0	7.2
TSS	x̄	24	49	52	39	39	41	32	44	40	32	53
mg/L	σ	39	105	118	80	71	78	44	79	72	61	84
Al	x̄	48	974	909	750	850	665	658	850	893	766	1063
	σ	733	1570	1580	1340	1260	1280	843	1690	1515	1390	1850
Cr	x̄	3.4	4.7	4.8	4.2	6.5	2.9	5.9	4.6	4.1	3.3	5.7
	σ	2.7	4.5	4.6	4.0	10	3.9	5.5	5.5	4.5	3.8	5.8
Cu	x̄	5.1	8.4	8.2	15	7.2	2490	6.3	4.9	5.5	5.4	6.2
	σ	7.4	17	18	18	8.4	1440	8.5	6.4	7.6	8.4	9.2
Ni	x̄	1.9	1.9	1.8	18	4.1	1.7	1.5	16	2.2	1.7	2.4
	σ	0.91	2.1	2.0	21	4.1	1.7	1.1	12	2.7	2.2	2.2
Pb	x̄	2.9	4.1	4.2	4.6	8.2	3.0	7.6	14	6.8	7.7	12
	σ	2.1	5.3	5.2	5.2	9.7	3.2	19	18	7.3	17	34
Zn	x̄	22	32	35	41	25	24	2900	15	96	5500	93
	σ	22	38	40	44	37	22	1450	15	63	2900	57
4-NP	x̄/r	<0.1	0.13	11.7	<3.5	*0.44*	Substances not analysed					
	σ	-	0.15	13.9	-	*0.88*						
	% cens.	100	71	12	98	68						
NP-1E	r	<0.1	<3.5	<0.5	<1.1	<1.1						
	σ	-	-	-	-	-						
	% cens.	100	95	100	100	100						
NP-2E	r	<0.1	<7.1	<3.0	<1.9	<2.7						
	σ	-	-	-	-	-						
	% cens.	100	95	83	100	100						
NP-3E	r	<0.1	<1.9	<3.8	<2.5	<4.6						
	σ	-	-	-	-	-						
	% cens.	100	100	93	100	100						
DEHP	x̄/r	<1	*1.1*	<1								
	σ	-	*1.2*	-								
	% cens.	100	74	100								
DIDP	x̄/r	<10	<200	*44*								
	σ	-	-	*24*								
	% cens.	100	100	69								
DINP	x̄/r	<10	264	*504*								
	σ	-	237	*699*								
	% cens.	100	0	21								

Figure 6 shows the event specific concentrations and loads of Cu in rain- and snowmelt-induced runoff from CUS, and the loads of Zn from ZNS and GAL. Experiments were performed using three separate panels of each material and the results exhibited good repeatability. Moreover, the Cu and Zn in the runoff samples were almost entirely in the dissolved (<0.45 μm) form, and their concentrations in snowmelt-induced runoff were lower than in rain runoff. However, because of the large volumes collected during snowmelt sampling, the latter trend was less pronounced for the loads. Rainfall events R9 and R10 had markedly higher metal concentrations than the other rainfall events but also had lower runoff volumes so their metal loads were similar to those for other events. Rainfall events R5.1 and R5.2 were two parts of a single rainfall event that featured a brief dry interval. The runoff concentrations for both parts were similar, so there was no apparent first flush effect. Finally, there was no apparent tendency for the concentrations of Cu and Zn to decrease over time between events R1 and R10.

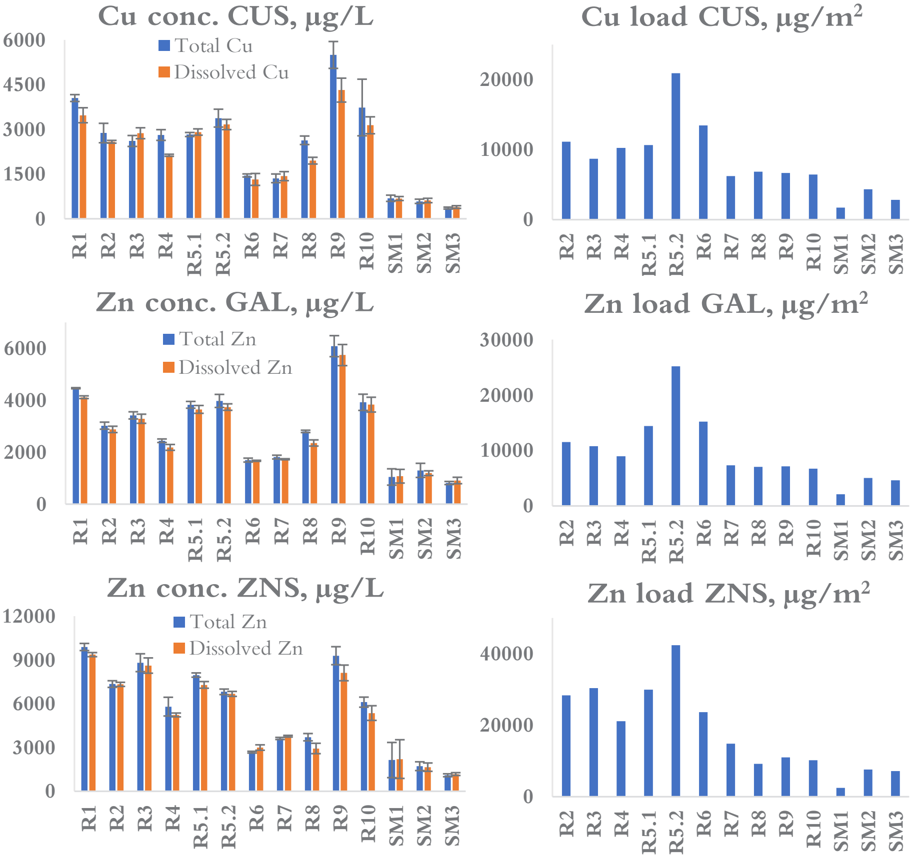


Figure 6 Concentrations vs. loads of Cu from CUS, and Zn from ZNS and GAL for rain events R1-10 and snowmelt events SM1-3. Error bars represent standard deviations based on triplicate samples. Loads were calculated from total concentrations. No loads could be calculated for R1. Figure adapted from Paper IV.

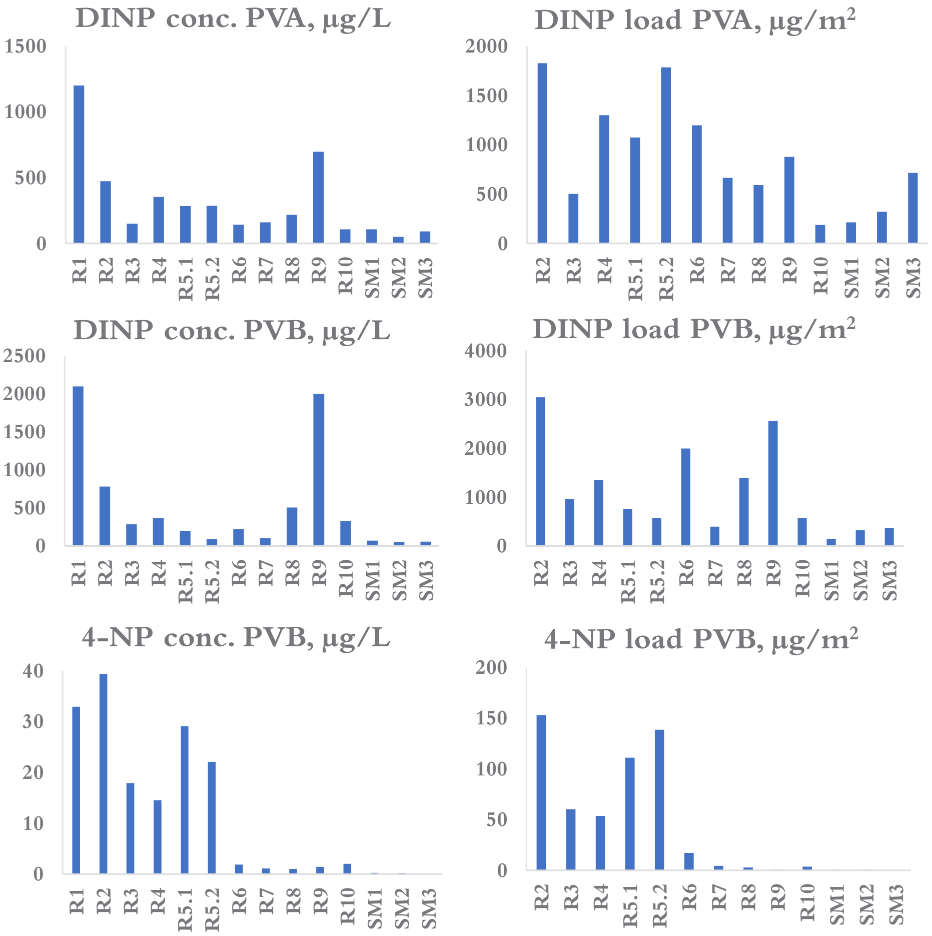


Figure 7 Concentrations vs. loads of DINP and NPs from PVA and PVB from rain events R1-10 and snowmelt events SM1-3. No loads could be calculated for R1. When calculating the averages for this figure, left-censored values were replaced with ½ RL. Adapted from Paper IV.

Figure 7 shows event-specific concentrations and loads of DINP in runoff from PVA and PVB, and of NPs in runoff from PVB. Data on NPs in runoff from PVA are not shown because their concentrations could only be quantified in a few samples. Rainfall events R1 and R9 had substantially higher DINP concentrations than the other events; this may be because the R1 samples represented the first runoff from the new panels while the R9 event was unusual in that it was a short rain shower following a long dry period. The DINP concentrations in the PVA runoff during events R5.1 and R5.2 were similar, but the concentrations of DINP and NPs in runoff from PVB were lower in R5.2 than R5.1. As previously observed for Cu and Zn, the DINP concentrations in snowmelt-induced runoff were generally lower compared than those in rain runoff. Moreover, whereas the

DINP concentrations in rain runoff did not decrease over time, the NP concentrations and loads were both considerably lower after event 5.2.

Table 6 presents the results of a paired Student's t-test for differences between event-specific metal (Al, Cr, Cu, Ni, Pb and Zn) concentrations in runoff from the tested materials and the control panels (STS), which were assumed to represent contributions from AD. Such comparisons could not be performed for the organic pollutants, because their concentrations in the STS runoff were always below the analytical RL, indicating that AD was not an important source of these pollutants in the study area. Significant differences in runoff concentrations were found for Cu, Ni, Pb, and Zn but not for Al or Cr, indicating that none of the tested materials release the latter two elements. In addition, the metal concentrations of runoff from PVA and PVB did not differ significantly from those in runoff from control panels. The other materials released concentrations that were significantly different from STS for at least one of the studied metals. The metal most frequently detected at elevated concentration was Zn, for which significantly elevated concentrations were detected in runoff from SHI, GAL, Corten steel (COR), CST, ZNS and coated zinc (CTZ). In addition, SHI and CUS yielded significantly elevated Cu releases, while SHI, BIF, and COR released elevated concentrations of Ni. Materials releasing significantly elevated Pb concentrations were BIF, COR, and CST.

Table 6 Results of a paired Student's t-test for differences between Al, Cr, Cu, Ni, Pb, and Zn concentrations in runoff from panels of the studied materials and control panels (STS). The results for the control panels are assumed to reflect the contributions of atmospheric deposition, while differences in concentration between the studied materials and the control are assumed to represent the contribution of the material in question. X denotes a significant difference based on a significance threshold of $\alpha=0.05$.

	PVA	**PVB**	**SHI**	**BIF**	**CUS**	**GAL**	**COR**	**CST**	**ZNS**	**CTZ**
Al										
Cr										
Cu			X		X					
Ni			X	X			X			
Pb				X			X	X		
Zn			X			X	X	X	X	X

4.3.2 Pollutants found in roadside snow

The results of the roadside snow sampling campaign are summarised for the different sites and sampling events (S1 and S2) in Table 7. The pH of the roadside snow was generally higher than that of the undisturbed snow at the reference site (REF) and the EC was considerably higher at the Stockholm site (E4S) than at the Luleå sites (LU1-LU7), likely because of the application of road salts at E4S. Moreover, the concentrations of TSS, metals, and organic pollutants were generally lower at the REF site than in roadside snow and many of the analysed substances were below the RL in the snow collected at the REF site. The only APs quantified in roadside snow were OPs, and no NPs were quantified in the roadside snow. The number of phthalates detected in roadside snow exceeded that in the panel runoff experiments: DEHP, dicyclohexyl phthalate (DCP), DIDP, and DINP were detected in snow samples, whereas the only phthalates detected in runoff samples were DINP and, in a few cases, DEHP and DIDP.

Table 7 Ranges (min-max) of pH, electric conductivity (EC), TSS (mg/L) and substance concentrations (μg/L) in the melted snow samples from the different sampling locations and two sampling occasions (S1/S2). The number of samples from each location and event were 3, except for LU3, S2 (n=1) and LU6 S2 (n=2). Table adapted from Paper V.

	E4S	**LU1**		**LU2**		**LU3**		**LU4**		**LU5**		**LU6**		**LU7**		**REF**	
	S1	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**
pH	7.8-8.5	7.2-7.4	7.9-8.4	8.3-8.8	8.0-8.6	7.9-8.1	8.5	7.7-8.0	8.0-8.5	7.7-8.6	7.8-8.2	8.6-9.0	8.3-8.5	7.2-7.4	7.9-8.0	6.5-6.9	6.5-6.7
EC μS/cm	6820-7620	71-95	51-78	424-448	72-96	137-169	165	93-97	86-113	55-68	27-34	519-841	51-59	26-36	20-24	8.6-9.3	7.1-8.0
TSS mg/L	4900-5100	650-1000	1700-2200	2100-4100	5700-9800	690-870	1600	930-1800	2200-4300	1500-3100	1300-2000	3300-5300	3700-4400	190-280	1000-1500	3.0-3.8	3.3-6.6
Al mg/L	59-74	21-31	43-55	63-172	166-253	171-278	39	23-44	61-65	40-92	29-37	108-196	105-110	6.0-10	22-31	0.08-0.11	0.10-0.15
Cd	0.69-0.95	0.19-0.23	0.27-0.39	0.52-1.4	1.2-1.7	0.12-0.20	0.21	0.16-0.38	0.36-0.37	0.23-0.59	0.12-0.25	1.1-2.4	0.96-1.0	<0.05-0.055	0.099-0.19	<0.05	<0.05
Cr	139-206	35-53	65-90	208-591	547-800	40-71	94	41-96	148-160	109-279	68-91	321-603	306-336	12-22	50-69	<0.9	<0.9
Cu	426-624	147-252	306-338	424-932	868-1150	114-207	176	73-177	195-214	132-320	112-147	574-1070	570-575	29.8-48.8	72.2-79.6	1.1-1.2	<1
Ni	55-88	17-27	38-45	87-264	235-370	17-32	40	18-47	69-74	48-128	34-41	136-272	126-138	5.4-8.8	24-37	<0.6	<0.6-0.63
Pb	60-93	19-30	37-45	58-178	142-194	16-301	30	14-33	45-49	32-78	22-32	98-189	98-102	5.4-8.4	16-23	0.62-0.69	<0.5-0.53
Zn	1410-1960	341-678	682-784	934-2270	2100-2840	243-401	518	215-480	612-694	421-960	313-385	1390-2690	1410-1460	64-98	215-253	5.3-6.3	6.7-9.8
DEHP	14-29	<1-1.9	<1-1	4.2-9.5	<1	2.2-3.7	<1	<1-1.4	<1	<1-2.7	<1	<1-3.8	<1-1.7	<1	<1	<1	<1
DCP	2.5-5.3	<1	<1	2.9-4.2	<1	<1	<1	<1	<1	<1	<1	1.6-4.9	<1-1.8	<1	<1	<1	<1
DIDP	130-250	<10	<10	<20-<50	<10-12	<20	<10	<10	<10	<20	<10	<10-<20	<10	<10	<10	<10	<10
DINP	260-540	<10-25	<10-13	43-100	<10-26	34-53	<10	<10-17	<10	<10-31	<10	<10-<50	<10-18	<10-<20	<10	<10	<10
4-OP	0.78-1.1	<0.054-0.13	0.038-0.044	0.51-0.70	0.12-0.14	<0.064-0.19	0.082	<0.066-0.10	0.057-0.063	0.20-0.30	0.035-0.054	0.59-0.96	0.078-0.088	<0.036	0.031-0.038	<0.01	<0.01
BPA	0.174-0.197	<0.05	0.057-0.069	0.088-0.11	<0.05-0.062	<0.05	0.084	<0.05-0.069	<0.05-0.091	<0.05	<0.05	0.106-0.209	0.067-0.072	<0.05	<0.05-0.052	<0.05	<0.05

Figure 8 presents the concentration ranges of selected micropollutants found in the roadside snow. It can be seen that the pollutants with the highest concentrations were Cr, Cu, Ni, W, and Zn, while the most concentrated organic substances were DINP and PAHs. OPs and BPA occurred frequently in the roadside snow (frequencies of detection were 50% for BPA and 81% for OPs) but in comparatively lower concentrations.

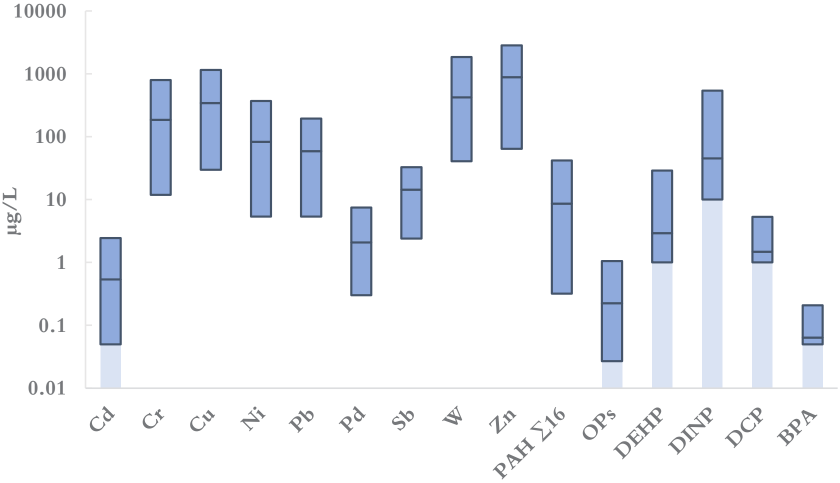
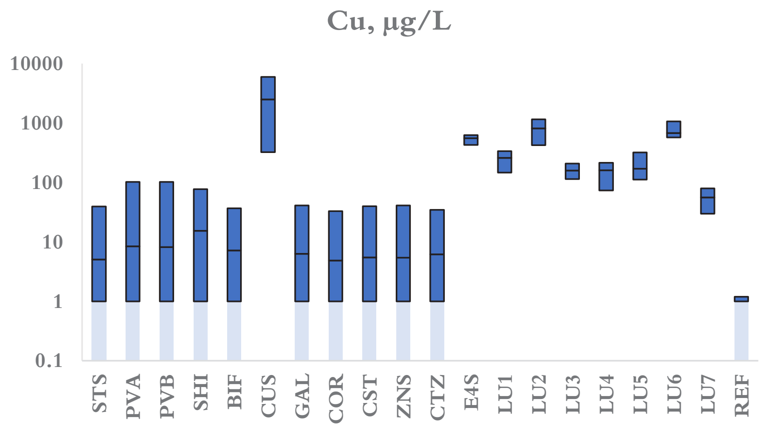


Figure 8 Minimum, mean and maximum total concentrations (in dark blue) of selected micropollutants: the metal(loid)s Cd, Cr, Cu, Ni, Pb Sb, W and Zn; polycyclic aromatic hydrocarbons (PAHs); octylphenols (OPs); di-(2-ethylhexyl)phthalate (DEHP); diisononyl phthalate (DINP); dicyclohexyl phthalate (DCP); and, bisphenol A (BPA), in all roadside snow samples (N = 42). Mean values were calculated using the NADA package in R using regression on order statistics. In cases where the minimum concentrations were below the reporting limits (RL), the pale blue colour represents the true distribution, which extends below the analytical RL. Data from the reference site were excluded from the analysis presented here. Adapted from Paper V.

4.3.3 Comparison of pollutants in building surface runoff and roadside snow

Concentrations of selected substances were compared between the pilot experiments (paper III and IV) and the roadside snow sampling (Paper V) to assess their potential contributions of pollution to urban runoff. Figure 9 shows the ranges of concentrations of Cu and Zn for each of the studied sources. It is readily apparent that the metallic materials were the largest contributors of Cu and Zn: CUS gave the highest concentrations of Cu, while ZNS and GAL gave the highest concentrations of Zn. However, the roadside snow had higher concentrations of Cu and Zn than the runoff from the other tested materials. Moreover, the concentration ranges were larger in the panel runoff than in the roadside snow, which can be explained by the larger number of runoff samples, the fact that the runoff samples included both rainwater- and snowmelt-induced runoff, and the five-year duration of the runoff sampling period.



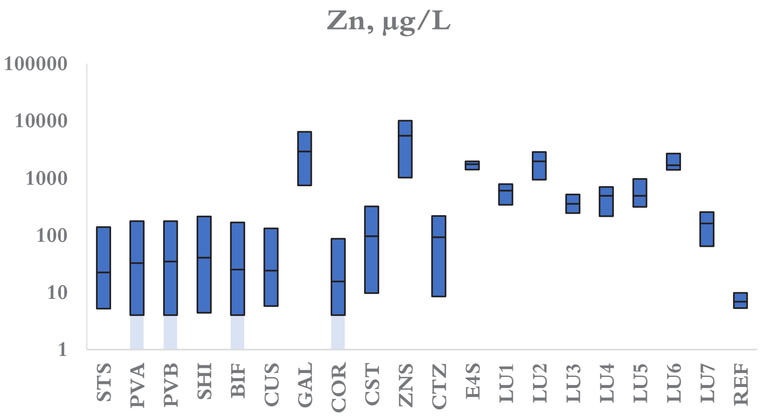


Figure 9 Cu and Zn ranges for different sources in open-air sampling. Data originate from Papers IV and V. In cases where the concentrations were below the reporting limits (RL), the pale blue colour represents the true distribution, which extends below the RL.

Figure 10 show the ranges of concentrations of DINP, NPs and OPs for the different sources studied in Papers III, IV, and V. It can be seen that the runoff from the PVC materials (PVA and PVB) and the roadside snow from Stockholm (E4S) had the highest concentrations of DINP, with similar average concentrations for both source categories. As also observed for Cu and Zn, the range of DINP concentrations was wider in the panel runoff than in the roadside snow, which can be explained by the larger number of samples and the length and diverse conditions of the runoff sampling period. In addition, the concentrations of APs differed markedly between the panel runoff and roadside snow: only NPs were quantified in the material panel runoff, while only OPs were quantified in the roadside snow samples. Moreover, the concentrations of DINP and APs were always below the RL at the reference sites and in runoff from control panels, which strongly suggests that AD contributed negligible quantities of DINP and APs in the study areas.

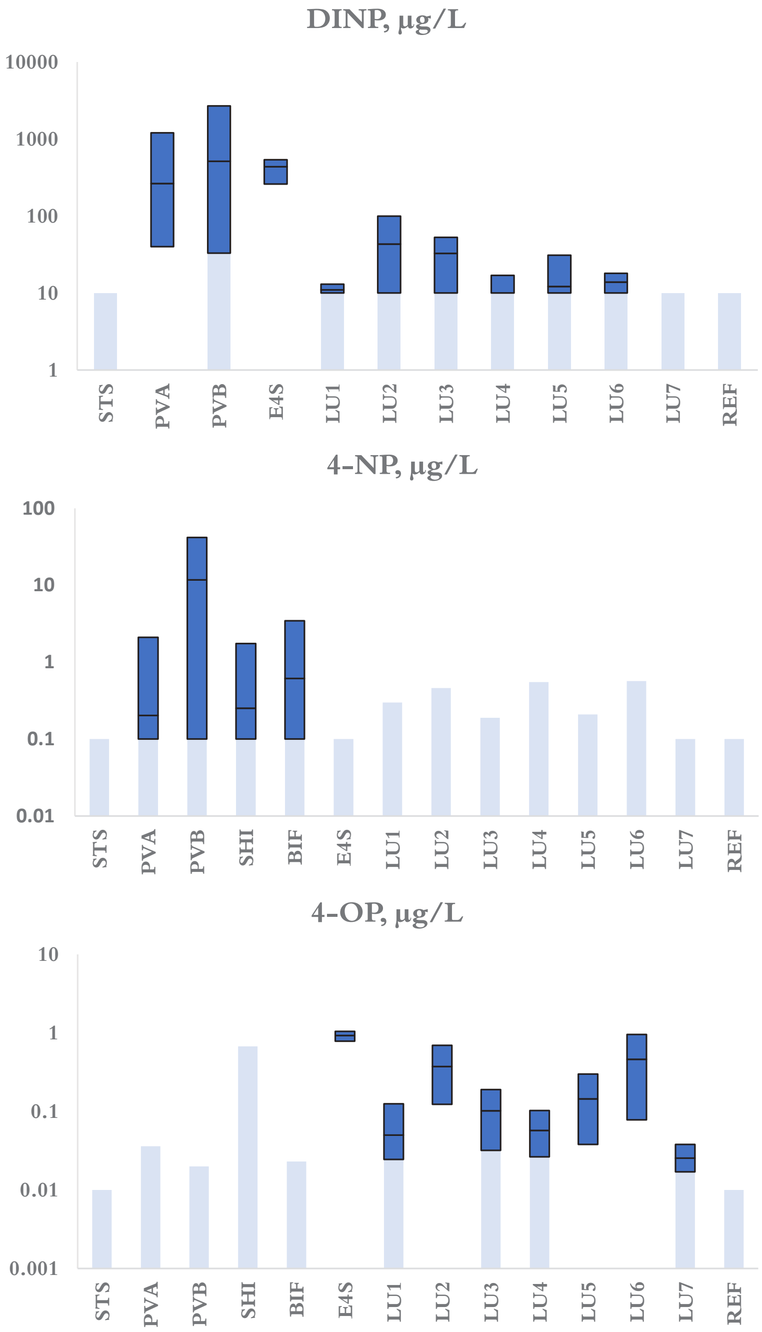


Figure 10 Concentration ranges of DINP, NP and OP for different sources in open-air sampling studies. Data originating from Papers IV and V. Concentrations that were below the RL or reported as elevated RLs (censored values) were replaced with ½ RL for the purposed of this figure. The pale blue colour represents the true distribution extending below the RL. Where only a pale blue bar is visible, only censored values were obtained for the substance in question.

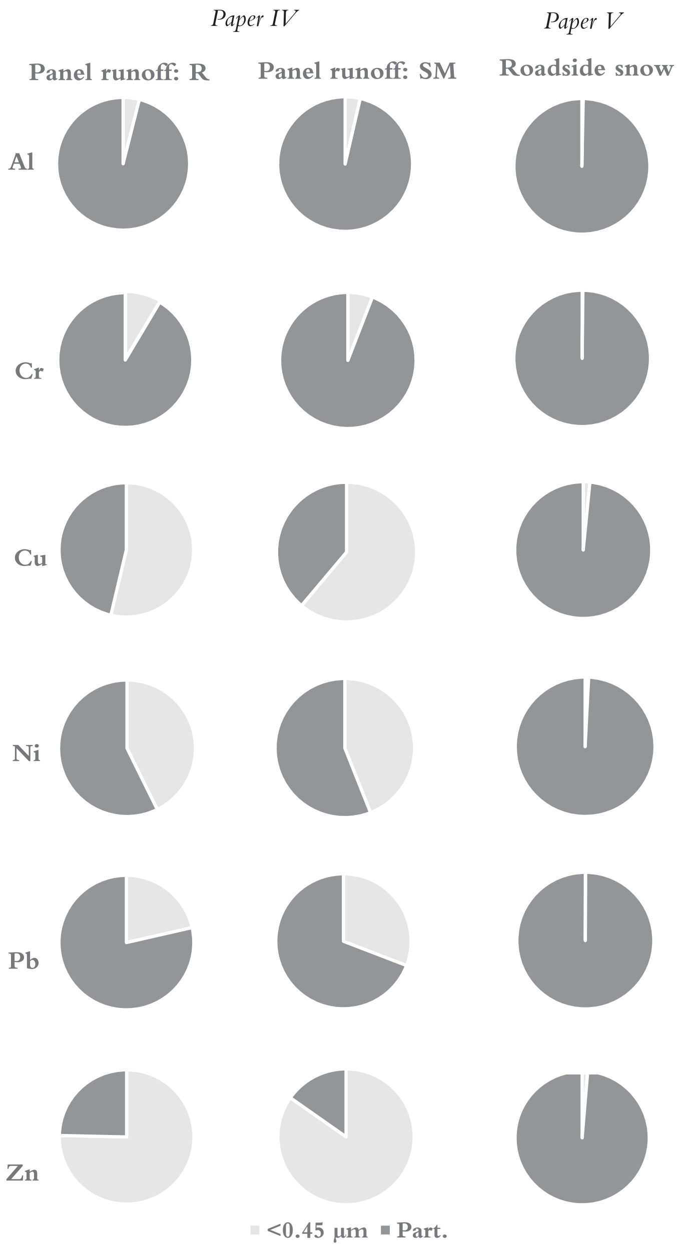


Figure 11 Proportions of dissolved (<0.45µm) and particulate metals (Al, Cr, Cu, Ni, Pb, Zn) in rain runoff (averages over 11 studied materials), snowmelt runoff (averages over 11 studied materials), and roadside snow (averages over all roadside snow samples). The particulate concentrations were calculated by subtracting the dissolved concentrations from the total concentrations.

Figure 11 show a comparison of the proportions of dissolved and particulate metals (Al, Cr, Cu, Ni, Pb, Zn) in the rain-induced panel runoff, snowmelt-induced panel runoff, and melted roadside snow. In general, metals were mainly attached to particles in roadside snow but were mainly dissolved in the panel runoff. These proportions did not generally differ greatly between rain- and snowmelt-induced panel runoff samples, although the proportion of dissolved Cu and Zn was higher in the snowmelt runoff. Moreover, some individual materials released relatively high proportions of dissolved metals – for example, the proportion of dissolved Zn in runoff from ZNS and GAL was 94%, while the proportion of dissolved Cu in runoff from CUS was 90%. The metals with the lowest proportions of dissolved species in the panel runoff were Pb and Cr. The dissolved proportions of metals in melted roadside snow were almost negligible; the metal with the highest proportion of dissolved material (2%) was Cu.

4.4 Considerations for planning source identification studies

The comparison of methods for identifying building surface materials as sources of urban runoff pollution (presented in Paper II) indicated that material composition screening studies are useful tools for identifying critical materials and/or substances warranting further study. This is because while screening studies can reveal the presence or absence of specific micropollutants in different materials, they provide no information on the leachability of these substances in contact with water. In contrast, the laboratory leaching experiments provided valuable data on pollutant leachability from the tested materials with the ability to control specific influential factors such as the composition of the leachant, the temperature, and the contact time between the material and the water. The open-air pilot experiments provided results that are likely to be more comparable to real building runoff but offered limited opportunities to isolate individual influential factors. Moreover, the labour and financial resources needed for each type of experiment differed substantially, as shown in Figure 12.

The estimates of the required labour resources were based on the working hours needed to perform the actual tests and excluded the time required for chemical analyses because the latter were performed by a contracted laboratory. The financial resource estimates were based on the costs of the chemical analyses, material and equipment, labour, and the construction of the pilot experimental site. Figure 12 shows that while material composition screening studies had a comparatively low resource demand, the laboratory leaching experiments were more labour-intensive and the open-air pilot experiments required considerable financial and labour resources.

Furthermore, the method used in the laboratory leaching experiments was unsuitable for studying the leaching of phthalates from the studied materials. In addition, the comparison of the results of the different studies highlighted the importance of analysing both APs and APEOs: NPEOs were detected in PVB during the material screening, but only NPs (and not NPEOs) were detected in the leachate and runoff from PVB, presumably because the NPEOs were degraded into NPs.

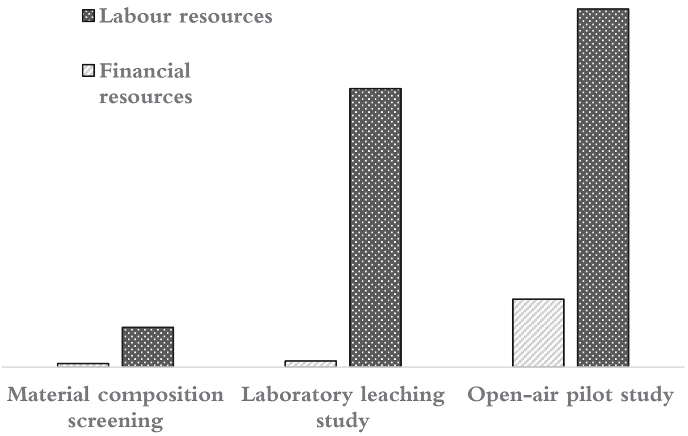


Figure 12 Relative comparison of the financial and labour resources required to study building surface materials as sources of targeted micropollutants using different methods. The cost estimates were based on the costs of chemical analyses, material and equipment, labour, and pilot site construction. The labour resource estimates were based on the work hours needed to perform the respective tests as described in the methods section (work hours needed for chemical analyses are excluded). Figure adapted from Paper II.

With regard to the accumulation of pollutants in the roadside snow, the results presented herein (Table 7) and in Paper V indicate that the traffic intensity was a more important factor for pollutant accumulation than the duration of accumulation. This inference is based on two facts: (i) the concentrations of pollutants in the E4S samples were generally higher than those from the Luleå sites, and (ii) pollutant concentrations did not differ markedly between sampling S1 and S2 at the sites in Luleå.

4.5 Important sources of urban runoff pollution

Table 8 summarises the sources of various pollutant groups as reported in the appended papers (I–V) and is based on the structure presented in Figure 5 (originally from Paper I). In the table, sources identified as 'major' contributors of the various substances are indicated by a capital X, while other sources are indicated by a lowercase x. The table also shows which appended paper(s) identified each source. It should be noted that the 'Road maintenance' source includes tunnel wash water. Obviously, the releases of pollution from industrial and construction activities depend heavily on the type of industry or construction/demolition work that is being performed. Littering and illegal dumping activities are hard to predict and measure because of their random occurrence (for example, they may occur accidentally) and the low likelihood that spills or dumping will be reported. In addition, Paper I identified littering of cigarette butts as a source of nicotine in stormwater runoff. Atmospheric deposition was identified as a potentially major source of various pollutants but can be seen as a 'secondary source' of pollutants that are generated by other anthropogenic or natural activities and transported over short or long distances before being deposited.

The tabulated results for roads and impermeable paved surfaces refer to the pollutant contributions of the corresponding surface materials rather than activities that cause wear of such surfaces. Building and structure surface materials were identified as sources of several different pollutants because of the great diversity of materials in this category that exist in urban environments and have been examined in runoff studies. Moreover, 'traditional' parks and lawns were mainly sources of nutrients, pesticides, and solids. Other substances listed in the table originated from artificial lawns and rubber mulch from e.g., playgrounds. SCMs were also identified as sources of many pollutant groups, possibly because of particles that originated from other sources in the urban environment and were deposited in the SCMs before being resuspended at a later stage. SCMs could thus be seen as a 'secondary source' of many pollutant groups. However, it should be noted that the materials used in their construction may also release pollutants. Finally, misconnections, pets, and wildlife were identified as sources of nutrients, faecal bacteria, and PPCPs in stormwater.

Table 8 Summary of the sources of various pollutant groups as identified by the appended papers (PI-V). Bold and capital X indicate the major sources.

	Vehicular traffic	Road maintenance	Industrial activities	Construction activities	Gardening activities	Littering and illegal dumping	Atmospheric deposition
Solids	**X** $^{PI, PV}$	**X** ^{PI}		**X** ^{PI}	x ^{PI}	x ^{PI}	**X** ^{PI}
Cu	**X** $^{PI, PV}$	x ^{PI}	x ^{PI}	x ^{PI}		x ^{PI}	**X** ^{PI}
Pb	**X** $^{PI, PV}$	x ^{PI}	x ^{PI}	x ^{PI}		x ^{PI}	**X** ^{PI}
Zn	**X** $^{PI, PV}$	x ^{PI}	x ^{PI}	x ^{PI}		x ^{PI}	**X** ^{PI}
Other metal(loid)s	**X** $^{PI, PV}$	x ^{PI}		x ^{PI}		x ^{PI}	**X** ^{PI}
Nutrients (N, P)		x ^{PI}		x ^{PI}	x ^{PI}	x ^{PI}	**X** ^{PI}
Organic matter							
Oil and grease	x ^{PI}					x ^{PI}	
Aromatic hydrocarbons	**X** $^{PI, PV}$	x ^{PI}	x ^{PI}	x ^{PI}		x ^{PI}	**X** ^{PI}
Phthalates	x $^{PI, PV}$					x ^{PI}	x ^{PI}
Alkylphenols and -ethoxylates	x $^{PI, PV}$		x ^{PI}				x ^{PI}
Bisphenol A	x ^{PV}		x ^{PI}			x ^{PI}	x ^{PI}
Pesticides					x ^{PI}		x ^{PI}
Microplastics	x ^{PI}		x ^{PI}	x ^{PI}		x ^{PI}	
PCBs				x ^{PI}			
PFAS			x ^{PI}				
PBDEs						x ^{PI}	
Nicotine						x ^{PI}	
Alkalinity		x ^{PI}					
Chloride		**X** ^{PI}					
Faecal bacteria							
PPCPs							
Thermal pollution							

	Roads and impermeable paved surfaces	Building and structure surface materials	Parks and lawns (incl. artificial turfs)	Stormwater control measures	Pipe materials	Misconnections	Pets and wildlife
Solids			x^{PI}	x^{PI}			
Cu		**X**^{PI}		x^{PI}			
Pb		**X**^{PI}	x^{PI}	x^{PI}			
Zn		**X**^{PI}	x^{PI}	x^{PI}	x^{PI}		
Other metal(loid)s	x^{PI}	**X**^{PI}	x^{PI}	x^{PI}			
Nutrients (N, P)			x^{PI}	x^{PI}		x^{PI}	x^{PI}
Organic matter			x^{PI}				
Oil and grease							
Aromatic hydrocarbons	**X**^{PI}		x^{PI}				
Phthalates		**X**$^{PI, PIII, PIV}$		x^{PI}			
Alkylphenols and -ethoxylates		**X**$^{PI, PIII, PIV}$		x^{PI}			
Bisphenol A				x^{PI}			
Pesticides		**X**^{PI}		x^{PI}			
Microplastics			x^{PI}			x^{PI}	
PCBs		x^{PI}					
PFAS							
PBDEs							
Nicotine							
Alkalinity	x^{PI}	x^{PI}		x^{PI}	x^{PI}		
Chloride							
Faecal bacteria						x^{PI}	x^{PI}
PPCPs						x^{PI}	x^{PI}
Thermal pollution	**X**^{PI}	x^{PI}		x^{PI}			

5 Discussion

This chapter discusses the results obtained in the experimental studies and literature review and places them into the broader context of urban runoff quality research. Section 5.1 addresses the sources, and associated pollutant groups, of importance for future urban runoff quality. Section 5.2 discusses options for mitigating the adverse effects of micropollutants in urban runoff on receiving waters, while Section 5.3 discusses the influence of climate change on pollutant releases. Finally, in Section 5.4, the implications for researchers and practitioners in the urban water sector are discussed.

5.1 Emerging sources and pollutants to consider in the future

In the pilot experiments, the highest releases of Zn to runoff were from ZNS and GAL with average concentrations of 5.5 mg/L and 2.9 mg/L, respectively (see Table 5), and the highest releases of Cu was from CUS, with average concentration of 2.5 mg/L in runoff. This corresponds well with the previous literature. For instance, Robert-Sainte et al. (2009) found 6.0 mg/L and 3.0 mg/L Zn in roof panel runoff of new zinc and galvanised steel, and Winters et al. (2015) reported a median concentration of 1.9 mg/L Cu in runoff from a copper panel. Regarding the organic micropollutants, no data for the concentrations in runoff from specific building surface materials was found. However, Bressy et al. (2011) measured NPs in runoff from a building catchment (including tile, zinc and flat roofs and a green space) and reported a median of 0.56 µg/L, which is lower than the average concentration in the runoff from PVB (12 µg/L), but on the other hand takes into consideration factors such as mixing and dilution effects. Wicke et al. (2021) found an average DINP+DIDP concentration of 12 µg/L in stormwater runoff from different catchment types in Berlin, Germany, which is more than a magnitude lower than the DINP concentrations found in the PVC pilot panel runoff, but again, includes dilution and mixing effects that are not considered in the pilot experiments. In addition, the DINP and DEHP concentrations in the melted roadside snow (Table 7) were higher than those reported for stormwater from Berlin (Wicke et al., 2021): in the roadside snow the concentrations of DINP and DEHP were up to 540 and 29 µg/L, compared to maximum concentrations of 130 and 14 µg/L in their study. Furthermore, Gasperi et al. (2022) studied the quality of road runoff in France and found median concentrations of 12 µg/L DEHP, 0.5 µg/L BPA, and 0.2 µg/L OP, which is in the same range as the concentrations found in the roadside snow (Table 7). Sb, which is a toxic element rarely reported in previous studies (Huber et al., 2016), was in the roadside snow samples present at levels similar to those found in road runoff in France (Gasperi et al., 2022). Altogether, these results are further indications of the research needs on the organic micropollutants in urban runoff from various sources or catchments, as was pointed out in Paper I, and e.g., by De Buyck et al. (2021a) and Awonaike et al. (2022).

In Paper I it was concluded that many sources currently seen as major contributors of pollution in urban runoff (e.g., vehicle traffic, metallic building and structure surface materials, and atmospheric deposition; see Figure 5 and Table 8) are expected to retain this assessment in the future, because of their ubiquitous presence in the urban environment. However, the specific sources releasing pollutants may change because of technical improvements or be entirely phased-out and replaced by more environmentally sustainable alternatives. Consequently, the pollutants released and the released amounts may change over time. For instance, the ongoing transition to electric vehicles could strongly affect pollution due to traffic. Revitt et al. (2022) developed an approach to predict current and future highway runoff pollutant concentration scenarios and found that vehicle electrification could reduce PAH levels in urban runoff but would not significantly affect Cu, Zn, Cd, and TSS concentrations. This was explained by the fact that exhaust emissions represent a minor source of metals and particles compared to road and tyre wear, and vice versa for PAHs. Moreover, in 2015 the U.S. EPA together with states and the automotive industry signed an agreement to achieve a nationwide phase-out of Cu in brake pads, which is a major source of Cu in highway runoff (Paper I). Early estimates indicate that the resulting changes in brake pad composition have reduced the concentration of Cu in urban runoff in California by 61% (U.S. EPA, 2021b). While these changes in the vehicle fleet appear to have predominantly positive effects on urban runoff quality, they also introduce potential new sources of pollution that need monitoring; it is possible that brake pads will become important sources of another pollutant, depending on the material chosen to replace Cu. Similarly, electric vehicles could become important sources of several pollutants including both rare earth elements (REEs) used in their production (Ilankoon et al., 2022) and pollutants released due to the different driving styles of electric vehicles when compared to conventional alternatives. REEs were described as contaminants of emerging concern with a high risk of ecotoxicological effects on various aquatic and terrestrial organisms (Gwenzi et al., 2018), and should therefore be examined in future stormwater quality studies. In addition, there are indications that the faster acceleration and higher weight of electric vehicles would increase their emissions from tyre and road wear compared to the equivalent internal combustion engine vehicles (Mirzanamadi & Gustafsson, 2022). Furthermore, vehicles and traffic activities may be important sources of diverse organic micropollutants (Awonaike et al., 2022), which is consistent with the results of Paper V and the data presented in Figure 8.

As noted in Paper I, the introduction of new materials and products to the built environment may affect urban runoff quality in a similar manner to changes in the inputs to road runoff. In particular, new synthetic materials and metallic materials with synthetic surface coatings are constantly being introduced into the urban environment. In accordance with one of the knowledge gaps identified in Paper I, a recent review on roof runoff contamination concluded that there is an overall lack of data on organic pollutants in roof runoff (De Buyck et al., 2021a). Moreover, the phasing-out of priority pollutants with known negative environmental effects often leads to their replacement with other chemicals that have similar properties and are thus likely to have similar environmental effects (Brack et al., 2018). A notable example is the EU priority pollutant DEHP, which is often replaced by the unregulated DINP or DIDP. Accordingly, Papers II-IV showed that PVC panels generally did not release the priority pollutant DEHP but frequently released DINP and DIDP (DEHP was released by PVA in a few runoff events, but at low concentrations; see Table 5). Moreover, while the current knowledge base is somewhat limited, it indicates that various potentially harmful substances may be released from the built environment and enter urban runoff. Together with the poor understanding of the potentially harmful mixture effects arising from simultaneous exposure to many substances (Masoner et al., 2019), this indicates a need for wide screenings of many pollutant groups in urban runoff quality studies, and for careful consideration of new products and materials that are introduced into the built environment. It should however be noted that changes in the pollutant burden of runoff over time are buffered to a degree by the relatively slow pace of change in the built environment and vehicle fleet, which leads to the formation of micropollutant 'stocks' (Mutzner et al., 2022). For example, PCBs were prohibited in Sweden already in 1972 and a decontamination campaign of Swedish buildings has been conducted since 1998 (Bernevi Rex, 2019), but PCBs were still frequently detected in sediments from Swedish urban stormwater ponds (Flanagan et al., 2021), likely because the removal of PCB-containing materials is a long (and so far, incomplete) process (Bernevi Rex, 2019).

5.2 Mitigation tools and their applicability for the different sources

The process of deciding at what point mitigative actions become necessary can be considered rather subjective and depends on several factors. A relatively straightforward decision criterion is the exceedance of relevant guideline values. However, the need for mitigative actions may also depend on the ecological sensitivity of the receiving waters, the level of dilution between the pollution source and the receiving waters, and (naturally) the pollutant concentrations or loads in the actual runoff. Most guideline values on water quality focus on surface water concentrations in the receiving waters, which may make it difficult to derive acceptable pollution levels for water being discharged into these receiving waters. Table 9 lists guideline values relevant to the results presented in this thesis. Three out of the four guidelines listed in this table refer to water quality in the receiving waters: the annual average environmental quality standards (AA-EQS) of surface waters specified in EU Directive 2013/39/EU; the freshwater maximum concentrations (MC) specified in the U.S. EPA National Recommended Water Quality Criteria for Aquatic Life; and the Swedish Agency for Marine and Water Management (SwAM) annual average (AA) concentrations for coastal surface waters (2019). The fourth column in Table 9 shows guideline values for stormwater discharges in Sweden's second largest city, Gothenburg (2020). Although copper and zinc are not listed among the priority pollutants in the EU WFD, they were identified as the pollutants posing the greatest threat to aquatic organisms in UK rivers (Johnson et al., 2017). Moreover, it should, however, be noted that stormwater runoff may contain pollutants whose concentration exceeds the guideline values for receiving surface water without having harmful effects on the actual receiving water because of dilution effects when runoff from various sources is mixed (Wicke et al., 2022).

Table 9 Guideline values relevant to the results of this thesis. The guideline values are the annual average environmental quality standards (AA-EQS) of surface waters specified in EU Directive 2013/39/EU, the freshwater maximum concentrations (MC) of the U.S. EPA's National Recommended Water Quality Criteria for Aquatic Life, the Swedish Agency for Marine and Water Management (SwAM), annual average (AA) concentrations in coastal surface waters (2019), and the guideline values for stormwater discharges in the city of Gothenburg (2020).

	EU WFD AA-EQS (Inland/other surface waters)	**U.S. EPA National Recommended Water Quality Criteria - Freshwater MC (acute/chronic)[d]**	**SwAM Coastal waters, AA**	**Gothenburg guidelines for stormwater discharges**
Cd	<0.08 - 0.25[a] / 0.2	1.8/0.72		0.9
Cr			3.4	7
Cu		-	0.87[b] *(Baltic Sea)*	10
Ni	4[b]/8.6	470/52 (dissolved)		68
Pb	1.2/1.3	65/2.5 (dissolved)		28
Zn		120/120	1.1 (dissolved, *Baltic Sea)*	30
BPA			0.11	
DEHP	1.3/1.3			
NPs	0.3/0.3	28/6.6		
OPs	0.1/0.01			
BaP	0.00017[c]			0.27

[a] Depending on water hardness

[b] Bioavailable

[c] BaP (benzo(a)pyrene), used as a marker for PAHs

[d] Function of water hardness, here corresponding to a hardness of 100 mg/L.

Figure 13 compares the pollution levels of Cu and Zn from the different sources studied within this thesis to the guidelines mentioned above, while Figure 14 presents the corresponding comparisons for NPs and OPs. As shown in Figure 13, the concentrations of Cu in roadside snow exceeded the stormwater discharge guideline values by roughly one order of magnitude at all roadside sites, while the copper sheet panel (CUS) runoff exceeded the same guideline concentrations by over two orders of magnitude. Similarly, the concentrations of Zn in the roadside snow at all sampled sites exceeded the Gothenburg and U.S. EPA guideline values, as did the concentrations in runoff from the galvanised (GAL) and zinc (ZNS) panels. An important difference between the panel runoff and the roadside snow is the proportion of dissolved metals, which is far greater in the panel runoff (see Figure 11), making these pollutants more mobile and bioavailable. Furthermore, a study of the speciation of Cu and Zn from the same pilot panels (CUS and ZNS) showed that the dissolved Cu and Zn was mainly present as free ions – the most bioavailable form (Lindfors et al., 2017). This implies that more advanced treatment technologies such as chemically active filtration are required to reduce the burden of Cu and Zn (Clark & Pitt, 2012). Studies on the removal of copper from roof runoff using a zeolite filter showed that the content of dissolved Cu could be reduced quite substantially (by 48–85%), but the Cu concentration of the effluent remained above the guideline values (Milovanović et al., 2022).

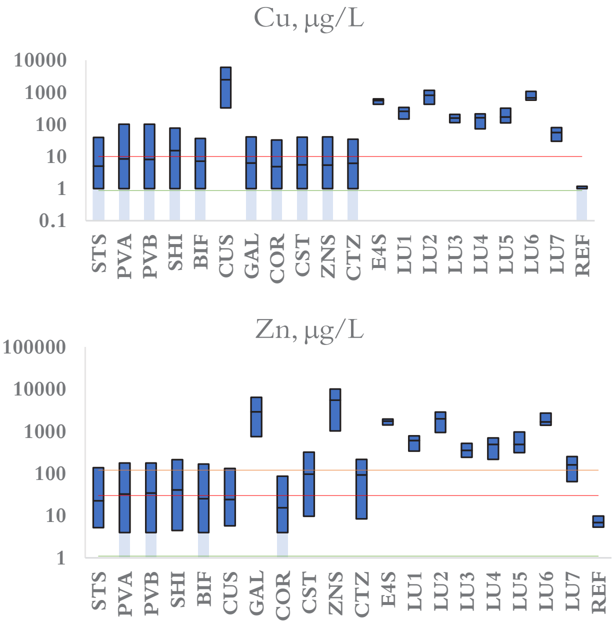


Figure 13 Cu and Zn concentration ranges for different sources in open-air sampling studies, and relevant guideline values indicated by red (Gothenburg guidelines for stormwater discharges), orange (U.S. EPA), and green (SwAM, annual average in coastal surface waters) lines.

Figure 14 compares the experimentally determined concentrations of 4-NPs and 4-OPs to the relevant guideline values, revealing that the 4-NP levels in the panel runoff were of the same magnitude as the U.S. EPA guideline values. Similarly, the 4-OP concentrations were generally of the same magnitude as the EU WFD guideline values, although those at the Stockholm location (E4S) substantially exceeded the guideline values. Moreover, as shown in both Figure 13 and Figure 14, some of the guideline values were comparable to or even below the analytical RLs of the substances in question. However, the SwAM guideline value for Cu refers to the bioavailable concentration, which is a proportion of the dissolved concentrations, thus, such comparisons are probably better made with the dissolved concentrations, for which the RL is also lower. For instance, Lindfors et al. (2021) compared the measured dissolved (<0.45 µm) and truly dissolved Cu concentrations (determined by ultrafiltration) to the bioavailable fraction (predicted with the model Bio-met) in urban runoff from three Swedish catchments, and found that on average, the truly dissolved Cu concentration exceeded the predicted bioavailable fraction by a factor of 22.

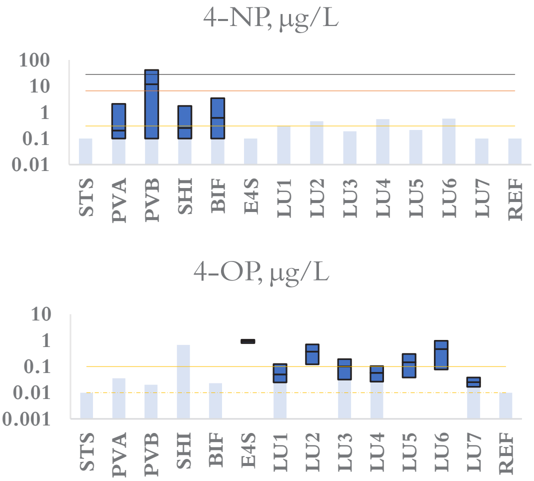


Figure 14 NP and OP concentration ranges for different sources in open-air sampling studies, and relevant guideline values indicated by black (U.S EPA acute), orange (U.S. EPA chronic), solid yellow (EU WFD inland waters), and dashed yellow (EU WFD other surface waters) lines.

Figure 15 compares the micropollutant levels in the roadside snow to the guideline values and the maximum dissolved concentrations in the samples. DEHP is the only phthalate for which guideline values exist and was present in roadside snow in concentrations up to 20 times higher than the EU WFD EQS. The measured concentrations of OPs and BPA were on the same order of magnitude as the guideline values, however. Figure 15 and Figure 11 both show that inorganic pollutants in roadside snow are mainly associated with particles, so their maximum dissolved concentrations rarely exceeded the corresponding guideline values. It should also be noted that the concentrations in the melted roadside snow are not equal to those in snowmelt road runoff, where a proportion of the pollutants would likely be retained in or near to the road environment (and possibly resuspended later), as discussed in Paper V. Treating such runoff using systems based on sedimentation or physical filtration of particles could therefore drastically improve the runoff quality and reduce the risks of negative effects in the receiving waters (Clark & Pitt, 2012). Moreover, because snow is a solid medium that accumulates pollutants until it melts, effective snow management practices could reduce melting-induced pollutant releases in ecologically sensitive areas. For example, polluted snow could be transported to less-sensitive areas or to snow treatment facilities for controlled melting (Viklander, 1999; Kuoppamäki et al., 2014; Borris et al., 2021).

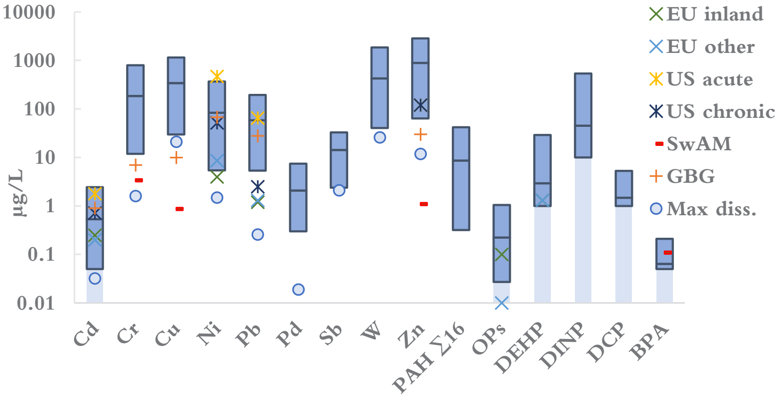


Figure 15 Concentration ranges of selected micropollutant in roadside snow samples (N = 42), and the corresponding guideline values (where available). The measured maximum dissolved concentrations of the metals are indicated by blue circles.

Table 10 Summary of the exceedances of applicable guideline values for selected micropollutants from the sources studied in Papers II–V, namely roadside snow (RSS) and 11 tested building surface materials. (From Table 9: EU refers to the AA-EQS of surface waters in EU Directive 2013/39/EU; U.S. refers to the MC in the U.S. EPA National Recommended Water Quality Criteria for Aquatic Life; Sw refers to the SwAM annual average in coastal surface waters; and GBG refers to the guideline values for stormwater discharges in the city of Gothenburg).

	RSS	**STS**	**PVA**	**PVB**	**SHI**	**BIF**	**CUS**	**GAL**	**COR**	**CST**	**ZNS**	**CTZ**
Cd	EU											
Cr	Sw GBG		Sw	Sw	Sw GBG	Sw	GBG	Sw	Sw	Sw		Sw
Cu	Sw	Sw	Sw	Sw	Sw	Sw	Sw	Sw	Sw	Sw	Sw	Sw
Ni	EU GBG				EU				EU			
Pb	EU GBG	EU	EU	EU	EU	EU	EU	EU	EU	EU	EU	EU
Zn	U.S. Sw GBG	Sw GBG	Sw GBG	Sw GBG	Sw GBG	Sw	Sw	U.S. Sw GBG	Sw	Sw GBG	U.S. Sw GBG	Sw GBG
BPA	Sw											
DEHP	EU											
NPs				U.S.[a]					Substance not analysed			
OPs	EU											
BaP	EU											

[a] Exceeds criteria for chronic exposure.

Table 10 summarises the exceedance of guideline concentrations of different pollutants in runoff and snow from the sources studied in Papers II–V. The number of substances present at concentrations above the guideline values was highest in roadside snow, for which the concentrations of all pollutants other than NPs exceeded at least one guideline value. However, it should be noted that some of the guideline values are close to the analytical RLs of the methods used in this work. This may indicate that the specific water bodies to which these guidelines apply are very sensitive to urban runoff inputs in general, because it is likely that the bioavailable concentrations of Cu and Zn in urban runoff would regularly exceed the Swedish Agency for Marine and Water Management annual average for the Baltic Sea. For instance, the Bio-met predicted bioavailable concentration of Cu in stormwater from industrial parks exceeded the SwAM guideline for Cu on several occasions, with concentrations of up to 1.4 µg/L bioavailable Cu (Lindfors et al., 2021).

Finally, as discussed in Paper I, it may often be both easier and more effective to limit the releases of pollutants instead of applying treatment to polluted runoff. Thus, source controls are often the most effective mitigative tool to reduce pollution (Marsalek & Viklander, 2011). This can be achieved by phasing out important sources, as exemplified by the previously discussed efforts to replace Cu in brake pads and the historically successful removal of Pb from gasoline, which dramatically reduced Pb levels in highway runoff (Kayhanian, 2012; Huber et al., 2016). Similar phase-outs could be performed for problematic building surface materials and drainage surfaces in the built environment. To counteract the risks of adverse effects on receiving waters because of pollution from building surface materials, mitigative measures (or careful material selection processes) should be integrated into the early stages of new construction projects. Where it is not feasible to remove or replace a specific pollution source, close-to-source treatment may be the best option because it could enable targeted treatment of specific pollutants or pollutant fractions using methods that could not be applied to stormwater from mixed sources at the end of a pipe. Practical features of buildings could also reduce the pollution of the building runoff. For instance, façades constructed with roof overhangs to reduce the runoff volume were suggested to reduce the pollutant contribution of façade materials (Wicke et al., 2022). However, such a roof overhang would likely have negligible effects on tall buildings.

5.3 The influence of climate on pollutant releases

The IPCC Sixth Assessment Report states that climate change has intensified the global hydrological cycle by increasing the occurrence of extreme floods and droughts. At the same time, urbanisation is increasing rapidly (Pörtner et al., 2022). Moreover, the ongoing global warming may increase the proportion of precipitation falling as rain instead of snow in cold climates. Based on the results presented in this thesis, such climatic changes could increase the release of pollutants from building surfaces and other surfaces with runoff, because the pollutant levels in rain-induced runoff were higher than those in snowmelt runoff (see Figure 6 and 7, and Paper IV). This also implies that the yearly pollutant loads from roof runoff would likely be higher in present and future climate conditions without seasonal snow covers (see Table 2 in Paper IV). In addition, Figures 6 and 7 show that the rain events preceded by long dry periods yielded runoff with unusually high concentrations of Cu, Zn, and DINP. Therefore, periods of drought may cause high concentrations of pollutants to be flushed off from such surfaces during subsequent rain events.

The global warming could potentially impact the use of road salt in cold climate regions. In regions where road salt use is now limited because of colder temperature (road salt is generally applied when temperature is around 0°C) future scenarios may involve an increased use of road salt and decreased use of grit materials, whereas those areas where road salt is generally applied today may decrease their use if the temperature falls below 0°C more seldom. This potential change could inflict changes in the dissolved metal, chloride, and TSS levels of snowmelt runoff (Marsalek, 2003; Westerlund & Viklander, 2006). Furthermore, the period with seasonal snow covers may in cold climate areas be shorter because of global warming, thus shortening the period of pollutant accumulation, which could potentially reduce the magnitude of the 'pollutant shocks' released during the melting period (Westerlund & Viklander, 2006; Meyer & Wania, 2008).

5.4 Implications for research and practice in the urban water sector

As demonstrated in the earlier sections of this thesis, a wide array of sources in the urban environment contribute to the pollution of urban stormwater runoff. As concluded in Paper I, advancements in technology and the implementation of regulations that cause harmful substances to be gradually removed from the urban environment mean that the list of important stormwater pollution sources and the associated pollutant groups can be expected to change continuously. Moreover, efforts to replace problematic materials will lead to the introduction of new substances and materials (and thus potential new sources of pollution) to the urban environment. Therefore, the work with identifying important sources of key pollutants in urban stormwater will continue to be needed for the foreseeable future.

At a larger scale, holistic thinking and innovative solutions are needed to cope with the water-related challenges of the urban environment, including diffuse pollution, floods and water scarcity. Larsen et al. (2016) stated that rapid urbanisation together with water scarcity and an ageing urban water infrastructure presents major challenges for urban water management. Mitigative measures should be introduced in the planning stage of new constructions to prevent negative effects on surface waters caused by releases of substances from building surface materials (Wicke et al., 2022). The environmental effects of different materials during their lifespans should therefore be considered carefully when selecting materials for use in new buildings and in environmental assessments. Risch et al. (2018) proposed an approach to account for wet-weather contributions of pollution to an urban (combined) wastewater system based on life cycle assessments (LCAs). After applying their method to a catchment in the Paris region, they concluded that stormwater flows had the greatest impact on freshwater ecotoxicity because of their high concentrations of Cu and Zn.

Moreover, Paper II showed that the methods suitable for different source identification studies depend on the specific aim of the study and should be chosen carefully in the planning process, based on the methods' capabilities and the available resources. While stormwater quality studies based on field measurements have the advantage of generating 'realistic' data on stormwater runoff, they have a relatively coarse (typically, catchment-scale) spatial resolution that prevents the identification of specific sources. Pilot-scale studies produce realistic data but are highly resource-intensive in terms of both labour and finances (see Figure 12). Conversely, small-scale laboratory studies and screenings are less resource-intensive but do not produce realistic data in terms of the concentrations released.

5.4.1 Challenges with analyses of organic micropollutants

The methods applied in the laboratory leaching experiments were unsuitable for identifying phthalate releases. Although the material screening studies showed that phthalates (mainly DINP) were present in the materials (see Table 4) and released into their surface runoff (Table 5), these compounds were not present in the laboratory leachates from either of the PVC materials. This could be due to a lack of particles for the hydrophobic phthalates to attach to in the leaching experiments; in the pilot panel studies, particles were deposited on the panels from the atmosphere, providing surfaces that the phthalates could adsorb onto. Previous research on phthalates in landfill leachates and stormwater showed that the leachability of phthalates was associated with dissolved organic matter (Kalmykova et al., 2013) and binding to humic acids (Zheng et al., 2007). Moreover, studies on DEHP migration from indoor PVC flooring found that dust particles effectively adsorbed DEPH, and that the dust uptake increased with time and temperature (Clausen et al., 2004; Clausen et al., 2012). These findings support the hypothesis that particles deposited on pilot panel surfaces act as carriers of phthalates with runoff from the PVC materials.

In general, the analysis of phthalates and APs/APEOs conducted in this thesis (Papers II-V) all suffered from problems with a high proportion of censored data and elevated reporting limits because of matrix effects. Mutzner et al. (2022) observed similar problems with organic micropollutant data in urban wet-weather flows, obtaining >50% censored data and analytical RLs exceeding the corresponding EQS; these authors concluded that improvements in chemical preparation and analysis of samples was needed. Moreover, Brack et al. (2018) suggested that advanced non-target screenings of chemicals could act as a support tool for risk assessments to counteract problems such as phased out chemicals being replaced by other chemicals with similar environmental effects. Non-target screenings of micropollutants in stormwater have also been applied in recent stormwater quality studies (e.g., Järlskog et al., 2021; Gasperi et al., 2022).

5.4.2 Factors affecting pollutant releases

Several factors may influence the releases of pollutants from various sources in the urban environment. Influential factors affecting releases from the building surface materials studied in Papers II-IV include rainwater pH (Wicke et al., 2014), ADD (Yaziz et al., 1989; Egodawatta et al., 2009), rain intensity (Winters et al., 2015; Charters et al., 2016) and air temperature, as suggested in Paper III. While some of the parameters revealed correlations between releases of pollutants from several different material panels (e.g., ADD), and air temperature correlated with the release of Cu from SHI and NPs from PVCB (see Table 7 in Paper III), the results presented in Papers III and IV did not reveal any single influential factors exerting significant effects on pollutant releases. As discussed in Paper III, this was expected because, in the natural environment, influential factors likely have simultaneous effects on substance releases. Moreover, the results from Papers III and IV indicated that the material properties mainly governed the pollutant releases and not the substance properties because the releases of the same pollutant displayed different release patterns from different materials.

The roadside snow sampling results (Paper V) indicated that the pollution levels in the snow collected in Stockholm were often higher than those at the Luleå locations, especially for the phthalate concentrations. This indicated that the much higher AADT and smaller snow volumes observed at E4S, had a greater influence on the pollutant concentrations than the duration of pollutant accumulation, which was much longer in Luleå both for the first and second sampling occasions (S1 and S2, corresponding to 56 and 72 days, respectively, compared to 13 days for E4S). Another explanation for the higher phthalate concentrations in Stockholm could be attributed to differences in the tyres used in the south of Sweden compared to the north (higher use of studded tyres in the northern regions of Sweden: almost 90%, as opposed to 40% in southern Sweden (Lundberg et al., 2019; Kriit et al., 2021)), or increased phthalate leaching or wearing because of higher amounts of road salts applied in Stockholm. The correlation tests performed in Paper V showed that the traffic intensity (AADT) correlated with concentrations of the metal(loids) Cu, Sb, W, and Zn, as well as DEHP and DINP in the roadside snow (see Table 3 in Paper V), and that pH and TSS were correlated to each other, likely because the TSS particles provided buffer capacity in the snow that increased the pH (Viklander, 1999). Valtanen et al. (2015) found that in runoff patterns are seasonal in cold climates, with wide differences between cold and warm periods because of differences in runoff generation (snowmelt/rain), and that runoff duration was the responsible factor for the cold periods.

6 Conclusions

The primary aim of the thesis was to provide new knowledge on the sources contributing to urban runoff pollution and to evaluate the specific contributions of micropollutants from two known major pollution sources: building and structure surface materials, and vehicular activities. From the results presented herein, the following conclusions can be drawn:

The results presented in the literature review (Paper I) confirmed that traffic activities and building surface materials are major sources of stormwater pollution, and that more attention needs to be paid to pollutants of emerging concern. Whilst results of the literature review identified atmospheric deposition (AD) as an important source of pollution in surface runoff, the matrices studied herein (pilot panel runoff, Papers III and IV, and roadside snow, Paper V) did not indicate AD as a significant contributor of the studied pollutants. However, AD may still be an important factor to consider in open-air studies and could play an important role in releases of other substances from building surface materials, e.g., phthalates from PVC sheets. Results presented in this thesis demonstrate that a wide range of metals and organic micropollutants may be found in runoff from building surface materials and in roadside snow. Among the studied sources, copper sheets gave rise to the highest concentrations of Cu, and zinc sheets and galvanised steel gave rise to the highest concentrations of Zn. PVC membranes were identified as sources of DINP and NPs. Vehicle traffic was identified as a source of Sb, W, OPs, BPA and DEHP, all of which were infrequently reported in previous studies. Many of the substances found in building runoff and roadside snow were present in concentrations exceeding available guideline values. Therefore, source control measures or other treatment options may be necessary to avoid adverse effects in receiving waters.

Comparisons of the two matrices studied showed that metals were mainly present in dissolved (<0.45 μm) form in pilot panel runoff (>90% in runoff from CUS, ZNS and GAL), unlike in roadside snow, where metals were almost entirely attached to particles. This implies that the two runoff types would require different treatment techniques for effective mitigation. The comparison of methods for identifying building surface materials as stormwater pollution sources (Paper II) indicated that laboratory leaching tests were generally effective for all studied substances except for phthalates, which were not released under the laboratory conditions. Among APs, NPs were predominantly found in building runoff, while OPs were predominantly found in roadside snow. Moreover, comparing the results from Papers II, III and VI demonstrated the importance of analysing both APs and APEOs because of their interconnected use and gradual degradation.

Finally, this thesis presented results from the in-situ ageing of building surface materials and analyses of runoff quality from both rainwater and snowmelt induced runoff, a topic not previously investigated. The results showed that the concentrations were generally higher in rainfall runoff than snowmelt runoff, and that most materials and substances exhibited no decreasing or increasing trend over time, except for the decreasing releases of NPs from a PVC material, possibly due to the washing out of NPs and material ageing.

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Paper I

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Review

The pollution conveyed by urban runoff: A review of sources

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HIGHLIGHTS

- Current knowledge of stormwater pollution sources varies among source categories.
- Atmospheric deposition, transportation and metallic materials are major sources.
- Some data from older stormwater quality studies may be obsolete and no longer valid.
- New materials and pollutants necessitate future re-examination of pollution sources.
- More attention needs to be payed to pollutants of emerging concern.

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Source controls

ABSTRACT

Urban stormwater and snowmelt pollution contributes significantly to the deterioration of surface waters quality in many locations. Consequently, the sources of such pollution have been studied for the past 50 years, with the vehicular transportation sector and the atmospheric deposition identified early as the major pollution sources. In search for mitigation of this pollution, source controls, besides other measures, were recognised as effective pollution mitigation tools, whose successful implementation requires a good knowledge of pollution sources. Even though great research efforts have been exerted to document specific sources of urban runoff pollution, or specific groups of pollutants present in urban runoff, a comprehensive overview of all known contributing sources is still missing. This review contributes to closing this gap by compiling findings of previous research and critically synthesizing the current knowledge of various stormwater pollution sources. As the emphasis is placed on the sources, the related issues of implications for urban surface water quality and possible source controls for individual sources are touched upon just briefly, where required. The review showed that the atmospheric deposition, vehicular transportation-related activities and metallic building envelopes continue to be among the major pollution sources, which have been studied in a far greater detail than other sources. Furthermore, it was noted that because of the rapid advances in clean manufacturing and pollution control technologies, a large part of the body of data on stormwater quality available in the literature should be considered as historical data, which may no longer describe well the current conditions. Progressing historical data obsolescence, combined with continuing releases of new materials and chemicals, and, in some cases of new substances of potential concern,

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into the environment, suggests that the identification of important stormwater runoff/snowmelt pollution sources, and the associated pollutants, has been and will remain to be a work in progress.

Contents

1. Introduction

Urban runoff, comprising stormwater and snowmelt in regions with seasonal snow, is widely recognised as a major transport vector of pollutants released in the urban environment, and, therefore, a significant contributor to the deterioration of urban receiving waters quality (Sartor and Boyd, 1972; Lee et al., 2007; Björklund et al., 2018). Urban stormwater as a concern in managing surface water quality has been studied since the mid-20th century and Åkerlindh (1950) and Weibel et al. (1964) were among the first to point out this concern. Some years later, the sources of pollutants occurring in urban stormwater and snowmelt attracted increased research interests, and the vehicular transportation-related sources were among those identified early as important pollution sources (Sylvester and DeWalle, 1972; Laxen and Harrison, 1977; Horkeby and Malmquist, 1977; Malmqvist, 1983). The early heuristic studies typically addressed such conventional pollutants as total suspended solids (TSS), chemical or biochemical oxygen demand (COD/BOD), trace metals (mainly Cd, Cr, Cu, Ni, Pb and Zn), and various species of N and P.

Starting in the 1980s, a number of ambitious, large-scale research programmes mapping stormwater quality over various land-use areas were established, with the U.S. Nationwide Urban Runoff Program (NURP) being the most extensive one (U.S. Environmental Protection Agency (EPA), 1983). In the U.S., a follow up on the NURP resulted in a recent National Stormwater Quality Database (NSQD), comprising data from >9100 urban runoff events, observed on six main urban land uses: residential, commercial, industrial, freeways, institutional, and open space. NSQD includes >100 various constituents, many of which are rather uncommon and documented only by sparse data (Pitt et al., 2018). Because of large variations of stormwater quality in time and place (Butler et al., 2018), the above extensive databases are helpful in e.g., estimating expected pollutant loads from whole catchments, planning treatment solutions where needed, or comparing pollution control options. However, these databases comprise data with a relatively coarse spatial resolution, equal to the catchment scale, and hence cannot be used for identifying the specific sources of diffuse pollution within the catchment, or their mitigation by source controls.

The EU Water Framework Directive (Directive 2000/60/EC) addressed the need to mitigate diffuse pollution and its amending priority pollutant directive (Directive 2013/39/EU) contributed to broadening the list of substances included in stormwater quality studies. The contemporary research often confirms the earlier findings concerning e.g., TSS, metals and polycyclic aromatic hydrocarbons (PAHs) (Zgheib et al., 2012; Gasperi et al., 2014), and produces new data on emerging pollutants in stormwater, such as phthalates (Björklund et al., 2011; Zgheib et al., 2012; Markiewicz et al., 2017; Müller et al., 2019), alkylphenols (APs) (Bressy et al., 2011; Björklund et al., 2011; Zgheib et al., 2012; Gasperi et al., 2014; Markiewicz et al., 2017; Müller et al., 2019), bisphenol-A (BPA) (Gasperi et al., 2014), and recently introduced pesticides (Zgheib et al., 2012; Gasperi et al., 2014). Moreover, because of rapid advancements in clean manufacturing and pollution control technology, much of the data from stormwater quality studies published in the literature may be dated and no longer valid in today's conditions. This resulted from the implementation of new technologies reducing emissions, as well as regulatory actions leading to virtual elimination of specific environmentally harmful substances. For instance, the earlier reported impacts of PAHs from steel plant emissions (Gu et al., 2003), or Pb from the use of leaded gasoline (Kayhanian, 2012) may no longer exist, or have been strongly abated.

Source controls, i.e. pollution prevention, represent fundamental steps towards minimising the presence of pollutants in urban stormwater and the concomitant potentially negative effects in receiving water bodies. Source control policies are recognised as the most cost-effective management tool in dealing with low-level diffuse pollution and there is a strong need to further advance this pollution control tool (Marsalek and Viklander, 2011). Often the opportunities for actually controlling the sources of pollution are limited or hard to achieve, and then it may be more feasible to control the release activities rather than the primary sources. Previous success stories concerning legislative actions leading to effective source control include the phasing out of lead from gasoline (Kayhanian, 2012; Huber et al., 2016). Recently implemented environmental policies such as the reduction of Cu in vehicle brake pads in the U.S. (U.S. EPA, 2015) and elsewhere are promising examples for future runoff quality improvements. For planning implementation of source control policies, adequate knowledge of the sources of urban stormwater pollution is essential (Loganathan et al., 2013).

Even though the urban stormwater pollution sources have been studied for more than half a century, a comprehensive overview of specific sources and the associated pollutant groups is still missing, and this review contributes to closing this gap by evaluating the current state of knowledge of various sources contributing to the pollution of urban stormwater. The scope of the review is fairly broad and focuses on well-documented sources, as well as the emerging sources, which have not been yet fully assessed in the scientific literature, and includes various types of pollutant groups, and the thermal pollution of stormwater. The approach used in this review, with focus on the sources rather than the nature or classification of pollutants, is a rather unique approach infrequently seen in other papers. In the context of this paper, urban stormwater was defined as urban runoff, generated by rainfall, snowmelt or both, normally conveyed by the public storm sewers in separate sewer systems, or other conveyance elements of contemporary drainage systems, including green infrastructure and stormwater control measures (SCMs). Hence, the terms 'urban runoff' and 'stormwater' are used synonymously, recognising that 'runoff' reflects the hydrological context and 'stormwater' focuses on the transported medium. Runoff conveyed in combined sewer systems, or in private drainage systems and/or treatment facilities, e.g. airport runoff, was considered outside the scope of this paper. Several conditions and factors may affect the transport and release of urban stormwater pollutants, but details about these factors were also considered outside the scope. When searching for relevant literature, contributions assessing urban runoff as a confirmed, or potential, transport vector were included. However, detailed discussions of the effects of urban runoff pollution on the receiving waters and control measures for mitigation of such effects were considered outside the scope of this review.

2. The classification of sources into categories

There are many ways of classifying and grouping sources of stormwater pollution, and the partition between the groups can be quite complex, with the boundaries between source categories rarely well defined. Depending on the classification approach taken, some sources may contribute the pollution to several source categories in different times or ambient conditions. For instance, one pollution source may be an operating vehicle releasing pollutants into the atmosphere (one source category), which may later be deposited on roads and other surfaces, and may thereby also contribute pollutants directly to road surfaces (another source category) and, hence, to stormwater runoff. The partitioning of sources is further complicated by source interactions (Thorpe and Harrison, 2008), caused, e.g., by resuspension of deposited pollutants, which in studies of stormwater quality and the application of study data may lead to double counting of pollutant contributions from a specific source. Thus, pollutant transformations and temporary storage during conveyance make it difficult to identify the contributions of pollution from specific sources on the basis of discharge concentrations (Lundy et al., 2012).

Various approaches to classification of stormwater pollution sources were noted in the literature. Loganathan et al. (2013) divided the sources contributing to road sediment pollution into the intrinsic sources (within the road environment, i.e., atmosphere, pesticide use, pedestrian littering, fences and railings, and all vehicular transportation related sources), and the extrinsic sources (buildings, industry, soils and vegetation). Lundy et al. (2012) classified sources based on land use types and activities, including, e.g., construction sites, highway surfaces, roof surfaces, open spaces, misconnections, and more. Similarly, Petrucci et al. (2014) grouped diffuse pollution sources into four main groups: activity-related (e.g., road transport emissions), land cover-related (buildings and infrastructure), behaviour related (e.g., pesticide and fertiliser use), plus atmospheric deposition (AD).

Building on the classifications of sources by the earlier researchers, in our review, the sources are grouped into four main categories: atmospheric deposition, drainage surfaces, anthropogenic activities, and urban drainage systems. Anthropogenic activities were defined as the activities practiced in the urban environment by humans, or resulting from such actions of humans, with varying frequencies and intensities. Examples of activity-related dynamic sources are, e.g., vehicular transportation, winter road maintenance, or construction work. The strength of these sources varies in time while the activity progresses, as in the case of construction works, which are temporary sources of pollutants, or may vary with season, as in the case of winter road maintenance or fertilisation of lawns. Other sources in the urban environment are static and generally relate to land covers, or surfaces; they may contribute pollution in wet weather regardless of any anthropogenic activities. The latter sources include, e.g., building envelopes, parks and infrastructure elements. However, the magnitude of the pollutant releases from surfaces may vary with a number of factors, such as the material age (Robert-Sainte et al., 2009), rainfall intensity (Charters et al., 2016), and others. The quantitative contribution of pollution from specific sources have been accounted for where such information was available and considered applicable. For some specific source categories, especially the activity related sources, the quantitative contribution of pollutants cannot be allocated to specific sources because of several sources producing simultaneous pollutant contributions to the same mass of runoff water, or because of high unpredictability, e.g., in the case of spills. Fig. 1 further describes the classification of pollution sources used in this review and also serves as a table of contents for the topics discussed herein. The sources are listed in the boxes and arrows indicate the main transport pathways of the pollution, and interactions among the source categories. This way of grouping sources also facilitates the discussion of source controls. Building upon the discussion in Marsalek and Viklander (2011), the strength of sources related to anthropogenic activities may often be more feasible to control by restricting the activity leading to pollutant release, instead of eliminating the actual source. On the other hand, the sources constituting drainage surfaces may be controlled by substitution of environmentally friendly materials for those releasing pollutants.

3. Important sources of urban stormwater pollution

3.1. Atmospheric deposition

Atmospheric deposition (AD) facilitates transfer of polluting substances and materials in the atmosphere to the urban catchment surface, with either precipitation or deposition in dry weather. Thus, AD comprises wet and dry components, with the former one contributing directly to pollution of surface runoff and the latter one contributing potentially after washoff of substances and materials from catchment surfaces (Marsalek et al., 2008). With respect to the runoff pollution, AD is particularly important in urban areas, which are characterised by numerous sources of air pollution and high likelihood of pollutant washoff into stormwater runoff, facilitated by the presence of impervious areas and runoff conveyance networks (Hobbie et al., 2017). Consequently,

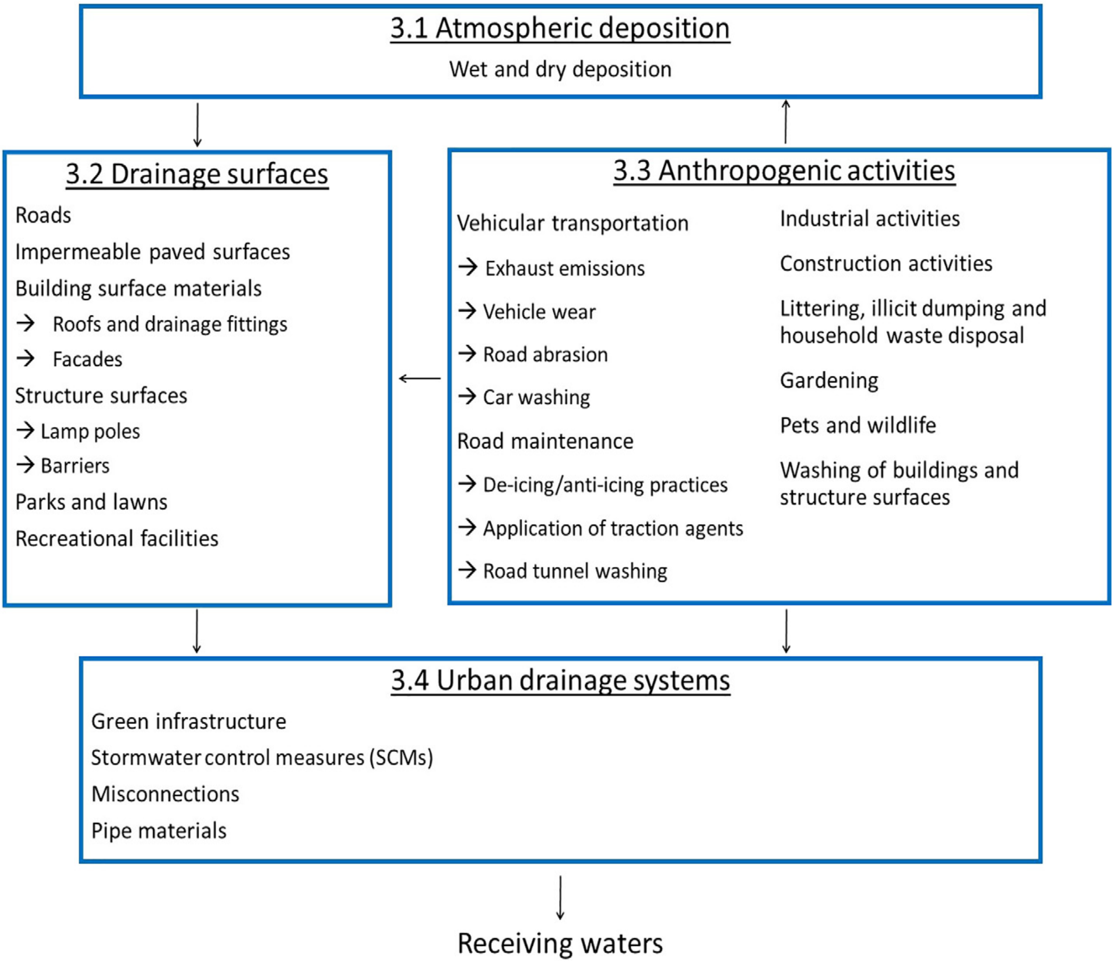

Fig. 1. Grouping of urban stormwater pollution sources, section numbers for the main source categories, and pollution transport pathways indicated by arrows.

AD has been generally identified as an important source of pollutants found in urban stormwater (e.g., Barkdoll et al., 1977; Malmqvist, 1983; Brinkmann, 1985; Davis et al., 2001; Pitt et al., 2004; Sabin et al., 2005; Davis and Birch, 2011; Gunawardena et al., 2012; Gunawardena et al., 2013; Petrucci et al., 2014; Omrani et al., 2017).

Concerning the stormwater pollution, the atmosphere serves more as a pollutant transport pathway, rather than an actual source of observed pollution (Petrucci et al., 2014). Atmospheric pollutants, from both natural and anthropogenic sources, are brought into the urban environment by emissions and atmospheric transport from local, regional and remote sources. The multitude of sources and atmospheric transport scales contribute to high variability of AD chemical characterisation and rates of deposition in both time and space (Malmqvist, 1983; Brinkmann, 1985; Boom and Marsalek, 1988; Rocher et al., 2004; Sabin et al., 2005). Among the sources listed in Fig. 1, AD is unique by including pollution sources located outside of urban catchments and contributing via long-range atmospheric transport, as documented, for example, by Li et al. (2007).

A quantitative assessment of AD contributions to pollutant exports with stormwater runoff from urban catchments is rather challenging because of such reasons as complexities of various pollution sources and air transport processes (Brinkmann, 1985; Morselli et al., 2003), changes in wet deposition chemistry on contact with surfaces (Polkowska et al., 2011), and uncertain pollutant entry from dry depositions into stormwater (Morselli et al., 2003; Murphy et al., 2015; Al Ali et al., 2017). Furthermore, Colman et al. (2001) pointed out that while the wet deposition is relatively simple to monitor, monitoring dry deposition and discerning between the vehicle-related deposition and the ambient urban atmospheric deposition is rather difficult and raises questions about comparison of data from various references. The lack of discernment between these two sources may then lead to double counting AD contributions. Finally, the historical AD data (e.g. Boom and Marsalek, 1988) have to be understood in the context of environmental conditions and AD sources existing when the data were collected. With time, some historical AD sources may be weakened by advances in implementation of clean air technologies and environmental policies reducing air pollution, but others (e.g. traffic) may be strengthened with the increasing intensity of the activity.

Among the chemicals transported through the atmosphere, there is a distinct class referred to as volatile organic compounds (VOCs). VOCs are widely used in many products (fuels, fumigants, paints, pesticides, precursors in manufacturing chemicals, refrigerants, and solvents) (Lopes and Bender, 1998; Moran et al., 2006), or are formed as by-products of processes occurring in urban areas (e.g., trihalomethanes formed as water disinfection by-products). Consequently, VOCs are ubiquitous in the urban environment, and may enter both surface waters, including stormwater, and groundwater from many sources (Lopes and Bender, 1998). Because of their toxicity, a number of VOCs were included in the U.S. EPA list of 129 priority pollutants and 12 of those were investigated in the NURP studies of urban runoff quality (U.S. EPA, 1983). In the list, this group includes three BTEX compounds, benzene, ethylbenzene and toluene, and their derivatives (including chlorinated benzenes). VOCs were rarely detected in the limited NURP sampling (U.S. EPA, 1983): four compounds in two to six of the 28 sampled cities, and in six samples per site or less. The primary sources of VOCs in stormwater can be identified as vehicle fuels (released as vehicle exhaust gases and particles, or at gasoline filling stations and in fuel spills), atmospheric transport and deposition, and industrial releases. Using the taxonomy of stormwater pollution sources introduced earlier (Fig. 1), and recognising broad uses and distribution of VOCs in urban areas, they are not discussed as a separate group, but in the appropriate review sections (Section 3.1 Atmospheric deposition, Section 3.3.1 Vehicular transportation, and Section 3.3.3 Industrial activities). One characteristic seems to be common to the stormwater studies of VOCs and the respective publications: although concerns about the stormwater pollution by VOCs were expressed, e.g., where stormwater serves for reuse (Liu et al., 2018b) or the recharging of groundwater (Yu et al., 2017), or that VOCs should be considered in planning community pollution reduction strategies (Li et al., 2018), the reported VOC concentrations were not assessed with respect to their environmental relevance and regulatory context.

Specific assessments of AD potential contributions to stormwater pollutant export loads were reported in about 20 references for total suspended solids (TSS), nutrients, metals, and trace organics. Such contributions were rated in this review with respect to their magnitude as "significant" (i.e., when representing 10–100% of stormwater export loads), or as "trace-to-low" contributions (up to several percent). A summary of such an assessment is presented in Table 1.

The references listed in Table 1 suggest that AD is a "significant" source of such stormwater quality parameters as TSS, nutrients (N and P), and metals associated with traffic and local industrial releases. The metals reported in AD included Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Ti, V, W, Zn, and Zr, but most studies focused just on the most environmentally relevant metals in urban stormwater, Cu, Pb, and Zn. For TSS and the above chemicals in urban catchments, the annual loadings in AD typically equalled 20–100% (or more) of the respective loads exported with urban stormwater. A number of studies emphasised the importance of local stationary sources of AD, in comparison to mobile emission sources (traffic and road dust). Other studies reported the presence of trace organics (mostly priority pollutants) in urban stormwater. Those occurred in low or trace amounts, and mostly in wet atmospheric deposition.

In summary, the current level of knowledge of AD indicates that depending on local circumstances, AD may be an environmentally important source of solids and conventional and emerging pollutants conveyed by urban stormwater, with some of such pollutants originating outside of the catchment. While wet deposition can be readily measured, dry deposition measurements and the entrainment of deposited chemicals by runoff are highly uncertain. In relation to other pollutant sources, AD may expand the list of pollutants found in urban stormwater and can be effectively controlled only at the source.

Table 1
Two-level assessment of atmospheric deposition contributions to urban stormwater quality.

Conventional pollutants	AD contributions equal to 10–100% of stormwater export loads
TSS	Murphy et al. (2015)
Nutrients (N, P)	Hobbie et al. (2017); Hou et al. (2012)
Metals associated with traffic (Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Ti, V, W, Zn, Zr)	Colman et al. (2001); Davis et al. (2001); Davis and Birch (2011); Gunawardena et al. (2012); Gunawardena et al. (2013); Huston et al. (2009); Liu et al. (2018a); Morselli et al. (2003); Murphy et al. (2015); Omrani et al. (2017); Ruban et al. (2010); Sabin et al. (2005); Al Ali et al., 2017 (a small, high traffic catchment, with AD contributions < 10%)
Trace organics (mostly priority pollutants)	AD contributions reported in low (only PAHs) or trace amounts (other substances than PAHs)
PAHs	Boom and Marsalek (1988); Ruban et al. (2010); Schifman (2014): Al Ali et al. (2017)
Pesticides	Ruban et al. (2010)
PFCs (perfluorinated compounds) or poly- fuorinated chemicals	Kim and Kannan (2007); Kwok et al. (2010); Murakami et al. (2009); Scott et al. (2006); Xiao et al. (2012); Zhao et al. (2013); Zushi and Masunaga (2009)
Xeno-estrogenic compounds	Peters et al. (2008)

3.2. Drainage surfaces

3.2.1. Roads and impermeable paved surfaces

Paved surfaces contribute to pollution of stormwater through two different processes: Mechanical wear of pavement surface by vehicle tires (discussed later in Section 3.3.1), and by elution of chemicals into water running off the pavement surface, discussed in this section. Coal tar-based sealants, used to enhance the structural integrity and visual appearance of asphalt driveways, sidewalks, walking trails, parking lots, roads and some playgrounds, were found to be a major source of PAHs in urban stormwater pond sediments in Minnesota, USA, accounting for 67% of the detected PAHs (Crane, 2014). Bitumen is a constituent of asphalt that contains PAHs and, therefore, a potential source of PAHs in runoff. Because of this environmental risk, the release of PAHs and selected metals from bitumen and asphalt has been studied in static and dynamic leaching tests (Brandt and De Groot, 2001; Legret et al., 2005). Both studies demonstrated that pollutant leaching was weak and most concentrations were below the existing regulatory limits for potable water, and concluded that leaching from asphalt is not an important source of metals or PAHs.

Similar to the effect of concrete pipes and other concrete structures on stormwater quality, the use of concrete pavement has the potential to provide the alkalinity needed to raise the runoff pH and alter the metal element partitioning (Sansalone and Buchberger, 1997). Concrete pavement materials were also reported to leach Cr; the source of Cr was Portland cement used in the concrete production (Kayhanian et al., 2009). The leaching of Cr was mainly influenced by the material age, permeability, temperature, and contact time. In a study comparing pollutant contributions from three pavement types, asphalt and crushed stone driveways produced the highest pollutant concentrations, while paver driveways had significantly lower pollutant concentrations (Gilbert and Clausen, 2006). Even though not explicitly stated by the authors, it is likely that the pollutants in their study were originally derived from e.g. AD, or traffic related activities, deposited on the driveways, rather than from the driveway material. Zhang et al. (2017) reported that natural stone-paved pedestrian paths produced the highest PAH surface load because of a high total solids content, with solids acting as pollutant carriers. However, the PAHs deposited in their study on the pedestrian path originated from other sources (i.e., vehicle emissions, coal and wood combustions, engine oil spills and vehicle tire debris). Furthermore, as urban impermeable surfaces are heated up by solar radiation, especially during summer months, they become an important source of thermal pollution of runoff, threatening cold water fisheries (Van Buren et al., 2000; Thompson et al., 2008; Janke et al., 2009).

In summary, notwithstanding the mechanical pavement wear by vehicle tires, discussed in Section 3.3.1, urban paved surfaces elute measurable contributions of PAHs and alkalinity. This source is closely related to, though less important than, the pavement wear by vehicle tires (Section 3.3.1). In regions with cold water fisheries, the thermal pollution of urban runoff may also be of concern to be fully considered in stormwater management planning.

3.2.2. Building materials and structure surfaces

All surfaces in contact with rainwater or stormwater surface runoff can potentially affect the quality of such waters. Various structures exposed to rainwater or stormwater exist in the urban environment: buildings, sculptures, lamp poles and crash barriers, to name a few. Their surfaces comprise a wide range of different materials, many of which have been studied extensively from the stormwater quality perspective. Similar to other impervious surfaces in the built environment, these surfaces can also act as sources of thermal pollution (Van Buren et al., 2000). Clay and concrete roofing tiles have been reported to increase runoff pH (Sulaiman et al., 2009; Lee et al., 2012), and corrosion of metal structures, commonly found on e.g. roofs and facades, is known to be a major source of Cu and Zn in runoff (Malmqvist, 1983). Gromaire et al. (2001) demonstrated that roof runoff was the main source (>80%) of Cd, Pb and Zn in wet weather flows in a combined sewer system serving a densely populated residential area in central Paris, because of the corrosion of roof cover materials. Slate roofs, window frames, ventilation holes, etc. on historical buildings were the main source of Pb, while zinc sheets used in roofs and gutters were the main source of Zn and Cd, which is a minor constituent of zinc products. The architecture in the catchment studied was considered representative of many large cities in Europe (Gromaire et al., 2001). Galvanised steel, used on various surfaces in the urban built environment such as building envelopes, crash barriers and lamp poles, is another important source of Zn. For example, Robert-Sainte et al. (2009) reported an annual average Zn concentration of 3081 μg/L in runoff from galvanised steel panels. Moreover, Boller and Steiner (2002) estimated that copper used on roofs accounted for up to 50% of the total copper load in urban drainage systems. Cu concentrations in runoff from copper panels were characterised by a median concentration of 1905 μg/L, over 20 rain events (Winters et al., 2015), and Müller et al. (2019) reported an average Cu concentration of 3090 μg/L from tests of triplicate panels for six rain events. In recent years, Corten weathering steel has been increasingly used on sculptures, architectural features and other surfaces in the urban environment, and was shown to contribute Ni to runoff (Raffo et al., 2016; Müller et al., 2019). However, metal sheets protected by surface coatings often exhibit lower releases of metals compared to raw metal sheets (Robert-Sainte et al., 2009; Müller et al., 2019). Furthermore, even though often considered as minor sources, non-metallic materials may also contribute metals to runoff. For example, pressure-treated and waterproof wood was reported to contribute Cu to runoff (Clark et al., 2008; Winters et al., 2015) and the EPDM (Ethylene propylene diene monomer) roof cover released Zn (Winters et al., 2015).

The release of various pesticides from building materials was reported in a number of studies. For instance, Burkhardt et al. (2011) showed that large amounts of pesticides (diuron, terbutryn, carbendazim, irgarol 1051) used in building envelopes entered stormwater. Similarly, Gromaire et al. (2015) reported high concentrations of benzalkonium chloride, used as a de-mossing agent, in roof runoff. Bucheli et al. (1998) concluded that bituminous roofing membranes were a major source of the pesticide Mecoprop, added as root penetration protector, and this finding was later confirmed by e.g. Vialle et al. (2013), who reported occurrence of Mecoprop in all samples of runoff collected in a suburban catchment, with measured concentrations of up to 4.8 μg/L. Paints applied to different kinds of surfaces can act as a source of Pb (Davis and Burns, 1999), pesticides (Jungnickel et al., 2008) and polychlorinated biphenyls (PCBs) (Jartun et al., 2009). Old façade plaster (mainly mid-20th century) was also found to be a potential source of PCBs (Andersson et al., 2004). Compared to the state of knowledge of metal and pesticide releases from building materials and other structure surfaces in the built environment, much less is known about releases of other organic micropollutants. Buildings were found to be a dominant source of APs in field measurements of atmospheric deposition and stormwater runoff in a suburban catchment near Paris (Bressy et al., 2011). They reported a median concentration of 0.56 μg/L nonylphenols (NPs) in building runoff and hypothesised that these NPs originated from additives in paints, pesticides, plastics and civil engineering materials. However, the specific materials (and, thus, potential sources) present in the catchment were not accounted for in their publication. Björklund (2010) performed a substance flow analysis and identified roofing and façade materials as important sources of phthalates, and concrete as an important source of NPs and nonylphenol ethoxylates (NPEOs). Pilot-scale outdoor experiments of runoff from building surface materials confirmed the release of phthalates (with average concentrations up to 455 μg/L Diisononyl phthalate, DINP), NPs (up to an average concentration of 26 μg/L) and lower levels of NPEOs from PVC roofing membranes, as well as the release of NPs (average concentration 0.99 μg/L) and lower levels of NPEOs from bitumen felt roofing (Müller et al., 2019).

In summary, a plethora of materials, both organic and inorganic, have been used in building envelopes to protect buildings and structures against adverse climatic effects and those of atmospheric deposition and stormwater. Most of these coatings, representing biocides and paints, contain potentially harmful substances, which eventually find their way into stormwater. Continuing development of new materials, surface coatings, paint formulations, etc. and their applications in the urban environment represent new potential sources of known or emerging pollutants in urban runoff. Material substitutions, policy controls and locally implemented stormwater treatment processes represent feasible control options. This source is closely related to the washing of building surfaces (Section 3.3.8), which represents a maintenance activity conducted with relatively low frequency (compared to the frequency of occurrence of wet weather).

3.2.3. Green areas (parks, lawns, urban forests and sport facilities)

Contemporary urban planning recognises the value and benefits of sustaining or expanding green areas in towns and cities (Swanwick et al., 2003). Such areas, of various forms and sizes, range from boulevards with grass and trees, to neighbourhood parkettes, district or central parks, and various sport fields, including golf courses. Among the benefits of urban green areas, one can name contributions to mitigation of urbanisation impacts with respect to the water cycle, local microclimate, air pollution, noise, urban ecology, and carbon footprint, and thereby the green areas contribute to the health and general well-being of urban population. Particularly significant are the benefits of urban forests, which were defined as the sum of all the trees within an urban area (City of Toronto, 2013), and in Toronto (Canada), such a forest encompasses 10.2 million of trees. The presence of green areas leads to inevitable interaction with traditional “grey” drainage infrastructure, including releases of dissolved organic matter (DOM) and its mixing and transport with stormwater from other sources in street gutters and storm sewers. DOM not only plays a major role in forming aquatic life systems, but also affects the fate and transport of pollutants (McElmurry et al., 2014; Zhao et al., 2015; Zhao et al., 2019; Yuan et al., 2019).

Characteristics of DOM at the catchment drainage outlet reflect both the catchment cover, determined by land use (Zhao et al., 2015), and local environmental factors. In urban areas, DOM measured by DOC (dissolved organic carbon) was in runoff at lower concentrations than in natural landscapes, and among the environmental factors, significance was attributed to solar radiation, and water temperature and conductivity (McElmurry et al., 2014), which are all modified in urban areas. Concerning the pollutant transport, Zhao et al. (2019) demonstrated that DOM in stormwater runoff from various land use areas exhibited strong binding affinities for heavy metals (Cd, Cu, Ni and Pb) and hence influenced their migration and transformation. Such processes are of great interest in stormwater treatment by vegetated surfaces, as demonstrated by Yuan et al. (2019) for grassy swales. While the environmental significance of DOM in urban stormwater has been demonstrated for a limited range of samples and environmental conditions, there is a need for continuing research expanding the published findings and defining their consequences for urban drainage planning and design.

A summary of sources of chemicals and faecal indicator bacteria in urban green areas is presented in the following paragraphs of the current section, under the catchment surfaces (covers), and in Section 3.3.6 on gardening, under activities.

Residential lawns and turf areas (e.g., sports fields, golf courses and parks) in the urban environment were shown to be 'hotspots' of nutrient input into stormwater (Center for Watershed Protection, 2003; Hobbie et al., 2017). Lawns and their soils are among the most important sources of total and dissolved phosphorus in urban runoff (Waschbusch et al., 1999; Hobbie et al., 2017), and Waschbusch et al. (1999) reported an average concentration of 0.79 mg/L P in runoff from lawns. Moreover, fallen leaves are a significant source of nutrients, especially phosphorus, in urban stormwater and accounted for >50% of the annual P output, winter season excluded (Selbig, 2016). Shaver et al. (2007) reviewed the literature data and reported that nutrient concentrations in runoff from grassy areas can be up to four times greater than those from other urban areas. Golf courses were found to be a source of pesticides in runoff (Metcalfe et al., 2016). Pervious surfaces, such as lawns, may contribute suspended solids to runoff during high intensity rain events causing soil erosion (Gromaire et al., 2001). The issues concerning soil erosion in urban areas are addressed in more detail in Section 3.3.4 on construction activities.

In recent years, the use of artificial turfs or recycled rubber mulch (e.g., in playgrounds) has become relatively common. Such a rubber mulch is an obvious source of microplastics (Magnusson et al., 2016) and a source of Zn, PAHs and phthalates released to runoff (Kanematsu et al., 2009; Bocca et al., 2009; Llompart et al., 2013). In addition, Celeiro et al. (2018) reported the presence of Cd, Pb and Cr in some rubber mulch samples and confirmed the leaching of several hazardous substances (including PAHs, phthalates, Cd, Pb and Cr) from synthetic play surfaces to runoff water.

In summary, recreational areas, parks and lawns are generally areas with high pedestrian traffic, and thus the places where littering (Sundt et al., 2014) and deposition of pet (or wildlife) faeces would commonly occur. Thus, these areas may be sources of faecal bacteria, nutrients and solids to urban runoff, assuming that they produce runoff, in spite of relatively high degree of perviousness. More information on pollution sources related to these areas can be found in Sections 3.3.5 and 3.3.7, respectively. Moreover, these areas are often closely connected to gardening activities and the associated pollution sources, such as fertiliser and pesticide applications, described in Section 3.3.6.

3.3. Anthropogenic activities

3.3.1. Vehicular transportation

Traffic related pollution has been studied extensively and the main pollution sources attributed to vehicular transportation have been identified as vehicle operation (Brinkmann, 1985), including exhausts, automotive fluid leakages (Markiewicz et al., 2017) and wear (Muschack, 1990); vehicle washing (Sörme et al., 2001; Björklund, 2010); and, road abrasion (Hvitved-Jacobson and Yousef, 1991), generating a complex mixture of pollutants. In cool temperate climate with seasonal snow, there is one more important source of pollutants: winter road maintenance involving applications of road salts and traction agents (grit materials) as discussed later in Section 3.3.2. Considering the urban stormwater pollution, the level of detail of specific transport related sources and the list of substances they contribute is much greater compared to other source categories, likely because road runoff was early identified as a major pollution source, depending on traffic intensity. In this connection, Marsalek et al. (1999) reported that among the selected sources of urban stormwater, runoff samples from two freeways (Average Daily Traffic (ADT) > 100,000 vehicles/24 h) produced the highest frequencies of moderate-to-severe toxicity detection by a battery of bioassays. In response to the reported sources of pollution in road runoff, the parameters traditionally studied include suspended solids (Westerlund and Viklander, 2006), petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), BOD and COD as well as trace metals in both solid and liquid fractions (Huber et al., 2016). Even though the specific sources contributing to pollutants released by vehicular traffic have been studied extensively, their quantitative contributions to actual concentrations in urban runoff cannot be readily discerned, because of simultaneous releases from several sources (e.g., brakes, tires and exhausts). A summary of pollutants released by vehicular traffic in urban areas is presented in Table 2; a detailed commentary follows.

Vehicle exhaust gases from internal combustion engines contain such pollutants as particulate matter (particles of soot and metals), hydrocarbons (including PAHs; Markiewicz et al., 2017), benzene series (BTEX) pollutants (Liu et al., 2018b), nitrogen oxides (NO_x), carbon monoxide (CO), sulphur dioxide (SO_2), and hazardous air pollutants (e.g., Pb; Brinkmann, 1985). Vehicle exhaust pollution is partly controlled by catalytic converters, which in turn were identified as sources of Rh, Pd and Pt (Rauch et al., 2005). The phasing out of Pb from gasoline resulted in a steady decrease in Pb concentrations in road runoff in recent decades (Kayhanian, 2012), but new additives were introduced and found their way into the environment, including oxygenates, such as Methyl tert-butyl ether (MTBE), ethanol, and alkylates (Nadim et al., 2001), and methylcyclopentadienyl manganese tricarbonyl (MMT) (Geivanidis et al., 2003). However, stormwater has yet not been confirmed as an important transport vector for these substances with the exception of MMT, which may cause increased Mn concentrations in road runoff (Huber et al., 2016). Exhausts from diesel engines were found to be a source of Ni (Duong and Lee, 2011). Other related

Table 2
Sources of pollutants released by vehicular traffic in urban areas.

Specific source	Pollutants released	References
Vehicle operation		
Exhaust gases and particles	Hydrocarbons, PAHs, NOx, Ni, BTEX	Markiewicz et al. (2017); Brinkmann (1985); Huber et al. (2016); Kayhanian (2012); Duong and Lee (2011); Liu et al. (2018b)
Catalytic converters	Rh, Pd, Pt	Rauch et al. (2005)
Vehicle wear		
Tires	TSS, Cd, Cu, Zn, PAHs, microplastics	Muschack (1990); Councell et al. (2004); McKenzie et al. (2009); Legret and Pagotto (1999); Kose et al. (2008); Horton et al. (2017a)
Tire studs	W	Huber et al. (2016)
Brakes	TSS, Cd, Cu, Ni, Pb, Sb, Zn, PAHs	McKenzie et al. (2009); Hjortenkrans et al. (2007); Markiewicz et al. (2017)
Engine and vehicle body wear	Cr, Ni	Gupta et al. (1981); Ward (1990)
Body paint	Pb	Kayhanian (2012)
Wheel balance weights	Pb, Fe (steel), Zn	Root (2000); Bleiwas (2006)
Vehicle washing		
Commercial car washing facilities	Pb, Cd, Cr, Zn	Sörme et al. (2001)
	Phthalates, NPs, NPEOs	Björklund (2010)
Road abrasion		
Abrasion by tires (non-studded and studded)	TSS	Hvitved-Jacobson and Yousef (1991); Van Duin et al. (2008) Lindgren (1996)
	PAHs	Markiewicz et al. (2017)
	Microplastics	Magnusson et al. (2016); Horton et al. (2017b); Vijayan et al. (2019a)

sources of pollutants are leakages of automotive fluids, among which the engine oil is the most important source of PAHs in the traffic environment (Markiewicz et al., 2017). Gasoline stations were reported as 'hotspots' of BTEX pollutants (Liu et al., 2018b) and, thus, represented a potential source of BTEX pollutants in stormwater.

Among the non-exhaust pollution sources, tire and brake wear were identified as the most important sources (Muschack, 1990), with respect to both the environmental relevance and the number of reported studies. The main pollutants associated with these sources were identified (Table 2) as follows:

- Tires: Zn (Councell et al., 2004), Cu (McKenzie et al., 2009), Cd (Legret and Pagotto, 1999), PAHs (Kose et al., 2008) and microplastics (Horton et al., 2017a)
- Brakes: Cu (McKenzie et al., 2009), Zn, Ni, Sb, Pb (Hjortenkrans et al., 2007), Cd (McKenzie et al., 2009) and PAHs (Markiewicz et al., 2017).

Other types of vehicle wear contributing to pollution included engine wear and welded metal plating (the vehicle body), both contributing Ni and Cr (Gupta et al., 1981; Ward, 1990). Paints (Kayhanian, 2012) and wheel balancing weights (Root, 2000; Bleiwas, 2006) were suggested as important sources of Pb in the traffic environment. Concerning the latter source, the use of Pb has been banned in some jurisdictions (e.g., EU) and other materials, Fe (steel) and Zn, were substituted. Tire studs used in some northern regions are made of W and are recognised as a source of this heavy metal in road runoff (Huber et al., 2016). However, W is rarely reported in stormwater studies and does not generate specific environmental concerns, considering its absence from lists of priority substances, e.g. the EU Directive (2013/39/EU) on priority pollutants (2013) and the U.S. EPA Priority Pollutant List (US EPA, 1983). Finally, it is worth mentioning that a range of material types and compositions are used in the vehicle industry (Thorpe and Harrison, 2008), e.g., for different vehicle types or in different regions, which creates large variations in the potentially released pollution. For instance, Hjortenkrans et al. (2007) stated that their results from 2005 showed that tires could be excluded as a significant source of Cr, Cu, Ni and Pb emissions in Stockholm.

Vehicle washing releases various chemicals and materials attached to the vehicles (Sörme et al., 2001), or contained in car-care products. Rain falling on stationary or moving cars could potentially have similar washing effects. Sörme et al. (2001) studied sources of heavy metals in urban wastewater in Stockholm (in both combined and separate sewer systems) by substance flow analysis and found that commercial car washes were an important contributor of Pb, Cd, Cr and Zn. Paint attrition during car washing may produce Pb (Kayhanian, 2012) and vehicle under-spray may activate other earlier mentioned sources of pollutants (e.g., leaked engine oil deposits). Using a substance flow analysis, Björklund (2010) reported that vehicle washing and wear were important sources of phthalates, NPs and NPEOs in urban stormwater. NPEOs are commonly used in commercial car wash detergents and degradation to NPs is a plausible contribution to NP concentrations found in stormwater (Rule et al., 2006). Where commercial car washes drain to storm sewers, they are obviously also a similar source, with the difference that the commercial wash water usually passes through an oil separator.

Road abrasion is an important source of particles (TSS) (Hvitved-Jacobson and Yousef, 1991), PAHs (Markiewicz et al., 2017), and microplastics (Magnusson et al., 2016), and the abrasion process is exacerbated by the use of studded tires (Lindgren, 1996) and applications of grit in winter road maintenance. Grit particles are ground by vehicle tires against the pavement and produce fine particles, which may either be washed off, or be incorporated into pavement pores (Van Duin et al., 2008). Microplastics may originate from both the bitumen used in road pavement construction and from road marking paints (Magnusson et al., 2016; Horton et al., 2017b).

When assessing traffic related pollution at specific sites, it has to be recognised that emissions of pollutants from their sources in the traffic environment greatly depend on such factors as traffic intensity (ADT) and composition (i.e., passenger cars vs. trucks), driving patterns, such as speed and brake use, and the pavement type. For instance, the rate of brake wear is largely dependent on the composition of the brake lining and the mode of driving, in which the brakes are engaged (Thorpe and Harrison, 2008). As synthesised by Loganathan et al. (2013), several studies showed that sediments deposited on road sections with high braking, accelerating and decelerating activities generally contained higher metal concentrations compared to other locations along the road. A literature review by Huber et al. (2016) concluded that roads with high annual ADT belong to the road category with the highest runoff concentrations of metals, because of braking and acceleration activities at traffic signals. The same literature review reported that concentrations in parking lot runoff varied widely depending on the main use of the parking lot (i.e., the frequency of entries and exits, presence of heavy vehicles, etc.). Revitt et al. (2014) reported that a coarser surface in car park areas and the pavement abrasion from increased frequency of stopping and starting of vehicles would result in larger sized particles released from the pavement. Increase of speed and traffic density was shown to increase pollutant concentrations in road dust mainly because of higher exhaust emissions and increased road abrasion (Duong and Lee, 2011), and the vehicle speed was found to be more important than traffic density (De Silva et al., 2016). Increased PAH concentrations in runoff were also explained by higher vehicular traffic (Burant et al., 2018). Duong and Lee (2011) reported that metal concentrations in road dust were higher for concrete highway pavements than for asphalt-concrete mixtures, mainly because of higher abrasion in the former case.

In summary, the current state of knowledge clearly shows that the sources related to vehicular transportation are major sources of many of the pollutants usually found in urban stormwater. Depending on traffic intensity (ADT), heavy metals may occur at toxic levels. The major contributors of such a pollution are vehicle exhausts, wear, washing and road abrasion. Thus, vehicle operation is one of the traffic pollution sources depending on the activity volume; hence, this source can be partly controlled by limiting the use of conventional vehicles and distances driven. Substantial reductions in exhaust gases pollution will result from a greater uptake of alternative fuel vehicles and the use of substitute materials reducing or eliminating some traditional sources of pollution. Other activities shown in Fig. 1 may also contribute to increased vehicular transportation intensity – e.g., catchment development in the form of urban sprawl, and industrial (Section 3.3.3) and construction (Section 3.3.4) activities. Finally, road maintenance, particularly in winter months, also contributes to runoff pollution, as discussed in Section 3.3.2.

3.3.2. Road maintenance

In climates with seasonal snow, snow clearance and de-icing practices are used to maintain roads passable and safe. In jurisdictions where the "bare pavement" policy was adopted for winter road maintenance (i.e. keeping roads and highways essentially clear of snow and ice during winter season), large amounts of road salts are applied to meet these policy requirements. In the U.S., it was estimated that 18 million tonnes of road salt were used annually (Corsi et al., 2010); the usage in Canada was 5 million tonnes annually (Government of Canada, 2018), and in Sweden, on average 240,000 t/y were used on state roads between the years 2000–2013 (Swedish EPA, 2013).

Common road salts contain chloride (typically about 60% by weight, in NaCl), anti-clumping agents, ferrocyanide, chromate or phosphate (Ramakrishna and Viraraghavan, 2005), and impurities reaching up to 5% of the total salt weight. Significant environmental effects have been associated with high concentrations of chloride discharged into receiving waters during the periods of snowmelt, as reviewed by Marsalek (2003) and Vignisdottir et al. (2019). Chemical effects of road salts are of two-fold nature, firstly as direct sources of pollutants (e.g., chloride), and secondly as agents increasing the dissolved phase (and effects on biota) of metals (Reinosdotter and Viklander, 2007). Ferrocyanide may form toxic free cyanide, which is removed by volatilization and, therefore, does not represent a significant environmental concern (Ramakrishna and Viraraghavan, 2005; Exall et al., 2011). Salt impurities contain mostly phosphorus, sulphur, nitrogen, copper and zinc. Other salts used in road de-icing include calcium, potassium and magnesium chlorides; those are generally more expensive than NaCl, but can be used effectively at lower temperatures. Urea, which is used mainly in aircraft and airport de-icing operations, and exceptionally was used in highway de-icing (Ramakrishna and Viraraghavan, 2005), is a potent source of nitrogen to runoff.

Common snow management practices also include application of traction agents (sand and grit) on pavements, streets, roads, highways and parking lots, and such materials may accumulate during the winter periods (Westerlund and Viklander, 2006) and remain in road gutters or roadside areas or gully pots, or become resuspended during snowmelt periods. The application of sand and grit is the main source of the high concentrations of TSS or coarser sediments often found in snowmelt-induced runoff (Westerlund et al., 2003; Galfi et al., 2016). Such solids serve as a carrier of pollutants, e.g. metals and PAHs (Stone and Marsalek, 1996; Helmreich et al., 2010; Loganathan et al., 2013; Zhang et al., 2015; Borris et al., 2016; Vijayan et al., 2019b). While small particles often hold the highest concentrations of metals, the highest metal loads were generally found in the largest particle size fraction (Loganathan et al., 2013), and large particles may act as collectors of smaller particles that can be released during runoff events (Borris et al., 2016). Helmreich et al. (2010) attributed heavy metal concentration increases during the snowmelt season to the increased tear and wear of vehicles and pavements due to applications of grit. The mineral composition (affecting e.g., material hardness) as well as particle size distribution of the abrasive materials applied was reported to affect the formation of road dust, and materials with high resistivity to fragmentation were preferred (Räisänen et al., 2003). Similarly, the mineral composition (i.e. natural metal content) of sand, grit and gravel materials may affect their release of metals. For instance, in some cases, sand used for anti-skid purposes was shown to contain high concentrations of phosphorus and several metals (Oberts, 1986). Furthermore, snow clearance from roads, parking lots and paved surfaces can increase abrasion of such surfaces and, thus, the occurrence of asphalt wear particles in runoff (Vijayan et al., 2019a).

Washing of road structures, e.g., traffic tunnels (Meland et al., 2010), or washoff of safety barriers or traffic signs by rain (Mayer et al., 2011), may also contribute to road runoff pollution. Depending on whether the wash water is collected and treated, it may be a source of pollution of stormwater. The washing process leads to removal of exhaust particles attached to tunnel walls and their entrainment by water. Meland et al. (2010) studied wash water from a traffic tunnel; such water was presettled in a small settler prior to discharge to a small stream. The settler effluent contained high concentrations of metals and PAHs, mostly associated with solids, and the estimated loadings from one wash event were 13 g Cu, 2.4 g Pb, 245 g Zn and 0.8 g of 16 PAHs. Wash waters may also contain detergents used in the washing process (Meland et al., 2010), which can increase their pH (Hallberg et al., 2014). The pollutants emitted in road tunnels showed tendencies to accumulate outside the tunnel and, thus, increase pollutant concentrations in runoff from road sections receiving wash water from road tunnels (Barbosa et al., 2007).

In summary, road maintenance in cool temperate climate involves applications of large quantities of road salt and grit during winter months, to ensure road safety. Both materials can be harmful in the receiving waters, by interfering with water quality processes, and in the case of salts, by causing toxicity. Future use of road salts may decline for several reasons: increasing awareness of environmental impacts of chloride, increasing occurrence of mild winters attributed to climate change, and advances in road salt management, including "smart" road salting and the development and increased usage of substitute de-icers (Stone and Marsalek, 2011). Such advances are somewhat offset by the lack of control over salt use on private or privately operated properties (e.g., parking lots) and the population growth increasing demands on road snow management (Chapra et al., 2009). Another maintenance activity contributing to runoff pollution by trace metals and PAHs (typical for road runoff) is the washing of traffic tunnels.

3.3.3. Industrial activities

Industrial activities are recognised as sources of pollutants (Duke and Chung, 1995), which may enter stormwater in two ways (Ellis, 1986): Via pollutant emissions into the atmosphere and subsequent wet and dry atmospheric deposition described earlier in Section 3.1, or by a direct surface runoff from industrial land. The contributions of pollution from industries to stormwater evidently depend on the types of industrial activities, and will change as such activities change with market demands and introduction of new technologies for both industrial production and pollution control. Some generic features of industrial sites may be common for most sites and include: vehicle operation, washing and storage (discussed earlier in Section 3.3.1); storage and handling of products and materials used in the industrial production; waste management, including pre-treatment of wastewaters; operation of equipment outdoors (Duke and Chung, 1995); and, operation of the on-site stormwater management system with quality control measures. Vehicular transportation activities at industrial sites cover a broad range of vehicles from passenger cars to heavy industrial trucks and equipment, with associate consequences for pollution emissions. Examples of industrial sources of pollutants entering stormwater follow, starting with conventional pollutants and followed by micropollutants.

Pitt et al. (1995) investigated sources of stormwater pollutants and concluded that in industrial and commercial areas the likely conventional pollutant hotspots were vehicle service areas, and parking and storage facilities. The industrial sites included in the U.S. NSQD produced some of the highest concentrations of Zn (median 199 μg/L), among the various land use categories (Pitt et al., 2004). Brown and Peake (2006) measured runoff quality from a catchment with combined residential, commercial and light industrial land use in Australia, and attributed the elevated levels of Pb and Cu to the industrial activities in the area. This finding was confirmed by the results of Tiefenthaler et al. (2008) and Liu et al. (2018a), who found that industrial and commercial areas produced higher metal concentrations in stormwater runoff, compared to other land uses, e.g., residential areas, especially with respect to Zn, Cu and Pb.

Gasperi et al. (2014) measured micropollutant concentrations in three French urban catchments of different land use, with the industrial catchment producing particularly interesting results. The catchment produced runoff with the highest concentrations of Cr and Ni (mean concentrations of 6 μg/L Cr and 7 μg/L Ni, respectively), most likely because of related industrial activities, but somewhat unexpectedly, the catchment generated the lowest PAH concentrations in runoff, possibly because of a low traffic density within the catchment. Further studies were conducted in this catchment, because it was considered representative of industrial catchments found in developed countries (Wiest et al., 2018). Contrarily to the Gasperi et al. (2014) results, a subsequent stormwater quality study in this catchment found that it had the highest concentration of PAHs, e.g., anthracene, with the event mean concentration (EMC) as high as 993 ng/L (Becouze-Lareure et al., 2019). Sediment samples from a detention basin in the catchment revealed the presence of NPs and NPEOs, which was consistent with the ubiquitous use of such chemicals in several industrial operations within the catchment. BPA was also present in the sediment samples, and was likely derived from the construction materials and automotive coatings, or from a paper recycling industrial facility also present in the catchment (Wiest et al., 2018). Moreover, Rule et al. (2006) found higher concentrations of

NPEOs in industrial developments (average concentration of 170 μg/L from one rain event) compared to housing developments (generally <20 μg/L), possibly because of the presence of such chemicals in commercial cleaning products, such as car wash detergents. Similarly, Xiao et al. (2012) found industrial activities to be an important source of perfluorooctane sulfonate (PFOS) released from local industrial sources, and Liu et al. (2018b) reported that industrial land use produced higher BTEX pollutant loads in stormwater.

Industrial activities such as production of microplastic pellets used in personal care products, plastic media used in abrasive blasting, plastic pellet production and various manufacturing processes, e.g. rubber, chemicals, paints and varnishes manufacturing represent potential sources of microplastics in stormwater from industrial sites (Cole et al., 2011; Sundt et al., 2014; Magnusson et al., 2016; Horton et al., 2017a). However, stormwater was not confirmed as the main transport vector of the microplastics from industrial activities, even though the stormwater detention ponds serving industrial and commercial areas produced the highest concentrations of microplastics (Liu et al., 2019).

In summary, industrial activities contribute both conventional pollutants and micropollutants to stormwater runoff. While the former group is connected with sources common to most industrial activities, the latter group of greater importance reflects the substances used in specific industrial operations. Industrial activities also contribute to increased traffic, which was discussed in Section 3.3.1.

3.3.4. Construction activities

Construction sites and related activities are known to contribute great amounts of sediments and soil particles to surface runoff and ultimately to the receiving waters. During catchment development, soil erosion is intensified in urbanising areas for two reasons: the stripping of natural protective vegetation cover of soils during construction, and increased runoff flows contributing to sheet erosion and scouring and transport of sediment in unlined channels (Marsalek et al., 2008). The issue of stormwater entrainment and transport of suspended solids and coarser sediments was first time identified in the literature more than fifty years ago (Wolman and Schick, 1967; Leopold, 1968). Wolman and Schick (1967) observed in Maryland (USA) that annual sediment yields from natural catchments could be as low as 100 t/km^2/y, but increased >100 times during urbanisation and catchment development. Marsalek (1992) pointed out that these high rates of sediment export represented a transitional state, because after completion of the urban development and establishment of the soil surface cover, those high yields would drop down to the predevelopment level, or even lower. In spite of advances in soil erosion protection during construction activities, in recent literature, TSS or turbidity still are among the most commonly documented parameters in runoff from construction sites (Wang et al., 2013; Murphy et al., 2014; Sillanpää and Koivusalo, 2015; Shen et al., 2018; Sajjad et al., 2019). Shaheen (1975) reported that a roadway across the street from a construction site received 14 times the expected amounts of deposited sediment based on contribution of traffic alone. TSS concentrations of 200–1200 mg/L were reported in stormwater runoff from construction sites (Center for Watershed Protection, 2003). Moreover, Sajjad et al. (2019) measured higher mean concentrations of TSS during the active construction phase, including excavation works (annual average EMCs of 1175 and 748 mg/L TSS, respectively, for two years of active construction), compared to post-construction phase, when the annual average EMCs for the following two years were around 600 mg/L TSS. Besides the physical impacts of stormwater sediment loads (e.g., silt blanketing of spawning beds in streams (Shaver et al., 2007)), stormwater sediment also carries adsorbed pollutants, e.g., metals and PAHs (Stone and Marsalek, 1996; Loganathan et al., 2013; Zhang et al., 2015; Borris et al., 2016), and thereby contributes to the pollution in the receiving waters. Ellis and Mitchell (2006) identified the construction industry to be a significant source of sediments, a documented source of nitrogen, and a possible source of metals, based on a survey of data in the UK literature. However, it was not stated what specific sources or activities within the catchments with ongoing construction activities were producing the sediments, nitrogen and metals.

Construction activities were shown to have profound impacts on water quality in a Finnish developing catchment (Sillanpää and Koivusalo, 2015), and earth moving works, paving, house construction and temporary wastewater discharges were among the most important factors explaining the variations in water quality. Construction work is often associated with the use of heavy vehicles and equipment, and materials that can potentially contribute various pollutants to the surroundings. Therefore, increased levels of pollution associated with vehicular transportation (Section 3.3.1), littering and oil spills (Section 3.3.5), and building materials (Section 3.2.2) may apply to construction sites as well. US EPA (2005) identified the fertiliser use (an important source of N and P), spills or littering, solid and sanitary wastes and debris, application of pesticides and other construction chemicals, and washout from concrete trucks as other important sources of pollution in construction areas. In demolition of old buildings, façade plaster was suggested to be a potential source of PCBs (Andersson et al., 2004). Construction and demolition work may also disperse microplastics to the surroundings, through the use of plastic building materials such as Polyvinyl chloride (PVC) and Polyethylene (PE), or through construction or maintenance work (e.g. sawing and drilling) using plastic materials (Magnusson et al., 2016). Expanded polystyrene (EPS) foam, used for insulation of e.g., pipes, roofs and walls, and house basements, was reported to break easily into smaller fragments during manipulation, and those can be transported by wind because of their low density (Magnusson et al., 2016). Such material properties may also increase the likelihood of transportation by stormwater.

In summary, construction activities represent a major source of stormwater solids generated by soil erosion and impacting on the receiving waters; a frequently reported source of nutrients (P and N), trace metals and PAHs attached to solids; and, episodically documented source of pesticides, construction chemicals, PCBs, and microplastics. In production of stormwater solids, construction activities are clearly the strongest source listed in Fig. 1, but little is known about the magnitude of contribution of other pollutants, including nutrients and trace metals.

3.3.5. Littering, illicit dumping and household waste disposal

Intentional and unintentional littering results in litter deposition both on catchment surfaces, where litter can be dislodged and transported with runoff, or directly into stormwater inlets and gully pots. Shaheen (1975) reported variations in seasonal roadway depositions of litter, unrelated to traffic, varying from 14.3 kg/km/day in winter to 24.8 kg/km/day in summer; such litter was defined as particles or objects >3.4 mm. However, Shaheen stated that "*it has already been determined that such litter is of minimal importance as a water pollutant*". Contrarily, recent findings point to the importance of fragmentation and degradation of e.g., plastic litter (bottles, bags used for collecting pet droppings, and others) as a source of microplastics to the marine environment (Lambert and Wagner, 2016; Magnusson et al., 2016). Plastic litter may also contain and carry adsorbed trace metals and organic pollutants that may be released to the surrounding environment and runoff (Nakashima et al., 2012; Hahladakis et al., 2018). As reasoned by e.g. Horton et al. (2017a) and Hahladakis et al. (2018), common plastic additives that were found to be released from plastic litter include many trace organic pollutants, such as phthalates, BPA and polybrominated diphenyl ethers (PBDEs), and metals, that are often used as or in colourings. Moreover, littering by disposing cigarette butts in the urban environment was considered a relevant threat to urban water quality, considering their rapid release of nicotine (Roder Green et al., 2014), as well as nano-scale particles and several metals (Chevalier et al., 2018). Littering may also attract rodents and other animals, which may contribute nutrients and faecal microorganisms to stormwater runoff, as further described in Section 3.3.7.

Illicit or accidental disposals and spills of wastes or chemicals from e.g. households, industries and other sources, may deteriorate stormwater quality, and can evidently be a source of various substances. Accidental spills occur on catchment surfaces draining into storm sewers, intentional disposal usually targets the sewer inlets (e.g., disposal of used engine oil, old paint) and can occur both in wet and dry weather. Accidental spills are likely to occur at industrial, commercial or vehicular transportation sites and are a significant source of illicit discharges to the stormwater sewers (Brown et al., 2004). A common example of dumping of liquids into the storm sewers is the cleaning of deep fryers in the parking lots of fast food operations (Brown et al., 2004). Furthermore, household cleaners and motor fluids or lubricants are also occasionally spilled or discarded into storm sewers (Butler et al., 2018). Dumping or spills of motor vehicle fluids may contribute hydrocarbons, phthalates, BPA, oil and grease, metals as well as other pollutants to storm sewers (Brown et al., 2004; Markiewicz et al., 2017). Moreover, personal communication with staff of Swedish municipalities revealed that illegal dumping of drilling residues from installations of downhole heat exchangers into storm sewers has occurred and thus contributed to increased TSS concentrations in stormwater. Other activities reported to produce improper discharges to storm sewers include draining of swimming pools involving discharges of chlorinated water into the sewers, and car washing in driveways, contributing sediments, nutrients and other pollutants to the storm sewers (Brown et al., 2004). Car washing was described with more detail in another section (3.3.1). A literature search revealed the lack of data on, and reporting of, such incidents, with practically no data on the measured effects on stormwater quality. Butler et al. (2018) estimated that domestic sources of chemical pollutants are usually minor compared to industrial spills or illicit toxic waste disposal.

In summary, the probabilistic nature of littering and illicit dumping and household waste disposal contribute to the unpredictability of these sources and their contributions to the pollution of stormwater. Recent identification of microplastics as pollutants of the marine environment exacerbates the concerns about the sources in this group, which are known to contribute plastics to urban runoff.

3.3.6. Gardening

Relatively few studies have been published on the topic of gardening activities as sources of stormwater pollution, perhaps because very little to no runoff is expected to occur from garden plots. In heavy thunderstorms, or when the ground is already saturated, runoff from pervious surfaces may occur and, thus, contribute suspended solids (Gromaire et al., 2001), or nutrients originating from e.g., fertilisers applied to grassed turfs (Malmqvist, 1983) to stormwater. In a recent study of nutrient budgets of urban catchments of various land use in the U.S., lawn fertilisers were among the dominating inputs of N and P (Hobbie et al., 2017). Gardening activities may also generate garden wastes, such as grass clippings or leaves, which, if deposited on nearby impervious surfaces, are a source of biodegradable organics, N and P to runoff (Dorney, 1986; Selbig, 2016). Pesticides used in gardening to control insects, weeds, and fungi can also potentially influence stormwater runoff quality (Bollmann et al., 2014). Wittmer et al. (2010) found elevated concentrations of the pesticide Mecoprop during the period May – September (up to 32 μg/L) compared to the rest of the year (below 0.1 μg/L), and attributed applications of this pesticide on lawns and in gardens as a likely source. Botta et al. (2012) reported frequent detections of 18 pesticides applied in the urban study area during the period of most frequent applications (May–July). Gardening activities are often closely connected to those concerning parks and recreational areas, which were described earlier in Section 3.2.3.

In summary, relatively little is known about gardening as a source of pollutants to urban runoff. This is probably caused by the fact that garden properties are highly pervious and may contribute little runoff. One can assume that gardening contributes solids originating from soil erosion of cultivated soils, and nutrients from over-fertilised gardens or lawns. In general, this source is closely connected with parks, lawns and recreational areas discussed in Section 3.2.3.

3.3.7. Pets and wildlife

Droppings from pets and birds are confirmed sources of nutrients and faecal microorganisms in urban stormwater. Concerning the former source, Hobbie et al. (2017) estimated household pet waste (particularly dog waste) as one of the top inputs of N and P to urban watersheds in St. Paul (Minnesota). In the case of N, pet waste was typically the third largest source (after residential fertilisers and atmospheric deposition), and with respect to P inputs, pet waste was the greatest source. Malmqvist (1983) estimated that a dog could contribute 700 g N and 90 g P per year to runoff, and a corresponding estimate for one bird in a catchment was 40–400 g N and 3–25 g P per year. These estimates were based on several assumptions, including the number of animals in the catchment and the probability of the droppings deposited on impermeable surfaces. Considering the large populations of pet dogs and cats worldwide (e.g., 90 and 94 million in the U.S. in 2017, respectively; https//en.wikipedia.org/wiki/Dogs_in_the_United_States, accessed Aug. 1, 2019), pet waste potentially represents a huge source of P, N, and faecal microorganisms. It is generally assumed that N comes from animal urine and P from faeces. This implies that the pet contribution of P could be controlled by pet owners picking up the droppings, while pet contribution of N is more difficult to control. Little has been published on dog owner practices of waste pickup; Hobbie et al. (2017) estimated that 40% of dog waste was left in the landscape.

Moreover, animal droppings are a source of faecal bacteria that can infect humans. Contamination of the urban environment by dog faeces is particularly of concern, because such faeces may harbour pathogenic bacteria (e.g., *Campylobacter, Salmonella* and *E. coli*) and parasites (e.g., *Giardia* and *Cryptosporidium*) threatening human health, and antibiotic resistant bacteria (e.g., *vancomycin-resistant enterococci* and *methicillin-resistant Staphylococcus aureus*) (Cinquepalmi et al., 2013). Faecal indicator bacteria (FIB), mostly *E. coli* and *enterococci*, are commonly used to assess the risk of microbiological contamination of urban stormwater and receiving waters (Galfi et al., 2016). Paule-Mercado et al. (2016) found that among agricultural, mixed land use and urban catchments, urban stormwater had the highest concentrations of faecal contaminants and domestic animal wastes were one of the sources. However, sanitary sewer contributions through e.g. misconnections (Section 3.4.2) or sewer overflows were probably the main source. O'Keefe et al. (2005) reported that droppings from dogs and birds were among the main sources of the FIBs found in their study catchment in Edinburgh. These FIBs sources were likely associated with a pigeon roost below a railway bridge and a guard dog kennel. Equestrian facilities in recreational areas were also shown to be a source of FIBs to stormwater (Tiefenthaler et al., 2011). Furthermore, microbial source tracking methods using molecular markers associated with specific sources make it possible to identify specific sources of bacteria. This was demonstrated by Steele et al. (2018), who detected animal faeces in stormwater, primarily associated with an avian marker (birds), but also associated with a canine marker. Microbial source tracking on urban beaches in Hamilton (Edge and Hill, 2007) and Toronto (Edge et al., 2007; Edge et al., 2010) indicated that in shallow water, the dominant FIB sources were bird droppings (stored in wet beach sand), rather than dog faeces or municipal wastewater in combined sewer overflows. Baral et al. (2018) found that stormwater runoff provided the main input of microorganisms to an urban creek during wet-weather, and that 75% of the microorganisms in stormwater was from materials washed off impermeable surfaces in the watershed. Pigeon faeces were predicted to account for a median of 14 to 21% of the microorganisms found in street sweepings, which were assumed to correspond to the materials washed off impermeable surfaces (Baral et al., 2018). Moreover, pharmaceuticals and personal care products (PPCPs) were detected in stormwater canals in New Orleans, USA, (Boyd et al., 2004) and even though the main source was wastewater contamination of stormwater, a potential source would also be veterinary pharmaceuticals found in pet waste.

In summary, pet waste represents an important source of N, P and FIBs in urban stormwater. Dog droppings are of particular concern, because of a potentially large mass of dog waste in urban areas, the presence of pathogenic bacteria and parasites threatening humans, occurrence of antibiotic resistant bacteria in such a waste, and an uncertain effectiveness of waste pick up by pet owners. Bird droppings are of concern in areas with large bird populations and opportunities for bacteria survival, such as interstitial water on urban beaches. This source is likely to be connected with those concerning urban green areas, which are likely to be frequented by pets and wildlife (Section 3.2.3).

3.3.8. Washing of buildings and structure surfaces

Building roofs and facades, and other structure surfaces, found in the urban environment collect deposited pollutants, may suffer from moss or algae fouling, and be subject to applications of protective or biocidal chemicals and materials. Occasionally, such surfaces need to be washed, by little trained individuals or specialised companies, to maintain or enhance their visual appearances. A similar activity of potential stormwater quality concern is the removal of graffiti from buildings. Sundt et al. (2014) reported washing of plastic-treated surfaces (coated or painted) as a source of microplastics and estimated the loss of particles due to surface maintenance as 5% of the surface layer. However, this estimate was based on scarce data, because relatively few studies were published on the building surface maintenance (Sundt et al., 2014). Furthermore, pressure washing can be applied to remove flaking paints from e.g. metal roofs. Depending on actions taken to collect and treat the wash water, the maintenance of building and structure envelopes by washing is a potential source of pollution of surface runoff and urban stormwater.

The wash waters contain constituents from atmospheric deposition, particles and dissolved constituents from the actual surface material, and any chemicals previously applied to the surface, e.g., biocides, or detergents used in cleaning. The contribution of pollution from building surface materials and structure surfaces is described in detail in Section 3.2.2. No reports on implications of these cleaning practices for stormwater quality were found in the scientific literature, but one report was found in Swedish media, the first washing in 27 years of the façade of the Stockholm Globe Arena (Lund, 2016). The 22,000 m^2 façade was pressure washed using hot water and concerns about the stormwater quality were addressed by treating the wash water, containing algae as well as metals and other pollutants originating from car and airplane emissions, by using filters inserted in road gullies. The washing of road tunnels as a source of stormwater pollution was described under the Road maintenance Section 3.3.2, because the associated pollutants are mainly derived from vehicular transportation and related activities.

In summary, there is little information available on generation of pollutants during the washing of buildings. The processes involved in this type of maintenance are similar to those described in Section 3.2.2 for Building surfaces and structures, with three distinctions: (i) the washing is likely to be more mechanically intensive (using e.g., pressure washers or other tools), (ii) wash detergents or chemicals may be used, but (iii) wash waters may be captured, contained and treated before disposal.

3.4. Urban drainage systems

The contemporary drainage systems represent complex systems of man-made and natural elements serving to convey stormwater runoff, improve its quality in green infrastructure (GI) and stormwater control measures (SCM), serve for beneficial uses of stormwater, and protect the receiving waters. In such systems, there are many opportunities for stormwater to elute or entrain, or reject various pollutants, as discussed in this section focusing on the underlying processes. The sources discussed are classified as Green infrastructure and stormwater control measures (SCMs), Sewer pipe materials, and Misconnections. GI and SCMs are considered as a part of the urban drainage systems, as they are specifically designed to collect and convey urban runoff, and often their effluents are connected to the storm sewers.

3.4.1. Green infrastructure and stormwater control measures (SCMs)

In general, GI and SCMs are designed to reduce runoff volumes and peak flows, and improve stormwater quality, and it is, therefore, somewhat counter-intuitive to discuss them in the context of sources of stormwater pollution. However, for such reasons as conflicting demands on these measures (e.g., stormwater treatment vs. aesthetical and recreational amenity features), outdated design, lack of maintenance, or lack of communications in the planning stage, the control measures may lead to deterioration of some aspects of stormwater quality within such systems. Examples of such cases, where GI and SCM facilities contributed to the pollution of stormwater, are relatively common, and some are listed below.

Permeable pavements were reported to increase significantly TSS concentrations in runoff due to the washout of sediments from the subgrade (Winston et al., 2016). Furthermore, such sediments may carry particle-bound metals, and possibly other substances as well. Concrete porous pavements and pervious concrete were shown to increase runoff pH and alkalinity (Kuang and Sansalone, 2011; Pilon et al., 2019), and sulphate concentrations (Pilon et al., 2019), though not necessarily to harmful levels. Green infrastructure, employing vegetated pervious surfaces, may leach out environmentally harmful chemicals into stormwater. Kondo et al. (2016) studied elemental concentrations in GI soils in Philadelphia (USA) and observed that even though the three elements of concern to human health, Cd, Hg, and Pb, were either no different or lower in GI soils, compared to non-GI soils, those concentrations were up to four times higher than soil clean-up objectives for residential use.

Green roofs may act as a source of nutrients, depending on enrichment of nutrients in the soils used and fertilising routines (Czemiel Berndtsson, 2010). If pesticides are applied to green infrastructure, to control insects, weeds, or fungi, they may also be present in the effluent water from such systems. At an experimental green roof site in Italy, Gnecco et al. (2013) found that green roofs could act as a source of solids, COD and some metals, and that the leaching of substances was greatly dependent on substrate characteristics. The characteristics of facility construction materials are of high importance also in other SCMs. For instance, Flanagan et al. (2019) showed that various pollutants, including phthalates, APs and BPA, were released from construction materials used in stormwater biofilters, such as a drain filter fabric, drain made of plastic, geomembrane, and asphalt. Similar conclusions were drawn by Gromaire et al. (2014) regarding the release of APs and BPA from materials used in green roof structures. In all SCM facilities with free water surface or conveyance materials exposed to solar radiation, the temperature of stormwater rises (Van Buren et al., 2000), and this temperature increase contributes to the thermal pollution of receiving waters, causing potential harm to cold water fisheries and other biota.

Primarily, SCMs or GI facilities may be acting as “secondary sources” of pollution, i.e. pollutants originally derived from other sources are released to effluent waters due to such processes as resuspension or leaching. Infiltration based systems bring up concerns about deterioration of soil quality (Kondo et al., 2016; Tedoldi et al., 2017) due to accumulation of road sediments and contamination from bypassing runoff, and such systems may therefore leach pollutants to the effluent water (Flanagan et al., 2019). The presence of road salts in the runoff water may mobilise metals and increase TSS levels in effluent waters (Winston et al., 2016; Søberg et al., 2017; Flanagan et al., 2019). In stormwater ponds, or other treatment facilities designed to trap stormwater sediments, there is a risk of sediment resuspension or releases of mobile elements (e.g. metals) in the case of high flows or changes in the ambient chemistry (Marsalek and Marsalek, 1997;

Marsalek et al., 2006; Wiest et al., 2018). Such changes can be induced by e.g., influx of chloride-laden snowmelt (Vijayan et al., 2019b). Chemical characteristics of sediments from six types of SCMs (ponds, constructed wetlands, an infiltration basin, biofilter, stormwater treatment clarifier, and oil grit separators) were assessed by Marsalek et al. (2006) against the Ontario Sediment Quality Guidelines and 80–100% of collected samples were found marginally to intermediately polluted by heavy metals. Severely polluted sediments were found for Cr, Cu, Mn, and Zn at several facilities, and sediment toxicity was confirmed at several sites (Marsalek et al., 2006).

In summary, in modern drainage systems, with SCM or GI facilities, attention needs to be paid to pollutant pathways and their ultimate fate. In most stormwater control facilities, pollutant "removal" is achieved by immobilisation and storage, with associated risks of subsequent releases. Hence, the facilities need to be designed with sufficient storage (e.g., of polluted sediment), be well and timely maintained and the removed pollutants need to be properly disposed at special sites.

3.4.2. Misconnections

The term misconnections used here includes both intentional and unintentional cross-connections of wastewater and stormwater sewers, and includes entry of household as well as industrial or commercial wastewaters (i.e. wash water, process water or other inappropriate flow) into storm sewers. Another closely related term found in the U.S. literature is "illicit discharges" defined as any direct or indirect non-stormwater discharges to the stormwater conveyance systems. Cross-connections with municipal sewage can occur where combined sewer systems were converted to separate sewers, while old industrial or commercial areas are more likely to have cross-connections with industrial or commercial wastewaters (Brown et al., 2004) and thus contribute with different types of constituents to stormwater. Illicit household discharges to storm sewer systems were described by Revitt and Ellis (2016) as a *"ubiquitous problem for urban receiving water quality"*. They reported that the biodegradable organic and nutrient loads from misconnections were likely to require dilution of up to 100:1 to conform to ecological criteria and that, in the UK, toilets, kitchen sinks and washing machines pose the main problems (Revitt and Ellis, 2016).

The best indicators of stormwater contamination by wastewater include chemical (e.g. caffeine) or microbiological human waste markers (Panasiuk et al., 2015). However, as reported by Irvine et al. (2011) because of wide ranges of concentration of many substances found in stormwater, it is difficult to find effective indicators for source identification. The detection of PPCPs in stormwater was interpreted as an indication of stormwater contamination by wastewater (Boyd et al., 2004). Misconnections are among the main sources of faecal coliforms found in stormwater sewers (Makepeace et al., 1995). Human source markers and pathogens were found present in stormwater regardless of the storm severity or sampling location, and were therefore assumed to come from a chronic pollution, such as sanitary sewer misconnections (Paule-Mercado et al., 2016; Steele et al., 2018). Considering the high occurrence of misconnected washing machines, misconnections may also be an important source pathway for microplastic fibres from synthetic clothes (Magnusson et al., 2016; Horton et al., 2017b) and household detergents, containing e.g. PO_4-P (Revitt and Ellis, 2016). The occurrence rate of such misconnections reported in the literature and summarised by Ellis and Butler (2015) showed great variation, but a valid average misconnection rate was 3–4% for UK, European and U.S. data, although specific areas with up to 30% misconnection rates were reported.

In summary, the risk of misconnections and stormwater contamination by wastewater depends on the structural integrity of the sewer infrastructure and its proper operation and maintenance. Generally, the presence of wastewater is commonly determined by the associated markers, which may be chemicals (e.g., caffeine) or faecal indicators. Higher risks of misconnections were reported in cities with an older sewer infrastructure.

3.4.3. Pipe materials

The quality and composition of stormwater may change during conveyance by storm sewers to the receiving waters, with both pipe materials and stormwater composition playing important roles. Davies et al. (2010) investigated the impact of PVC and concrete pipes on urban water chemistry by laboratory experiments and found that concrete pipes can affect water quality significantly, mainly by increasing its pH. Wright et al. (2011) also concluded that concrete pipes are responsible for changes in the geochemistry in urban streams, resulting in higher pH compared to non-urban streams. Metal release from different pipe materials in laboratory submersion tests was studied by Ogburn et al. (2013) and they found that concrete, high-density polyethylene (HDPE) and vinyl materials released small or no concentrations of metals and can, therefore, safely be used as stormwater drainage materials. Borris et al. (2017) conducted laboratory tests with conveyance of three types of stormwater by sewer pipes made of concrete, galvanised corrugated steel, and PVC. Their results confirmed the earlier reported increases in pH in concrete pipes, and indicated reductions in stormwater turbidity in concrete and corrugated steel pipes. Flocculated settling of fine solids in relatively new concrete pipes, and solids settling and retention in bottom corrugations might be the causes of such reductions. Furthermore, significant releases of Zn (up to a concentration of 1406 μg/L Zn) from the galvanised corrugated steel pipe were observed. The results also depended on the type of stormwater used: two synthetic stormwaters mimicking the locally observed chemical composition of stormwater and one actual stormwater enhanced by gully pot sediments. Among these stormwater media, the last one was considered as the best with respect to mimicking the actual field conditions.

Among trenchless technologies for pipe repair, sewer relining with synthetic liners is becoming a more common practise and a number of studies addressed the effect of this technology on water quality. For instance, Grella et al. (2016) suggested coating of insides of concrete pipes with epoxy to avoid large pH increases. It has been demonstrated that inorganic and organic contaminants, including carcinogenic and endocrine disrupting compounds, may be released from certain storm sewer coatings into the conveyed waters (Whelton et al., 2013; Tabor et al., 2014; Ra et al., 2018; Li et al., 2019). Ren and Smith (2012) studied the potential release of BPA, di-(2-ethylhexyl) phthalate (DEHP), and benzyl butyl phthalate (BBP) from two common sewer pipe repair procedures in laboratory batch experiments, but did not detect any of the aforementioned three plasticisers in the water exposed to the pipe-repair materials. However, the experimental setup of their experiments do not mimic well the conditions in actual storm sewers, characterised by continual changes of properties of the conveyed stormwater, including changes of temperature, flow rate, and stormwater chemical composition, with respect to, e.g. organic matter content and sediment concentrations, which may potentially affect releases of substances. Furthermore, the analytical method used in their study had relatively high detection limits (0.029, 0.191, and 0.447 mg/L for BPA, DEHP, and BBP, respectively), compared to the environmentally relevant concentrations. For example, the maximum allowable concentration of DEHP in surface waters is 1.3 μg/L, according to the EU directive on priority substances (Directive 2013/39/EU).

In summary, the choice of sewer pipe material (i.e., concrete, plastics, or corrugated steel) may affect the quality of conveyed stormwater. Where such changes would bear adverse consequences for conditions in the receiving waters, pipe materials preventing these changes should be used. Alternately, special coatings (e.g., by epoxy) hold promise in avoiding interactions between the pipe material and stormwater quality.

4. Implications of stormwater pollution source analysis and future outlooks for urban stormwater quality

The knowledge of the specific sources contributing to diffuse pollution through transport vectors such as stormwater is necessary for identifying opportunities for implementation of source controls and other SCMs, and to ensure their effective design and operation. This review summarises the current knowledge of the sources contributing to the pollution of stormwater and, thus, the sources of urban diffuse pollution. Several of the sources described herein were identified as requiring more research. These included anthropogenic activities such as washing of buildings and structure surfaces, and construction activities (concerning other pollutants than TSS) as well as specific elements of urban areas or surfaces, such as non-metallic building surface materials, and gardens, parks and other green areas, among others. In the context of the ongoing climate change and global warming, which may lead to, e.g., longer dry periods and increased rain intensities in many parts of the world, the effects that these factors can exert on runoff quality may increase concentrations of harmful substances in runoff, and may also increase the problems associated with the thermal pollution of stormwater. The major stormwater pollution sources, identified in this review as: vehicular transportation, metallic building envelopes and AD will likely remain major sources due to their widespread presence in the urban environment. Moreover, AD should undoubtedly be considered in stormwater quality studies (Liu et al., 2018a), even in relatively unpolluted areas, because the global AD pollution load due to contributions from highly polluted areas may impact also unpolluted catchments (Omrani et al., 2017).

For stormwater quality concerns, a number of stakeholders need to contribute to achieving sustainable management of stormwater quality. Researchers should continue the work of identifying and quantifying the contributing pollution sources, as well as developing control strategies and treatment technologies, in collaboration with the industry. Future stormwater quality programs should to a larger extent reflect the societal developments and include the pollutants of emerging concern, defined e.g. in the lists of priority pollutants (such as the Directive 2013/39/EU, 2013) or released with the introduction of new products, materials, or chemicals to the urban environment. Synergistic environmental effects of the micropollutants present in urban stormwater are poorly understood (Masoner et al., 2019) and need to be studied further in parallel with collecting the data on their occurrences in stormwater. Furthermore, policy makers should: (i) develop control policies and regulations for reducing the actual entry of harmful pollutants into the environment, including the stormwater, (ii) provide guidance to practitioners implementing such policies, and (iii) establish programs for follow up and evaluation of these pollutant control policies (Marsalek and Viklander, 2011). Past successes of pollutant control policies supporting stormwater quality, including the earlier mentioned phasing lead out of gasoline (Kayhanian, 2012; Huber et al., 2016), or substitution of harmless materials for copper in brake pads, indicate that source controls are much more effective in actually removing diffuse pollutants from the environment than stormwater treatment facilities (Marsalek and Viklander, 2011). Regarding the building surfaces and structures exposed to rainwater or stormwater, material substitutions are effective pollution control measures, when comparing various materials. One exception could be historical buildings, where the original materials need to be retained to preserve the historical appearance. In that case, on-site treatment of polluted building runoff should be implemented. In any case, cooperation and communications among different stakeholder groups, including the public, is necessary to build acceptance for the implementation of innovative acceptable solutions (Barbosa et al., 2012).

5. Conclusions

The knowledge of sources of pollution of urban stormwater and snowmelt is required for selecting effective control options, including source controls, for preventing or mitigating such a pollution and its impacts on the receiving waters. The status of knowledge in this field varies among the source categories, with much of the past research focused on highly influential sources including the atmospheric deposition, vehicular transportation, and metallic building envelopes and structure surfaces. Such sources have been considered as major contributors of urban runoff pollution, and are likely to retain this assessment, because of their central role in urban land use activities involving releases of atmospheric pollutants (contributing to atmospheric deposition, e.g., industries), vehicular transportation, and the use of metallic materials exposed to rainfall.

Concerning the other urban stormwater pollution sources, a number of knowledge gaps were identified: the extent of potential contributions of pollution from washing of buildings and structure surfaces; the contribution of other pollutants than TSS from construction activities; the contribution of pollutants from non-metallic building surface materials (mainly with respect to organic micropollutants other than pesticides); the significance of the pollution contribution from gardens, parks and other green areas, especially in anticipation of future climate changes characterised by increased rainfall depths and intensities in many regions of the world; and, the significance of the faecal pollution caused by urban pets and wildlife.

More attention needs to be paid to the emerging pollutants by conducting systematic studies (reaching beyond opportunistic episodic sampling) reporting the concentrations needed for the environmental risk assessment of emerging pollutants. Such data would serve to broaden the database of stormwater pollutants and guide material substitutions, where needed.

Rapid advancements in clean manufacturing and pollution control technologies, as well as increased awareness concerning the environmental impacts of anthropogenic (behavioural) activities among the public, may further increase the differences in pollutant emissions between historical and recent data. Hence, caution is urged when using historical data in current environmental studies. The tendency of progressing data obsolescence is likely to continue in the future, possibly at even faster rates. Moreover, the continuing introductions of new materials and products, and potentially of new pollutants, into the urban environment suggests that the identification of important stormwater pollution sources, and of the associated pollutants, is a continuing process.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Paper II

Alexandra Müller, Heléne Österlund, Jiri Marsalek, Maria Viklander (2021)

Comparison of three explorative methods for identifying building surface materials contributing pollutants to stormwater

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Comparison of three explorative methods for identifying building surface materials contributing pollutants to stormwater

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ABSTRACT

Runoff from building and structure surfaces may contribute to the pollution of urban stormwater and, thereby, to the degradation of the receiving water quality. Various micropollutants have been found in surface runoff from buildings in the urban environment, including metals and organic micropollutants. Effective methods for identification of such pollutants and their sources are the prerequisites for the development of control measures. In this paper, three different methods for the identification of building surface materials acting as sources of metals (Cd, Cr, Cu, Ni, Pb and Zn), nonylphenols and phthalates are presented: (i) screening of the material composition, (ii) laboratory leaching experiments with synthetic rainwater, and (iii) open-air pilot testing of material panels exposed to actual rainfall and runoff. These three methods cover a wide span of experimental aspects, including, e.g., size of material samples, resource demands, and control of influential factors. Nine materials commonly used on building and structure surfaces in the urban environment were tested: metal sheets of zinc, copper, galvanised steel, coated corrugated steel and stainless steel; and, four different roofing membranes of bitumen as well as polyvinyl chloride (PVC). The experimental results indicated that all three methods were meritorious in providing some information contributing to the identification of pollutant sources. The screening of material composition for targeted pollutants is relatively quick and inexpensive, but may fail to identify minor sources of pollutants, or may identify the substances present in the material, but not released in contact with water. Laboratory leaching was generally effective in identifying sources of substances present in surface runoff, but was unsuitable for estimating the magnitude of actual concentrations in building runoff. Open-air pilot studies of material samples (exposed area = 2 m^2) were thought to provide the results corresponding well to concentrations in runoff from actual building surfaces, but required relatively large financial and labour resources. Thus, the choice of the method for pollutant identification should be based on study objectives, and some benefits may be achieved using more than one method in an integrated manner; e.g., composition screening and lab or open-air leaching of targeted materials.

1. Introduction

Urban stormwater is known as a vector transporting a wide variety of chemicals of known or potential environmental concerns from urban landscapes to surface waters and groundwater aquifers (Masoner et al., 2019). Many of these chemicals, including, e.g., metals, are also associated with concerns on human health risks, where surface waters are used for drinking water production (Makepeace et al., 1995), or where rooftop runoff is harvested and considered, after treatment, for potable water uses (Lee et al., 2012). Consequently, adequate knowledge of the sources of such contaminants is required for effective development and implementation of control measures, including material substitutions. Surface materials of buildings and structures in urban areas were identified as potential sources of various micropollutants, which are released on contact with rainwater running off such surfaces, and contribute to the pollution of urban stormwater (Müller et al., 2020). While the releases of metals from the metallic building envelopes (e.g., Malmqvist, 1983; Robert-Sainte et al., 2009; Charters et al., 2021) and of biocides from, e.g., renders and paints (Bollmann et al., 2014; Gromaire et al., 2015) have been relatively well described in the literature, there is a scarcity of information on releases of other types of organic micropollutants from building surfaces into the urban environment (DeBuyck

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et al., 2021). Furthermore, introductions of new products and construction materials into the built environment, as well as the legacy pollution sources, drive a continual need for identification of new contaminants of concern and their sources (Müller et al., 2020), standardised testing of construction materials (Bandow et al., 2018), and the development of source control policies for both conventional pollutants and pollutants of emerging concern (Marsalek and Viklander, 2011).

Exploratory studies of stormwater quality confirmed occurrences of a wide range of micropollutants, some of which are considered as pollutants of emerging concern (Masoner et al., 2019). Two such model groups of substances are phthalates and alkylphenols (APs), which are used widely by the chemical industry (Priac et al., 2017). Among APs, nonylphenols (NPs) and octylphenols (OPs), as well as their ethoxylates (nonylphenol ethoxylates, NPEOs, and octylphenol ethoxylates, OPEOs), are used as industrial additives to plastics products, paints and varnishes, and are most frequently detected in environmental studies. Phthalates are commonly used as plasticisers in the production of polyvinyl chloride (PVC) and other plastics materials. Both phthalates and NPs were detected in urban stormwater in environmentally relevant concentrations (Björklund et al., 2009; Zgheib et al., 2012; Gasperi et al., 2014; Becouze-Lareure et al., 2019) and may cause adverse effects on aquatic organisms (Staples et al., 1997; Huang et al., 2007; Forner-Piquer et al., 2017). Moreover, NPs and the phthalate Di-(2-ethylhexyl)phthalate (DEHP) are listed among the 45 priority substances of major concern for European waters (Directive, 2013/39/EU).

Several approaches to identifying building surface materials as potential, or confirmed sources of micropollutants were found in the literature: (i) substance flow analysis (SFA), (ii) laboratory leaching, and (iii) pilot-scale, open-air leaching of material panels exposed to rain. The selection of individual approaches depends on study objectives, as further elaborated below. Björklund (2010) used SFA to identify the building surface materials as likely sources of phthalates and NPs, and concluded that there was a lack of information on emission behaviour of these chemicals in the open-air environments. Indeed, lack of knowledge of release mechanisms in open-air conditions is a major limitation of this approach, which on the other hand is well suited for screening the chemicals to be targeted in more advanced searches.

Laboratory leaching offers more specific information than SFA and has been used in standardised testing of construction materials, as reviewed by Bandow et al. (2018). For this purpose, specific standardised tests have been developed, including the dynamic surface leaching test (DSLT), whose main intent is to reproduce diffusion-controlled leaching processes. A critical operating parameter of this test is the ratio of the leachant volume (usually deionised water) to the exposed surface area of the tested material. The leachant is changed according to a prescribed schedule, and the contact time ranges from 6 h to 28 days. Release rates are calculated from targeted chemical concentrations in the leachant. However, the measured leaching rates cannot be used for extrapolation of results to the actual open-air conditions, because of differences between the lab and open-air environments (Bandow et al., 2018). Furthermore, because chemical protocols for identifying toxicants in leachate are inherently incomplete, chemical testing is supplemented by testing ecotoxicity of the leachate. Other types of lab leaching tests were conducted for the research purposes of identifying sources of pollutants to be targeted for further studies. Lamprea et al. (2018) performed laboratory leaching experiments with shredded pieces of automotive and construction materials and found several of them to be potential sources of bisphenol A and alkylphenols (APs). While both standardised leaching tests (Bandow et al., 2018) and exploratory leaching in search for new sources of contaminants deal with the same process, the objectives greatly differ – in the former case, the focus is on standardised procedures and environmental compliance of construction materials, in the latter one, the objective is screening potential sources of contaminants for further research. The main advantages of lab testing include controlled experimental conditions and in the limited exploratory testing also moderate costs.

The pilot-scale leaching of material panels by actual rainwater and runoff, in an open-air setting, is another method of testing source materials under realistic conditions. This method was used to identify building surface materials as sources of such metals as Cu and Zn (Clark et al., 2008; Robert-Sainte et al., 2009; Winters et al., 2015; Müller et al., 2019), as well as phthalates and NPs (Müller et al., 2019). The main advantage of this approach is the similarity to material leaching on actual building surfaces, including the exposure to rain events and wet and dry cycles (Bandow et al., 2018). The leaching results obtained by this method need to be corrected for contributions of atmospheric deposition. Among the methods addressed here, pilot-scale leaching was most costly.

The literature survey yielded only limited information on comparative evaluations of various experimental methods for estimating the leaching of pollutants from building surface materials. To mitigate this knowledge gap, the three methods recommended in the literature for identifying the sources of micropollutants in building runoff were compared and assessed in this study: material composition screening, laboratory leaching tests (excluding the standardised testing of construction materials, which represent a different class of issues), and open-air pilot-scale leaching of material panels by actual rainwater. The selected methods represent procedures with widely varying demands on resources, but also various degrees of reproduction of the actual washoff of building surface materials by rainwater. The objectives of the paper that follows are to assess the above three methods with respect to: (i) capacity for identifying sources of metals, NPs and phthalates in runoff from nine materials commonly used on building or structure surfaces, (ii) the strength of the identified pollution sources, and (iii) the benefits and limitations of individual methods and their applicability in future studies.

2. Materials and methods

Three methods were selected for studying the potential and actual releases of the targeted chemicals from a set of nine materials: metal sheets of zinc (ZN), copper (CU), galvanised steel (GAL), coated corrugated steel (CST) and stainless steel (STS); and, roofing membranes of bitumen felt (BIF) and bitumen shingles (SHI), as well as PVC from two manufacturers (PVCA, PVCB). Such materials are commonly used on single-family houses and apartment buildings, as well as on institutional, industrial and commercial buildings. The material selection was based on a report of The Swedish National Board of Housing Building and Planning (Boverket, 2010) on the technical status of Swedish buildings, and was done in dialogue with commercial suppliers of construction materials and a roofing company based in Luleå, Sweden.

The material composition screening was intended to identify potential pollutant sources by determining the chemicals present in the material, while laboratory leaching experiments mimicked the releases of the targeted chemicals from the materials tested in contact with water. Lastly, the open-air pilot study was intended to test the materials studied for releases of the targeted chemicals in authentic conditions of actual rainfall/runoff events. All the materials tested were subject to the same three methods.

2.1. Material composition screening

The main objective of the material composition screening was to determine the actual presence (or absence) of metals (Cd, Cr, Cu, Ni, Pb and Zn), phthalates, NPs and NPEOs in the materials tested. Metal sheets (ZN, CU, GAL, STS) were excluded from analyses of phthalates and NPs, because it was highly unlikely that they would contain any organic micropollutants. The full list of chemical analyses, to which the individual materials were subject to, is presented in Table 1. For sample preparation, the coating of the coated, corrugated steel (CST) was scraped off using stainless steel tools. The other materials, cut to an appropriate size, were treated as whole samples, because their surface

Table 1
Analytical methods and list of chemical analyses applied to each material tested by the three methods: Material composition screening (screening), Laboratory leaching (lab), and Open-air pilot experiments (pilot).

	Metals	Phthalates (13 compounds)[a]	NPs and NPEOs
Analytical method	Solid samples were digested with HNO_3/HCl/HF, and water samples were autoclaved with HNO_3, prior to analysis on ICP-SFMS, following standards SS EN ISO 17294-2: 2016.	Samples were analysed using GC-MS, following standard DIN ISO 18856 (water samples) and E DIN 19742:2014–08 (solid samples). Water samples were extracted using hexane, and solid samples were extracted with ethyl acetate.	Samples were analysed on LC-MS-MS, based on ISO 18857-2, after acidification and extraction with dichloromethane (water samples).
Materials analysed in the screening	All 9 materials	BIF, SHI, PVCA, PVCB	CST, BIF, SHI, PVCA, PVCB
Materials analysed in the lab-leaching	All 9 materials	BIF, SHI, PVCA, PVCB	CST, BIF, SHI, PVCA, PVCB
Materials analysed in the pilot study	All 9 materials	STS, PVCA, PVCB	STS, BIF, SHI, PVCA, PVCB

[a] The following phthalates were analysed: dimethylphthalate, diethylphthalate, di-n-propylphthalate, di-n-butylphthalate, diisobutyl phthalate, di-n-pentylphthalate, di-n-octylphthalate, di-(2-ethylhexyl)phthalate, butylbenzylphthalate, dicyclohexylphthalate, diisodecyl phthalate, diisononyl phthalate, and di-n-hexylphthalate.

layer could not be separated from the underlying layers. One sample per material was prepared and sent for analyses to an accredited laboratory (ALS Scandinavia AB), where the chemical analyses were performed. The analytical methods applied are presented in Table 1, and the reporting limits (RL) of the analysed substances can be found in the Supplementary material.

2.2. Laboratory leaching experiments

A synthetic rainwater was used as a leachant and prepared according to the rainwater quality data reported in Swedish studies (Granat, 1990; Kindbom et al., 2001; Karlsson et al., 2003). A solution of Sartorius ultrapure arium® pro water (0.055 μS/cm), 9.45 M hydrochloric acid (HCl) and six salts ($NaNO_3$, KNO_3, $(NH_4)_2SO_4$, $CaCl_2 \times 2H_2O$, $MgSO_4 \times 7H_2O$ and NaCl) was prepared and yielded the following concentrations: 3.0 mg/L Cl^-, 0.42 mg/L NH_4^+-N, 0.49 mg/L NO_3^--N, 0.73 mg/L SO_4^{2-}-S, 0.20 mg/L Ca^{2+}, 0.21 mg/L Mg^{2+}, 0.10 mg/L K^+, 1.8 mg/L Na^+, and pH of 4.4 ± 0.2. A similar composition was proven to successfully simulate rainwater in Swedish field conditions (Odnevall Wallinder et al., 2002). Relatively low pH of the synthetic rainwater was preferred, hypothesising that it would increase the leaching of substances from the roofing materials.

The leaching experiments were performed separately for metals and organic compounds, in order to avoid adsorption of analytes to the container walls. The synthetic rainwater was added to polypropylene (PP) beakers (for metal analyses) or glass beakers (organic analyses) to a volume corresponding to the rainfall of 32 mm, which is the rain depth of a 24 h event with one-year average recurrence interval in Sweden (Wern and German, 2009). Subsequently, the material samples were immersed in the beakers (see Fig. 1) and the beakers were covered with PP lids (PP beakers) or aluminium foil (glass beakers) in order to avoid cross-contamination by splashing, and contamination from the surrounding environment. In order to limit the leaching to the sample surface that would be in contact with rainwater/washoff on actual buildings, the material edges and back faces were covered with three layers of a metal-free lacquer (for metal analyses), or the samples were screwed back-to-back or pressed to the glass beaker walls (for organic analyses). Control material samples were made of Plexiglas coated with the metal-free lacquer (metal analyses), and glass beakers without any material samples were also tested (organic analyses). All materials were tested in duplicate samples. After 24 h of leaching, under gentle agitation of 60 revolutions per minute, the material samples were removed from beakers and left to dry for a minimum of 24 h. In order to avoid biased concentrations resulting from higher chemical releases from brand new materials, the leachate from the first testing round was discarded. The procedure was thereafter repeated, and the leachates from the second round of leaching were sent to ALS Scandinavia AB laboratory for substance analyses, according to the details available in Table 1. Table 1 also presents a list of substances, which were analysed in the leachates from each material sample. The laboratory leaching experiments were previously reported in Andersson Wikström et al. (2015).

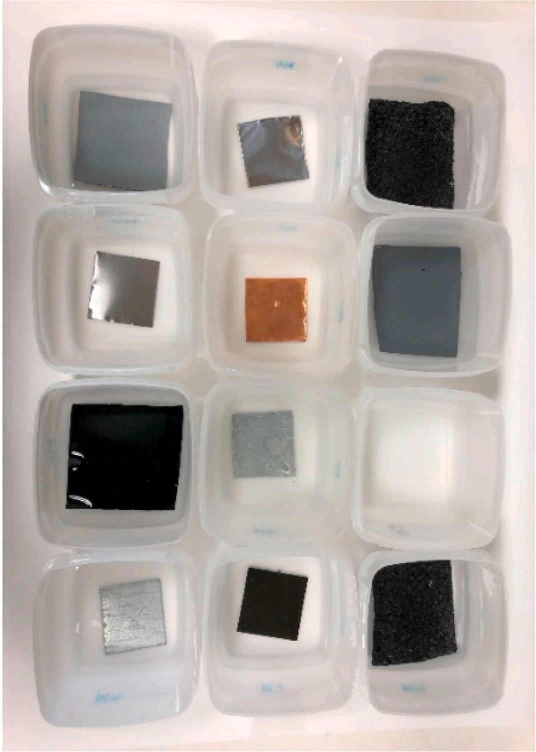

Fig. 1. Experimental setup of leaching experiments, with small (0.5 L) polypropylene containers holding material samples and the synthetic rainwater.

2.3. Open-air pilot study

Triplicates of 1 × 2 m rectangular panels were made of the individual materials and installed with a gentle slope in the open air on the campus of Luleå University of Technology (LTU) in northern Sweden. Luleå has a subarctic climate (Köppen climate classification code Dfc). Measurements of precipitation pH at the study location were in the range of 5.5 ± 0.4. The study location surroundings consist of office and residential buildings, parking lots, green areas and a small road. Potential nearby (within 8 km) sources of airborne pollution include a district heating plant and a steel production plant. Stainless steel gutters, attached to the panels at the lower end, were used to collect the runoff from individual panels and were protected by over-hanging overlays against a direct rainwater entry into the gutters. Stainless steel was also tested on triplicate panels and considered as a reference material serving to monitor the pollution contributed by the atmospheric deposition. All panels were installed in a random order over the experimental site approximately 6 months before the runoff sampling started, and during this initial period were exposed to actual weather conditions, including approximately 145 mm of rain and snow.

For the purpose of this study, six rain events were sampled over the period of one year. Weather data, including, e.g., the precipitation depth and air temperature for the events used in tests, were obtained from a weather station of the Swedish Meteorological and Hydrological Institute (SMHI) located approximately 9 km from the campus area. The whole runoff volume from each panel was collected in one perfluoroalkoxy alkane (PFA) bag and treated as a single sample, yielding the event mean concentration (EMC). The PFA bags were dispatched and connected to the gutters of each panel (see Fig. 2) some hours before the expected rain, and the collected runoff was transported to the LTU-laboratory as soon as possible, but not later than 15 h after the rain had stopped. The studied metals were analysed in runoff from all the tested and reference materials, while the organic substances were analysed only in runoff from (i) BIF, SHI, PVCA and PVCB, based on the results of previous testing, and (ii) in runoff from STS to detect contributions of any airborne sources of NPs or phthalates (for details, see Table 1). The samples were submitted to ALS Scandinavia AB for chemical analyses; for details, see Table 1. Average concentrations in runoff from each material were calculated from the triplicate samples for six rain events, yielding 18 data points per material. The pilot study was presented in detail in a previous publication (Müller et al., 2019).

2.4. Chemical analysis

In Table 1, a list of the chemical analyses applied to each of the tested materials by all three methods is presented. Metal analyses were applied to all materials in all three methods, while the organic analyses were applied to a selection of materials, based on likelihood of their presence/release and results of previous testing of the materials. NPs, NPEOs and phthalates were analysed in runoff from STS in the outdoor pilot experiment as a control to determine any airborne contribution of these substances. The chemical analyses of the material and water samples were performed by the accredited laboratory ALS Scandinavia AB, and the analytical methods for the different substances are described further in Table 1. The laboratory accreditation certifies compliance with international standards for quality assurance and quality control (QA/QC). The reporting limits (RL) of the applied methods can be found in the Supplementary material. All analyses were performed using inductively coupled plasma-sector field mass spectrometry (ICP-SFMS), gas chromatography-mass spectrometry (GC-MS), or liquid chromatography–tandem mass spectrometry (LC-MS-MS).

3. Results and discussion

The concentrations of the studied substances in each material screening sample, as well as in the leachates and runoff from respective materials are presented in Fig. 3 (metals) and Fig. 4 (NPs, NPEOs and 2 phthalates). The specific data for all the materials and studied substances can be found in Table S1 of the Supplementary material.

3.1. Metals

In the material composition screening, ZN and GAL were identified as potential sources of Zn, and CU as a source of Cu; all three identifications were confirmed by both the laboratory leaching study and the open-air pilot study. Similarly, SHI was identified by all three methods as a source of Cu and Ni. CST showed a high content of Zn in the screening, but significantly lower releases, by more than an order of magnitude, than the releases of Zn from ZN and GAL in the laboratory leaching and the pilot study. A possible explanation for this was the interference of the underlying layers when the coating was scraped off in the material composition screening; those layers were not in contact with the leachant/runoff in the other two methods. Moreover, STS, ZN and CST showed relatively high content of Cu in the material composition screening, but did not display releases of Cu to water under the laboratory and open-air study conditions tested in this study. The material composition screening showed that two materials, STS and SHI, contained noteworthy concentrations of Cr and Ni: STS contained 149 000 mg/kg of Cr and 1070 mg/kg of Ni, and SHI contained 460 and 1140 mg/kg of Cr and Ni. However, with the exception of releases of Ni from SHI, the releases of Cr and Ni to water were below the RL (0.9 and 0.6 μg/L, respectively) in the laboratory leachate samples, and were consistently low amongst the tested materials in the open-air pilot study (mean concentrations of Cr < 4 and Ni < 3 μg/L). Recognizing that these low Cr and Ni concentrations were observed even for the materials whose screening showed no contents of Cr and Ni, the source of Cr and

Fig. 2. a,b. (a) Overview of the test site of the open-air pilot study with different materials mounted on separate panels and (b) Experimental setup of the open-air pilot study, with stainless steel overlays and gutters collecting the runoff. The black buckets were holding the PFA bags.

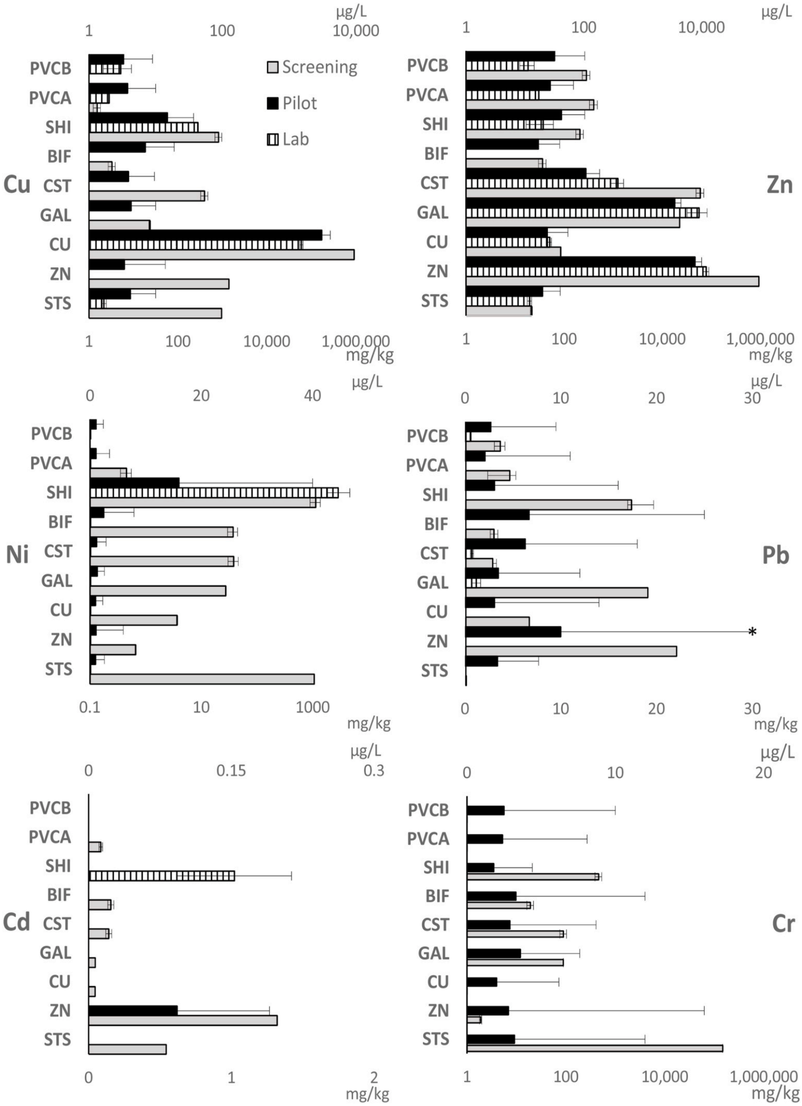

Fig. 3. Lower axis: Metal concentrations (mg/kg) in the materials (screening). Upper axis: Average metal concentrations (µg/L) in duplicate samples (lab), and in the runoff from triplicate samples and six rain events (pilot). Error bars represent analytical measurement uncertainty in the screening, and min/max values in the laboratory and pilot studies. No measurement uncertainty was specified for the metal analysis of the metal sheets, because the method was not accredited, but the laboratory reports a general uncertainty of ca 30%. *The maximum Pb concentration in runoff from ZN in the pilot experiments was 105 µg/L.

Ni was assumed to be atmospheric deposition (except for the Ni release from SHI). Moreover, these concentrations correspond to the representative concentrations of Cr and Ni in rainwater in urban areas (3 and 2 µg/L, respectively) suggested by Göbel et al. (2007). From the results of the material composition screening, Pb was present in the highest concentrations in ZN, GAL and SHI, but in the laboratory leaching study, Pb concentrations were under – or close to – the RL. In the open-air pilot study, the Pb concentrations in runoff displayed large variations among material triplicates, but the highest average and maximum concentrations of Pb were found in runoff from ZN. Regarding Cd, concentrations found in the tested materials and their leachates/runoff were both fairly low, and none of the studied methods indicated that any of the tested materials were likely sources of Cd.

3.2. *Phthalates, nonylphenols and –ethoxylates*

PVCA and PVCB were identified in the material composition screening as potential sources of diisononyl phthalate (DINP), Diisodecyl phthalate (DIDP), and contained comparatively lower levels of Di-n-octyl phthalate (DNOP). In PVCA, the phthalate DEHP was present, and PVCB contained NPEOs. Both PVC materials released DINP, DIDP and lower levels of DNOP in the open-air pilot study, whereas PVCA released detectable concentrations of DEHP for some of the studied rain events. To the contrary, no phthalates were released in concentrations above the RL from any of the tested materials in the laboratory leaching study. A possible explanation for this is the hydrophobicity of these phthalates, with log $K_{ow} > 8.0$ for DINP and DIDP (Staples et al., 1997), and their high affinity to adsorb to suspended solids (Björklund et al., 2009), which while absent in the laboratory leachant, were present in the open-air environment as a result of atmospheric deposition of particles on the pilot panel surfaces. The average total suspended solids (TSS) concentrations in runoff from PVCA and PVCB were 15 and 20 mg/L respectively (Supplementary material 1 of Müller et al., 2019). Furthermore, the leachability of such hydrophobic organic compounds

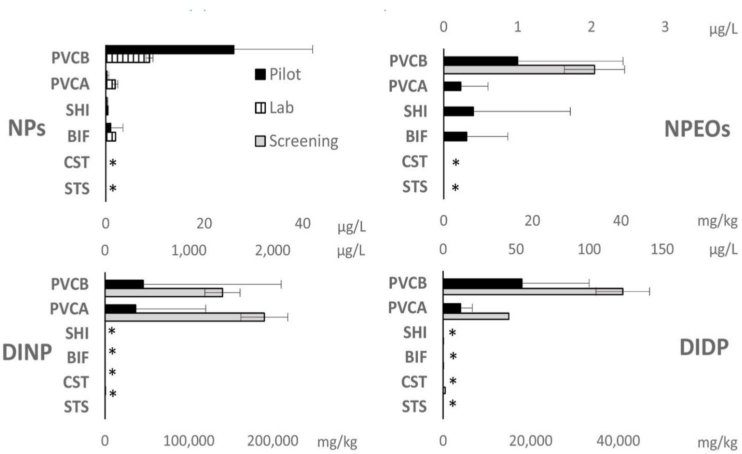

Fig. 4. Lower axis: NP, NPEO, Diisononyl phthalate (DINP) and Diisodecyl phthalate (DIDP) concentrations (mg/kg) in the materials (screening). Upper axis: Average concentrations (µg/L) in duplicate samples (lab) and in runoff from triplicate samples and six rain events (pilot). Error bars represent analytical measurement uncertainty in the screening, and min/max values in the lab and pilot studies. *STS: organic contaminants (OC) were only analysed in the pilot study; CST: OC were not analysed in the pilot study; BIF and SHI: phthalates were not analysed in the pilot study.

as phthalates is known to be associated with the presence of dissolved organic matter. For instance, Zheng et al. (2007) studied the distribution of phthalates in dissolved fractions of landfill leachates and found that the investigated phthalates had high affinity to bind to humic acid, and Kalmykova et al. (2013) studied the partitioning of organic compounds in landfill leachates and stormwater, and suggested that the dissolved organic carbon would decrease the K_{ow} of hydrophobic substances, including phthalates.

Regarding NPs and/or NPEOs, PVCB was identified by all methods as a source. NPEOs (but not NPs) were detected in PVCB in the material composition screening, while higher concentrations of NPs were present in the lab leachates and runoff samples, and lower concentrations of NPEOs in the runoff in the pilot study. This indicates that the environmentally unstable NPEOs were added to the material formulation, and subsequently degraded to NPs after contact with water (Priac et al., 2017). This highlights the importance of analysing both NPs and NPEOs in leachates and runoff. Moreover, even though the NP/NPEO concentrations were below the RL for BIF, SHI and PVCA in the material composition screening, NPs were still released from the materials in contact with water, indicating that they were present in the material composition at levels below the reporting limits available in the current method (5 and 10 mg/kg, respectively). The concentrations of all the studied phthalates, NPs, NPEOs, in the surface layer of CST were below RL in the material composition screening, as were the concentrations of these substances in the leachates in the laboratory leaching study, which led to a decision not to analyse these substances in runoff from CST in the open-air pilot study.

3.3. Differences in study conditions among the tested methods

There were principal differences among the studied methods for assessing the pollutant leaching from building materials. The material composition screening, while helpful for planning advanced studies, only indicates the presence or absence of substances in the material, without considering their leachability in contact with water. Laboratory leaching addresses the leachability issue in a relatively clean lab environment with good control of influential factors, including the choice of leachant (e.g., actual or synthetic rainwater), temperature variations, water/material contact time (Lamprea et al., 2018), wet and dry cycling (Bandow et al., 2018), exposed surface area, and solar radiation. Finally, open-air pilot experiments expose the tested materials to actual atmospheric conditions, but should consider influences of such external factors as particles, dust and chemicals from the atmospheric deposition, on releases of pollutants (DeBuyck et al., 2021). Another external factor to consider in outdoor experiments are bird droppings, which are acidic, accelerate corrosion of metal roof structures, and impact on rooftop runoff quality (Spennemann and Watson, 2018).

The material composition screening may serve as a good indicator of the pollutants that could be released from the studied materials, in a similar way as a SFA. However, our results indicate that such screenings may fail to detect some substances present in runoff and leachate samples, as was the case with NPs from BIF, SHI and PVCA, or identify substances present in the materials that are unlikely to be released in contact with water, as was the case, e.g., with the high concentrations of Cr in STS. With the exception of releases of phthalates from the studied materials, the results of the laboratory leaching and the open-air pilot studies were consistent with respect to identifying the substances released. This was especially true for the “major” releases, such as the releases of Cu and Zn from the metal sheets, and the release of NPs from PVCB. Accordingly, leaching experiments, similar to those applied herein, may be useful for identifying the sources of specific pollutant groups, with smaller resources required (i.e., in terms of the equipment, labour, safety, and costs). However, the leachate concentrations from such laboratory experiments did not agree well with the respective concentrations in runoff from the open-air pilot panels, assumed to agree fairly well with the actual building surfaces, and should not be used for comparisons to concentrations measured in the field (Bandow et al., 2018). Lamprea et al. (2018) performed leaching experiments similar to those presented in our study, and identified PVC materials, concrete, Styrene-Butadiene-Styrene (SBS)-modified bitumen, car bodies and brake fluids as potentially important sources of NPs. Because the tested materials were shredded prior to leaching, and methanol and deionised water were used as leachants, the comparison of their results to actual outdoor conditions is not possible. However, their leaching method, using methanol, may have been more suitable to achieve leaching of the phthalates that were obviously present in both PVCA and PVCB, but not detected in the synthetic rain leachates in this study. In addition, Lamprea et al. (2018) stated that because of the shredding of materials prior to leaching, their estimated emissions rates are very likely to be overestimated. In our study, the longer contact time between the materials and water in the laboratory leaching experiments than in the open-air pilot study does not seem to have resulted in an overestimation of the concentrations present in the leachates compared to runoff concentrations, exemplified, e.g., by the higher concentrations of Cu found in runoff from CU than in the laboratory leachates of CU (Fig. 3).

Another advantage of performing studies in the controlled laboratory environment is the possibility of isolating single factors and study their effects on the potential releases of pollutants from certain materials. For instance, Wangler et al. (2012) tested the importance of temperature changes on biocide releases from façade coatings by tests in a weathering chamber, varying the temperature in several steps. Such studies would be almost impossible to perform outdoors, or would demand a vast amount of data and close monitoring of numerous meteorological parameters, in order to discern the effects of single factors or parameters. Consequently, material composition screenings, laboratory studies and pilot scale outdoor studies should serve different purposes and the successful integration of results from all three categories should lead to a better knowledge of the phenomenon being studied. Moreover, researchers and practitioners may be restricted by limited resources in terms of finances and time when planning studies for the identification of new sources of stormwater pollution. The resource demands may differ widely among the methods studied, as illustrated in Fig. 5, presenting a relative comparison of the resource demands in terms of financial resources and labour (work hours) for the three methods. The estimations of the financial resource demands in Fig. 5 were based on the costs of the chemical analyses, material and equipment needs, labour costs and pilot site construction, while the labour resources were estimated based on the working hours needed to perform the respective tests as described in the methods section (excluding the working time for performing the actual chemical analyses, which were outsourced). These estimates do not take into consideration any costs of renting the laboratory facilities or land plots necessary to perform the experiments, or the labour resources needed to analyse/interpret the data from experiments. It can be inferred from Fig. 5 that while the material composition screening was comparatively quick and inexpensive, the laboratory leaching experiments were relatively labour intensive, and the open-air pilot experiments required significant resources in terms of planning, costs and labour.

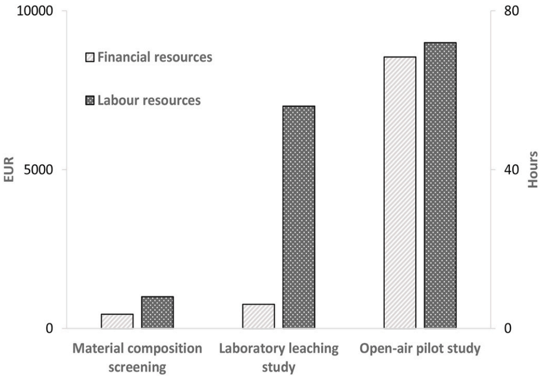

Fig. 5. Comparison of the financial and labour resources required for investigations of building surface materials as sources of targeted micropollutants. The cost estimates were based on the costs of chemical analyses, material and equipment needs, labour and pilot site construction. The labour resource estimations were based on the work hours needed to perform the respective tests as described in the methods section (excluding the work hours needed for chemical analyses).

4. Conclusions

Quick and inexpensive small-scale exploratory studies of sources of the stormwater pollution (i.e., scales smaller than studies of runoff from actual buildings or catchments) are most helpful for planning effective field monitoring of stormwater quality, by identifying: (i) sources of pollutants of emerging concern that should be included in future studies, and (ii) new sources of conventional pollutants. Moreover, these small-scale studies provide opportunities for identifying the sources of diffuse pollution and guidance for selecting mitigation options, such as material substitution or near-source treatment.

The results presented herein highlight the importance of: (i) considering the atmospheric deposition of metals when performing open-air experiments, and (ii) analysing both NPs and NPEOs in products as well as their leachates and/or runoff, because of their interconnected use and gradual degradation from NPEOs to NPs. Moreover, the specific method used in the laboratory leaching experiments was unsuitable to investigate the leaching of phthalates, and possibly other hydrophobic compounds, from the studied materials.

Chemical screening of material composition appears to be less resource intensive, but potentially suffers from two limitations: (i) failure to identify minor sources of pollution, or (ii) may correctly identify substances present in the material, but without indicating their susceptibility to be released in contact with water. While laboratory leaching experiments are generally effective in identifying sources of substances present in surface runoff, they are unsuitable for estimating the magnitude of actual concentrations in such a runoff. Outdoor pilot studies are thought to provide the results corresponding well to the concentrations in runoff from actual building and structure surfaces, but require large financial and labour resources. Some benefits may be achieved by integrated use of more than one method; e.g., composition screening and laboratory leaching or open-air testing of targeted materials. Furthermore, in open-air studies, it is important to take into consideration the atmospheric deposition, as well as other influential factors that may affect the releases of pollutants from building and structure surfaces. Consequently, the results of such studies may be harder to transfer to other locations. Hence, when planning future studies of the stormwater pollution from washoff of building and structure surfaces, researchers and practitioners need to consider the above findings when selecting the "best" method of pollutant assessment meeting the specific objectives and the funding of their study. In future applications of methods similar to the open-air pilot study, it is recommended to consider strategies for separating pollution contributions of atmospheric deposition from material leaching, e.g., by direct measurements of atmospheric deposition.

Credit author statement

Alexandra Müller: Conceptualisation, Methodology, Formal analysis, Investigation, Visualisation, Writing – original draft, Funding acquisition. Heléne Österlund: Conceptualisation, Methodology, Writing – review & editing, Supervision. Jiri Marsalek: Conceptualisation, Methodology, Writing – review & editing, Supervision. Maria Viklander: Conceptualisation, Methodology, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.

org/10.1016/j.jenvman.2021.113574.

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Table S1 Total concentrations of the studied substances found in the tested materials, their leachates and their runoff respectively. The figures represent a single sample in the material composition screening, average of duplicate samples, ± the difference from the average in the laboratory leaching experiments, and average of triplicate samples over six rain events (± standard deviation) in the outdoor pilot study. Cases where elevated RL were obtained instead of actual concentrations are presented in italics. CST has higher reporting limits for phthalates because of differences in the analytical methods.

		Cd	Cr	Cu	Ni	Pb	Zn	NPs	NPEOs	DINP	DIDP	DNOP	DEHP
Material composition screening (mg/kg)	**STS**	0.54	149 000	960	1070	0.15	22	n/a	n/a	n/a	n/a	n/a	n/a
	ZN	1.3	1.9	1410	0.66	22	941 000	n/a	n/a	n/a	n/a	n/a	n/a
	CU	0.045	<0.8	920 000	3.7	6.7	85	n/a	n/a	n/a	n/a	n/a	n/a
	GAL	0.046	89	23	28	19	22 800	n/a	n/a	n/a	n/a	n/a	n/a
	CST	0.14	89	399	38	2.9	60 000	<5.0	<10	<1000	<1000	<1000	<1000
	BIF	0.16	19	3.3	37	3	36	<5.0	<10	*<150*	*<150*	<10	<10
	SHI	0.2	460	826	1140	17	211	<5.0	<10	*<100*	*<100*	<10	<10
	PVCA	0.085	0.61	1.5	0.45	4.7	403	<5.0	<10	190 000	*<30 000*	2700	770
	PVCB	<0.02	0.2	<0.5	<0.2	3.7	285	<5.0	34	140 000	41 000	*<2000*	*<100*
Laboratory leaching experiments (µg/L)	**STS**	<0.05	<0.9	1.7 ± 0.15	<0.6	<0.5	12 ± 4.7	n/a	n/a	n/a	n/a	n/a	n/a
	ZN	<0.05	<0.9	<1	<0.6	<0.5	12 000 ± 1400	n/a	n/a	n/a	n/a	n/a	n/a
	CU	<0.05	<0.9	1530 ± 85	<0.6	<0.5	26 ± 1.9	n/a	n/a	n/a	n/a	n/a	n/a
	GAL	<0.05	<0.9	<1	<0.6	1.2 ± 0.47	9120 ± 3380	n/a	n/a	n/a	n/a	n/a	n/a
	CST	<0.05	<0.9	<1	<0.6	0.74 ± 0.16	380 ± 98	<0.100	<0.100	n/a	n/a	n/a	n/a
	BIF	<0.05	<0.9	<1	<0.6	<0.5	<4	2.0 ± 0.085	<0.100	n/a	n/a	<1.0	<1.0
	SHI	0.15 ± 0.062	<0.9	43 ± 0.80	45 ± 2.1	<0.5	21 ± 10	0.41 ± 0.007	<0.100	n/a	n/a	<1.0	<1.0
	PVCA	<0.05	<0.9	2.0 ± 0.01	<0.6	<0.5	17 ± 0.05	1.9 ± 0.93	<0.100	*<10*	*<10*	<1.0	<1.0
	PVCB	<0.05	<0.9	3.0 ± 1.4	<0.6	0.59 ± 0.076	11 ± 3.1	8.9 ± 0.69	<0.100	*<10*	*<10*	<1.0	<1.0
	Blank	<0.05	<0.9	5.1 ± 2.5	<0.6	0.69 ± 0.080	6.7 ± 1.8	<0.100	<0.100	*<10*	*<10*	<1.0	<1.0
Outdoor pilot study (µg/L)	**STS**	<0.05	3.2 ± 3.1	4.2 ± 3.1	1.0 ± 0.59	3.4 ± 2.6	20 ± 8.5	<0.1	<0.1	<1	<1	<1	<1
	ZN	0.093 ± 0.057	2.8 ± 3.6	3.4 ± 3.6	1.1 ± 1.3	10 ± 24	7770 ± 1406	n/a	n/a	n/a	n/a	n/a	n/a
	CU	<0.05	2.0 ± 1.9	3090 ± 534	1.0 ± 0.58	3.1 ± 3.3	24 ± 12	n/a	n/a	n/a	n/a	n/a	n/a
	GAL	<0.05	3.6 ± 2.4	4.3 ± 2.6	1.3 ± 0.66	3.5 ± 3.1	3530 ± 690	n/a	n/a	n/a	n/a	n/a	n/a
	CST	<0.05	2.9 ± 2.5	3.9 ± 2.2	1.2 ± 0.74	6.3 ± 4.6	109 ± 37	n/a	n/a	n/a	n/a	n/a	n/a
	BIF	<0.05	3.3 ± 3.2	7.0 ± 5.3	2.5 ± 2.0	6.7 ± 6.2	17 ± 9.6	0.99 ± 1.2	0.31 ± 0.21	n/a	n/a	n/a	n/a
	SHI	<0.05	1.8 ± 1.1	15 ± 12	16 ± 13	3.1 ± 4.1	42 ± 33	0.15 ± 0.14	0.40 ± 0.29	n/a	n/a	n/a	n/a
	PVCA	<0.05	2.4 ± 2.3	3.8 ± 2.7	1.1 ± 0.78	2.1 ± 2.5	27 ± 19	0.23 ± 0.17	0.23 ± 0.087	365 ± 257	12 ± 7.1	1.7 ± 1.6	1.0 ± 0.93
	PVCB	<0.05	2.5 ± 2.7	3.3 ± 2.7	1.1 ± 0.63	2.7 ± 2.4	32 ± 30	26 ± 9.3	1.0 ± 0.69	455 ± 517	54 ± 25	2.0 ± 2.1	<1

Table S2 Report limits (RL) for the analytical methods applied in the study.

Substance	RL, solid samples (mg/kg)	RL, water samples (µg/L)
Cd	0.02	0.05
Cr	0.1	0.9
Cu	0.5	1
Ni	0.2	0.6
Pb	0.2	0.5
Zn	1	4
Phthalates (13 compounds)*	10	1
NPs	5	0.1
NPEOs	10	0.1

* The following phthalates were analysed: dimethylphthalate, diethylphthalate, di-n-propylphthalate, di-n-butylphthalate, diisobutyl phthalate, di-n-pentylphthalate, di-n-octylphthalate, di-(2-ethylhexyl)phthalate, butylbenzylphthalate, dicyclohexylphthalate, diisodecyl phthalate, diisononyl phthalate, and di-n-hexylphthalate.

Paper III

Alexandra Müller, Heléne Österlund, Kerstin Nordqvist, Jiri Marsalek, Maria Viklander (2019)

Building surface materials as sources of micropollutants in building runoff: A pilot study.

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Building surface materials as sources of micropollutants in building runoff: A pilot study

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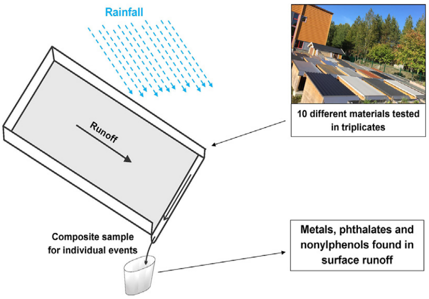
HIGHLIGHTS

- Runoff quality from building surface materials was studied in pilot scale outdoors.
- Building materials contributed metals, phthalates and nonylphenols to runoff.
- Up to 2100 μg/L Diisononyl phthalate and 42 μg/L nonylphenols in runoff from PVC.
- Substance release from soft, flexible materials seemed to increase with temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Control of diffuse pollution is critical for achieving good surface water quality status. In this context, pollutant contributions from building materials have received increased attention in recent decades. This study examined the releases of metals, nonylphenols and phthalates from ten common building surface materials (installed in triplicates) into rainwater runoff from six rain events. The highest releases of metals were from copper and zinc sheets (average concentrations of 3090 μg/L Cu and 7770 μg/L Zn respectively), while other metal materials, e.g., Corten weathering steel, exhibited lower releases. PVC roofing released high concentrations of nonylphenols and phthalates (average concentrations of up to 26 μg/L nonylphenols and 455 μg/L Diisononyl phthalate, DINP) which have not been investigated in the earlier studies. Pollutant releases varied between events, likely because of weather conditions and rainfall characteristics. Study findings should be valuable for environmentally responsible applications of the existing building materials and the development of new ones, as well as the investigations and risk assessment of specific pollutants in stormwater.

1. Introduction

A cocktail of pollutants in urban stormwater includes contributions from many types of drainage surfaces as well as the ambient air. Actual entry of pollutants into stormwater occurs through such processes as wash-off, weathering and leaching (Malmqvist, 1983). It is recognised that pollutants carried with stormwater may severely affect aquatic life in receiving waters (Makepeace et al., 1995). The European Water Framework Directive (2000) specifically points out the need to address diffuse pollution.

The contribution of pollutants from building materials has gained increased research interest during the recent decades. Malmqvist (1983) was among the first to point out the importance of roof runoff for stormwater quality and demonstrated that roof runoff was a major source of copper and zinc, originating from corrosion of metal

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structures. Förster (1999) studied the variability of roof runoff quality and concluded that factors such as roofing material, dry deposition, precipitation and other meteorological characteristics generate a high degree of variability between storm events, locations, roofing materials and groups of pollutants. Rainfall intensity and antecedent dry days (ADD) were reported as influential factors for roof runoff quality, with respect to pollutant accumulation growing with increasing ADD, more effective wash-off with greater rainfall intensities (Yaziz et al., 1989), and affecting the formation and removal of corrosion products from metal surfaces (He et al., 2001). However, low-intensity rainfalls may generate higher concentrations of e.g. copper derived from dissolution of the material surface (Charters et al., 2016).

In several studies, increased releases of metals were correlated to lower runoff pH (Quek and Förster, 1993; Wicke et al., 2014). The runoff run length and surface slope were suggested as important parameters affecting copper concentrations in runoff from strips of roofing copper (Bielmyer et al., 2012). Furthermore, material surface characteristics (i.e. roughness and adhesiveness) were shown to have great importance for the accumulation and wash-off of deposited pollutants during wet-weather (Wicke et al., 2012), and removal of deposited pollutants by wind and air turbulence (Quek and Förster, 1993).

The previous research on contribution of pollutants from building surface materials focused mostly on metals (e.g. Clark et al., 2008; Robert-Sainte et al., 2009; Winters et al., 2015) and pesticides (Burkhardt et al., 2007; Bollmann et al., 2014; Gromaire et al., 2015). However, much less is known about other organic micropollutants. Nonylphenols (NPs) and phthalates are industrial chemicals that are common additives in a wide range of e.g. plastic products and many of these compounds have been documented as harmful to aquatic life (Huang et al., 2007; Swedish Chemical Agency, 2015; Forner-Piquer et al., 2017). NPs and the phthalate Di-(2-ethylhexyl)phthalate (DEHP) are priority substances listed in Annex I of the European Union directive on priority substances (Directive 2013/39/EU, 2013). Previous laboratory leaching tests indicated the potential of several commonly used roofing materials to release NPs to stormwater (Andersson Wikström et al., 2015) and large quantities of NPs were leached from PVC materials (Lamprea et al., 2018). A substance flow analysis by Björklund (2010) identified roofing and façade materials as important sources of phthalates and concluded that there was a significant lack of knowledge concerning the emission behaviour of these substances in the outdoor environment. No literature references were found in which nonylphenols and phthalates were analysed in runoff from building surface materials. Bressy et al. (2011) studied alkylphenols in atmospheric deposition as well as runoff from a residential catchment near Paris and found that building runoff emissions were the predominant source of alkylphenols in stormwater. However, the questions concerning the effect of influential factors on their release remain unanswered.

In this study, common building surface materials that are used on roofs, facades or other surfaces in the built environment were tested in the outdoor environment under varying weather conditions to assess their releases of pollutants, both emerging and well known, to rainwater runoff. The primary study objective was to collect unique data on releases of micropollutants not studied earlier from building surface materials and the secondary objective was to identify influential factors worthy of further research.

2. Material and methods

2.1. Experimental setup

Ten different building surface materials were installed on mildly sloping pilot-scale panels outdoors at the Luleå University of Technology (LTU) campus, with one material per panel and three replicates of every material. All panels were 1 × 2 m (width × length) with a slope of approximately 10% in the northwest to southeast direction. The following materials were studied: bitumen-based roofing felt (BIF), bitumen-based shingle (SHI), Corten weathering steel (COR), corrugated and coated steel (CST), coated zinc sheets (CTZ), copper sheets (CU), galvanised steel (GAL), two different roofing membranes made of polyvinyl chloride, PVC (PVCA and PVCB), and titanium-zinc sheets (ZN). The selection was done in dialogue with stakeholders and was based on a report by the Swedish National Board of Housing Building and Planning (Boverket, 2010) on the technical status of Swedish buildings as well as the results of previous laboratory studies (Andersson Wikström et al., 2015). In order to distinguish contributions of pollutants from the atmospheric deposition from those by the tested panels, triplicates of stainless steel (STS) were used as control material. Stainless steel was in previous work confirmed not to release detectable concentrations of the pollutants evaluated in this study to water (Andersson Wikström et al., 2015). All panels, including the control panels, were installed in a randomised order over the experimental site. The tested materials were new, as received from manufacturers, installed roughly six months before the start of sampling, and during this "warm-up" period were exposed to winter and spring weather conditions, including approximately 145 mm of precipitation in the form of snow and rain. The following material surface albedos were determined: BIF 0.09, COR 0.10, CST 0.08, CTZ 0.16, CU 0.09, GAL 0.31, PVCA 0.25, PVCB 0.21, SHI 0.05, ZN 0.18, STS 0.54. These values were calculated as the ratios of the reflected solar radiation to the incoming solar radiation, both of which were measured using a pyranometer (Kipp & Zonen CMP3, zero offset $<15\ \mathrm{W/m^2}$). The panels had stainless steel gutters with overlays preventing rainwater from entering directly into the gutters. Perfluoroalkoxy alkanes (PFA) bags of approximately 20 L volume were used to collect the panel runoff. Photographs of the experimental setup are provided in Supplementary information.

The surroundings of the experimental site (at LTU campus) consist of office and residential buildings, a small road and green areas. A satellite photo of the experimental site and surroundings can be found in Supplementary information. The City of Luleå is located in the northernmost part of Sweden at 65.62° N, 22.12° E and altitude 6 m above sea level. The town has a steel production plant and a district heating plant as potential sources of airborne pollutants, both of which are located about 7 km south-east from the experimental site. The most common prevailing wind direction in the region is southerly or south-westerly winds. Luleå has a subarctic climate and belongs to the Köppen climate classification code Dfc. Typical precipitation pH in this region ranges around 5 (EBAS, 2017). Precipitation and air temperature data were obtained from a weather station of the Swedish Meteorological and Hydrological Institute (SMHI) located approximately 9 km from the campus area.

2.2. Material composition screening

To expand the knowledge on the content of phthalates, nonylphenols, octylphenols and their ethoxylates in the studied materials, a substance screening was conducted on small material samples, one per each material. The purpose of the material composition screening was to facilitate the decision process of what substances to analyse for in runoff from each material by providing information on in which materials the substances were present and could be potentially released. Metal plates were excluded, as it was unlikely that these organic substances would be present. From CST the surface coating was scraped off using metal tools. SHI, BIF, PVCA and PVCB were cut into pieces, because it was impossible to separate the surface layer from the underlying layers. The material pieces and coating scrapings were sent to an accredited laboratory (ALS Scandinavia AB) for analysis. Phthalates were analysed using Gas chromatography–mass spectrometry (GC–MS) according to the method E DIN 19742 (2014-08). Nonylphenols, octylphenols and their ethoxylates were analysed using Liquid Chromatography - Tandem Mass Spectrometry (LC-MS-MS). The results from the material screening are presented in Table 1 together with the

Table 1
Test material content of selected phthalates, nonylphenols, octylphenols and their ethoxylates.

Substance concentration (mg/kg)	BIF	CST	PVCA	PVCB	SHI
Di-n-octyl phthalate (DNOP)	<10	<10	2700	*<2000*	<10
Di-(2-ethylhexyl)phthalate (DEHP)	<10	<10	770	*<100*	<10
Diisodecyl phthalate (DIDP)	*<150*	<10	*<30,000*	41,000	*<100*
diisononyl phthalate (DINP)	*<150*	<10	190,000	140,000	*<100*
Nonylphenol ethoxylates	<10	<10	<10	34	<10

*Substances that were below the reporting limits for all materials were excluded. The cases where elevated reporting limits were obtained instead of concentrations are presented in italics.

Table 3
Stormwater discharge guideline values (limits) and concentrations measured in stormwater in reference locations.

		Guideline value Gothenburg[a]	Sampling in Umeå, Sweden[b]	France, three towns[c]	Paris, France[d]
Substance (μg/L)	Cu	10	11–134	15–38	30–220
	Zn	30	54–538	126–240	154–520
	Ni	40	1.9–100	2.9–6.6	–
	Cr	15	3.1–252	2.0–6.2	<LOQ-45
	Cd	0.4	0.1–0.04	0.32	–
	Pb	14	1.8–23	22	<LOQ-129
	NPs	–	<0.1–3.8	0.4	0.3–9.2
	DEHP	–	<1.0–34	–	3.0–58
	DINP	–	<1.0–140	–	–
	DIDP	–	<1.0–11	–	–

[a] Guideline values for stormwater discharge quality in the Swedish City of Gothenburg (2013).
[b] Event mean concentration (EMC) ranges for areas with different land use. Unpublished data sampled by researchers at LTU.
[c] Means or ranges of means for different urban catchments in three towns in France (Gasperi et al., 2014).
[d] Concentration ranges for areas with different land use in Paris, France (Zgheib et al., 2011).

corresponding reporting limits. Reporting limits for the analyses presented below were <10 mg/kg for both phthalates and nonylphenol ethoxylates.

2.3. Sampling and analysis

The database analysed in this paper comprises panel-runoff from six rain events, of which characteristics are listed in Table 2. Even though events 5.1 and 5.2 represent parts of the same rain event, divided by an intermediate break, they were considered as two separate events for practical reasons (the PFA bags were close to full) and in order to enable a comparison between the early and late parts of a rain event.

The PFA bags for collecting runoff were attached to the stainless steel gutters some hours before the expected rain. The total runoff volume from the whole rain event was collected in one PFA bag per surface panel and treated as a single composite sample, producing EMCs (event mean concentrations). The collected runoff was transported to the laboratory within hours after the rain stopped. The collected volume was measured by weighing. Basic water quality parameters (pH, conductivity and total suspended solids (TSS)) were measured in The Environmental Laboratory of the Luleå University of Technology. Samples for analysis of dissolved metals were filtrated through a <0.45 μm membrane filter. All substance analyses were sent to an accredited laboratory (ALS Scandinavia AB). The accreditation certifies the laboratory compliance with international QA standards, confirmed both by an initial assessment and by recurrent audits. Laboratory blanks and controls/reference materials are prepared and analysed in parallel with the samples. Metals were analysed following SS EN ISO 17294-2: 2016 and EPA method 200.8: 1994 using inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). Samples intended for dissolved metal analysis were acidified using 1 mL 14 M HNO_3 (supra-pure) per 100 mL sample before analysis and samples for total metal analysis were extracted by autoclaving 12 mL sample with 1.2 mL 14 M HNO_3 (supra-pure). In order to correct for instrumental drift and matrix induced signal variations, indium internal standard was added to a concentration of 25 μg/L to every sample, blank, control and calibration standard prior to analysis. Nonylphenols, octylphenols and their ethoxylates were analysed based on ISO 18857-2. Acidified (pH 2 ± 0.2) and homogenised samples were loaded on styrene-divinylebenzene columns and extracted with dichloromethane. The extracts were derivatised with N-Methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) and analysed on gas chromatography (GC)-MS. Phthalates were analysed according to the method DIN EN ISO 18856. Samples were loaded on reversed phase C18 columns. The columns were dried with nitrogen and extracted using hexane. Analysis was carried out on GC–MS. Reporting limits for all runoff water analyses can be found in Tables 4 and 5 together with the results, and as a separate table in Supplementary information.

Total and dissolved metal concentrations were analysed in runoff from all materials. Six metals that are commonly reported in stormwater studies, namely cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), were included in this paper. More metals and major elements were analysed, but not presented here, because their concentrations were environmentally insignificant. Phthalates were analysed in samples of runoff from the PVC materials, and nonylphenols, octylphenols and -ethoxylates were analysed in runoff samples from PVCA, PVCB, BIF and SHI. All substances were analysed in the runoff from the control material (STS) and corresponding results are presented together with the results for the other materials. The selection of organic compounds to be analysed in runoff from each material was based on the results of an earlier laboratory leaching study (Andersson Wikström et al., 2015), the material screening described in Section 2.2, as well as a trial sampling at the pilot site with a simplified setup.

The sampling results were compared to guideline values from the second largest Swedish city (Gothenburg, 2019 population ~580,000), unpublished LTU data for stormwater from various land use areas, and two literature references (Table 3).

To evaluate which of the studied materials were relevant contributors of the studied pollutants to runoff, the pollutant event mean concentrations (EMC) in runoff from individual materials were compared to those of the control material (STS). The fractions of the total number of events for which the pollutant concentration in material panel runoff exceeded the corresponding STS concentration were tested for statistical significance using a two-sample *t*-test assuming unequal variance and $p < 0.1$. Pearson correlation analyses were performed in order to

Table 2
Characteristics of the six sampled events. Cumulative precipitation includes the total precipitation depth on the surfaces starting from the date of installation (Source: SMHI).

Event	Date	Precipitation (mm)	Rain duration (h)	Antecedent dry days, ADD	Average air temperature (°C)	Cumulative precipitation (mm)
1	12-6-2017	10.4	9	6	11	145
2	04-7-2017	5.6	7	5	15	194
3	26-10-2017	3.7	11	0 (23 h)	1.8	527
4	07-5-2018	6.3	5	2	5.2	848
5.1	27-6-2018	7.5	9	4	13	923
5.2	28-6-2018	8.4	10	0	10	931

evaluate correlations between the influential factors and the substance releases from the building materials.

3. Results and discussion

Concentrations of substances released in runoff from the six events sampled are presented in Tables 4 and 5. The total number of samples were 18 for individual materials (one sample per each material replicate and event), except for few exceptions listed in table footnotes. Average runoff pH was below neutral for all materials and varied between 6.0 and 6.4 for all materials. Dry atmospheric deposition may cause a slight increase in runoff pH (Göbel et al., 2007), which corresponds well with these measurements. Corresponding variations in electrical conductivity and TSS were 4.2–21 µS/cm and 14–49 mg/L, respectively. Basic water quality data for specific materials can be found in Supplementary information.

Table 4

Min, max and average total concentrations and standard deviation (SD) of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) for all the sampled events in µg/L. Average concentration of dissolved metals, expressed as percentage of average total metal concentration, is shown in the parentheses next to average total concentrations.

		Cd	Cr	Cu	Ni	Pb	Zn
BIF	Min	<0.05	<0.9	1.1	0.72	0.63	5.1
	Max	0.080	12	19	7.9	25	39
	Av.	0.028 (0.25)	3.3 (4.7)	7.0 (60)	2.5 (57)	6.7 (21)	17 (56)
	SD	0.013	3.2	5.3	2.0	6.2	9.6
COR	Min	<0.05	<0.9	1.1	11	1.3	7.8
	Max	0.067	10	11	43	54	23
	Av.	0.027 (0.2)	3.7 (1.6)	4.5 (34)	23 (82)	16 (28)	15 (49)
	SD	0.010	2.9	2.8	10	16	4.6
CST	Min	<0.05	<0.9	1.5	<0.6	0.65	73,0
	Max	<0.05	8.7	9.6	2.9	18,0	186
	Av.	n/a	2.9 (3.8)	3.9 (33)	1.2 (28)	6.3 (28)	109 (79)
	SD	n/a	2.5	2.2	0.74	4.6	37
CTZ	Min	<0.05	<0.9	<1	0.78	0.87	77
	Max	0.053	14	15	5.4	19	176
	Av.	0.028 (0.2)	5.6 (4.2)	6.4 (71)	1.9 (12)	6.4 (34)	110 (79)
	SD	0.0092	4.9	4.9	1.7	6.7	37
CU	Min	<0.05	<0.9	2400	<0.6	0.58	12
	Max	<0.05	6.2	4160	2.3	14	54
	Av.	n/a	2.0 (1.2)	3090 (93)	1.0 (30)	3.1 (19)	24 (76)
	SD	n/a	1.9	534	0.58	3.3	12
GAL	Min	<0.05	<0.9	2.1	0.76	0.98	2390
	Max	0.076	7.6	10	2.6	12	4490
	Av.	0.049 (1.4)	3.6 (19)	4.3 (25)	1.3 (20)	3.5 (10)	3530 (94)
	SD	0.019	2.4	2.6	0.66	3.1	690
PVCA	Min	<0.05	<0.9	1.9	<0.6	<0.5	7.0
	Max	<0.05	8.1	10	3.5	11	67
	Av.	n/a	2.4 (4.7)	3.8 (44)	1.1 (28)	2.1 (11)	27 (64)
	SD	n/a	2.3	2.7	0.78	2.5	19
PVCB	Min	<0.05	<0.9	1.1	0.62	<0.5	8.3
	Max	<0.05	10	9.0	2.4	9.5	104
	Av.	n/a	2.5 (3.5)	3.3 (46)	1.1 (35)	2.7 (25)	32 (68)
	SD	n/a	2.7	2.7	0.63	2.4	30
SHI	Min	<0.05	<0.9	2.2	2.9	0.64	9.4
	Max	0.33	4.4	37	40	16	104
	Av.	0.048 (0.5)	1.8 (10)	15 (76)	16 (84)	3.1 (28)	42 (89)
	SD	0.072	1.1	12	13	4.1	33
ZN	Min	<0.05	1.1	<1	0.64	0.52	5240
	Max	0.19	16	14	6.0	105	10,100
	Av.	0.093 (2.1)	2.8 (1.1)	3.4 (40)	1.1 (22)	10 (12)	7770 (95)
	SD	0.057	3.6	3.6	1.3	24	1406
STS (control)	Min	<0.05	0.92	<1	<0.6	<0.5	5.5
	Max	<0.05	12	10	2.6	7.7	40
	Av.	n/a	3.2 (11)	4.2 (57)	1.0 (32)	3.4 (20)	20.1 (68)
	SD	n/a	3.1	3.1	0.59	2.35	8.5

*In calculations of averages, values below reporting limits (RL) were assumed to equal 0.5 × RL. CTZ was installed later than the other materials and was only sampled starting from event 4 and onwards (9 samples). Total number of samples for BIF is 17, because one triplicate failed to generate runoff on one occasion.

**n/a = not applicable.

3.1. Metals

Table 4 displays metal concentrations for all events and for each of the studied building surface materials. The highest contribution of Zn to runoff was from ZN and GAL with average concentrations of 7770 µg/L and 3530 µg/L, respectively. These are even higher than the annual average concentrations reported by Robert-Sainte et al. (2009) for roof panels of new zinc (6064 µg/L) and galvanised steel (3081 µg/L) in Paris. Unsurprisingly, the CU was the largest contributor of Cu to runoff, with an average concentration of 3090 µg/L over the six events. This is in line with results from similar studies. For instance, Winters et al. (2015) reported a median concentration over 20 rain events of 1905 µg/L in runoff from a copper panel and Persson and Kucera (2001) reported a 12-month mean value of 3575 µg/L Cu from a copper surface in Stockholm. It is also worth noting that of the above-mentioned concentrations from this study, both Cu and Zn were > 90% dissolved and hence fairly mobile and bioavailable. The concentrations found in this study were considerably higher than those measured in stormwater from different catchments and would need to be diluted >100 times in order to comply with the guideline values from Gothenburg (Table 3). The release of metals from the coated metal sheets CST and CTZ was low, likely as a result of the surface coatings. Similar observations were made on release of metals from coated galvanised steel (Robert-Sainte et al., 2009).

As the concentrations of Cr, Cu and Ni displayed small variations among different materials and small deviations from the control material, except for the release of Cu from CU and Ni from COR and SHI, the atmospheric deposition appeared to be the main source of these three metals. COR produced the highest average release of Pb, but displayed a large range between the minimum and maximum concentrations for all the materials, making presumptions about the origins of Pb difficult. Concerning Cd, the concentrations were close to the reporting limit for all the materials and, therefore, neither the materials nor the atmospheric deposition conditions studied seemed to contribute Cd to surface runoff.

3.2. Organic substances

As can be inferred from Table 5, PVCA and PVCB released high concentrations of diisononyl phthalate (DINP), with average of 365 and 455 µg/L respectively. To the best of authors' knowledge, no similar studies exist for comparison. However, concentrations measured in this study were considerably higher than reported for stormwater in Umeå; Table 3 (unpublished data). PVCA also released DEHP, a priority substance according to the EU directive on priority substances (Directive 2013/39/EU, 2013). DINP is today the most commonly used phthalate and substitute for DEHP (Swedish Chemical Agency, 2015). Recent research suggested adverse effects on aquatic organisms after exposure to DINP (Forner-Piquer et al., 2017). In their study, female zebrafish were exposed to three different concentrations of DINP via water for three weeks and the negative effects could be seen already at the lowest concentration (0.42 µg/L).

Nonylphenols (NPs) were detected in runoff from all of the studied materials, except for the stainless steel control (STS), indicating that, at the study location, NPs were derived from the materials and not from atmospheric deposition. Concentrations of NPs in runoff from PVCB (average 26 µg/L) were higher than the concentrations presented in Table 3. Bressy et al. (2011) measured NPs in runoff from a building

Table 5
Min, max, average total concentrations and standard deviation (SD) of Di-n-octyl phthalate (DNOP), Di-(2-ethylhexyl)phthalate (DEHP), Diisodecyl phthalate (DIDP), diisononyl phthalate (DINP), 4-tert-octylphenol triethoxylate (OP-3E), 4-nonylphenols (tech. mixture)(NP), 4-nonylphenol monoethoxylate, diethoxylate and triethoxylate (NP-1E, NP-2E, NP-3E) for all the sampled events in μg/L.

		DNOP	DEHP	DIDP	DINP	OP-3E	NP	NP-1E	NP-2E	NP-3E
BIF	Min					<0.01	0.21	<0.1	<0.1	<0.1
	Max					<0.01	3.5	0.080	0.55	0.25
	Av.					n/a	0.99	0.062	0.15	0.11
	SD					n/a	1.2	0.018	0.14	0.072
PVCA	Min	<1	<1	1.8	91	<0.01	<0.1	<0.1	<0.1	<0.1
	Max	*<14*	4.0	*<40*	1200	0.38	0.61	0.21	0.18	0.21
	Av.	1.7	1.0	12	365	0.079	0.23	0.075	0.085	0.071
	SD	1.6	0.93	7.1	257	0.11	0.17	0.045	0.039	0.042
PVCB	Min	<1	<1	23	75	<0.01	13	<0.1	<0.1	0.12
	Max	*<19*	<1	100	2100	0.25	42	0.20	0.35	1.9
	Av.	2.0	n/a	54	455	0.028	26	0.084	0.18	0.76
	SD	2.1	n/a	25	517	0.056	9.3	0.043	0.093	0.60
SHI	Min					<0.01	<0.1	<0.1	<0.1	<0.1
	Max					<0.01	0.40	0.16	0.85	0.70
	Av.					n/a	0.15	0.078	0.16	0.16
	SD					n/a	0.14	0.039	0.19	0.19
STS (control)	Min	<1	<1	<1	<1	<0.01	<0.1	<0.1	<0.1	<0.1
	Max	<1	<1	<1	<1	<0.01	<0.1	<0.1	<0.1	<0.1
	Av.	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	SD	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

*In calculations of averages, values below reporting limits (RL) were assumed to equal 0.5 × RL. Substances that were below reporting limits for all materials have been excluded. Cases with elevated reporting limits are presented in italics. Total number of samples is 16 for all phthalate analyses as the triplicates were combined to a composite sample at the first event. Total number of samples for BIF is 17, because one triplicate failed to generate runoff on one occasion.
**n/a = not applicable.

catchment (including tile, zinc and flat roofs and a green space) and reported a median of 0.56 μg/L but with relatively high variability (0.15–0.75 μg/L as 1st and 9th deciles). They also reported that NP concentrations were significantly higher in building runoff compared to bulk atmospheric deposition and thus concluded that NPs were derived from building structures.

3.3. Materials and substances of concern

Table 6 presents the fractions of the total number of events for which the pollutant EMC in material panel runoff exceeded the corresponding STS EMC with a significant margin ($p < 0.1$). Shaded cells indicate the cases for which the pollutant EMC were at least ten times greater than those of STS for two events or more, and this somewhat arbitrary condition was considered to denote important sources of each substance. Exceedances for one event only were disregarded. The information provided in Table 6 can be used for environmentally responsible applications of the existing building materials and the development of new ones, as well as the investigations and risk assessment of specific pollutants in urban stormwater.

Apart from CU, BIF and SHI were probable contributors of Cu. CST and CTZ were probable contributors of Zn apart from the obvious

Table 6
Evaluation of substances released from each material and fraction of samples exceeding the control material (STS) average concentrations.

		Material									
		BIF	**CST**	**CTZ***	**COR**	**CU**	**GAL**	**PVCA**	**PVCB**	**SHI**	**ZN**
Substance	**Cd**						0.33				0.67
	Cr										
	Cu	0.67				1.0				0.67	
	Ni	0.50			1.0					0.83	
	Pb	0.33									
	Zn	0.33	1.0	1.0*			1.0	0.50	0.50	0.50	1.0
	NPs	0.83	n/a	n/a	n/a	n/a	n/a	0.83	1.0		n/a
	NP-1E		n/a	n/a	n/a	n/a	n/a		0.50	0.33	n/a
	NP-2E	0.33	n/a	n/a	n/a	n/a	n/a	0.50	0.83		n/a
	NP-3E		n/a	n/a	n/a	n/a	n/a		1.0		n/a
	DNOP	n/a	n/a	n/a	n/a	n/a	n/a	0.50	0.50	n/a	n/a
	DEHP	n/a	n/a	n/a	n/a	n/a	n/a			n/a	n/a
	DIDP	n/a	n/a	n/a	n/a	n/a	n/a	1.0**	1.0**	n/a	n/a
	DINP	n/a	n/a	n/a	n/a	n/a	n/a	1.0**	1.0**	n/a	n/a

Exceedance in only one event was disregarded. Shaded cells indicate concentrations exceeding STS concentrations at least ten times in two or more events. Concentrations below the reporting limits were assumed to equal 0.5× the reporting limits. n/a = not applicable.
*Data for CTZ were available only for three rain events.
**Data for only five events were available for statistical calculations (see the text below for full description).

sources in GAL and ZN. Concerning Ni, COR and SHI were important contributors. COR had the highest average release of Pb among the studied materials (Table 4), but because of large variations among the event samples, the differences from STS-means were not statistically significant. None of the studied materials was identified as a relevant contributor of Cr. In some events, Cd concentrations in runoff from GAL and ZN were significantly higher than from STS. However, the concentrations were of the same order of magnitude as for other materials and close to the reporting limit (Table 4). Furthermore, none of the materials released Cd in concentrations comparable to those listed in Table 3. Therefore, Cd was not considered a substance of critical concern in the studied materials.

PVCB was identified as the largest contributor of organic substances, with respect to both mass loads and the total number of substances. For event 1, composite samples for phthalate analysis were prepared from the triplicates and, therefore, concentrations could not be assessed statistically. However, as the DIDP and DINP concentrations were greater than an order of magnitude, for both PVCA and PVCB, compared to STS, such differences were still considered significant. Furthermore, BIF was an important source to NPs.

3.4. Variations in runoff concentrations between events

Inter-event variations in runoff concentrations were observed for the majority of the studied materials, as evident in Fig. 1, showing concentrations of selected substances in runoff from selected materials for the events sampled. The largest variations were noted for soft, flexible materials (i.e. SHI, BIF, PVCA and PVCB), while hard metal sheets (i.e. CU, ZN, GALV, COR, CTZ, CST, STS) displayed smaller variations. Concerning the Cu release from SHI, high concentrations were released in event 1 and were followed by a decrease in concentrations. In event 3, concentrations were in the same order of magnitude as STS, and finally, in events 4, 5.1 and 5.2, the concentrations were again higher. The high release in event 1 could be attributed to a wash-off of Cu from the new material, which is in agreement with the findings of Winters et al. (2015). In their study, metal runoff from roofing materials in pilot scale experiments in the state of Washington indicated significantly lower releases of Cu from asphalt shingles in the second round of sampling, compared to the first round. However, the sampling rounds were conducted during different seasons (February–April and October–January) and other climatic factors (e.g. air temperature, and atmospheric deposition) may have affected the differences in data. The release pattern of Cu from SHI was similar to that of other substances as well as to the release pattern of substances from BIF, which is a similar material. The release of NPs from PVCB also followed a similar pattern, but with higher concentrations for event 2 than event 1, and showed no clear decreasing trend or first wash-off from the material when it was newest.

Air temperature, within a relatively low range of temperatures encountered in this study (Table 2), seemed to correlate with the releases of substances from these softer and flexible materials, with higher release during events with higher air temperature and vice versa. Daytime air temperatures prior to events 1, 2 and 5.1 were up to 20 °C and with solar radiation could potentially have warmed up the surfaces before the start of the rain. It is also likely that differences in albedo among these materials will affect the heat absorption and the albedo of SHI and BIF were among the lowest out of the tested materials. Interestingly, metals and organic substances showed similar release patterns for these materials, indicating that the release was associated with material characteristics rather than substance properties. This release process may be caused by the softening of the materials at higher temperatures, which make them more prone to release substances (e.g., by material expansion). Conversely, low temperatures reduce the material softness and hence the release of substances. Some organic substances are known to be affected by temperature changes; e.g. Manzano et al. (1999) found a correlation between the increased temperature and biodegradation of nonylphenol ethoxhylates in water, and increased temperature was suggested to facilitate conversion of nonylphenol ethoxylates to nonylphenols (Isobe et al., 2001).

The release of DINP from PVCA was clearly highest in event 1, indicating a wash-off of phthalates from newer material. As earlier stated, the materials had been exposed to weather conditions, including precipitation, before the sampling of event 1, which complicates such inferences. However, no tested correlations were found that supported this high release in event 1 and the occurrence of a first wash off during the materials' earliest period of exposure to the weather cannot be excluded. Furthermore, the release in the subsequent events was still considered high and showed no clearly decreasing trend over time. The release of DINP from PVCB showed similar patterns and its corresponding figure can be found in Supplementary information. Phthalates are not chemically bound to the PVC polymers and, therefore, can be released throughout the material's lifetime (Clausen et al., 2012). For event 1, a composite sample for phthalate analysis was prepared from the triplicates, and therefore standard deviation could not be

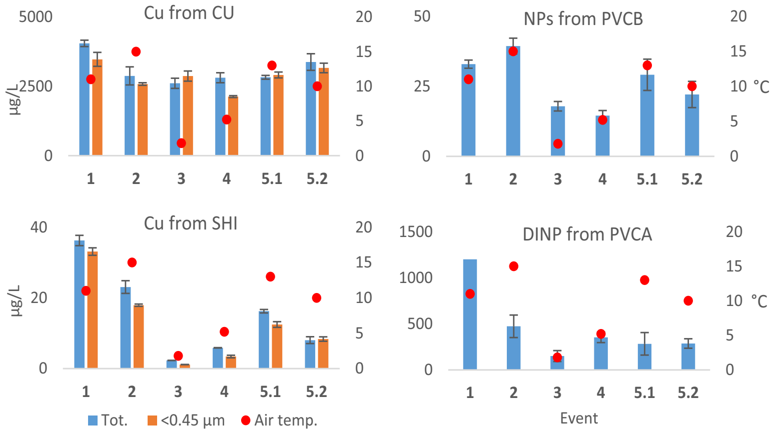

Fig. 1. Releases of dissolved and total Cu from copper sheets (CU) and shingles (SHI), total NPs from PVCB and total DINP from PVCA in individual events. Error bars represent standard deviations among the material triplicates. For event 1, composite samples for phthalate analysis were prepared by combining the triplicate samples and, therefore, no standard deviation is available for DINP in event 1. Event-average air temperature (red dots) on secondary axis.

determined. The release of DINP did not show a clear correlation to air temperature, but the releases from both PVCA and PVCB was clearly lower in event 3, when air temperature was close to 0 °C (Table 2). Emissions of the phthalate DEHP was earlier proved to increase significantly with increasing temperature, in a study on emissions of DEHP from PVC flooring in a laboratory study (Clausen et al., 2012).

The release of Cu from CU in the upper left corner of Fig. 1 shows that the highest concentrations were released in event 1. However, no clear decreasing trend could be detected during the 12 months of sampling. Robert-Sainte et al. (2009) reported higher Cu release from old copper (approximately 25 years) than new and hypothesised that it was due to higher presence of soluble corrosion products on the old copper sheet. A similar reasoning was offered by Clark et al. (2008), who performed laboratory leaching experiments with pristine and aged (60+ years) galvanised metals and concluded that pollutant release may occur over long time periods. In our study, no decrease in Cu concentrations in the runoff from CU was noted between event 5.1 and 5.2, indicating that if there is a first flush behaviour, earlier suggested by e.g. Wicke et al. (2014) and He et al. (2001), it was not of great importance with respect to the released Cu concentrations over longer rain durations. Other metal sheets, e.g. ZN, GAL and CST, showed similar release patterns of their corresponding metals of concern, as can be found in Supplementary information.

3.5. Influential factors

The correlations between the substance release and event-average rainfall intensity, air temperature, ADD as well as TSS, were analysed for individual materials and the substances which they released (Table 6) using Pearson correlation analyses. Results of the Pearson correlation analysis are presented in Table 7. A significance level of $p < 0.1$ was used in all cases; insignificant correlations were excluded for brevity. No correlations were found with event-average rainfall intensity. The only significant correlations with air temperature are the Cu release from SHI (excluding event 1) and NP release from PVCB. This is in agreement with the hypothesis formulated earlier in Section 3.4. It is likely that a larger temperature range would have increased the number of statistically significant correlations. More statistically significant correlations were found with ADD and TSS. It is plausible that the correlations for SHI and BIF are partly caused by the rough surface of these materials, which creates protected spaces for accumulation of substances originating from both atmospheric deposition and material surface degradation. Considering atmospheric transport of pollutants, materials with a rough surface, such as SHI and BIF, have a thicker boundary layer facilitating more effective entrapment of atmospheric deposition particles than smooth materials like STS. SHI, BIF and STS were the only materials that had a positive correlation between Cu and Ni concentrations and TSS, indicating that these metals originated from the atmosphere as hypothesised earlier in Section 3.1. Dislodging of trapped particles from SHI and BIF would require higher rainfall intensities compared to STS with a smooth surface. Egodawatta et al. (2009) studied build-up and wash-off of pollutants from model roofs of corrugated steel and concrete tiles, and found that fine particles could remain on roof surfaces during smaller rainfall intensities. Thus, a series of low intensity rainfalls may allow particles to accumulate on rough surfaces, such as those of SHI and BIF, while smooth surfaces are washed off. Yaziz et al. (1989) described this phenomenon and reported that the rainfall intensity played a major role in the “cleaning” process. Wind would also play an important role in the removal of deposited particles (Quek and Förster, 1993), and would likely remove more particles from a smooth surface than from a rough surface. The surfaces of the PVCA sheets are smooth, PVCB surfaces are only vaguely textured, and were therefore assumed to have similar capacities to collect atmospheric deposition as STS. Therefore, combined with high concentrations and absence of correlations with TSS, the correlations between DINP release and ADD were not likely to be due to atmospheric deposition. Instead, it is hypothesised that the correlation with ADD was caused by material degradation, causing DINP migration to the material surface and possible adsorption to dust particles, and finally wash off with runoff. Emissions of the phthalate DEHP from PVC flooring to air in a field and laboratory emission cell was shown by Clausen et al. (2004) to increase with time and dust was an effective adsorbent. The dust uptake of DEHP also showed increasing concentrations with time.

Table 7
R-values for significant ($p < 0.1$) Pearson correlations between substance release and influential factors, with *p*-values in brackets.

	Air temperature	ADD	TSS[a]
Cu from SHI (all events)	–	0.91 (0.01)	–
Cu from SHI (event 2–5.2)	0.93 (0.02)	0.87 (0.05)	0.89 (0.04)
Cu from BIF	–	0.88 (0.02)	0.82 (0.09)
Cu from STS	–	–	0.84 (0.08)
Zn from SHI	–	0.82 (0.05)	–
Zn from PVCA	–	0.82 (0.05)	–
Zn from PVCB	–	0.77 (0.08)	–
Zn from GAL	–	–	−0.91 (0.03)
Cd from ZN	–	0.83 (0.04)	–
Ni from SHI	–	0.89 (0.02)	0.81 (0.1)
Ni from BIF	–	0.94 (0.01)	0.84 (0.07)
Ni from STS	–	–	0.93 (0.02)
NP from PVCA	–	0.80 (0.05)	–
NP from PVCB	0.86 (0.03)	0.80 (0.05)	–
NP from BIF	–	0.81 (0.05)	0.87 (0.05)
DINP from PVCA	–	0.74 (0.09)	–
DINP from PVCB	–	0.77 (0.08)	–

[a] TSS was measured starting from event 2, and, thus, correlations were made with data from event 2–5.2.

The metal sheets and the release of the corresponding metals of concern (Cu or Zn) did not show any correlation to ADD. A correlation was found between Cd concentration in runoff from ZN and ADD, and a negative correlation between TSS and Zn release from GAL was found.

The absence of statistically significant correlations between substance releases and influential factors points to a somewhat obvious fact that in the natural environment, no single factor can control the release of a substance. The complexity of processes affecting the release in a natural environment is governed by many factors, which conjunctively affect such releases, and isolation of single factors would require an extensive body of sampling data for robust statistical tests. The results of this study also imply that different types of materials are affected by different influential factors. One factor that may affect the release of certain substances from one material does not necessarily affect the release of the same substances from another material – or of other substances from the same material. Winters et al. (2015) performed pairwise correlations between metal concentrations from roof surfaces and climatic factors and found an inverse correlation between the metal concentration and rain intensity. Such findings agree with findings of laboratory rain simulations on new and aged panels of copper and zinc performed by He et al. (2001), who reported that rain intensity had exerted a clear effect on metal releases, especially the first flush concentrations. They also concluded that the inter-event time had significant effects on the released metal quantities. In contrast, Winters et al. (2015) did not report a significant correlation with ADD, further highlighting the difficulties with identifying important influential factors in a complex, natural environment. Finally, the study reported here was based on a set of rain events with a relatively limited range of characteristics (see Table 2) and this would limit the likelihood of discerning influential variables from such data.

4. Conclusions

For the current climate and atmospheric deposition conditions in the study area, this study shows that several of the studied building surface materials are environmentally relevant contributors of the studied substances to stormwater runoff. Specifically, metal sheets of copper, zinc and galvanised steel released high concentrations of dissolved Cu and Zn. High concentrations of NPs and DINP (not studied previously) were released from the two types of PVC roofing. Factors affecting the release of substances in a natural environment appear to be mutually related, while the material characteristics govern processes of release and entrapment of substances. The release of both organic and inorganic substances from soft and flexible materials (i.e. SHI, BIF, PVCA and PVCB) seemed to increase with increasing temperature, but such a trend was not found in the case of metal sheets (i.e. CU, ZN, GALV, COR, CTZ, CST, STS).

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Building surface materials as sources of micropollutants in building runoff: A pilot study

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Supplementary material 1
Basic parameters measured in runoff from all studied materials

Table S1 Minimum, maximum and average pH, conductivity and total suspended solids (TSS) for all events

	pH			**Conductivity (µS/cm)**			**TSS (mg/L)**		
	Min	**Average**	**Max**	**Min**	**Average**	**Max**	**Min**	**Average**	**Max**
BIF	6.0	6.4	6.7	6.4	19	53	<2	22	59
CST	5.5	6.2	6.7	2.7	7.3	13	<2	27	86
CTZ	5.8	6.1	6.4	2.7	4.2	5.1	<2	49	160
COR	5.3	6.0	6.7	3.7	6.4	12	<2	26	80
CU	5.5	6.0	6.4	6.3	9.7	15	<2	20	100
GAL	6.0	6.3	6.7	7.9	12	17	<2	21	82
PVCA	5.7	6.2	6.5	2.9	8.2	16	<2	20	58
PVCB	6.0	6.3	6.5	3.4	8.6	16	<2	15	67
SHI	5.9	6.3	6.5	7.4	19	41	2.2	14	34
STS	5.3	6.1	7.4	3.1	6.5	11	<2	23	130
ZN	6.0	6.3	6.7	13	21	30	<2	17	110

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Supplementary material 2
Event concentrations of substances in runoff from all studied materials

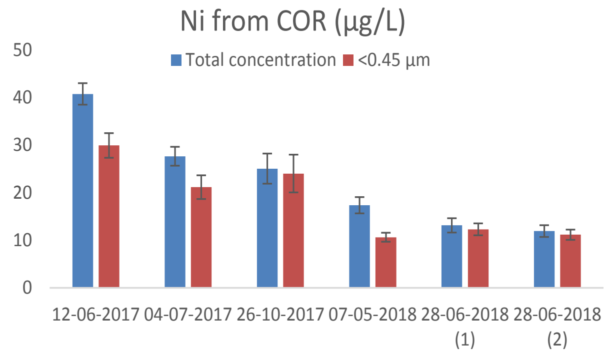

Figure S1 Event concentrations of Ni in runoff from COR

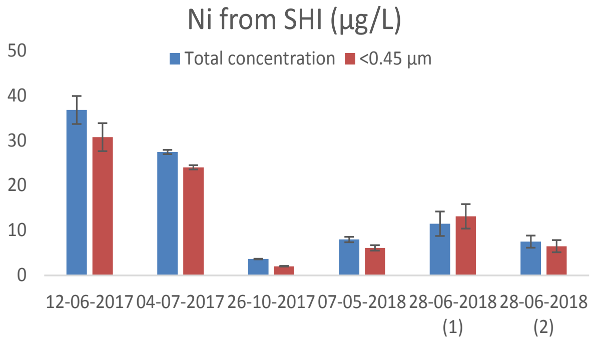

Figure S2 Event concentrations of Ni in runoff from SHI

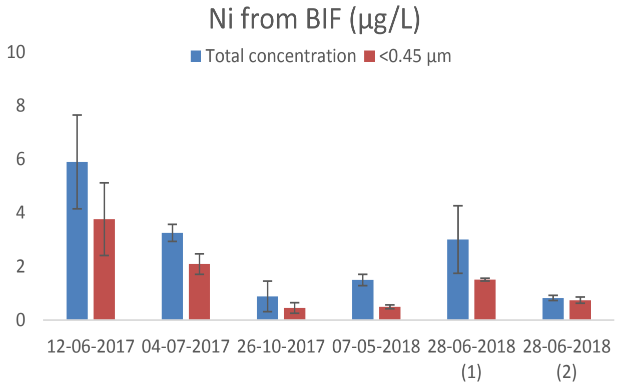

Figure S3 Event concentrations of Ni in runoff from BIF

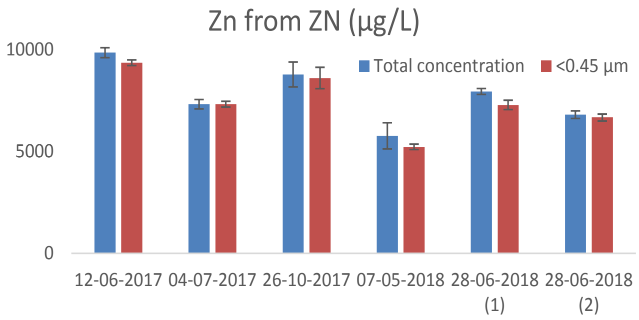

Figure S4 Event concentrations of Zn in runoff from ZN

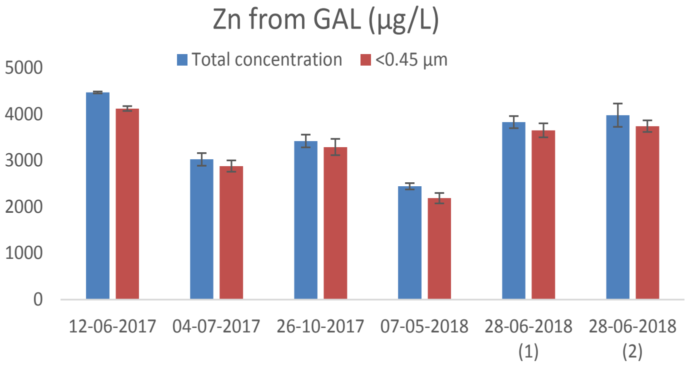

Figure S5 Event concentrations of Zn in runoff from GAL

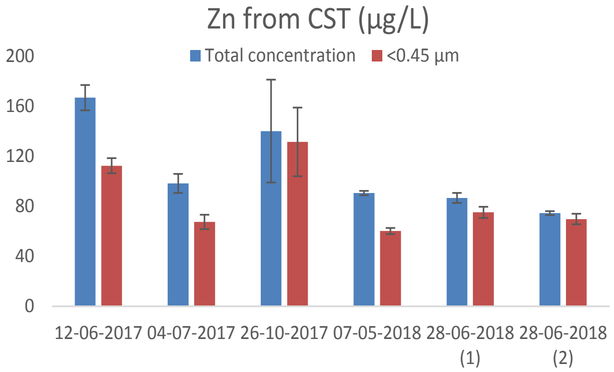

Figure S6 Event concentrations of Zn in runoff from CST

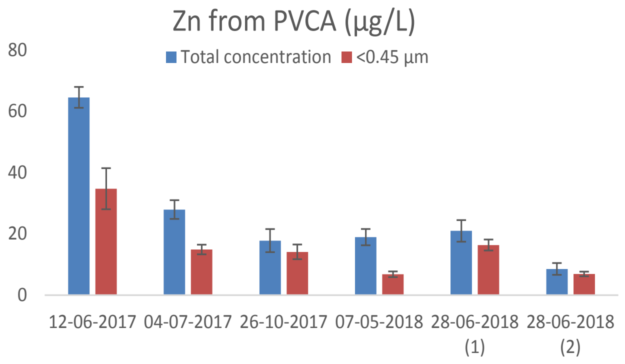

Figure S7 Event concentrations of Zn in runoff from PVCA

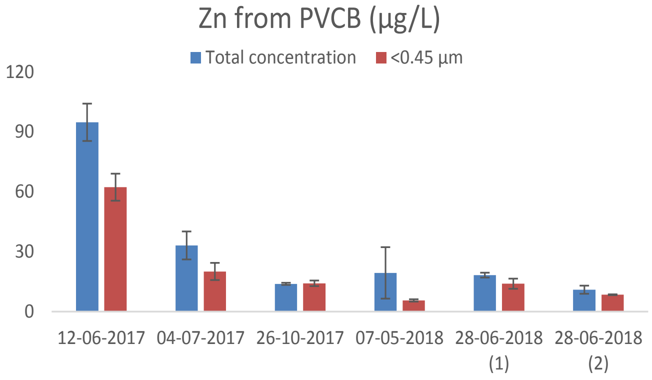

Figure S8 Event concentrations of Zn in runoff from PVCB

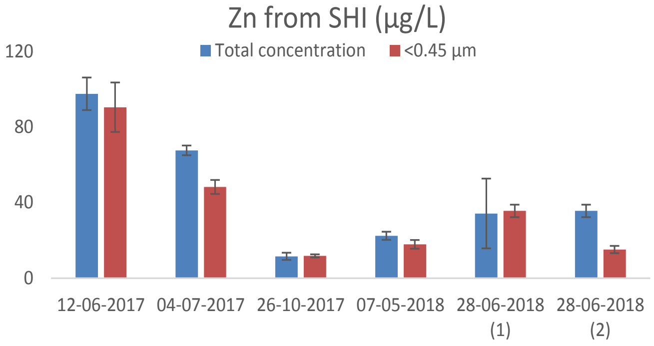

Figure S9 Event concentrations of Zn in runoff from SHI

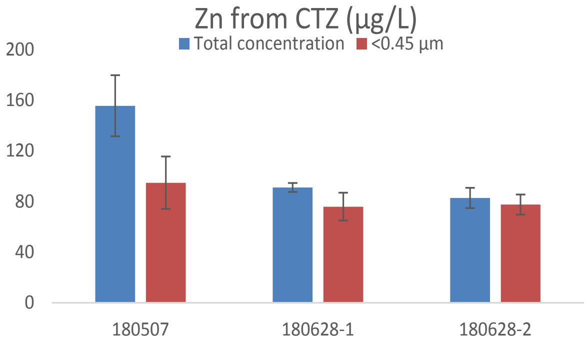

Figure S10 Event concentrations of Zn in runoff from CTZ

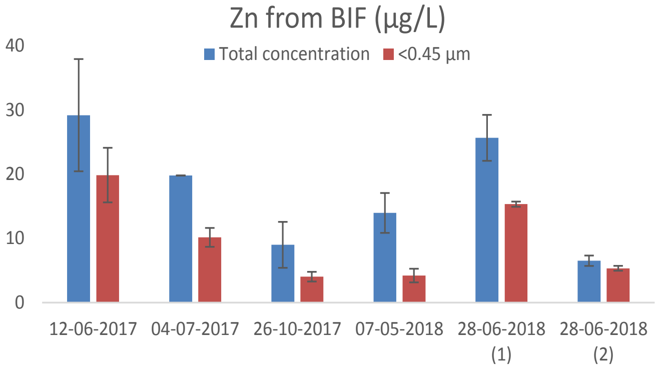

Figure S11 Event concentrations of Zn in runoff from BIF

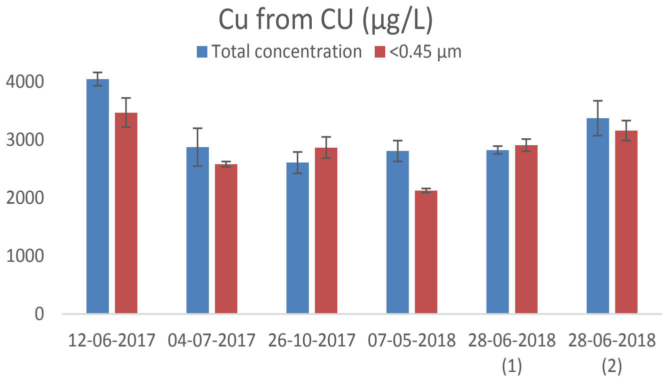

Figure S12 Event concentrations of Cu in runoff from CU

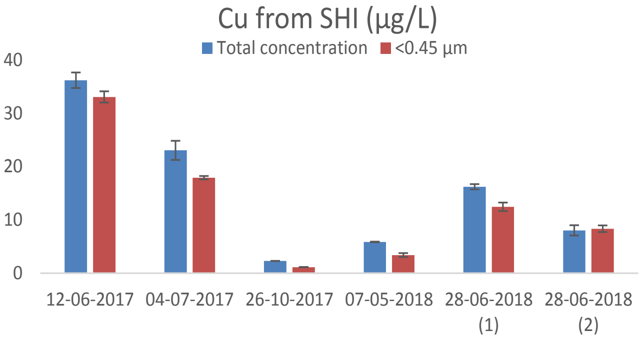

Figure S13 Event concentrations of Cu in runoff from SHI

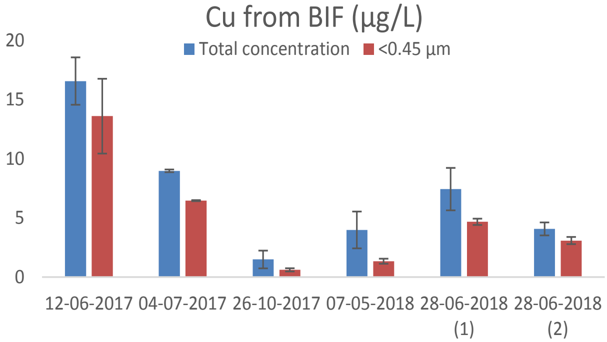

Figure S14 Event concentrations of Cu in runoff from BIF

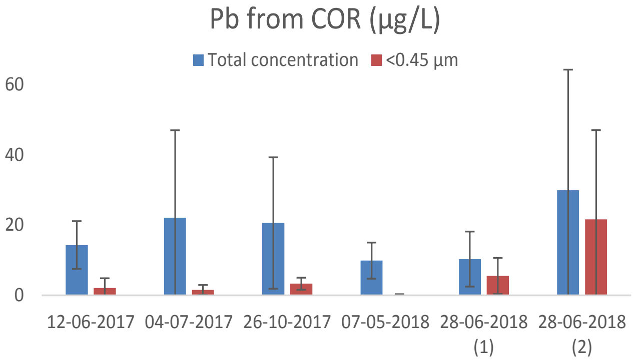

Figure S15 Event concentrations of Pb in runoff from COR

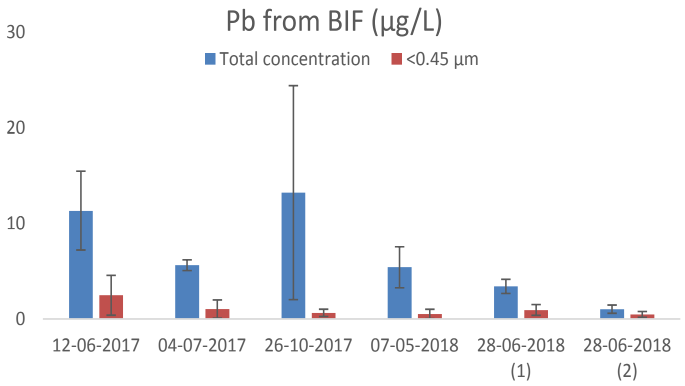

Figure S16 Event concentrations of Pb in runoff from BIF

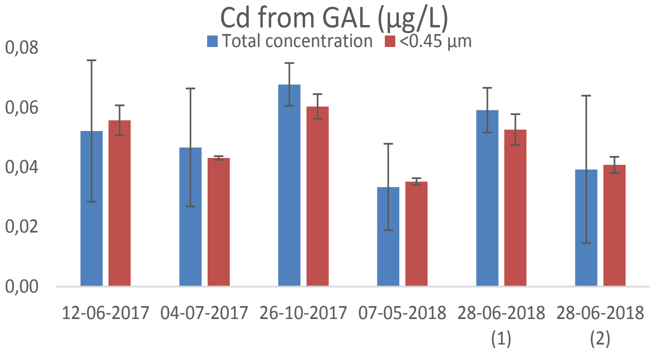

Figure S17 Event concentrations of Cd in runoff from GAL

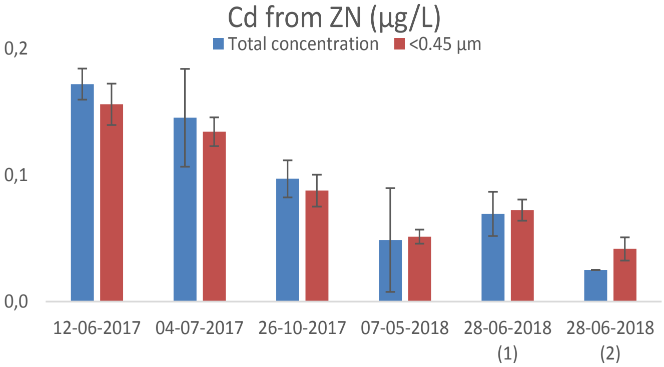

Figure S18 Event concentrations of Cd in runoff from ZN

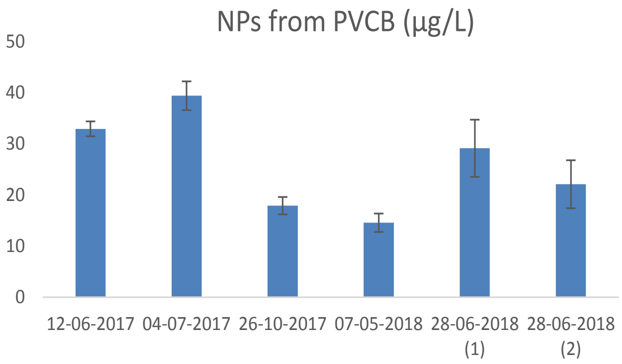

Figure S19 Event concentrations of NPs in runoff from PVCB

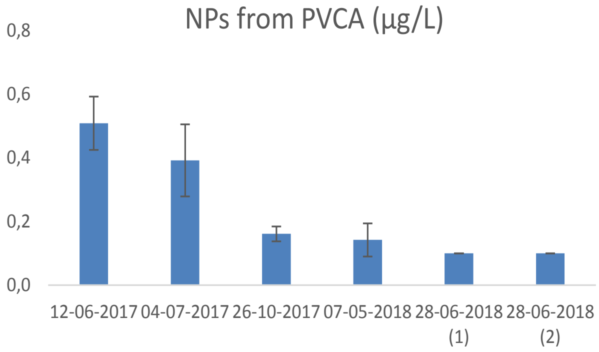

Figure S20 Event concentrations of NPs in runoff from PVCA

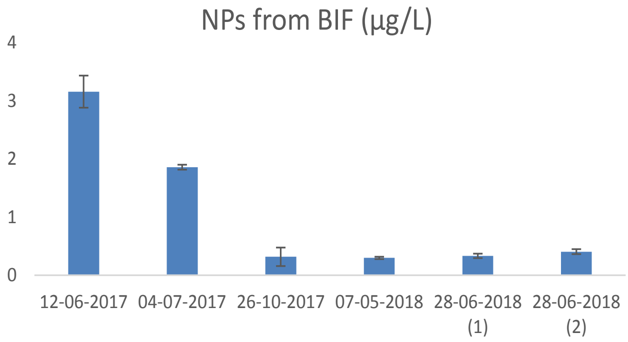

Figure S21 Event concentrations of NPs in runoff from BIF

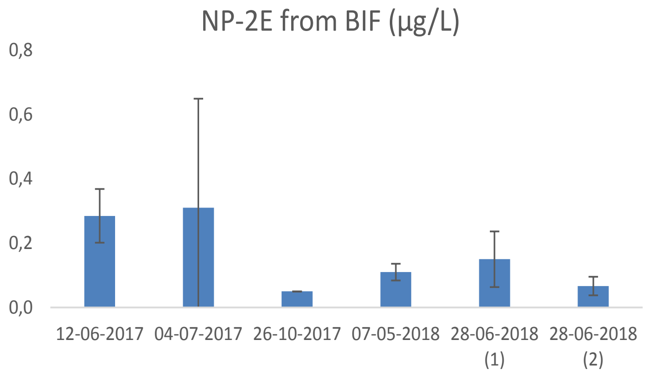

Figure S22 Event concentrations of NP-2E in runoff from BIF

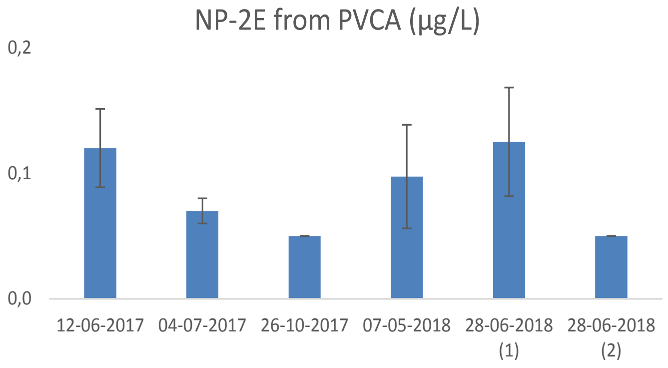

Figure S23 Event concentrations of NP-2E in runoff from PVCA

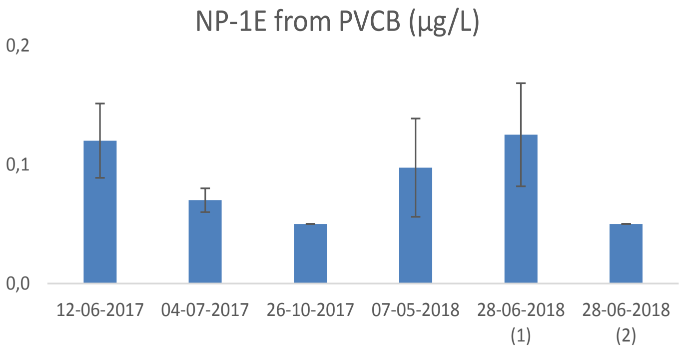

Figure S24 Event concentrations of NP-1E in runoff from PVCB

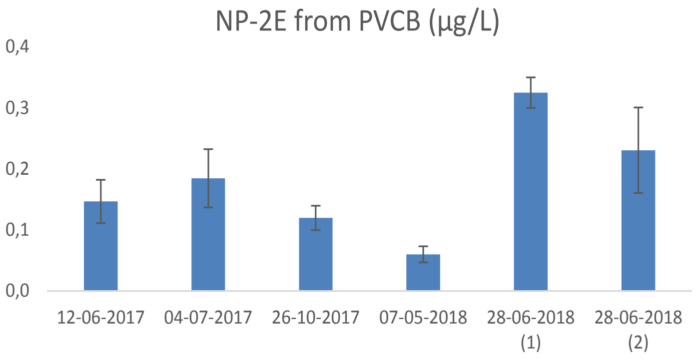

Figure S25 Event concentrations of NP-2E in runoff from PVCB

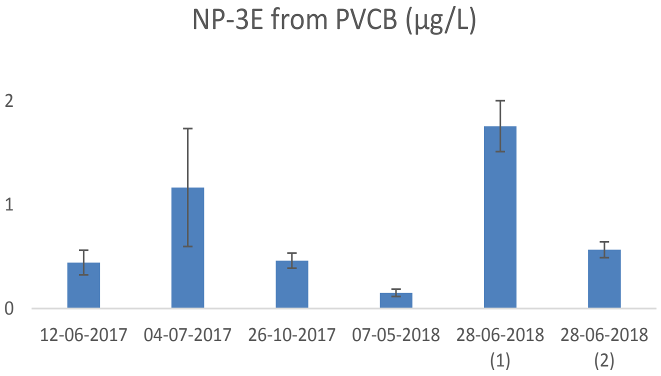

Figure S26 Event concentrations of NP-3E in runoff from PVCB

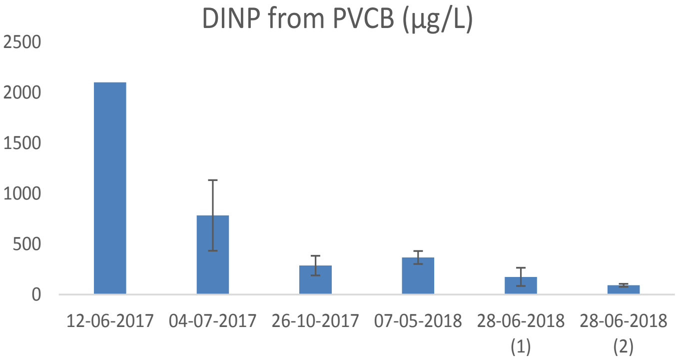

Figure S27 Event concentrations of DINP in runoff from PVCB

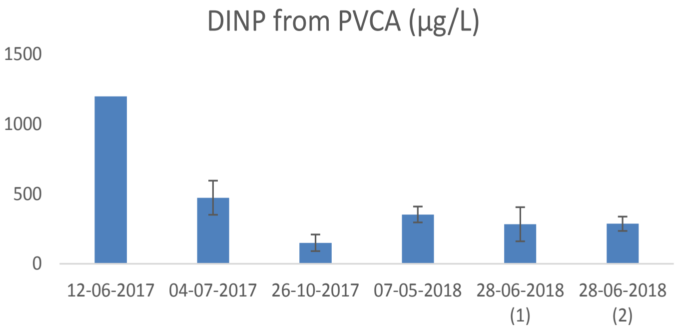

Figure S28 Event concentrations of DINP in runoff from PVCA

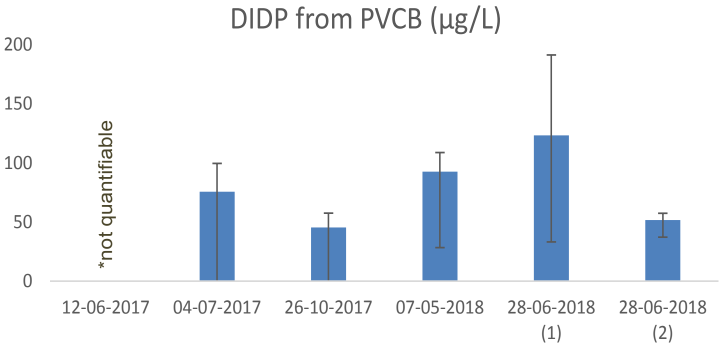

Figure S29 Event concentrations of DIDP in runoff from PVCB

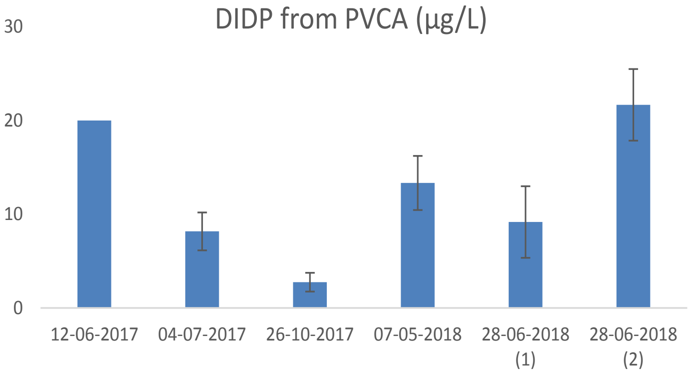

Figure S30 Event concentrations of DIDP in runoff from PVCA

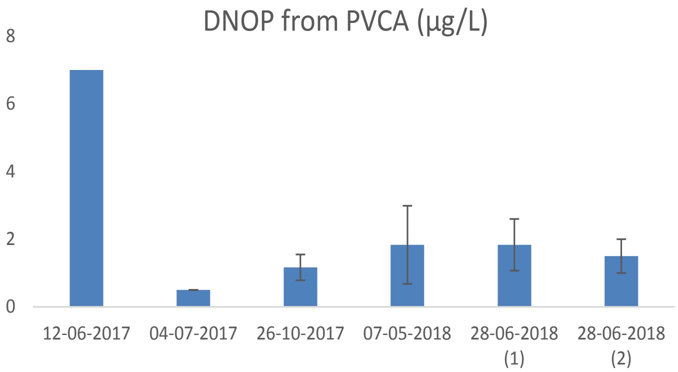

Figure S31 Event concentrations of DNOP in runoff from PVCA

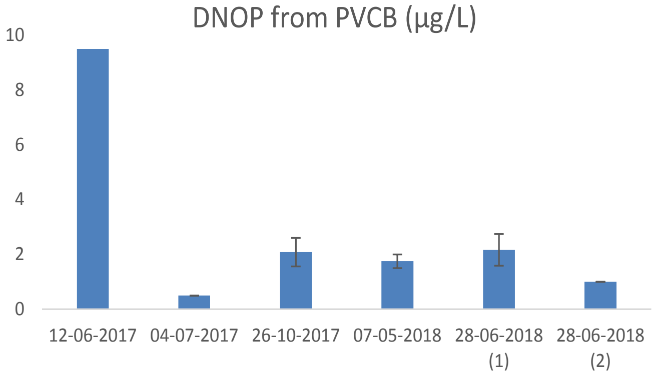

Figure S32 Event concentrations of DNOP in runoff from PVCB

Building surface materials as sources of micropollutants in building runoff: A pilot study

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Supplementary material 3

Experimental site and sampling setup – photos and maps

Figure S1 Satellite photo showing location of the experimental site (marked in red) and surroundings consisting of buildings (LTU campus and residential), a small road, parking spaces and green areas. Retrieved from https://kartor.eniro.se/m/jkg7L

Figure S2 Experimental site and pilot surfaces showing randomised placement of different materials

Figure S3 Sampling setup with stainless steel gutters for runoff collection and overlays for prevention of rainwater entry. Plastic buckets were used to stabilise the PFA bags used for sample collection.

Figure S4 Sampling setup and attachment of PFA bags for sample collection to the stainless steel gutters. PFA bags were placed in plastic buckets for stability.

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Supplementary material 4
Reporting limits for substances analysed in runoff

Table S1 Reporting limits (RL) for the analysed metals (total and dissolved): cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) as well as organic substances (total): Di-n-octyl phthalate (DNOP), Di-(2-ethylhexyl)phthalate (DEHP), Diisodecyl phthalate (DIDP), Diisononyl phthalate (DINP), 4-tert-octylphenol triethoxylate (OP-3E), 4-nonylphenols (tech. mixture)(NP), 4-nonylphenol monoethoxylate, diethoxylate and triethoxylate (NP-1E, NP-2E, NP-3E).

Substance	RL, total (µg/L)	RL, dissolved (µg/L)
Cd	0.05	0.002
Cr	0.9	0.01
Cu	1	0.1
Ni	0.6	0.05
Pb	0.5	0.01
Zn	4	0.2
DNOP, DEHP, DIDP, DINP	1	n/a
OP-3E	0.01	n/a
NP,NP-1E, NP-2E, NP-3E	0.1	n/a

*n/a= not applicable

Paper IV

Alexandra Müller, Heléne Österlund, Kerstin Nordqvist, Jiri Marsalek, Maria Viklander

Releases of micropollutants from building surface materials into rainwater and snowmelt induced runoff

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Releases of micropollutants from building surface materials into rainwater and snowmelt induced runoff

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Abstract

Building surface materials, exposed to wash-off by rainwater or snowmelt, are recognised as one of the significant urban diffuse pollution sources contributing to the impairment of stormwater quality. The resulting stormwater runoff, which is often discharged untreated to receiving waters, may cause adverse effects on aquatic organisms. The pollution conveyed by roof runoff originates from two potential sources, migration of surface material constituents, or from wash-off of pollutants deposited on the building surface by atmospheric deposition. The present study investigated the releases of Cu and Zn, as well as of several groups of contaminants of emerging concern: alkylphenols, alkylphenol ethoxylates, and phthalates, from commercially available materials, which are commonly used on building envelopes and structure surfaces in the urban environment. The materials tested included the following: metal sheets of stainless steel, copper, zinc, galvanised steel, Corten steel, corrugated and coated steel, coated zinc; and roofing membranes of bitumen felt and bitumen shingles, as well as polyvinyl chloride (PVC) from two manufacturers. The stainless steel was considered a control material serving to estimate pollutant contributions deposited on the pilot panels from the surrounding environment. Moreover, this study presents novel data on roof snowmelt runoff quality, not reported in the previous literature. The experimental setup consisted of 2-m^2 rectangular panels mounted in three replicates of each material and placed in an open-air setting on the campus of Luleå University of Technology, Sweden. Runoff leaving the gently sloping material panels was collected during 11 rain and three snowmelt driven runoff events occurring over a period of five years. The results showed that, in general, the micropollutant concentrations and loads were lower in snowmelt than rain runoff, and no decreasing trend could be detected in the releases of phthalates or metals during the study period. Moreover, on a yearly basis, copper sheets were estimated to release 0.6 g/m^2 Cu to runoff, zinc and galvanised sheets were estimated to release 1.3 and 0.7 g/m^2 Zn, respectively, and, PVC sheets were estimated to release up to 78 mg/m^2 of diisononyl phthalate (DINP).

Keywords: Material ageing, Metals, Nonylphenols, Phthalates, Snowmelt runoff, Stormwater quality

1 Introduction

The contribution of numerous pollutants from urban drainage surfaces and flows (Müller et al., 2020) may cause the impairment of the receiving waters quality. Specific concerns were expressed about the chemical cocktail effects, which can be attributed to a wide variety of chemicals occurring in urban stormwater runoff, whose interactions are poorly understood (Masoner et al., 2019). The first step towards mitigation of the harmful effects caused by stormwater pollution is developing the adequate knowledge of the sources of these pollutants. Drainage surface material is one of the driving factors of runoff quality (Charters et al., 2021), and in this context, building surface materials are recognised as one of the major sources of stormwater pollution (Müller et al., 2020). Several of the organic and inorganic micropollutants found in building runoff produced documented negative effects on aquatic organisms, as indicated by their inclusion in, e.g., the U.S. Environmental Protection Agency (EPA) list of Toxic pollutants under the Clean Water Act (U.S. EPA 401.15), and the EU Directive on priority pollutants (Directive 2013/39/EU) amending the Water Framework Directive. The wide variety of building surface materials used in urban environments include various metallic materials, with or without coatings, as well as wooden and concrete structures, and membranes of e.g., polyvinyl chloride (PVC), bitumen, or ethylene propylene diene terpolymer (EPDM), among others. This wide variety of surface materials implies a long list of contaminants potentially being released with runoff. Furthermore, other factors such as precipitation pH (Wicke et al., 2014), rainfall intensity (McIntyre et al., 2019), and material surface characteristics (Wicke et al., 2012), may greatly influence the concentrations released to surface runoff.

There are two main mechanisms governing the entry of pollutants into building runoff: leaching of material constituents (including corrosion of the metallic materials), and wash-off of pollution deposited on the surfaces from the atmosphere (De Buyck et al., 2021). Several approaches have been used to study the contribution of pollution from building surface materials at different scales. These include e.g., laboratory leaching tests, which are suitable to determine leaching potential of chemicals from specific materials, but unsuitable to assess the concentrations released with runoff (Bandow et al., 2018), and, pilot scale open-air studies, considered to better reflect the releases of chemicals under actual conditions (Müller et al., 2021). Previous research efforts in open-air conditions have established major releases of metals such as Cu from copper sheets (Persson & Kucera, 2001; Winters et al., 2015; Müller et al., 2019) and Zn from zinc sheets and galvanised steel (Robert-Sainte et al., 2009; Winters et al., 2015; Müller et al., 2019), and, releases of the same metals from other materials, such as pressure treated wood, EPDM (synthetic rubber), and coated steel sheets (Clark et al., 2008; Robert-Sainte et al., 2009; Winters et al., 2015).

Even though many regions of the world have seasonal, or occasional, snow covers, the pollution of roof snowmelt runoff is a rather unexplored research topic. We found only one study, in which roof snowmelt, from a relatively fresh snow (<10 days), was sampled in Bayreuth, Germany, and analysed for suspended solids, polycyclic aromatic hydrocarbons (PAHs), dissolved organic carbon, electric conductivity (EC) and pH (Daub et al., 1994). Moreover, despite an increased research interest in the presence of organic micropollutants in stormwater and indications on their releases from building surfaces, there is still an overall lack of data on organic micropollutants in building runoff (De Buyck et al., 2021). For instance, while several studies have confirmed the occurrence of various pesticides in building runoff (Bucheli et al., 1998; Burkhardt et al., 2011; Gromaire et al., 2015), only few studies investigated releases of alkylphenols (APs) and phthalates from building surface materials, despite concerns about their adverse environmental effects, and the assessment by substance flow analysis that these drainage surfaces represent important sources (Björklund, 2010). PVC roofing membranes were in a previous study confirmed as sources of phthalates and nonylphenols (NPs) through analysis of pilot panel rainwater runoff (Müller et al., 2019), and, in a similar study, phthalates were analysed in runoff from several building surface materials, but were detected in generally low concentrations, and only the pressure treated wood exhibited detectable DEHP concentrations (Winters & Graunke, 2014).

In the present study, the releases of metals, phthalates, and APs from 10 different building surface materials to rainwater and snowmelt induced runoff were investigated through an open-air pilot study set-up with sampling spanning over a five-year period, and compared to contributions from the atmospheric deposition. To the best of our knowledge, in-situ ageing of several of the investigated building surface materials and studied pollutants has not been published before, nor have analyses of the quality of roof snowmelt runoff been adequately addressed in the previous literature. In this study, temporal changes in pollutant releases over a five-year period as well as an estimation of the magnitude of the released pollutant mass loads on a yearly basis are presented. Furthermore, in the current study, the influence of the pilot sheet surface temperatures on the releases of pollutants with runoff, as well as correlations to other influential factors of importance, were studied. The study objectives were to investigate the development of releases of micropollutants from building surface materials over time (up to 5 years), compare them to releases from new materials, presented in Müller et al. (2019), and, to study the importance of influential factors, such as surface temperature and antecedent dry days (ADD), on the releases. Furthermore, the present study produced novel data on roof snowmelt runoff quality, and addresses the importance of material characteristics, such as e.g., surface coatings, material hardness and flexibility, etc., for the releases of pollutants under the study conditions.

2 Material and methods

2.1 Experimental setup

The experimental site consisted of rectangular low slope (approximately 10%) pilot panels of 1 x 2 m size, located in an open-air setting on the campus of Luleå University of Technology, Sweden. Luleå has subarctic climate, code Dfc according to the Köppen climate classification. Measurements of the rain pH at the experimental site were in the range of 5.6±0.4. On the 33 panels, 11 different building surface materials were tested in triplicates, all of which were installed in a randomised order. The tested materials are commonly applied to roofs and facades of detached residential houses, apartment, commercial and industrial buildings, and some other surfaces in the urban environment. Specifically, the tested materials were metal sheets of stainless steel (STS), copper (CUS), zinc (ZNS), galvanised steel (GAL), Corten steel (COR), corrugated and coated steel (CST), coated zinc (CTZ); and roofing membranes of bitumen felt (BIF) and bitumen shingles (SHI), as well as PVC from two manufacturers (PVA, PVB). The stainless steel was considered a control material to estimate pollutant contributions deposited on the pilot panels from the surroundings, and the gutters collecting runoff from all individual pilot panels, as well as their overlays preventing direct rainwater entry, were also made of stainless steel. The experimental setup and sampling were described in an earlier publication (Müller et al., 2019). Moreover, the surface temperature of one replicate of each of the tested materials (i.e., 11 panels in total) was continuously recorded every 30 minutes by Tinytag Plus 2 loggers with surface thermistor probes (Tinytag PB-5003), mounted in one of the upper corners of every pilot panel material. Precipitation data were collected from a weather station located approximately 700 m southwest of the experimental site.

2.2 Sampling of runoff

Runoff was collected from 11 rain events, which occurred between June 2017 and July 2021, as well as three snowmelt events in March 2022. The rain events were characterised by, e.g., different seasons, antecedent dry periods, and rain characteristics. One of the rain events was characterised by an intermediate break of no rain of approximately one hour, during which the sampling bags were exchanged because they were almost full, and to be able to analyse the early and latter parts of the rain event separately (denoted as events 5.1 and 5.2). Characteristics of the rain (R1-R10) and snowmelt events (SM1-SM3) are presented in Table A1 of the Appendix. Prior to forecasted rain, Perfluoroalkoxy alkanes (PFA) bags with capacity of approximately 20 L were attached to the stainless-steel gutters collecting the runoff. The whole runoff volume was collected in one bag per pilot panel, meaning that, after thorough mixing, the concentrations in the analysed PFA bags could be considered to represent event mean concentrations (EMC). The samples were collected as soon as possible (within a maximum of 15 hours) after the rain had stopped. CTZ was installed at a later stage of the field program and was included in the measurements starting with event R4. For the snowmelt (SM) sampling, the same PFA bags had been attached to the gutters in the early morning, before melting started, and removed after the melting had stopped in the evening (SM event 1), or at the time when (some of) the bags were full to prevent overfilling (SM events 2 and 3).

2.3 Physical and chemical analysis of samples

The samples were brought to The Environmental Laboratory of the Luleå University of Technology, where the collected volumes of all individual samples were recorded, and pH, EC and total suspended solids (TSS) were measured. Chemical analyses of the samples were performed by an accredited laboratory (ALS Scandinavia AB), and their accreditation is a confirmation that their laboratory procedures are in accordance with international standards for quality assurance and quality control (QA/QC). Total and dissolved (<0.45 µm) metals were analysed in all runoff samples, while APs were analysed in runoff from PVA, PVB, BIF, SHI and STS (control), and phthalates were analysed for PVA, PVB and STS (control), following the results of previous tests and pollutant screening of the materials (for details, see Müller et al., 2019). The specific substances analysed for as well as the analytical methods used are summarised in Table 1.

Table 1 The analytical methods and reporting limits (RL) for all substances analysed in runoff from the pilot surfaces. The chemical analyses were performed by ALS Scandinavia AB, using inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) and gas chromatography-mass spectrometry (GC-MS).

Analysed parameter (RL, µg/L)	Analytical method	Materials analysed
Total suspended solids, TSS (2 mg/L)	Vacuum filtration through 1.6 µm glass fibre filters, following the Swedish standard EN 872:2005. The filters were oven dried at 105°C ± 2°C.	All 11 materials
Total metals: Al (10), Cd (0.05), Cr (0.9), Cu (1), Ni (0.6), Pb (0.5), Zn (4)	Samples were digested by autoclaving with 1.2 mL 14M HNO_3 per 12 mL sample, prior to analysis on ICP-SFMS, following the standard SS EN ISO 17294-2: 2016.	All 11 materials
Dissolved (<0.45 µm) metals: Al (0.2), Cd (0.002), Cr (0.01), Cu (0.1), Ni (0.05), Pb (0.01), Zn (0.2)	Samples were acidified by 1 mL 14M HNO_3 per 100 mL sample, and analysed on ICP-SFMS, following the standard SS EN ISO 17294-2: 2016.	All 11 materials
Phthalates: dimethylphthalate, diethylphthalate, di-n-propylphthalate, di-n-butylphthalate, diisobutyl phthalate, di-n-pentylphthalate, di-n-octylphthalate, di-(2-ethylhexyl)phthalate, butylbenzylphthalate, dicyclohexylphthalate, diisodecyl phthalate, diisononyl phthalate, and di-n-hexylphthalate (1)	Samples were extracted with hexane and analysed on GC-MS, following standard DIN ISO 18856.	PVA, PVB and STS
Alkylphenols and -ethoxylates: 4-tert-octylphenol, 4-tert-octylphenol monoethoxylate, 4-tert-octylphenol diethoxylate, 4-tert-octylphenol triethoxylate (0.01) 4-nonylphenols (tech. mixture), 4-nonylphenol monoethoxylate, 4-nonylphenol diethoxylate, 4-nonylphenol triethoxylate (0.1)	Samples were acidified and extracted with dichloromethane, and analysed on GC-MS, based on the ISO standard 18857-2.	BIF, SHI, PVA, PVB and STS

2.4 Data analysis

The total number of runoff samples from the 33 pilot surfaces was 451. Among the phthalate and AP analyses, some of the concentrations were reported as elevated RL instead of actual concentrations, due to matrix effects. Furthermore, all samples had some substances below the RL. For the statistical analyses of such left-censored data, the Nondetects and Data Analysis for Environmental Data package (NADA) in R was applied. Means were calculated using the regression on order statistics (ROS) method. Substances quantified in at least 25% of samples were included in the analyses.

A principal component analysis (PCA) was performed using the software SIMCA 17, in order to visualise the dataset and analyse overall correlations among the different parameters. The following parameters were included in the PCA: pH; EC; TSS; sample volume (weight); total and dissolved Cr, Cu, Ni, Pb and Zn; DINP; NP; number of antecedent dry days (ADD); precipitation depth, and average material surface temperature (i) during the rain, (ii) since the last rain event, and, (iii) 24 hours before the rain event. All parameters were pre-treated with unit variance scaling, and all parameters except for pH, weight, the temperatures, and precipitation were logarithmically transformed to account for skewness. All individual samples from the 11 rain events were included in the PCA, but the snowmelt events were excluded because the external factors (ADD, precipitation) were irrelevant for the snowmelt evets. Censored data were replaced with ½RL for the purpose of the PCA.

In order to estimate the yearly contributions of pollution from the different materials, the site mean concentrations (SMC) were calculated separately for all 11 materials by Equation 1:

$$SMC = \frac{\Sigma(\,EMC_{sample} \times V_{sample})}{V_{tot}} \qquad (Eq.\ 1)$$

where EMC_{sample} is the concentration of a specific substance in a single runoff sample, V_{sample} is the specific sample volume, and V_{tot} is the total volume of all samples from that specific material. The SMCs were then multiplied by the yearly and seasonal average precipitation normals in Luleå the latest 30-year period (1991-2020), for which the data collected by the Swedish Meteorological and Hydrological Institute, SMHI, was available). The estimations were separated into rain and snow seasons and, therefore, SMCs were calculated separately for rain and snowmelt data, and afterwards multiplied with the average precipitation of the rain season (i.e., combining spring, summer and autumn, 430 mm) and snow season (winter, 130 mm) separately.

3 Results and Discussion

For brevity, the focus of the results presented herein is on the metals Cu and Zn, as well as the organic micropollutants NPs and diisononyl phthalate (DINP). The selection of these substances was based on a number of reasons: (i) these chemicals showed clear deviations in releases from some of the materials compared to the control panels, indicating that some of the tested materials were sources of these chemicals, (ii) these chemicals represent a known or potential threat to the aquatic life, and (iii) these chemicals were quantified in >25% of the samples. For information on other metals, phthalates, alkylphenols and -ethoxylates, as well as TSS, pH and EC in the samples, see Table A2 in the Appendix.

3.1 Metals

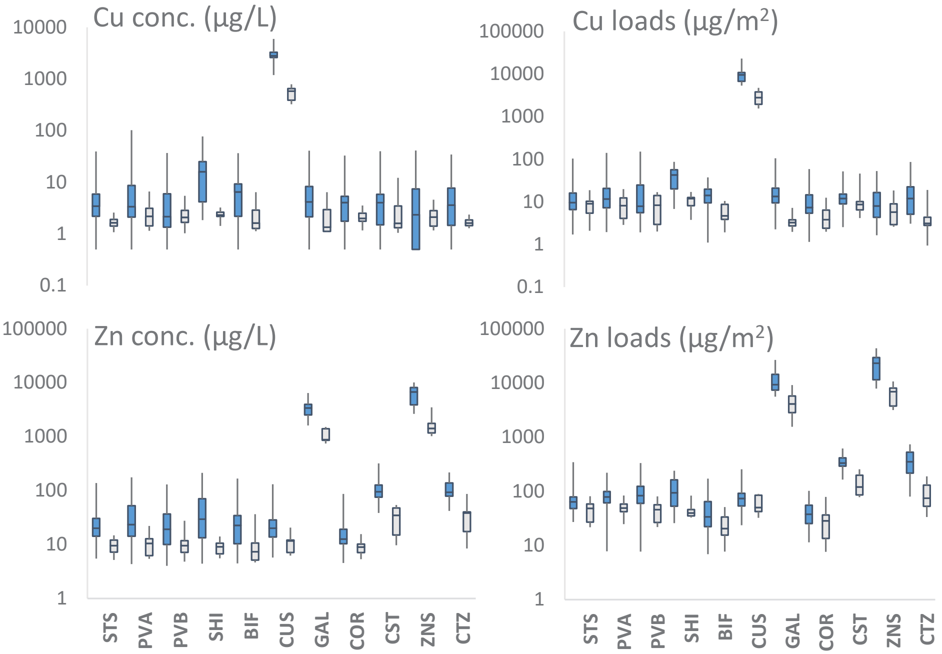

Figure 1 Boxplots of Cu and Zn concentrations (µg/L) and loads (µg/m²) in rain (blue) and snowmelt (grey) runoff from the tested materials. Horizontal lines indicate 1st quartile, median and 3rd quartile, while whiskers represent the full range of the samples.

In Figure 1, concentration ranges of Cu and Zn for the different materials in rain (blue) and snowmelt (grey) induced runoff are presented. Besides the obvious that CUS was the major source of release of Cu and that ZNS and GAL were the major sources of releases of Zn, which is in line with the previous research (Clark et al., 2008; Robert-Sainte et al., 2009; Müller et al., 2019), Figure 1 indicates that the concentrations are overall higher in rain induced runoff compared to snowmelt induced runoff. One reason that could partly explain this observation is that the snow cover on the panel surfaces limits the contact between the runoff water and the surface materials, and that the runoff run length on the actual material surface, previously found to be an important factor (Bielmyer et al., 2012), would therefore be shorter for the snowmelt runoff than the rainwater runoff. Moreover, while a surface coating is known to reduce Zn concentrations in runoff (Robert-Sainte et al., 2009; Müller et al., 2019), CST and CTZ still represent sources of Zn, releasing concentrations of >100 µg/L (and loads of >100 µg/m²) to runoff. The releases of Cu from SHI were higher than those of the control panels (STS), indicating material contribution of Cu. The other materials had Cu and Zn concentrations and loads in the same order of magnitude as each other, and STS, indicating that atmospheric deposition was the main source of Cu and Zn in the collected runoff from these materials. Other metals analysed in runoff did not show strong deviations from STS and, therefore, atmospheric deposition was assumed to be the major source of those metals. For details, see Table A2 in the Appendix. Furthermore, a common characteristic for Cu and Zn analysed in the panel runoff was that both were mainly in dissolved form, as can be seen for Zn in runoff from ZNS (Figure 3) and in the Appendix for the other materials studied.

3.2 Organic micropollutants

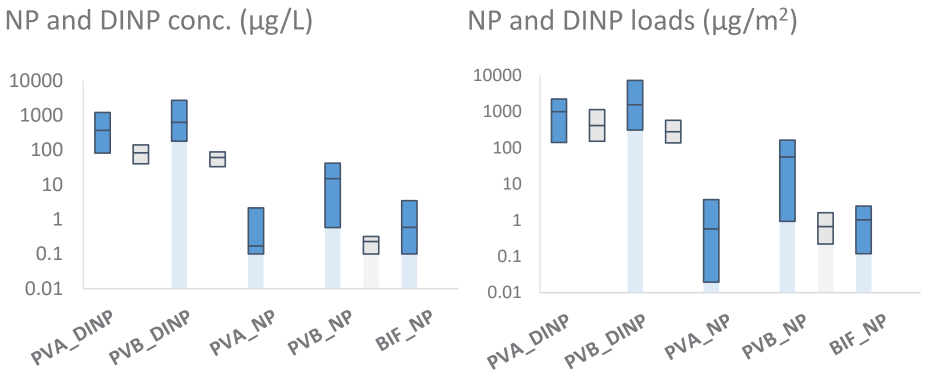

Figure 2 Minimum, mean and maximum total concentrations of diisononyl phthalate (DINP) and 4-nonylphenol (NP) concentrations (µg/L) in rain (blue) and snowmelt (grey) runoff from the tested materials. Mean values were calculated with the NADA package in R using regression on order statistics. When calculating the loads for this figure, left-censored values were replaced with ½ RL. In cases where the minimum concentrations were below the RL, the pale colour represent the true distribution extending below the analytical RL to an unknown extent. The materials STS and SHI were not presented in the figure, because all measurements were below the RL, or reported as elevated RLs.

The concentration and load ranges of DINP and NPs in rain (blue) and snowmelt (grey) induced runoff from the test panels is presented in Figure 2. Because a fraction of the concentrations were left-censored, regular median and quartile values could not be calculated. Instead, mean values calculated using ROS with NADA, and minimum and maximum values are presented in the figure. For the pollutant load calculations, which were obtained by a multiplication of sample-specific concentration and volume, the censored values were replaced by ½ RL for lack of a better solution. For STS, all concentrations were below the analytical RL, and for SHI, all concentrations were censored values and, thus, they were excluded from the figure. Similarly, in the snowmelt samples, all NP concentrations in runoff from PVA and BIF were below the analytical RL. The pale coloured bars in the figure indicate where the results were partly based on the censored values, and where the minimum concentrations extend below the given minimum value to an unknown extent. Similar to Cu and Zn, all the organic micropollutants display lower concentrations in snowmelt runoff compared to rain runoff. PVB represents the largest source of both DINP and NPs, while DINP releases from PVA were of the same order of magnitude as the releases from PVB, and the releases of NPs were of the same order of magnitude, and relatively close to the RL for PVA and BIF. Moreover, all organic micropollutant concentrations in runoff from STS were below the analytical RL, indicating that there were no significant contributions of the studied organic micropollutants from atmospheric deposition in the study area and that the actual materials represent the sources of micropollutant releases.

Overall, many of the studied organic micropollutants had a large proportion of censored data. DEHP was detected in runoff from PVA, but 74% of the data were below the RL (see Tab. A2 of the Appendix). Octylphenols and -ethoxylates were not quantified in any of the runoff samples, and were therefore excluded from further analyses, and while the nonylphenols and -ethoxylates (NPs/NPEOs), as well as the phthalates DIDP, had a large proportion of left-censored values (from Tab. A2 of the Appendix: 12-98% for NPs, 83-100% for NPEOs, and 69-100% for DINP, respectively), their RLs were elevated because of matrix disorders, sometimes up to two orders of magnitude over the original reporting limit. The likely explanations for the matrix disorders were high concentrations of another substance with similar properties, e.g., DINP in the case of DIDP, were disturbing the analysis. Furthermore, the higher occurrences of NPs compared to NPEOs, together with the results from a material composition screening showing that PVB contained NPEOs but not NPs (Müller et al., 2021), indicate that NPEOs are released to runoff and subsequently degraded to NPs.

3.3 Event specific concentrations and loads

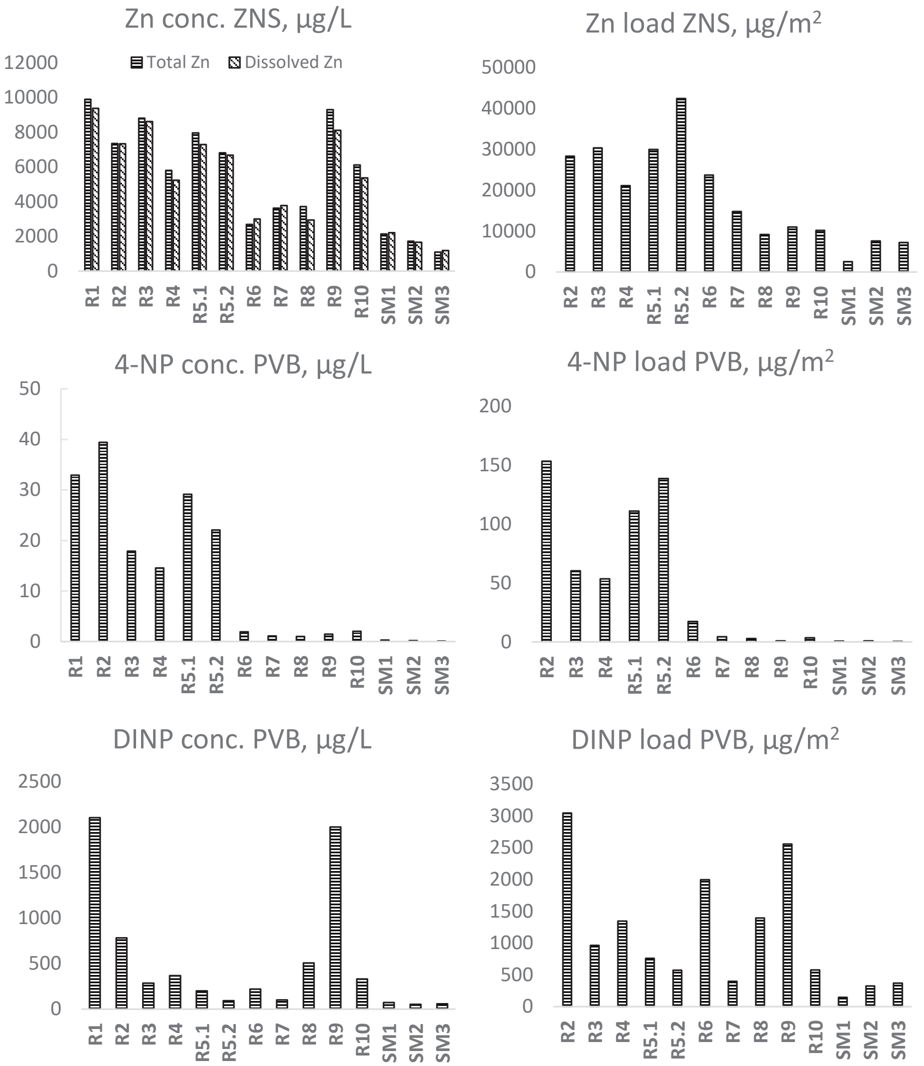

Figure 3 Event specific concentrations (µg/L) and loads (µg/m²) of Zn from ZNS, and, 4-NP and DINP from PVB. No loads could be calculated for R1. In this figure, left-censored values were replaced with ½ RL.

Over the course of the five-year study period, no decreasing (or increasing) trends in the releases of Cu and Zn could be detected, neither for the metal sheets with (CST, CTZ) or without (CUS, ZNS, GAL) coating, or SHI. In Figure 3, the concentration and loads of Zn from ZNS at the sampled events are presented, together with the corresponding releases of NPs and DINP from PVB. ZNS was selected because it represented the highest concentrations metals, but the releases of e.g., Zn from GAL and Cu from CUS followed the same pattern. Plots of substance releases per event for the other materials studied are available in the Appendix. The release patterns are in agreement with the results of e.g., McIntyre et al. (2019), who found relatively constant releases of Cu and Zn from both metal roofing materials and asphalt shingles with copper granules over two sampling campaigns stretching over approximately one year each and separated by a 'weathering interval' of roughly 2 years. Moreover, the subsequent degradation of a surface coating or lacquer may lead to increased releases of pollutants over time (McIntyre et al., 2019). As no such trends could be seen for the coated metals sheets in the present study, i.e., CTZ and CST, their surface coatings are assumed to be intact five years after installation. Results from previous studies comparing new copper and zinc sheets to old and used sheets (material age 40-55 years) have shown that old metal sheets release higher concentrations of Cu and Zn to runoff, compared to newer materials (Robert-Sainte et al., 2009; Wicke et al., 2014), possibly because of the corrosion creating a porous surface layer that enhances metal dissolution (Wicke et al., 2014). In this context, the metal sheets tested in the present study are, five years after installation, still to be considered as relatively new. However, the tested roofing membranes of e.g., bitumen or PVC have a shorter lifespan (roughly 15-20 years for a bitumen felt roof), and, thus, the five-year study period represents a substantial part of their normal time-of-use.

From Figure 3, the releases of NPs from PVB show a decreasing trend over time. The events R1-5.2, representing the first 12 months of the sampling campaign, are characterised by distinctly higher NP concentrations compared to the following events. This may potentially be caused by leaching out of NPs from the new materials, and subsequent ageing of the material. No such trends were observed for the other organic micropollutants, e.g., DINP. Instead, DINP releases were highest in R1 and R2, followed by fairly constant concentrations in events R3-R8, and loads varying with the collected sample volume (i.e., amount of precipitation). In R9, characterised by a long preceding dry period, higher temperature, and high TSS concentrations in runoff, the releases of DINP from PVB to runoff are on the same level as the first events. In the following R10, the DINP levels returned to the same levels as in R3-R8.

Overall, the differences between the sampled events are more pronounced for the organic micropollutants compared to the metals. It is important to note that, likely, different processes are governing the releases of metals and organic micropollutants. While corrosion and leaching are the main factors for metallic structures (He et al., 2001), hydrophobic organic substances, such as phthalates, may not be released from the material surface in contact with water (Müller et al., 2021). Instead, the leachability of phthalates in stormwater and landfill leachates was suggested to be dependent of the presence of organic carbon (Kalmykova et al., 2013) and humic acids (Zheng et al., 2007). Moreover, a study on DEHP migration from PVC flooring found that dust particles effectively adsorbed DEHP, and that the dust uptake increased with time (Clausen et al., 2004). In addition, the migration of DEHP was significantly increased with increasing temperature (Clausen et al., 2012). Therefore, in the present study, the particles deposited on the panel surfaces are assumed to play an important role in the releases of phthalates from the PVC materials, acting as surfaces for phthalates to adsorb to, and as carriers in subsequent runoff.

3.4 Estimated yearly loads

Table 2 presents the estimated yearly loads of Cu, Zn, DINP and NPs per m^2 of the studied materials under the current climatic conditions at the study location. The estimations are rough and based on several assumptions, especially for the snowmelt estimations, which were based on just three measurements of snowmelt quality during a single year. The highest estimated load was Zn from ZNS, with a total estimated contribution of 1.3 g/m^2 and year. Even though the average Zn concentrations (Tab. A2 in Appendix) were in the same range in this study compared to measurements from zinc panels in Paris (Robert-Sainte et al., 2009), their annual runoff loads were higher, up to 3.8 g/m^2, possibly as a result of more precipitation, or because our experimental site has a snow cover for at least four months without runoff. The estimated yearly loads follow the same pattern for all studied pollutants, with higher loads in rainfall induced runoff than snowmelt. Furthermore, the effects of climate change on temperature and precipitation patterns may lead to less snow and more rain in the future, which will subsequently risk worsening the problem with pollution of building surface runoff in areas with seasonal snow covers. Similarly, periodic droughts, or long periods without precipitation, may lead to wash-off of large quantities of phthalates that seem to be dependent on the accumulation of particles on the surfaces in order to be released, as discussed in the preceding section 3.3.

Table 2 Estimated average yearly load per m^2 (in mg) of Cu, Zn, diisononyl phthalate (DINP), and 4-nonylphenols (NPs) from rainfall induced runoff (R) and snowmelt induced runoff (SM) from the tested materials. When calculating the loads for this table, left-censored values were replaced with ½ RL. <RL indicate that 75% of the measurements, or more, were left-censored.

	STS	PVA	PVB	SHI	BIF	CUS	GAL	COR	CST	ZNS	CTZ
Cu R	0.86	1.3	1.2	2.3	1.1	542	1.0	0.77	0.75	0.73	1.1
Cu SM	0.11	0.11	0.12	0.13	0.078	32	0.053	0.097	0.15	0.098	0.078
Zn R	4.7	4.8	4.9	6.4	3.5	4.3	628	2.5	19	1213	22
Zn SM	0.58	0.59	0.61	0.55	0.34	0.63	63	0.55	1.7	88	1.5
DINP R	<RL	55	74	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
DINP SM	<RL	4.9	3.7	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
NPs R	<RL	0.034	3.0	<RL	0.070	n/a	n/a	n/a	n/a	n/a	n/a
NPs SM	<RL	<RL	0.0090	<RL	<RL	n/a	n/a	n/a	n/a	n/a	n/a

3.5 Principal component analysis (PCA)

The PCA model consisted of 10 components explaining 93% of the data variation, of which the first and second component explained 30% and 14%, respectively (Figure 3). Samples from ZNS and GAL are clearly clustered together in the bottom of the score plot, because of the Zn concentrations (located in the lower parts of the loading plot). CST and CTZ samples are also located below the centre line, likely because of higher Zn concentrations compared to the other samples. Moreover, a majority of the SHI samples are located in the top left corner of the score plot, suggesting correlation to TSS, ADD, and surface temperature (S.temp), located to the left in loading plot. In the loading plot, TSS, ADD and the surface temperature variables are clustered together on the right-hand side, indicating simultaneous 'mutual' influence on the model. Overall, several of the potentially influential factors are naturally interlinked, impeding the possibility of distinguishing the influence of single factors on releases of substances in open-air experiments. For instance, as already established, high TSS concentrations in runoff result to a large extent from the duration of accumulation time, or ADD (Yaziz et al., 1989). Thus, the detailed investigations of the influential factors affecting pollutant releases from building surface materials are best performed in environments, which allow to control specific parameters, not possible in open-air experiments with sampling of runoff induced by natural precipitation. Moreover, a PCA model with loads instead of concentrations produced similar results but with lower degree of explanation.

Scores - PCA_0.5RL_logtrans (M1, PCA-X)

Colored according to classes in M1

R2X[1] = 0,298; R2X[2] = 0,141; Ellipse: Hotelling's T2 (95%)

Loadings - PCA_0.5RL_logtrans (M1, PCA-X)

R2X[1] = 0,298; R2X[2] = 0,141

Figure 4 Score and loading plots from the principal component analysis (PCA), where values <RL were replaced with ½RL.

4 Conclusions

- This study presents results of snowmelt quality in building surface runoff, not reported in the previous literature. In general, the concentrations and loads of Cu, Zn, NPs and DINP were lower in snowmelt runoff compared to rain runoff. Thus, in regions with seasonal snow covers, increased temperatures resulting from climate change imply risk of worsening the pollution of building runoff in the future, when larger proportions of the precipitation will fall as rain instead of snow.
- The 'major sources' among the studied materials may contribute large quantities of the studied pollutants to runoff. Under the current climatic conditions at the study location, CUS was estimated to release 574 mg Cu per m^2, ZNS and GAL were estimated to release 1301 and 691 mg Zn per m^2, and PVA and PVB were estimated to release 60 and 78 mg DINP per m^2, respectively, on a yearly basis.

- Phthalates detected in runoff from the PVC materials in spite of their known hydrophobicity. This was suggested to be due to the migration of phthalates from the material surfaces to the particles deposited on the pilot panels, and subsequent wash-off with rain and snowmelt runoff.
- A decreasing trend over time could be noted for the releases of NPs from the tested materials, especially PVB, which was the largest source of NP releases. Likely, this was an effect of wash off from the new materials combined with material ageing.
- No decreasing trends were observed in the releases of phthalates or metals over the five-year study period. This suggests that the materials tested will continue releasing the respective pollutant(s) over their life span.

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Supplementary material to:

Releases of micropollutants from building surface materials into rainwater and snowmelt induced runoff

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Table A1 Characteristics of the sampled rainfall (R) and snowmelt (SM) induced runoff events.

Event	**Date**	**Precipitation (mm)**	**Average daily temperature**[b] (°C)	**Antecedent dry days**
R1	12/6/2017	10[b]	12	6
R2	4/7/2017	3.5	11	7
R3	26/10/2017	3.2	1.0	0 (23 h)
R4	7/5/2018	3.3	5.2	2
R5.1	28/6/2018	4.6	11	4
R5.2	28/6/2018	5.3	11	0
R6	30/8/2019	9.7	16	5
R7[a]	2/11/2019	3.4	-0.5	2 (snow)
R8	20/8/2020	2.9	16	16
R9	9/6/2021	1.8	16	17
R10	15/7/2021	1.2	20	4
SM1	17/3/2022	0	-0.3	n/a
SM2	18/3/2022	0	2.7	n/a
SM3	21/3/2022	0	4.2	n/a

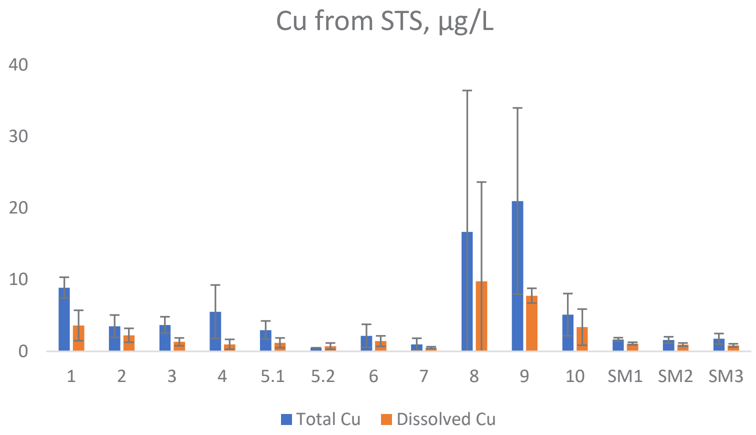
[a] Approximately 3 cm of snow cover was lying on the panels before the rain started.

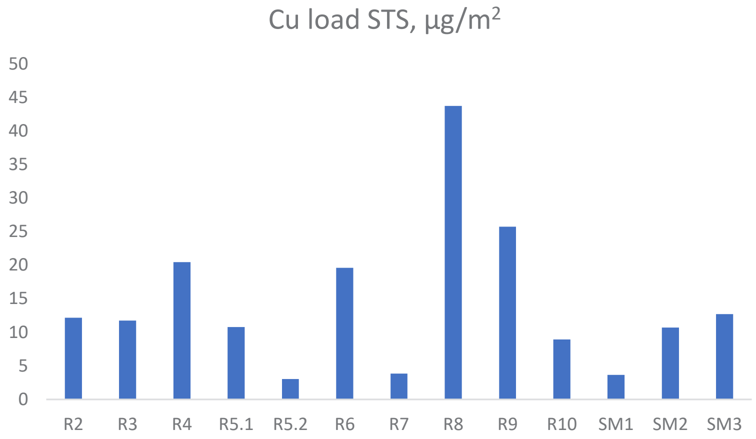
[b] Data was collected from the SMHI station approximately 9 km south of the experimental site.

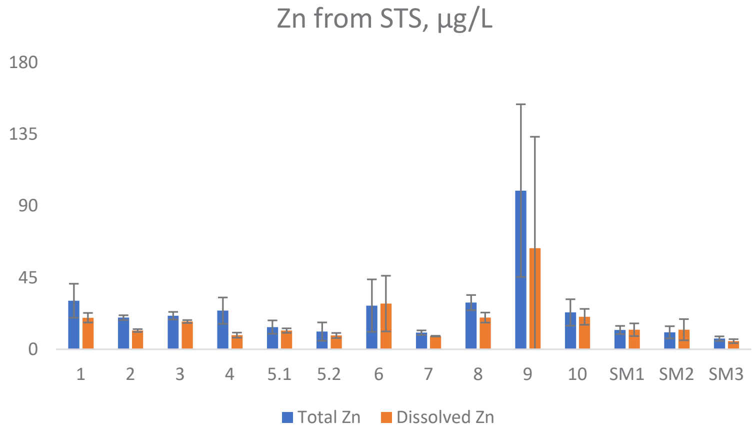
Table A2 Average ($\bar{x}$), standard deviation (σ) of pH, electric conductivity (EC), total suspended solids (TSS), the metals Al, Cr, Cu, Ni, Pb and Zn, 4-Nonylphenols (4-NP), 4-nonylphenol monoethoxylate, diethoxylate and triethoxylate (NP-1E, NP-2E, NP-3E), and the phthalates Di-(2-ethylhexyl)phthalate (DEHP), Diisodecyl phthalate (DIDP), diisononyl phthalate (DINP). $\bar{x}$ and σ calculated with R using regression on order statistics are presented in italics. For substances with >75% unquantified samples, the highest reported RL (r) is presented instead of the average.

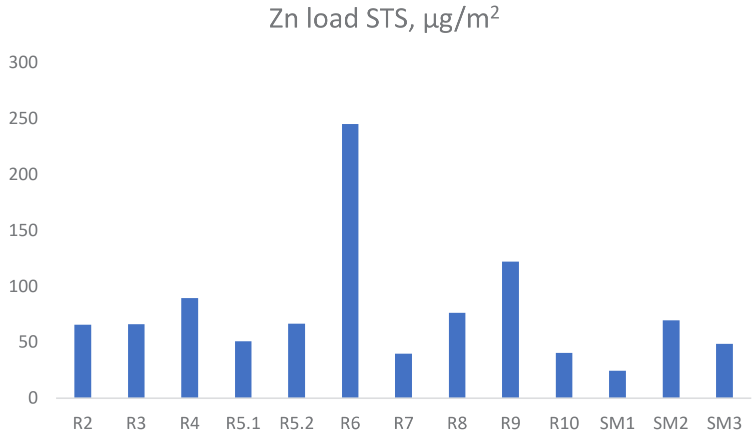
		STS	**PVA**	**PVB**	**SHI**	**BIF**	**CUS**	**GAL**	**COR**	**CST**	**ZNS**	**CTZ**
		n=41	n=42	n=42	n=42	n=41	n=42	n=42	n=42	n=42	n=42	n=33
pH	$\bar{x}$	5.9	5.9	6.0	6.0	6.2	6.0	6.3	6.0	6.0	6.4	5.9
	σ	0.47	0.33	0.33	0.48	0.35	0.21	0.22	0.33	0.36	0.22	0.29
EC	$\bar{x}$	8.7	16	12	18	21	11	15	8.5	9.7	20	9.5
µS/cm	σ	4.5	17	10	15	20	5.3	12	4.8	6.5	9.0	7.2
TSS	$\bar{x}$	24	49	52	39	39	41	32	44	40	32	53
mg/L	σ	39	105	118	80	71	78	44	79	72	61	84
Al	$\bar{x}$	48	974	909	750	850	665	658	850	893	766	1063
	σ	733	1570	1580	1340	1260	1280	843	1690	1515	1390	1850
Cr	$\bar{x}$	3.4	4.7	4.8	4.2	6.5	2.9	5.9	4.6	4.1	3.3	5.7
	σ	2.7	4.5	4.6	4.0	10	3.9	5.5	5.5	4.5	3.8	5.8
Cu	$\bar{x}$	5.1	8.4	8.2	15	7.2	2490	6.3	4.9	5.5	5.4	6.2
	σ	7.4	17	18	18	8.4	1440	8.5	6.4	7.6	8.4	9.2
Ni	$\bar{x}$	1.9	1.9	1.8	18	4.1	1.7	1.5	16	2.2	1.7	2.4
	σ	0.91	2.1	2.0	21	4.1	1.7	1.1	12	2.7	2.2	2.2
Pb	$\bar{x}$	2.9	4.1	4.2	4.6	8.2	3.0	7.6	14	6.8	7.7	12
	σ	2.1	5.3	5.2	5.2	9.7	3.2	19	18	7.3	17	34
Zn	$\bar{x}$	22	32	35	41	25	24	2900	15	96	5500	93
	σ	22	38	40	44	37	22	1450	15	63	2900	57
4-NP	$\bar{x}$/r	<0.1	0.13	11.7	<3.5	*0.44*						
	σ	-	0.15	13.9	-	*0.88*						
	% cens.	100	71	12	98	68						
NP-1E	r	<0.1	<3.5	<0.5	<1.1	<1.1						
	σ	-	-	-	-	-						
	% cens.	100	95	100	100	100						
NP-2E	r	<0.1	<7.1	<3.0	<1.9	<2.7						
	σ	-	-	-	-	-						
% cens.		100	95	83	100	100			Substances not analysed			
NP-3E	r	<0.1	<1.9	<3.8	<2.5	<4.6						
	σ	-	-	-	-	-						
	% cens.	100	100	93	100	100						
DEHP	$\bar{x}$	<1	*1.1*	<1								
	σ	-	*1.2*	-								
	% cens.	100	74	100								
DIDP	$\bar{x}$/r	<10	<200	*44*								
	σ	-	-	*24*								
	% cens.	100	100	69								
DINP	$\bar{x}$	<10	264	*504*								
	σ	-	237	*699*								
	% cens.	100	0	21								

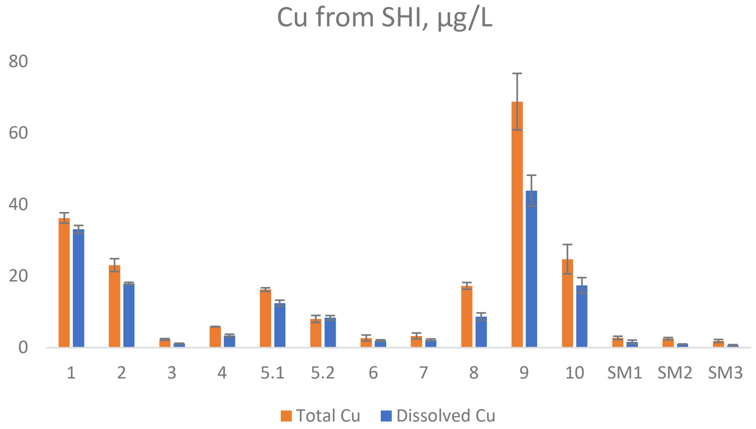
Figures A1-16 (below): Event specific concentrations (µg/L) and loads (µg/m^2) of Cu, Zn, DINP and NPs from the studied materials.

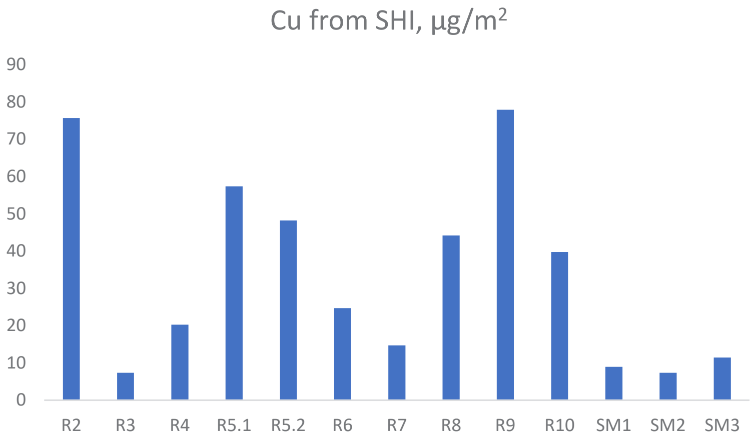




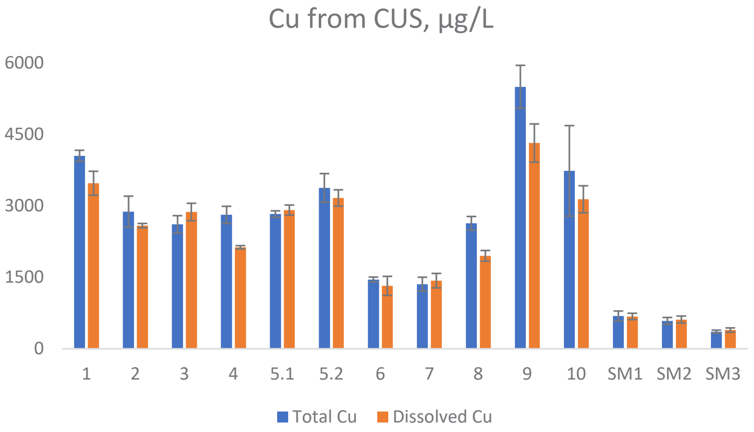



Zn load STS, µg/m²
300
250
200
150
100
50
0
R2
R3
R4
R5.1
R5.2
R6
R7
R8
R9
R10
SM1
SM2
SM3

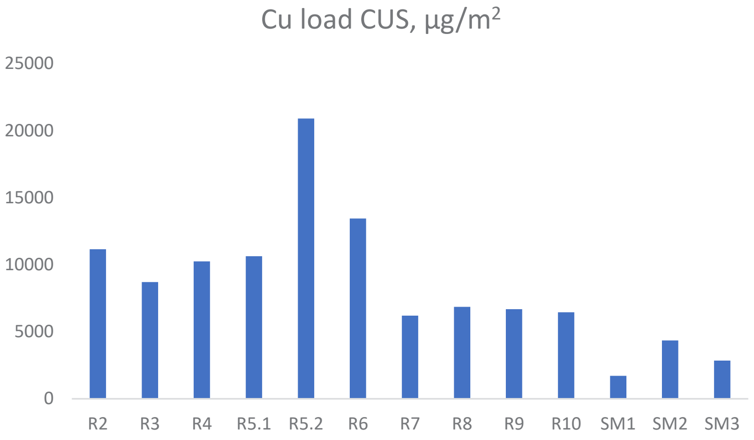

Cu from SHI, µg/L
80
60
40
20
0
1
2
3
4
5.1
5.2
6
7
8
9
10
SM1
SM2
SM3
Total Cu
Dissolved Cu



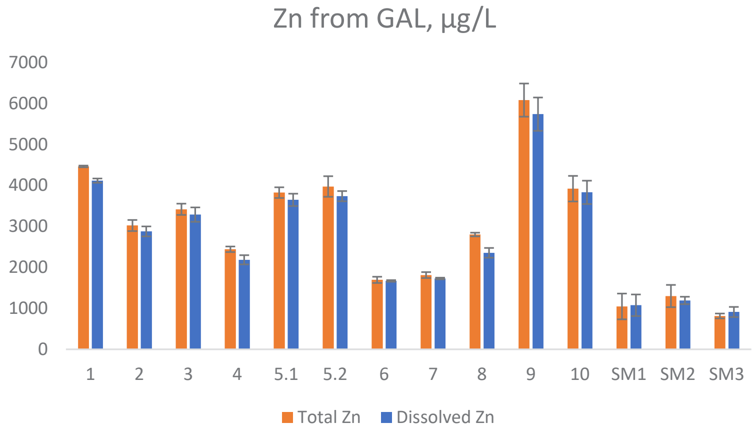
Cu from SHI, µg/m^2



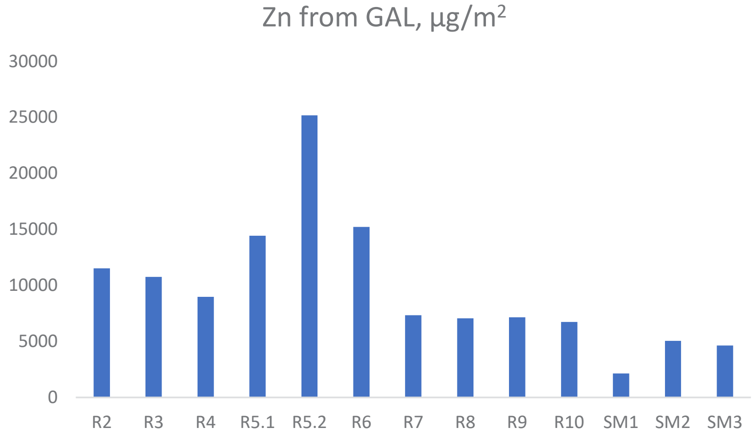
Cu from CUS, µg/L



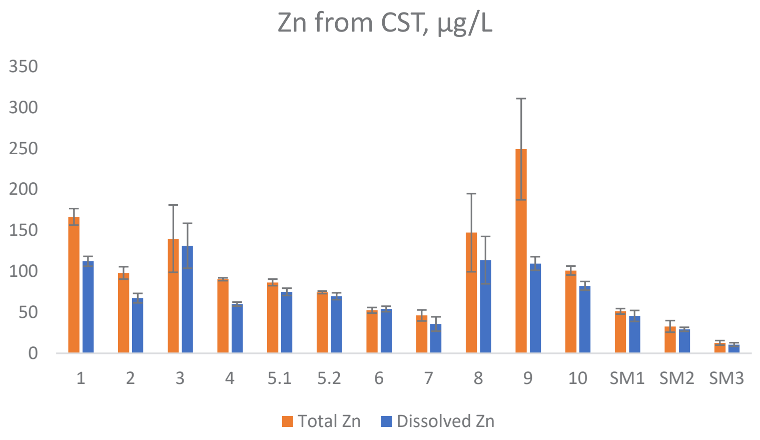
Cu load CUS, µg/m^2

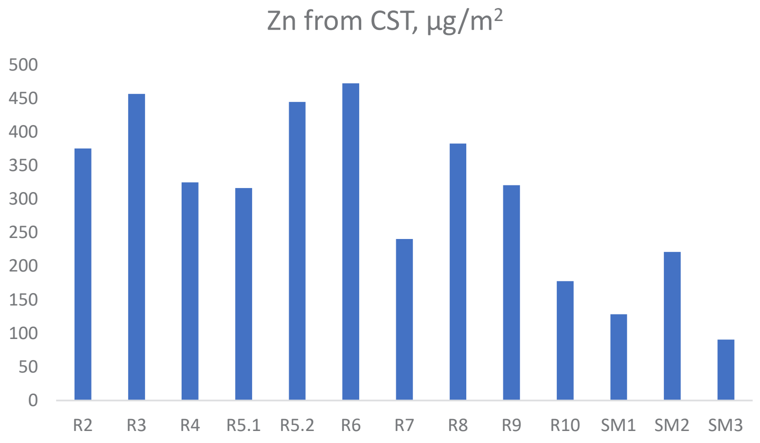


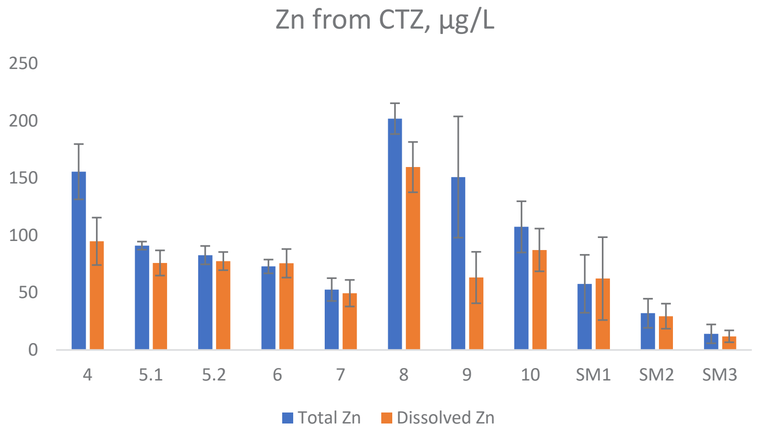
Zn from GAL, µg/L
7000
6000
5000
4000
3000
2000
1000
0
1
2
3
4
5.1
5.2
6
7
8
9
10
SM1
SM2
SM3
Total Zn
Dissolved Zn

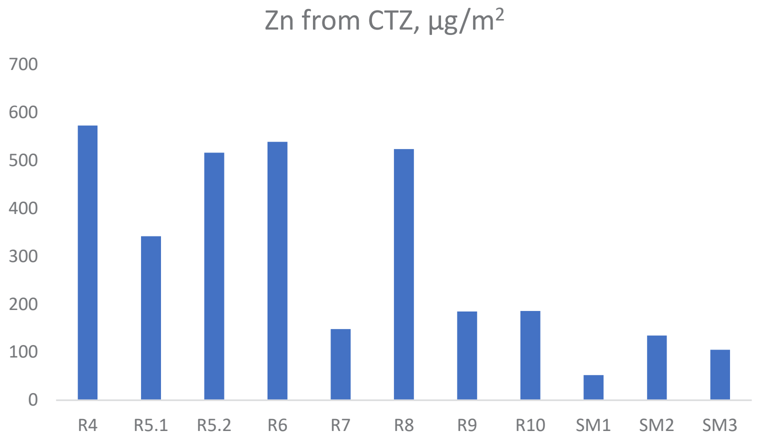


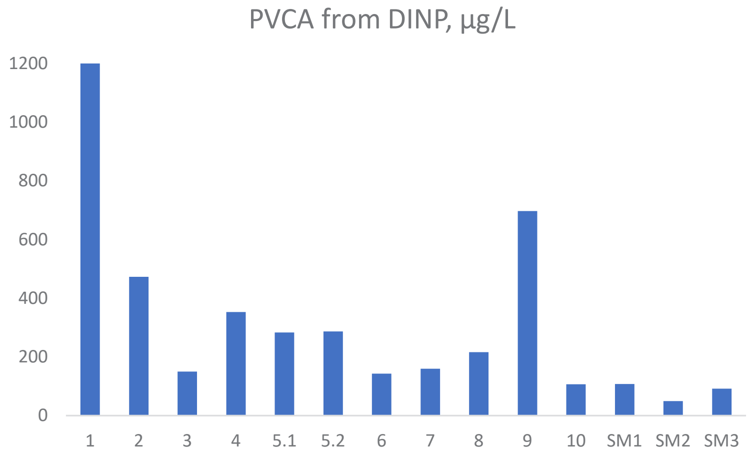
Zn from GAL, µg/m²
30000
25000
20000
15000
10000
5000
0
R2
R3
R4
R5.1
R5.2
R6
R7
R8
R9
R10
SM1
SM2
SM3

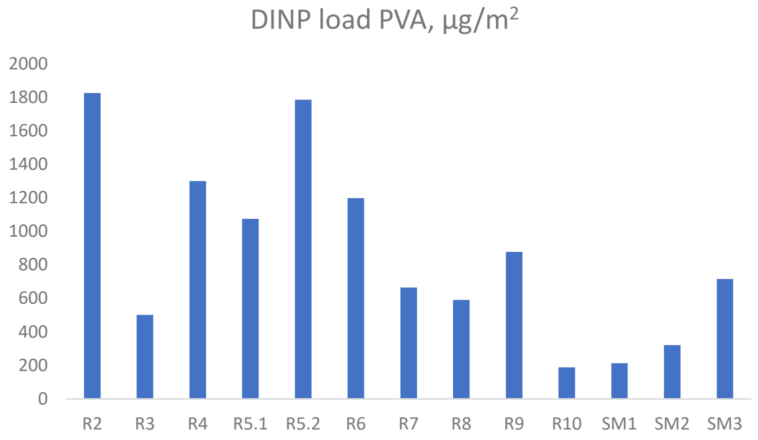

Zn from CST, µg/L
350
300
250
200
150
100
50
0
1
2
3
4
5.1
5.2
6
7
8
9
10
SM1
SM2
SM3
Total Zn
Dissolved Zn


Zn from CST, µg/m2
500
450
400
350
300
250
200
150
100
50
0
R2
R3
R4
R5.1
R5.2
R6
R7
R8
R9
R10
SM1
SM2
SM3


Zn from CTZ, µg/L
250
200
150
100
50
0
4
5.1
5.2
6
7
8
9
10
SM1
SM2
SM3
Total Zn
Dissolved Zn


Zn from CTZ, µg/m²
700
600
500
400
300
200
100
0
R4
R5.1
R5.2
R6
R7
R8
R9
R10
SM1
SM2
SM3


PVCA from DINP, µg/L
1200
1000
800
600
400
200
0
1
2
3
4
5.1
5.2
6
7
8
9
10
SM1
SM2
SM3


DINP load PVA, µg/m²
2000
1800
1600
1400
1200
1000
800
600
400
200
0
R2
R3
R4
R5.1
R5.2
R6
R7
R8
R9
R10
SM1
SM2
SM3

Paper V

Alexandra Müller, Heléne Österlund, Jiri Marsalek, Maria Viklander (2022)

Exploiting urban roadside snowbanks as passive samplers of organic micropollutants and metals generated by traffic

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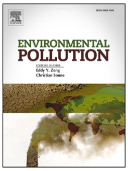

Exploiting urban roadside snowbanks as passive samplers of organic micropollutants and metals generated by traffic[☆]

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Emerging pollutants
Metals
Phthalates
Stormwater

ABSTRACT

Stormwater and snowmelt runoff is known to contribute to the deterioration of quality of urban surface waters. Vehicular traffic is recognised as a major source of a wide range of pollutants to urban runoff, including conventional pollutants, such as suspended solids and metals, and those referred to as 'contaminants of emerging concern'. The aim of this study was to investigate the contribution of selected metal(loid)s (Cd, Cr, Cu, Ni, Pb, Pd, Sb, W, Zn), polycyclic aromatic hydrocarbons (PAHs), nonylphenols, octylphenols and –ethoxylates, phthalates and bisphenol A (BPA) from vehicular traffic by sampling urban roadside snow at eight sites, with varying traffic intensities, and one control site without direct impacts of traffic. Our results confirmed that vehicles and traffic-related activities were the sources of octylphenols, BPA and phthalates as well as the metal(loid)s Sb and W, infrequently reported in previous studies. Among metal(loid)s, Cu, Zn and W occurred in the highest concentrations (up to 1.2 mg/L Cu, 2.4 mg/L Zn and 1.9 mg/L W), while PAHs and phthalates occurred in the highest concentrations among the trace organic pollutants (up to 540 μg/L phthalate diisononyl phthalate). Among the phthalates, di-(2-ethylhexyl)phthalate had the highest frequency of detection (43% of the roadside samples). While BPA and octylphenols had relatively high frequencies of detection (50% for BPA and 81% for octylphenols), they were present in comparatively low concentrations (up to 0.2 μg/L BPA and 1.1 μg/L octylphenols). The control site displayed generally low concentrations of the pollutants studied, indicating that atmospheric deposition was not a significant source of the pollutants found in the roadside snow. Several of the pollutants in the roadside snow exceeded the applicable surface water and stormwater effluent guideline values. Thus, the transport of these pollutants with runoff posed risk of causing adverse effects in the receiving surface waters.

1. Introduction

Urban stormwater, including snowmelt in regions with seasonal snow, is widely known to contribute to the deterioration of receiving waters with respect to quality and fish habitat (e.g., Makepeace et al., 1995; Sillanpää & Koivusalo, 2013; Masoner et al., 2019). Among anthropogenic activities polluting stormwater, vehicular traffic was identified as one of the most important sources of stormwater pollution early in the history of stormwater quality research (e.g., Laxen & Harrison, 1977) and has since then been studied extensively with regard to a wide range of pollutants released and their transport with stormwater runoff (Müller et al., 2020). As reviewed in Müller et al. (2020), the early studies largely focused on the now conventional pollutants, e.g., suspended solids, nutrients, metals, polycyclic aromatic hydrocarbons (PAHs) and chloride, while the most recent studies report findings of the pollutants of emerging concern in road stormwater runoff. Awonaike et al. (2022) highlighted that traffic is a major source of a wide range of organic pollutants to road runoff, and consequently to the receiving waters. For instance, relatively recent stormwater quality studies detected a number of organic pollutant groups of environmental concern, including alkylphenols (APs) (e.g. Bressy et al., 2011), phthalates (Björklund et al., 2009) and bisphenol A (BPA) (Gasperi et al., 2014), and indicated that traffic activities were a likely contributing source. Phthalates are commonly used as plasticisers in plastics production, mainly for the production of polyvinyl chloride (PVC). Historically, the phthalate di-(2-ethylhexyl)phthalate (DEHP) was used most commonly, but after its ban for certain uses, based on toxicological studies (Jamarani et al., 2018), it is increasingly being replaced by, e.g., diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP). APs and BPA are used as industrial additives to plastics products, epoxy resins,

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paints and varnishes and, among APs, nonylphenols (NPs) and octylphenols (OPs), as well as their ethoxylates (NPEOs and OPEOs), are most frequently detected in environmental studies. Hence, these pollutant groups could enter the road environment, encompassing the road and its direct surroundings, through mechanical wear of plastics details of vehicle bodies as well as tyres (Masoner et al., 2019).

Regarding the conventional pollutants, the extensive research on pollution in the road environment has identified the sources contributing specific pollutants. For instance, exhaust gases and particles are known to release PAHs (Markiewicz et al., 2017) and Ni (Duong & Lee, 2011), tyres release Zn (Councell et al., 2004) and Cu (McKenzie et al., 2009), and brakes may release Cu (McKenzie et al., 2009), Sb, Zn, Ni and Pb (Hjortenkrans et al., 2007). Metal(loid)s infrequently reported in previous urban runoff quality studies, but with known sources of releases in the road environment (Müller et al., 2020), include Pt, Rh, Pd, Sb and W. Tyre studs, used in cold climates to provide traction on slippery roads, are recognised as the main source of W (Huber et al., 2016), and catalytic converters, used in the exhaust systems of internal combustion engine vehicles, were identified as sources of Rh, Pd and Pt (Rauch et al., 2005). These metals generally do not occur in concentrations causing high environmental concerns, but may serve well as indicators of vehicular traffic activities (Huber et al., 2016). Regarding organic micropollutants, the current knowledge of their occurrence and sources of releases in the urban environment is more limited. As earlier stated, previous stormwater quality studies detected a range of organic micropollutants in urban runoff (e.g., Boom & Marsalek, 1988; Björklund et al., 2009; Bressy et al., 2011; Gasperi et al., 2014), but few studies have established clear connections to releases in the road environment. For instance, a recent study of road runoff in Paris, France, detected a wide range of organic micropollutants, among which phthalates (primarily DEHP), benzotriazoles, PAHs, BPA and APs were present in the highest concentrations (up to 20 μg/L) (Gasperi et al., 2022). Vehicles and traffic-related activities were identified as important sources of a number of organic micropollutants, including APs, phthalates and BPA, through substance flow analyses (Björklund, 2010; Markiewicz et al., 2017). One of the latest additions to the list of vehicular traffic generated pollutants are the tire and road wear particles (TRWPs), which were found to be abundant in roadside snowbanks (Vijayan et al., 2019b). Moreover, laboratory-leaching experiment results point to the potential releases of APs, BPA and phthalates from car bodies and tyres (Lamprea et al., 2018; Deshayes et al., 2019). Some of these substances (phthalates, NPs, OPs and several metals) may cause adverse effects in the receiving waters, and consequently are listed among the 45 priority substances of major concern for European waters (Directive, 2013/39/EU), and among the Toxic and Priority Pollutants under the U.S. Clean Water Act (U.S. EPA, 2021).

Roadside snowbanks may serve as effective passive samplers of pollutants generated in the winter road environment, because such pollutants can accumulate in the snow mass during longer periods, up to the whole snow cover season, which may facilitate the detection of pollutants occurring in low concentrations (Björklund et al., 2011). Other than PAHs, which, similar to metals, were subject to previous screenings (e.g., Boom & Marsalek, 1988; Reinosdotter et al., 2006; Kuoppamäki et al., 2014; Vijayan et al., 2019a), studies on organic pollutants of environmental concern in urban snow are scarce. Fries and Püttmann (2004) detected NPs in urban fresh fallen snow in Germany and Belgium, and, grab samples of roadside snow in Gothenburg, Sweden, showed frequent detections of NPs and phthalates (Björklund et al., 2011). The accumulation of pollutants during a whole snow season may cause peak concentrations of pollutants during snowmelt (Westerlund & Viklander, 2006; Meyer & Wania, 2008). However, in cold climates, snow management strategies make it possible, to some extent, to control where the polluted snow is disposed of and the pollutants end up after melting (Viklander, 1999). Furthermore, the sampling of roadside snow enables discernment of the contribution of pollution from other stationary sources in the road environment, e.g., road fences, traffic barriers and signs and other galvanised steel elements, representing a source of Zn (Huber et al., 2016), or plastics materials, as the snow would not come into contact with these surfaces to the same extent as rain and runoff.

Because of the above-mentioned scarce reports of organic micropollutants as well as the metal(loid)s Pt, Rh, Pd, Sb and W, and, clear connections to their releases in the road environment, the aim of the present study was to investigate the occurrence of selected metal(loid)s (Cd, Cr, Cu, Ni, Pb, Pd, Pt, Sb, W, Zn), PAHs, nonylphenols (NPs), octylphenols (OPs) and –ethoxylates (NPEOs, OPEOs), phthalates and BPA in the road environment by sampling urban roadside snow. While NPs, OPs, NPEOs, OPEOs, BPA, phthalates and Pt, Rh, Pd, Sb and W were rarely reported in the earlier literature, others may, in the context of the present study, be seen as reference pollutants serving to establish connections to the earlier studies and the road environment, and determine if a correlation to pollutant releases from vehicles and traffic-related activities can be observed.

2. Material and methods

2.1. Sampling locations

For the purpose of the present study, samples of roadside snow were collected at eight roads and highways with varying annual average daily traffic (AADT) counts in Luleå (seven locations) and Stockholm (one location). Luleå is located in the northernmost part of Sweden and has a subarctic climate (Köppen climate classification code Dfc) with a snow cover lasting several months in the winter season, while Stockholm is located approximately 900 km south of Luleå and has a humid continental climate (Köppen climate classification code Dfb) with occasional snow covers. Details of the sampling locations are presented in Table 1, and maps of the sampling locations may be found in Appendix D. The AADT at the sampling site in Stockholm is among the highest AADTs for Swedish roads, with >50 000 vehicles per traffic direction and day. The traffic intensity of roads in Luleå is smaller (up to around 10 000 vehicles per traffic direction and day), but as Luleå has a colder climate and usually longer periods with snow cover, it experiences longer snow accumulation times. All sampling sites represent typical Swedish roads and highways with respect to appearance, traffic conditions, as well as snow clearance and de-icing practices. The selection of sampling locations was based on the highest possible AADT (in Luleå, except for site

Table 1
Presentation of sampling locations. AADT data are given for one traffic direction, and were collected from the Swedish Transport Administration website (https://vtf.trafikverket.se/SeTrafikinformation).

Sampling location name	Site characteristics	AADT (year of measurement)	No. of lanes per traffic direction	Speed limit, km/h
E4S	Highway north of Stockholm.	50 860 (2018)	4	110
LU1	Highway deceleration zone in Luleå	10 591 (2017)	2	90
LU2	Beginning of main road from central Luleå	9623 (2018)	2	70
LU3	Road in central Luleå	9693 (2018)	2	70
LU4	Road in central Luleå	6318 (2015)	1	50
LU5	Road in central Luleå	4917 (2020)	1	70
LU6	Road in Luleå city centre	4806 (2020)	2	50
LU7	Residential main street in Luleå	2031 (2020)	1	50
REF	Control site, ca 150 m from the nearest road. Near the Luleå city centre.	n/a	n/a	n/a

LU7, which was added as a 'low-AADT location' for comparisons), and the appropriateness of the location with respect to snow removal practices at the actual location. Specifically, it was important that the snow was left in a snowbank next to the road and that (i) no fence, pedestrian and bicycle path, or other obstacle, was in the way of leaving a snowbank next to the road, and (ii) the snow was not pushed away from the side of the road, or entirely removed, for space or visibility reasons. At the Stockholm site (E4S), road salt is used for de-icing, while at all Luleå locations, the application of sand and grit is the main strategy to maintain pavement traction during winter, and road salt is only used at critical spots, such as bus stops and busy road stretches. In Luleå, snow samples were also collected at a control site in an urban setting but approximately 150 m away from the nearest road, in order to detect airborne sources of pollution in the vicinity. Other than airborne transport of pollution from vehicles and traffic-related activities, Luleå has a steel production plant and a district heating plant as potential sources of airborne pollutants, both located about 5 km south-east from the control site. According to the Swedish Meteorological and Hydrological Institute (SMHI), the most frequent prevailing wind direction in the study region is from the south or south-west.

2.2. *Snow sampling procedure*

Sampling took place in February and March 2021. Snow samples were collected once at the Stockholm location: February 10th, after 13 days of snow cover, and two times at all locations in Luleå: February 17th (further denoted as S1) and March 5th (further denoted as S2), after 56 and 72 days of snow cover respectively. At S1, the snow was ice-free and showed no signs of melting, while at S2, there were ice formations in the snow and visible signs that some melting had occurred. The snow samples were collected from the snowbanks directly adjacent to the roads (0.5–4 m from the wheel tracks, depending on the location of the snowbank) using a conventional snow shovel made of aluminium. At some locations, it was also necessary to use a titanium ice-drill to detach the snow because of ice formations in the snowbank. Triplicate samples were collected at all locations, with a 1–2 m distance from each other in the traffic direction. It was considered important to collect the snow nearest to the roadway, as it was hypothesised that this would be where the largest proportion of the pollutants from vehicles and traffic-related activities would be deposited. Results of snow quality studies in Sweden and Finland showed that the concentrations of PAHs, total suspended solids (TSS) and several metals decreased considerably with distance from the roads (Reinosdotter et al., 2006; Kuoppamäki et al., 2014). The full depth of the snow bank was collected as one sample and stored in perfluoroalkoxy alkanes (PFA) bags of approximately 20 L capacity. Vertically composed samples (top to bottom) were previously used in several studies (e.g., Viklander, 1999; Sillanpää & Koivusalo, 2013) and provided good estimates of the pollutant load in roadside snowbanks (Hautala et al., 1995) in spite of variations in snow quality with depth. A total of 5–6 kg of snow was collected per sample, and the PFA bags were stored in plastic pails for stability. For the control samples of undisturbed snow, not exposed to traffic, the snow from the entire snow depth was collected (in triplicate samples) approximately 10 m away from the nearest pedestrian path using the same aluminium shovel and PFA bags as for the other samples. The samples from Stockholm were shipped in a Styrofoam box to Luleå University of Technology, without any visible signs of melting, and were otherwise treated as the rest of the samples. After the sampling, the samples were left to thaw at room temperature until they were completely melted, after which physical and chemical analyses of the samples were performed. The total number of samples was three at E4S (Stockholm) and six at each of the Luleå locations, with the exception of LU3 (four samples in total) and LU6 (five samples in total), where holes in the PFA bags caused leaking of some of the samples while melting.

2.3. *Physical and chemical analyses of samples*

Basic water quality parameters (pH, electrical conductivity and TSS) were measured in The Environmental Laboratory at the Luleå University of Technology as soon as possible after the snow samples were completely melted, which occurred within 48 h after the start of the melting. TSS measurements were performed according to the Swedish standard EN 872:2005, meaning vacuum filtration through glass fibre filters with a 1.6-μm pore size, and determination of suspended solids contents through weighing of the filters after oven drying. The lower limit of determination was 2 mg/L. Samples for analysis of dissolved metal(loid)s were filtrated through a 0.45 μm membrane filter. Samples for chemical substance analyses were submitted to an accredited laboratory (ALS Scandinavia AB) with certified compliance with international quality assurance standards. PAHs, APs, phthalates and BPA were analysed by Gas chromatography-Mass spectrometry (GC-MS), while metal(loid)s were analysed using inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). Samples serving for analysis of total metal(loid)s were autoclaved with HNO_3 prior to analysis (for Pt, Pd and Rh, aqua regia was used instead of HNO_3), with exception of W, which was digested with HF and HNO_3 in hot block. Further details about the analytical methods and their reporting limits (RL) are presented in Table 2.

Table 2
Analytical methods, analysed substances and their analytical reporting limits (RL) in μg/L.

Substance group	Analytical methods	Substances (reporting limit, μg/L)
Metals	Analysis on ICP-SFMS, following standards SS EN ISO 17294–2: 2016 and US EPA Method 200.8:1994.	Al (10), As (0.5), Ba (1), Cd (0.05), Co (0.2), Cr (0.9), Cu (1), Fe (10), Mn (0.9), Mo (0.5), Ni (0.6), Pb (0.5), V (0.2), Zn (4), Sb (0.1), Pt, Pd, Rh (0.02)
PAHs	Analysis on GC-MS according to a method based on standards US EPA 8270D, US EPA 8082 A, CSN EN ISO 6468 and US EPA 8000D.	Naphthalene (0.030), acenaphthylene (0.010), acenaphthene (0.010), fluorine (0.010), phenanthrene (0.020), anthracene (0.010), fluoranthene (0.010), pyrene (0.010), benzo(a) anthracene (0.010), chrysene (0.010), benzo(b)fluoranthene (0.010), benzo(k)fluoranthene (0.010), benzo(a)pyrene (0.010), dibenzo(ah)anthracene (0.010), benzo(ghi)perylene (0.010), indeno(123cd)pyrene (0.010)
Alkylphenols	Analysis on GC-MS according to a method based on standard ISO 18857–2.	4-tert-octylphenol, 4-tert-octylphenol-monoethoxylate, -diethoxylate, and -triethoxylate (0.01), 4-nonylphenols (tech. mixture), 4-nonylphenol -monoethoxylate, -diethoxylate and -triethoxylate (0.1)
Phthalates	Analysis on GC-MS, following standard DIN EN ISO 18856:2005.	Dimethyl phthalate, diethyl phthalate, di-n-propyl phthalate, di-n-butyl phthalate, diisobutyl phthalate, di-n-pentyl phthalate, di-n-octyl phthalate, di-(2-ethylhexyl) phthalate, butylbenzyl phthalate, dicyclohexyl phthalate, diisodecyl phthalate, diisononyl phthalate, and di-n-hexylphthalate (1)
Bisphenol A	Analysis on GC-MS according to a method based on standard ISO 18857–2.	Bisphenol A (0.05)

2.4. Data analysis

Data analyses were performed using Excel and R, and included basic statistical calculations as well as studies of correlations among various parameters (e.g., substance concentrations, TSS, EC, pH, and AADT at the different sites). Some of the samples had concentrations below the reporting limits (RL) of the respective analysis; and among the organic substances, some of the substance concentrations were reported as elevated RL instead of actual concentrations, due to matrix effects. When analysing such left-censored data, statistical methods developed for the analyses of nondetect data (Helsel, 2005) were applied through the Nondetects and Data Analysis for Environmental Data package (NADA) in R. Statistical analyses were only applied to substances quantified in at least 25% of samples, and, means were calculated using the regression on order statistics (ROS) method, while the significance of correlations was tested using the nonparametric Kendall's tau test. Moreover, commonly adopted diagnostic ratios were applied to identify the likely sources of PAHs in the roadside snow, by parent PAH ratios of e.g., low molecular weight (LMW) PAHs and high molecular weight (HMW) PAHs, Flouranthene (FLA) and Pyrene (PYR), and, Benzo(g,h,i)perylene (BghiP) and Indeno(1,2,3-cd)pyrene (IcdP). This approach was previously used in several studies, e.g., by Yunker et al. (2002) and (Karlsson and Viklander, 2008).

3. Results and discussion

3.1. Substance concentrations

In Fig. 1, minimum, mean and maximum total concentrations of selected micropollutants in all samples of roadside snow (42 samples in total) are presented. To account for samples with concentrations below the RL, mean values were calculated with the NADA package in R using regression on order statistics (ROS). In cases where the minimum concentrations were below the reporting limits (RL), the pale blue colour denotes the true distribution, extending below the analytical RL to an unknown extent. Moreover, Fig. 1 includes relevant guideline values for comparisons to the results of this study. The guideline values apply to: (i) annual average environmental quality standards of inland and other surface waters in the EU Directive 2013/39/EU (in Fig. 1: EU inland/EU other); (ii) freshwater maximum concentrations according to the U.S. EPA National Recommended Water Quality Criteria for Aquatic Life (in Fig. 1: US acute/US chronic); (iii) the Swedish Agency for Marine and Water Management (SwAM) annual average in coastal surface waters (2019), and; (iv) guideline values for stormwater discharges in the second largest city in Sweden, of Gothenburg (2020) (in Fig. 1: GBG). Because some of the guidelines correspond to the dissolved, or bioavailable concentrations of pollutants, the maximum dissolved (in Fig. 1: Max diss.) concentrations of the metal(loid)s in the roadside snow are indicated by the blue circles in Fig. 1. Data from the control site (REF) was excluded from the analysis presented here, in order to indicate only the occurrence of the micropollutants in the road environment. From Fig. 1, the most abundant metals were W and Zn, while the most abundant organic micropollutant was DINP.

The ranges of concentrations of the analysed substances in the melted snow samples from the various sampling locations are summarised in Table A1 of Appendix A, together with the basic parameters pH, conductivity, and TSS. Selected elements with little environmental relevance, as well as substances that were not quantified in any of the 48 samples, were excluded for brevity. As the samples were collected at the part of the snowbank closest to the road, and not the highest point of the snowbank (sometimes several meters away from the road), the samples were not considered to be representative of the whole snowbank volume and, thus, unit area mass loads were not presented. Moreover, as the metal(loid)s were predominantly present in the particulate form, in agreement with the results from previous snow quality studies, e.g., Reinosdotter et al. (2006), all metal(loid) concentrations are presented as total concentrations, except in Fig. 2, showing both total and dissolved (<0.45 μm) concentrations of Sb and W. Fig. 2 and Table A1 of the Appendix A both show that the substance concentrations were low at the control site (REF), compared to the samples collected in the road environment, indicating low atmospheric deposition rates at the site. Neither phthalates, APs, APEOs nor BPA were present in concentrations above the RL in the snow collected at the control site. This is a clear indication that the main sources of the studied substances were the vehicles and traffic-related activities, and evidence that the deposition of traffic-related pollutants takes place mainly in the proximity of roads (Kuoppamäki et al., 2014).

Regarding metal(loid)s in the roadside snowbanks, Cu, Zn and W occurred in the highest concentrations. Pt was quantified in one single sample close to the RL (0.06 μg/L), and was, therefore, excluded from further analyses of the collected data. W, Sb, Pd, Rh, Cd, Cr and Ni were below the RL at the control site (REF), while Cu, Pb and Zn were detected, at concentrations lower than those in the roadside snow samples. The comparatively low Al concentrations at REF, compared to the road environment sites, indicate that the use of an Al shovel for sample collection did not largely affect the Al-results. Moreover, Sb, which is a toxic element rarely reported in previous studies (Huber et al., 2016), was in the roadside snow samples present at levels similar to those found in road runoff in France (Gasperi et al., 2022).

Four phthalates were detected in the roadside snow samples: DEHP, dicyclohexyl phthalate (DCP), DINP and DIDP, all of which occurred in concentrations higher in E4S samples than those from the Luleå

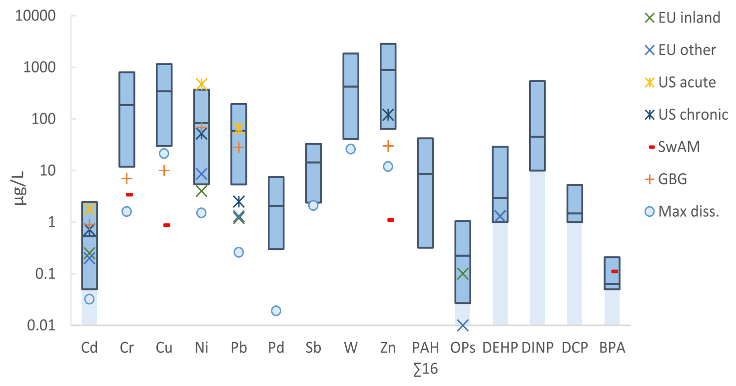

Fig. 1. Minimum, mean and maximum total concentrations (in dark blue) of selected micropollutants: the metal(loid)s Cd, Cr, Cu, Ni, Pb Sb, W and Zn; polycyclic aromatic hydrocarbons (PAHs); octylphenols (OPs); di-(2-ethylhexyl)phthalate (DEHP); diisononyl phthalate (DINP); dicyclohexyl phthalate (DCP); and, bisphenol A (BPA), in all samples of roadside snow (N = 42), and relevant guideline values where applicable. The maximum dissolved concentration of metals is indicated by the blue circles. Mean values were calculated with the NADA package in R using regression on order statistics. In cases where the minimum concentrations were below the reporting limits (RL), the pale blue colour represent the true distribution extending below the analytical RL. Data from the control site was excluded from the analysis presented here. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

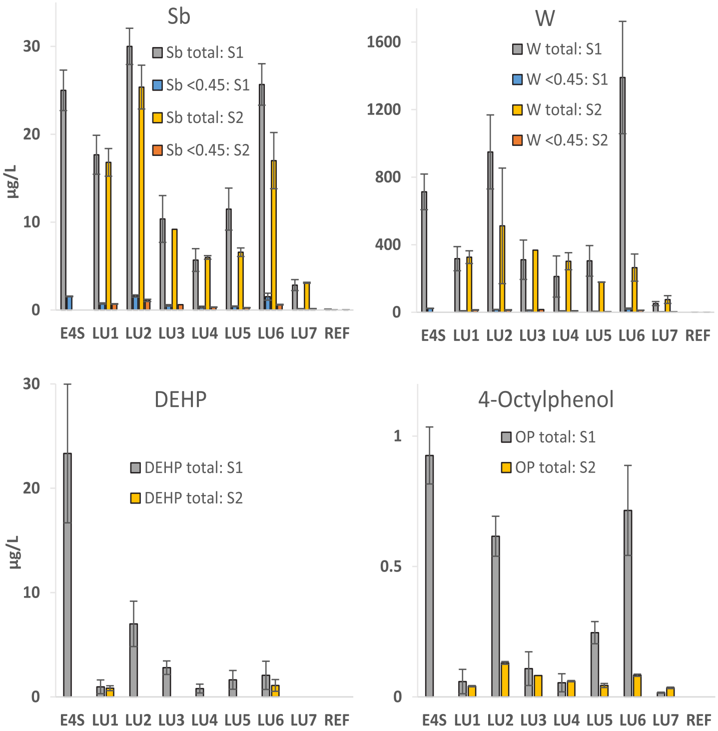

Fig. 2. Average Sb, W, di-(2-ethylhexyl)phthalate (DEHP) and 4-octylphenol (OP) concentrations (µg/L) in the roadside snow from all sampling locations, and the control site (REF), from sampling occasions S1 and S2. Error bars represent standard deviations between triplicate samples. Metals were measured as total or dissolved (<0.45 µm, in this figure denoted as <0.45) concentrations, while organic compounds were only measured as total concentrations. When calculating the averages and standard deviations for this figure, left-censored values were replaced with ½ RL.

locations. Among the phthalates, DEHP had the highest frequency of detection, followed by DINP, both present in <50% of roadside snow samples, but in relatively high concentrations. DIDP was only quantified in the three samples from Stockholm (at an average concentration of 210 µg/L), as well as one single sample from the Luleå locations, but in other cases was below the RL, or reported as an elevated RL due to matrix effects interfering with the analysis, possibly caused by other phthalates. BPA and OP had higher frequency of detection compared to the phthalates, exceeding 50% and 80%, respectively, but were present in comparatively low concentrations. Among APs, OP was the only substance that was quantified (in concentrations up to 1.1 µg/L), while the other APs and alkylphenol ethoxylates (APEOs) analysed were below RL, or displayed elevated RL due to matrix effects. However, the concentrations of OPs were in all samples above the corresponding RL for other APs and APEOs, indicating that OPs were the dominating APs present in the samples. PAHs were present in all samples, including the control samples (but in lower concentrations). Finally, BPA was quantified in roughly 50% of the samples from the road environment (i.e., excluding REF-samples), in concentrations up to 0.2 µg/L.

3.2. *Variations between sampling campaigns and sites*

The average site-specific concentrations of Sb, W, DEHP and OP for S1 and S2, and standard deviations (error bars) are displayed in Fig. 2. Sb, W, DEHP and OP were selected because of their environmental relevance, frequent detection in the present study, and, infrequent reporting in the literature. In general, snow samples from the site LU7, characterised by the lowest AADT among the sites, displayed the lowest concentrations of the studied substances among the data from roadside sampling locations. Sites LU6 and LU2 displayed the highest concentrations among the Luleå locations, and, for several metal(loid)s, the concentrations were higher than in the samples from E4S, Stockholm, possibly as a result of the much longer accumulation time in Luleå. For instance, the LU6 and LU2 peak concentrations of W, used in tyre studs (Huber et al., 2016), could be attributed to the higher use of studded tyres in the northern regions of Sweden (almost 90%), as opposed to 40% in Southern Sweden (Lundberg et al., 2019; Kriit et al., 2021), or because of increased wear of the studs caused by braking and accelerating at the specific sites. Fig. 2 also shows the low proportion of dissolved Sb and W, which generally applied to all metal(loid)s.

Regarding the organic micropollutants at the Luleå sites, phthalate and OP concentrations were higher in S1 than S2, while PAHs were at similar levels at S1 and S2. BPA was detected at more sampling sites at S2 compared to S1 (Appendix A), but the highest concentrations among Luleå sites were recorded at LU6 and LU2 at S1. Although the accumulation time of samples collected at E4S was shorter, the concentrations of the organic micropollutants in general, and the detected phthalates in particular, were higher compared to the Luleå locations. Possible reasons for this include the considerably higher AADT of E4S, and sample dilution by larger snow volumes in Luleå. On the other hand, with a few exceptions, most Luleå sites displayed higher levels of pollution during S1 than S2, possibly as a result of dilution by larger amounts of snow at S2 (Reinosdotter & Viklander, 2005). The most distinct exception from this were the pollution levels in the snow collected at LU2 at S2, also corresponding to the high TSS levels at this specific location and occasion. Regarding the basic parameters, E4S indicated higher TSS and conductivity (see Appendix A) compared to all Luleå sites, except site LU2 during the second sampling. The higher conductivity can likely be explained by the more extensive use of road salts on roads in Stockholm compared to Luleå. The pH (Appendix A) was also higher at the sites with higher AADT, compared to the control site (REF) and the low-AADT site (LU7), in agreement with the earlier research, possibly as a result of higher TSS providing buffering capacity to the snow (Viklander, 1999). Moreover, from Fig. 2, it can be inferred that the repeatability between triplicate samples was overall good (average relative standard deviation: 21%). In summary, considering both the differences between E4S and the Luleå sites as well as the differences between S1 and S2 at the Luleå sites, the results indicated that the traffic intensity was a more important factor for pollutant accumulation than the duration of accumulation.

3.3. Substance ratios as indicators of sources

Different PAH ratios were used to confirm the source of the PAHs in the roadside snow samples. The ratio between LMW PAHs and HMW PAHs may be used to distinguish between pyrogenic sources, i.e., incomplete combustion of e.g., fossil fuels or wood, and petrogenic sources, i.e., petroleum products or oil. A LMW/HMW ratio of <1 indicates pyrogenic sources, while a ratio of >1 indicates petrogenic sources (Soclo et al., 2000). Calculated LMW/HMW ratios for the roadside snow samples were in the range of 0.01–0.20, indicating pyrogenic sources, likely incomplete combustion of fossil fuels. As the PAH concentrations in the control site (REF) samples were in many cases below the RL, no such ratios could be calculated. A IcdP/(IcdP + BghiP) ratio between 0.20 and 0.50 likely implies fossil fuel combustion, with vehicle emissions usually indicating this ratio between 0.24 and 0.40 (Yunker et al., 2002), and, all ratios for the roadside snow samples fall within this range, except those that were below the RL. FLA/(FLA + PYR) ratios ranged between 0.40 and 0.54 for the roadside snow samples, and the FLA/(FLA + PYR) ratios between 0.40 and 0.50 are characteristic for fossil fuel combustion, while ratios of >0.50 are in general characteristic of grass, wood or coal combustion. However, the use of this ratio is complicated by such factors as, e.g., different PAH composition between different diesels fuels (Yunker et al., 2002) and possibly others. It is noteworthy that the FLA/(FLA + PYR) ratios in the samples collected at the control site on the first sampling occasion were 0.59 (all three samples), corresponding well to the ratios found in urban air, or indicating grass, wood or coal combustion as the likely source (Yunker et al., 2002), which could possibly be explained by wood burning inside houses or outdoors around campfires in the vicinity. On the second sampling occasion, the concentrations were below the RL, and no ratios could be calculated. Altogether, as expected, the use of PAH ratios as indicators of sources points to petroleum products or combustion of fossil fuels (i.e., traffic) being the likely source of PAHs in all quantified samples of roadside snow.

Similar to the PAHs, elemental ratios can be useful to indicate the relative contribution from specific sources. For instance, Hjortenkrans et al. (2006) investigated the Cu:Sb ratio of roadside topsoil samples, because both metal(loid)s are closely related to brake lining releases, and found the ratio values between 3.6 and 150 (average 20 ± 19), and explained the large range with other inputs of Cu from e.g., tyres. In the current study, the Cu:Sb ratio ranged between 9.9 and 51 (average 22) in the roadside snow samples, and 2.2–9.9 in the REF samples from the first sampling (at S2, both Cu and Sb were $<$RL at REF). Moreover, the site-average Cu:Sb ratio was higher at all roadside Luleå locations (LU1-LU7) at S2 compared to S1, possibly indicating accumulation of pollution from sources other than brake wear (e.g., tyres). For this purpose, the Zn:Sb ratio was used for comparisons, as Sb emissions are entirely attributed to brake wear (Budai & Clement, 2018), and the Zn:Sb ratios (between 23 and 125, average 60) showed a similar pattern with higher site-average for LU1-LU7 at S2 compared to S1. Budai & Clement (2018) reported a Zn:Sb ratio of 38 in urban road runoff (presented as a Sb:Zn ratio of 0.026 in their publication and was inverted herein), which is of the same order of magnitude as the Zn:Sb ratios of the roadside snow samples in the present study. Moreover, the Zn:Cu ratio in urban road runoff was 2.7 (presented as a Cu:Zn ratio of 0.37 in their publication and was inverted herein) (Budai & Clement, 2018). According to Hwang et al. (2016), the Zn:Cu ratios in road dust is relatively constant worldwide, e.g., they report that most U.S. road dust ratios fall within the range 2.6–5.1, and that an unusually high or low ratio would indicate inputs from other sources than traffic. Camponelli et al. (2010) reported a total Zn:Cu ratio of 5.1 in roadway runoff and 2.3 in road dust from the same road. The Zn:Cu ratios of the roadside snow samples in the current study were in the range 1.8–3.5 (average 2.6), thus close to the ranges reported in road dust and roadway runoff, and were 4.5–5.7 at REF (S1). Furthermore, elemental ratios of specific sources in the road environment (tyre and brake wear) presented by McKenzie et al. (2009) showed that Cu was enriched in brakes, (Zn:Cu ratio >1), and Zn was highly enriched in tyres (Zn:Cu ratio $\ll 1$). Even though the calculated ratios in the roadside snow are not directly comparable, it could be noted that the Zn:Cu ratio of <1 in our study implies that tyre contributions (in combination with other sources) dominated the pollutant contributions from brakes. The above presented results indicate that the main contribution of the metal(loid)s (Cu, Zn and Sb) accumulated in the roadside snow was from emissions from traffic sources, e.g., brake and tyre wear. These results are in agreement with those of other methods of ‘source tracking’. For instance, Hong et al. (2018) developed a method for source tracking of heavy metals in road deposited sediment using a ‘flag element ratio’, and found that braking and tyre wear were the major sources of Cu and Zn.

3.4. Correlations between parameters

Table 3 presents the results of the Kendall’s tau tests for correlations between selected substance concentrations (censored and uncensored) in the roadside snow samples ($N = 42$) and the basic parameters TSS, conductivity and pH, as well as the sampling site AADT. P-values for the correlations may be found in Appendix C. For brevity, selected elements with little environmental relevance and those that were quantified in $<25\%$ of the samples were excluded from the analyses. The results display correlations between TSS and metal(loid)s, PAHs, DCP, and BPA. AADT was correlated to the concentrations of Cu, Sb, W, Zn, DEHP and DINP, and, among those, all metal(loid)s have confirmed sources of releases from vehicles, and the phthalates had considerably higher concentrations at E4S which could explain the correlation with AADT. Conductivity was correlated to all substances included in Table 3 but Pd, as well as AADT and pH, possibly as a result of the generally higher substance concentrations at E4S compared to the Luleå sites, combined with the much higher AADT (five-fold or more) and conductivity (road salt usage) at this specific site. The correlation between pH and TSS may be, as described earlier, a result of particles providing buffering capacity to the snow (Viklander, 1999). Furthermore, all metal(loid)s were correlated to each other, as well as to PAHs, OPs, and BPA. The control site (REF) results were not included in the correlation analysis, but the overall low pollution levels at the site still provide relevant information to the clear correlation between traffic and the studied pollutants. Since the atmospheric deposition conditions at REF are considered applicable to all other Luleå sites (LU1-LU7), the atmospheric deposition can be ruled out as an important source of the studied pollutants. It is harder to make such inferences for the E4S site, because of the low number of samples in Stockholm ($n = 3$) and the lack of reference samples. Moreover, the high number of correlations between the parameters analysed (as evident from Table 3) is a further indication that no other sources than traffic made important contributions to the pollutant storage in the roadside snow, which, in turn, points to the advantage of using roadside snowbanks as passive samplers of pollutants generated by traffic, because of their potential to act as a temporary storage media and negligible interaction with other types of sources, e.g. road fences, compared to rainwater induced runoff.

3.5. Environmental impacts

The accumulation of pollutants in roadside snowbanks implies risks of large pollutant fluxes during snowmelt events (Westerlund &

Table 3
Results of Kendall's tau test for correlation between concentrations of selected substances in the roadside snow samples (N = 42) and TSS, pH, conductivity, and, sampling site annual average daily traffic (AADT). Significant correlations, considering α = 0.05, are marked with x. Data from the control site (REF) was excluded from the analysis presented here.

	Cd	Cr	Cu	Ni	Pb	Pd	Sb	W		PAH 16	OP	DEHP	DINP	DCP	BPA	TSS	pH	Cond	AADT
Cd	n/a	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Cr		n/a	x	x	x	x	x	x	x	x	x			x	x	x	x	x	
Cu			n/a	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Ni				n/a	x	x	x	x	x	x	x			x	x	x	x	x	
Pb					n/a	x	x	x	x	x	x	x		x	x	x	x	x	
Pd						n/a	x	x	x	x	x				x	x			
Sb							n/a	x	x	x	x	x	x	x	x	x	x	x	x
W								n/a	x	x	x	x	x	x	x	x	x	x	x
Zn									n/a	x	x	x	x	x	x	x	x	x	x
PAH 16										n/a	x			x	x	x	x	x	
OP											n/a	x	x	x	x	x	x	x	
DEHP												n/a	x	x	x			x	x
DINP													n/a	x	x			x	x
DCP														n/a	x	x	x	x	
BPA															n/a	x	x	x	
TSS																n/a	x	x	
pH																	n/a	x	
cond.																		n/a	x
AADT																			n/a

Viklander, 2006: Meyer & Wania, 2008). The transport of pollutants from melting urban snowpacks includes complex processes and is dependent on a number of influential factors, such as snowmelt flow, particle sizes and presence of salts (Reinosdotter & Viklander, 2007), the physical properties of the snowpack, and, runoff over frozen or thawed ground (Meyer & Wania, 2008). For instance, pulse releases of large amounts of chemicals are more likely to occur during intense melting or heavy rain on large, homogenous snowpacks accumulated over the whole season, than in shallow snow covers in temperate climates with recurrent melting over the season, and the resulting runoff may inflict the greatest stress on the receiving waters when running over frozen ground (Meyer & Wania, 2008). Moreover, large proportions of the dissolved metals are often transported in the beginning of the melt period, and, their concentrations may be further amplified by the presence of salts (Reinosdotter & Viklander, 2007). In studies of laboratory melting of roadside snow samples, Reinosdotter and Viklander (2007) estimated that 7–20% of the total Cu and Zn load was transported with the meltwater, and, Vijayan et al. (2019a) estimated that 5–12% of the PAHs followed the meltwater. Even though it is hard to accurately estimate the mass of pollutants that will settle on the ground next to the road (for possible latter resuspension with heavy rains) and the mass that will enter the receiving waters with snowmelt runoff, the comparison to the available guideline values may provide valuable information for risk evaluations. Snow management and disposal practices and the transportation of polluted snow from sensitive areas to less-sensitive areas, or even to snow treatment facilities, is possible and was suggested in previous studies as a control measure (e.g., Viklander, 1999; Kuoppamäki et al., 2014; Borris et al., 2021). Moreover, as the metal (loid)s in the roadside snow samples were primarily in the particulate form, which is often also the case in road runoff (e.g., Gasperi et al., 2022), treatment techniques based on the settling of particles, or filtration, would likely improve the water quality dramatically.

The substance concentrations found in the roadside snow samples were compared to the applicable guideline values for surface waters from the EU Water Framework Directive (WFD), the U.S. EPA, and, the SwAM, as well as the guideline values for stormwater discharges in the second largest Swedish city, of Gothenburg (2020), used for guiding stormwater quality management in the city. Such guideline values are presented in Fig. 1, as well as Table B1 of Appendix B. Moreover, the WFD, U.S. EPA and SwAM guidelines all apply to ambient water quality, and it is important to note that the snowmelt quality presented herein would likely be mixed with other runoff waters and would also be greatly diluted upon entry into the receiving waters. Nevertheless, such comparisons may provide information on, e.g., the critical substances in need of further monitoring. Not all of the studied pollutants were included in the guidelines considered relevant to this study. Regarding the metals, with the exception of Cd, the concentrations in the roadside snow exceeded all the various guidelines listed, except for the acute (toxicity) Ni maximum concentrations (MC) according to the U.S. EPA, which was in the same range as the Ni concentrations in the roadside snow. However, the U.S. EPA guidelines for Ni and Pb correspond to the dissolved concentrations, which were below the guidelines in the roadside snow samples, as illustrated in Fig. 1. Cu and Zn concentrations, mainly released from brakes and tyres, both exceeded the Gothenburg stormwater discharge guidelines by one order of magnitude, and the SwAM surface water guidelines for the Baltic Sea by two and three orders of magnitude, respectively. Even though the SwAM surface water guidelines for the Baltic Sea refer to the bioavailable fraction of Cu and Zn, which in this context is perhaps best compared to the dissolved concentrations, it can be inferred from Fig. 1 that the dissolved concentrations still exceeded the guidelines by one order of magnitude. The only phthalate listed in these guidelines was DEHP, which was present in the roadside snow in concentrations up to 20 times higher than the EU WFD EQS (Environmental Quality Standards). Moreover, the benzo(a) pyrene (BaP) concentrations, which can be found in Table A1 of Appendix A, exceeded the EU WFD guidelines at all the roadside sampling locations, and were of the same order of magnitude as, or above, the Gothenburg guideline. In terms of traffic, vehicle exhaust was shown to be the major source of PAHs, and, the ongoing transition to electric vehicles may partly mitigate this concern (Revitt et al., 2022). BPA and OPs were only listed in one of the guidelines each (SwAM and EU WFD, respectively), and the concentrations in the roadside snow were of the same order of magnitude as listed for both the BPA and OP concentrations. Furthermore, other pollutants that are not listed in any guidelines may also cause environmental damage. For instance, DINP, not yet listed in any of the above-mentioned guidelines, was shown to decrease fertility of aquatic organisms at far lower concentrations (0.42 μg/L) (Forner-Piquer et al., 2018) than those in the roadside snow samples.

Overall, considering that many of the studied substances exceeded the available guidelines, and more substances were present in high concentrations but not listed in any currently applicable guidelines, the roadside snow may potentially pose risk to aquatic life during uncontrolled snowmelt and transport to the receiving waters. Especially considering the poor understanding of the potential mixture effects from many substances being present in proportionally low concentrations (Masoner et al., 2019), sometimes referred to as a chemical cocktail effect. This would warrant toxicity testing of roadside snow in future studies. Furthermore, traffic byproducts and road surfaces are being increasingly recognised as important sources of a wide range of organic contaminants, and deserve the full attention of those working with urban water quality (Awonaike et al., 2022). A number of substances of environmental relevance may warrant future investigations of the contribution of pollution from the road environment to roadside snowbanks. For instance, Per- and Polyfluoroalkyl Substances (PFAS), that were previously found in street sweepings (Ahmadireskety et al., 2021) and road runoff (Gasperi et al., 2022), Benzotriazoles (Awonaike et al., 2022), and, rare earth elements (REEs), considering their environmental risks and increasing use in, e.g., the production of electric cars (Masoner et al., 2019).

4. Conclusions

This study investigated the occurrence of selected metal(loid)s and organic micropollutants in the road environment by sampling urban roadside snow at sites with different traffic intensities and pollution accumulation periods, as well as at one control site in an urban setting, but without a direct exposure to traffic emissions. It was confirmed that the road environment, including vehicles and traffic-related activities, were the source of OPs, BPA and phthalates (DEHP, DINP, and DCP) as well as the metal(loid)s Sb and W, infrequently reported in previous studies. Furthermore, the conventional pollutants, including TSS, Cu, Pb, and Zn, helped establish connection to releases from traffic-related activities. The control site displayed generally low, or even unquantifiable, concentrations of the studied pollutants, indicating that no airborne source exerted large effects on the pollutant levels in the roadside snow. Likely, the pollutants found in the roadside snowbanks would be entrained by road runoff, or partly remain deposited in the road environment, susceptible for later resuspension. Furthermore, the pollution levels in the snow collected in Stockholm were in many cases higher than those at the Luleå locations, indicating that the higher AADT and smaller snow volumes were more important than the duration of pollutant accumulation. This was especially true for the phthalate levels. Because concentrations of several of the studied pollutants in the roadside snow exceeded the available surface water and stormwater discharge guideline values, e.g., DEHP, the transport of these pollutants with snowmelt runoff posed risk of causing adverse effects in the receiving surface water bodies. Therefore, snow management practices, or other control measures, including source controls, may need to be considered in ecologically sensitive areas.

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CRediT author statement

Alexandra Müller: Conceptualisation, Methodology, Formal analysis, Investigation, Visualisation, Writing - Original Draft, Writing - Review & Editing. **Heléne Österlund:** Conceptualisation, Methodology, Writing - Review & Editing, Supervision. **Jiri Marsalek:** Conceptualisation, Methodology, Writing - Review & Editing, Supervision. **Maria Viklander:** Conceptualisation, Methodology, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.119723.

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Appendix A

Exploiting urban roadside snowbanks as passive samplers of organic micropollutants and metals generated by traffic

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Table A1 *Ranges (min-max) of pH, electric conductivity (EC), TSS (mg/L) and substance concentrations (µg/L) in the melted snow samples from the different sampling locations and two sampling occasions (S1/S2), and indication of the number of samples from each location.*

	E4S	LU1		LU2		LU3		LU4		LU5		LU6		LU7		REF	
Parameter (µg/L)	**S1, n=3**	**S1, n=3**	**S2, n=3**	**S1, n=3**	**S2, n=3**	**S1, n=3**	**S2, n=1**	**S1, n=3**	**S2, n=3**	**S1, n=3**	**S2, n=3**	**S1, n=3**	**S2, n=2**	**S1, n=3**	**S2, n=3**	**S1, n=3**	**S2, n=3**
pH	7.79-8.52	7.20-7.36	7.89-8.41	8.32-8.79	8.02-8.59	7.91-8.14	8.46	7.71-7.99	8.02-8.48	7.71-8.60	7.82-8.15	8.57-8.97	8.34-8.49	7.21-7.41	7.91-8.04	6.50-6.92	6.52-6.71
EC (µS/cm)	6820-7620	70.8-95.1	51.1-78.0	424-448	71.8-95.7	137-169	165	92.9-96.7	86.0-113	55.1-68.3	26.5-34.1	519-841	50.7-58.7	26.4-35.6	20.4-23.6	8.60-9.30	7.10-8.00
TSS (mg/L)	4900-5100	650-1000	1700-2200	2100-4100	5700-9800	690-870	1600	930-1800	2200-4300	1500-3100	1300-2000	3300-5300	3700-4400	190-280	1000-1500	3-3.8	3.3-6.6
Al	58800-74100	20500-30500	43200-55000	62600-172000	166000-253000	17100-27800	39000	22900-43800	61000-64500	40400-92000	28600-36700	108000-196000	105000-110000	5970-10400	21900-30500	80.2-114	100-146
As	9.62-13.5	6.56-11.3	15.8-17.4	18.7-41	33.6-48.1	4.42-7.46	8.06	4.55-16.1	17.4-18.2	9.19-18.1	6.27-8.35	33.0-59.6	31.8-37.5	0.881-2.06	4.16-5.31	<0.5	<0.5
Ba	537-746	284-416	580-699	859-2250	2210-3640	221-356	479	295-524	761-788	482-1150	329-411	1460-2680	1330-1450	74.3-134	254-358	2.04-2.36	1.8-2.39
Cd	0.688-0.951	0.194-0.234	0.272-0.394	0.522-1.42	1.16-1.7	0.116-0.197	0.209	0.157-0.381	0.36-0.374	0.231-0.589	0.124-0.245	1.06-2.44	0.962-1.02	<0.05-0.0547	0.099-0.186	<0.05	<0.05
Cr	139-206	34.9-52.9	64.8-89.6	208-591	547-800	40.4-70.6	93.8	41-95.9	148-160	109-279	68.4-91.2	321-603	306-336	11.9-22.1	50.2-68.6	<0.9	<0.9
Cu	426-624	147-252	306-338	424-932	868-1150	114-207	176	73.1-177	195-214	132-320	112-147	574-1070	570-575	29.8-48.8	72.2-79.6	1.1-1.19	<1
Fe	104-148	29.4-46.2	66-87.2	115-319	309-480	23.7-41.9	64.1	32.6-67.9	107-113	66.4-162	46.6-62.4	202-376	198-210	6.98-14	32-48.2	0.126-0.188	0.134-0.184
Ni	55.2-88.1	16.9-26.7	37.6-45.4	86.5-264	235-370	17.1-31.7	40.4	18-47.1	69-73.7	48.1-128	33.8-40.9	136-272	126-138	5.39-8.81	24.2-37.2	<0.6	<0.6-0.626
Pb	60.1-93.2	19.3-30.4	37.2-45.4	58-178	142-194	16.4-30.5	30.2	13.8-32.6	44.8-48.7	32-78.3	22.2-32.4	98.3-189	98-102	5.38-8.36	16.3-22.6	0.623-0.693	<0.5-0.526
V	192-281	64-102	136-176	261-773	742-1140	70.3-116	171	87-175	345-371	184-458	119-161	483-904	442-476	17.6-34.3	82.4-124	1.01-1.2	0.886-1.24
Zn	1410-1960	341-678	682-784	934-2270	2100-2840	243-401	518	215-480	612-694	421-960	313-385	1390-2690	1410-1460	63.9-98	215-253	5.32-6.27	6.68-9.79

Pd	0.3-2.02	1.04-1.36	1.64-2.28	1.91-4.74	4.05-5.57	0.398-1.31	1.24	1.04-1.99	1.47-1.64	2.44-6.66	1.24-1.3	3.56-7.45	2.55-3.2	0.3-0.34	0.736-0.903	<0.02	<0.02
Rh	<0.02	0.0208-0.0269	<0.02	0.0393-0.0629	0.0245-0.0345	0.03-0.0352	0.0282	0.0254-0.032	<0.02-0.0212	0.0442-0.0925	0.0343-0.0487	0.059-0.0676	0.0289-0.0368	0.1-0.154	0.0549-0.0774	<0.02	<0.02
Sb	22-27.6	14.8-20.2	15.4-19	27.9-32.8	22.7-28.7	7.31-13.8	9.18	4.56-7.5	5.8-6.27	8.45-14.3	5.9-7.03	23.9-29	16.1-17.9	2.39-3.72	3.01-3.15	<0.1-0.12	<0.1
W	569-819	259-418	274-361	666-1200	236-994	213-475	368	123-384	232-348	224-431	177-180	1140-1860	167-362	40.6-68.2	45.8-102	<0.4	<0.4
di-(2-ethylhexyl)phthalate (DEHP)	14-29	<1-1.9	<1-1	4.2-9.5	<1	2.2-3.7	<1	<1-1.4	<1	<1-2.7	<1	<1-3.8	<1-1.7	<1	<1	<1	<1
dicyclohexylphthalate (DCP)	2.5-5.3	<1	<1	2.9-4.2	<1	<1	<1	<1	<1	<1	<1	1.6-4.9	<1-1.8	<1	<1	<1	<1
diisodecyl phthalate (DIDP)	130-250	<10	<10	<20-<50	<10-12	<20	<10	<10	<10	<20	<10	<10-<20	<10	<10	<10	<10	<10
diisononyl phthalate (DINP)	260-540	<10-25	<10-13	43-100	<10-26	34-53	<10	<10-17	<10	<10-31	<10	<50	<10-18	<10-<20	<10	<10	<10
4-tert-octylphenol	0.784-1.05	<0.054-0.125	0.038-0.044	0.513-0.697	0.123-0.136	<0.064-0.19	0.082	<0.066-0.103	0.057-0.063	0.196-0.3	0.035-0.054	0.593-0.959	0.078-0.088	<0.036	0.031-0.038	<0.01	<0.01
naphthalene	0.058-0.327	0.068-0.088	<0.03-0.063	0.218-0.265	0.048-0.22	0.086-0.115	0.081	0.181-0.308	0.369-0.527	0.13-0.162	0.038-0.053	0.252-0.453	0.171-0.175	<0.03-0.032	0.033-0.036	<0.03	<0.03
acenaphthylene	0.011-0.067	0.011-0.012	<0.022	0.044-0.056	<0.01-0.052	<0.03	<0.03	<0.18	<0.13	<0.04-0.022	<0.04-0.018	<0.15	<0.12	<0.01	<0.01	<0.01	<0.01
acenaphthene	0.012-0.067	<0.01	<0.022-0.023	0.057-0.087	0.012-0.122	<0.14	<0.02	<0.37	<0.28-0.211	<0.17	<0.02-0.011	<0.19	<0.1	<0.02	<0.01	<0.01	<0.01
fluorene	0.038-0.277	0.038-0.044	<0.022-0.077	0.169-0.228	0.028-0.268	<0.06-0.072	0.067	<1.87	0.875-1.14	<0.1-0.071	0.047-0.067	0.528-0.625	0.296-0.316	0.011-0.017	0.019-0.022	<0.01	<0.01
phenanthrene	0.59-4.78	0.451-0.567	0.121-1.05	1.42-1.83	0.224-2.56	0.71-0.907	0.796	6.93-7.52	4.47-6.3	0.661-1.16	0.671-0.755	3.64-4.87	2.49-2.66	0.151-0.217	0.313-0.39	<0.02-0.026	<0.02
anthracene	0.039-0.336	0.027-0.032	<0.022-0.046	0.109-0.147	0.019-0.22	0.04-0.062	0.049	0.196-0.301	0.105-0.314	0.032-0.094	0.052-0.074	0.113-0.327	0.218-0.22	<0.01-0.01	0.012-0.026	<0.01	<0.01
fluoranthene	0.77-6.88	0.427-0.527	0.056-1	1.8-2.16	0.288-3.27	0.69-0.869	0.692	0.619-1.09	0.825-1.37	0.693-1.37	0.848-0.932	2.51-4.17	2.32-2.41	0.168-0.272	0.41-0.515	0.024-0.029	0.011-0.012
pyrene	1.11-9.94	0.476-0.557	0.066-1.17	2.38-2.93	0.389-4.86	0.755-1	0.989	0.592-1.18	0.983-1.67	0.813-1.68	0.944-1.1	3.22-5.42	3.05-3.24	0.146-0.262	0.414-0.543	0.017-0.02	<0.01
benzo(a)anthracene	0.178-1.43	0.088-0.111	<0.022-0.232	0.607-0.724	0.096-1.22	0.152-0.207	0.189	0.113-0.258	0.227-0.423	0.199-0.428	<0.23-0.28	<1.64	0.778-0.842	0.032-0.065	0.082-0.112	<0.01	<0.01
chrysene	0.294-1.8	0.11-0.155	<0.022-0.254	0.583-0.634	0.113-1.6	0.26-0.383	0.407	0.4-0.868	0.364-0.661	0.34-0.587	<0.39-0.395	<3.95	0.644-0.685	0.066-0.09	0.137-0.156	<0.01	<0.01
benzo(b)fluoranthene	0.627-4.51	0.262-0.34	0.038-1.03	1.41-1.76	0.282-4.16	0.428-0.568	0.61	0.295-0.676	0.675-1.14	0.459-1.02	<0.73-0.767	<2.57	1.98-2.01	0.089-0.146	0.333-0.46	<0.01	<0.01
benzo(k)fluoranthene	0.127-1.02	0.061-0.083	<0.022-0.237	0.413-0.468	0.072-0.983	0.114-0.153	0.111	0.076-0.149	0.158-0.265	0.128-0.214	<0.17-0.172	<0.78	0.481-0.49	0.024-0.041	0.075-0.099	<0.01	<0.01
benzo(a)pyrene	0.276-2.17	0.0897-0.105	<0.022-0.365	0.545-0.668	0.108-1.69	0.142-0.197	0.26	0.107-0.29	0.254-0.514	0.208-0.495	<0.28-0.323	<1.36	0.678-0.704	0.0308-0.0487	0.0882-0.179	<0.01	<0.01
dibenzo(ah)anthracene	0.123-1.01	0.025-0.051	<0.03	0.156-0.297	<0.8-0.036	0.084-0.092	0.139	0.045-0.166	0.162-0.268	0.088-0.207	<0.16-0.172	<0.57	0.303-0.332	0.014-0.027	0.067-0.12	<0.01	<0.01

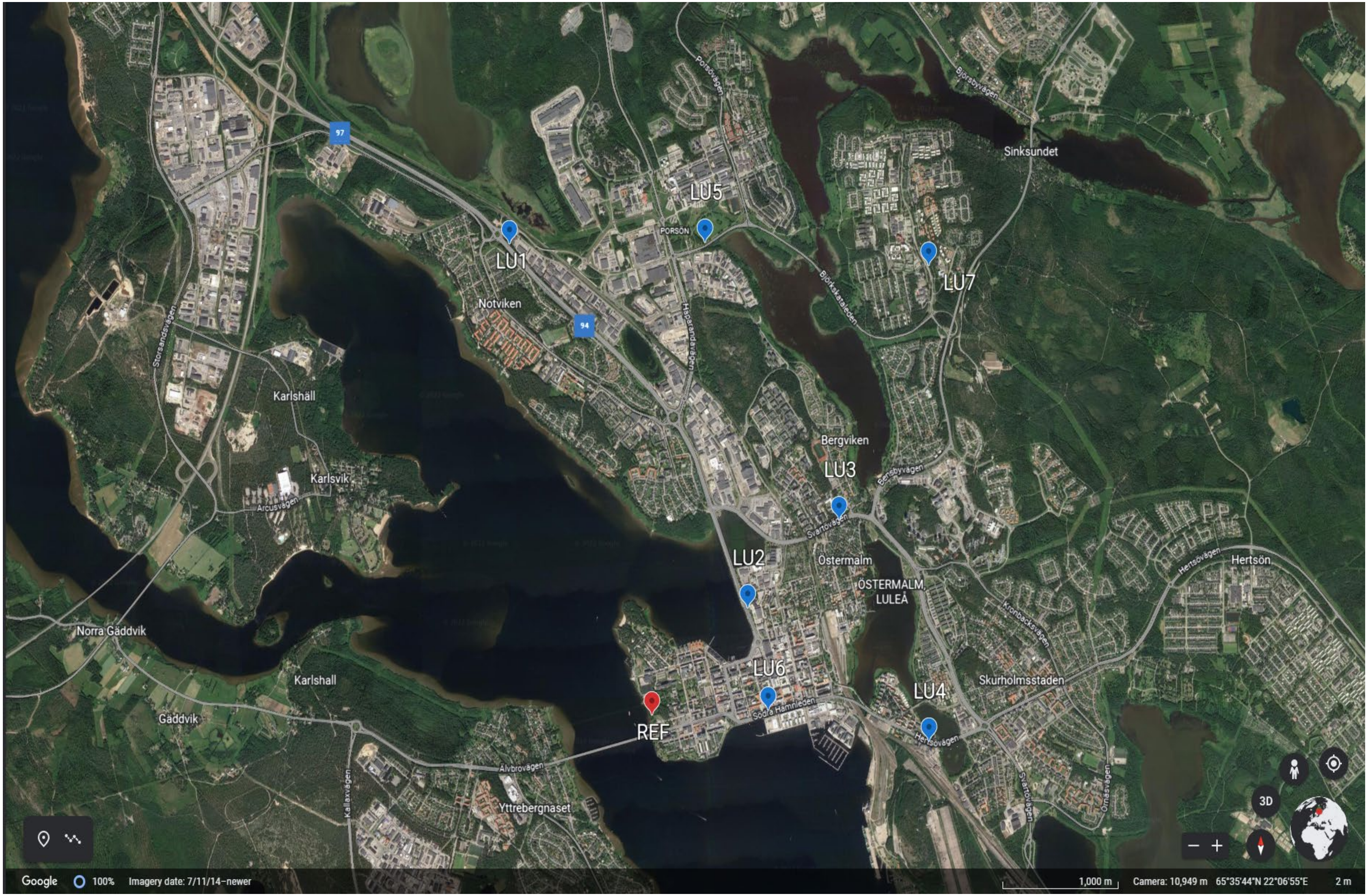
benzo(ghi)perylene	0.552-5.6	0.224-0.245	<0.4-0.047	0.705-0.862	0.169-0.698	0.299-0.427	0.737	0.212-0.474	0.715-1.06	0.406-0.744	<0.74-0.79	<1.92	1.49-1.68	0.067-0.108	0.377-0.51	<0.01	<0.01
indeno(123cd)pyrene	0.181-1.92	0.072-0.099	<0.31	0.34-0.493	<1.13-0.091	0.142-0.213	0.219	0.096-0.323	0.295-0.508	0.212-0.346	<0.28-0.344	<1.13	0.49-0.709	0.039-0.059	0.151-0.207	<0.01	<0.01
bisphenol A	0.174-0.197	<0.05	0.057-0.069	0.088-0.11	<0.05-0.062	<0.05	0.084	<0.05-0.069	<0.05-0.091	<0.05	<0.05	0.106-0.209	0.067-0.072	<0.05	<0.05-0.052	<0.05	<0.05

Table B1 Relevant guideline values for comparisons to the results of this study. The guideline values apply to annual average environmental quality standards (AA-EQS) of surface waters in the EU Directive 2013/39/EU, freshwater maximum concentrations (MC) according to the U.S. EPA National Recommended Water Quality Criteria for Aquatic Life, and, the SwAM annual average (AA) in coastal surface waters (2019), as well as guideline values for stormwater discharges in the city of Gothenburg (2020).

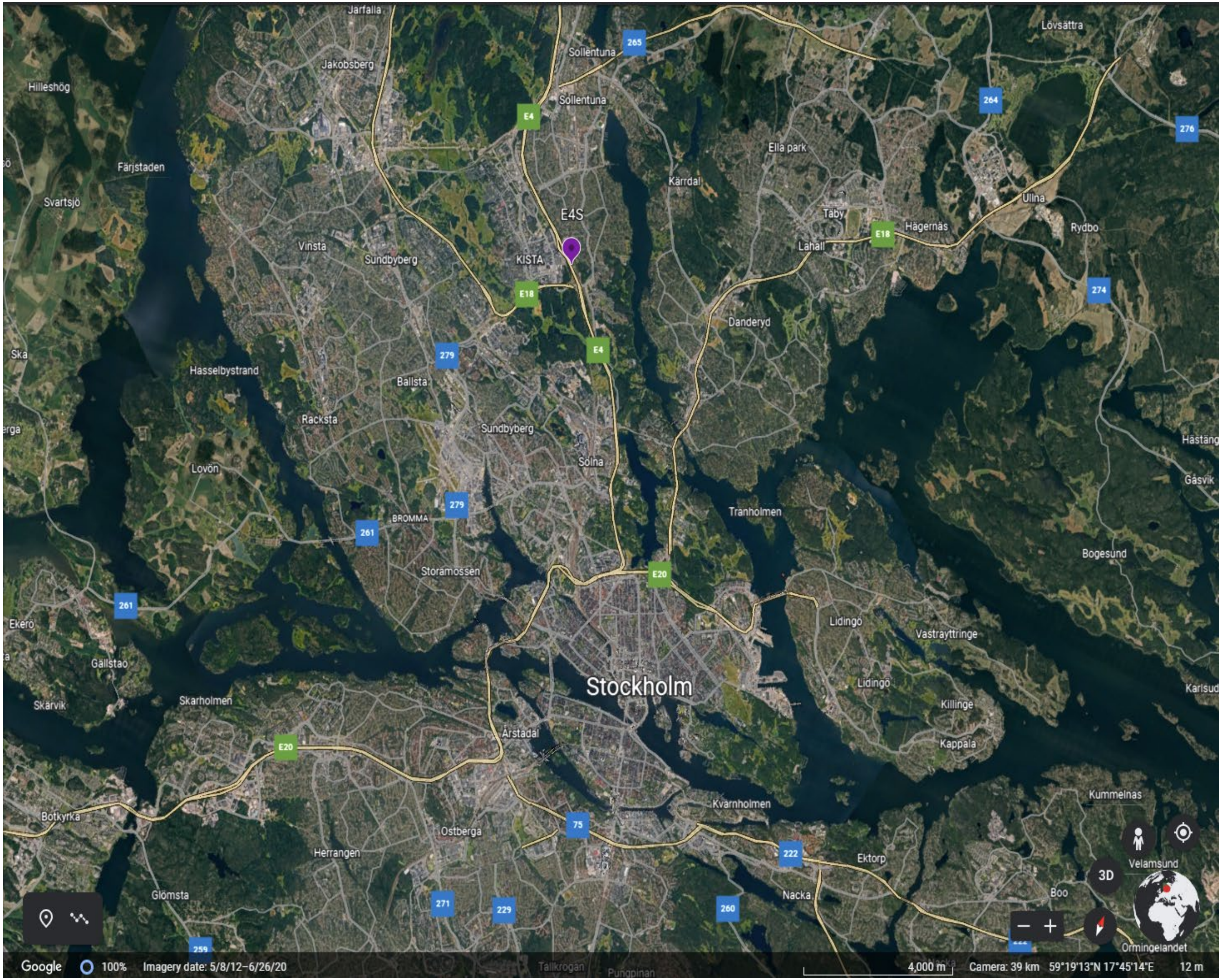
	EU WFD AA-EQS (Inland/other surface waters)	**U.S. EPA National Recommended Water Quality Criteria - Freshwater MC (acute/chronic)**	**SwAM Coastal waters AA**	**Gothenburg guidelines for stormwater discharges**
Cd	<0.08 - 0.25* / 0.2	1.8/0.72		0.9
Cr			3.4	7
Cu		-	0.87* *(Baltic Sea)*	10
Ni	4**/8.6	470/52 (dissolved)		68
Pb	1.2/1.3	65/2.5 (dissolved)		28
Zn		120/120	1.1 *(Baltic Sea)*	30
BPA			0.11	
DEHP	1.3/1.3			
NPs	0.3/0.3	28/6.6		
OPs	0.1/0.01			
BaP	0.00017***			0.27
Remarks	**depending on water hardness* *** bioavailable* **** BaP (benzo(a)pyrene), used as a marker for PAHs*	*Function of water hardness, here corresponding to a hardness of 100 mg/L.*	**bioavailable*	

Table C3 P-values from the Kendall's tau test for correlation between concentrations of selected substances in the roadside snow samples (N=42) and TSS, pH, conductivity, and, sampling site annual average daily traffic (AADT). Data from the control site (REF) was excluded from the analysis presented here.

	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Pd**	**Sb**	**W**	**Zn**	**PAH 16**	**OP**	**DEHP**	**DINP**	**DCP**	**BPA**	**TSS**	**pH**	**cond.**	**AADT**
Cd	n/a	1.23E-13	4.95E-14	3.55E-14	0.00E+00	1.11E-10	8.11E-09	1.35E-08	6.66E-16	5.57E-06	4.58E-07	1.84E-02	4.51E-02	1.17E-04	1.78E-06	2.88E-13	2.46E-05	7.49E-04	1.12E-01
Cr		n/a	4.75E-11	0.00E+00	3.55E-15	1.56E-09	1.50E-06	1.34E-06	2.53E-12	1.95E-06	4.86E-07	7.50E-02	1.47E-01	3.30E-04	2.17E-05	4.70E-13	5.78E-07	5.35E-03	7.76E-01
Cu			n/a	1.82E-11	1.53E-14	4.79E-09	2.01E-12	1.13E-10	2.22E-16	1.36E-04	6.44E-07	2.23E-03	6.96E-03	3.42E-05	3.36E-06	3.96E-11	2.85E-05	6.06E-05	5.61E-03
Ni				n/a	6.66E-16	3.22E-10	1.02E-06	7.31E-07	3.51E-13	2.29E-06	5.14E-07	6.92E-02	1.28E-01	2.76E-04	6.97E-06	2.24E-14	4.35E-07	4.22E-03	6.61E-01
Pb					n/a	5.43E-11	1.19E-08	1.36E-08	2.22E-16	5.58E-06	7.63E-07	3.37E-02	7.01E-02	1.60E-04	3.77E-06	4.80E-14	3.30E-06	8.77E-04	1.82E-01
Pd						n/a	4.08E-06	1.85E-05	7.88E-10	7.76E-04	8.78E-05	2.96E-01	4.50E-01	7.24E-02	7.82E-03	1.20E-07	3.47E-01	8.67E-02	9.65E-01
Sb							n/a	4.95E-10	3.73E-10	6.52E-03	1.20E-07	1.48E-04	8.18E-04	7.44E-06	5.45E-05	4.49E-06	3.32E-04	1.14E-05	8.08E-04
W								n/a	4.83E-09	4.27E-04	1.52E-07	1.63E-05	4.41E-04	3.58E-06	9.30E-07	9.18E-06	5.88E-04	3.46E-08	1.39E-03
Zn									n/a	3.00E-05	8.04E-07	1.84E-02	3.47E-02	1.03E-04	1.11E-06	1.28E-13	4.35E-05	2.82E-04	2.70E-02
PAH 16										n/a	1.20E-04	5.86E-02	6.47E-02	3.05E-03	2.13E-03	4.31E-07	6.71E-03	5.23E-04	6.14E-01
OP											n/a	1.61E-06	2.25E-05	2.22E-06	3.53E-05	3.62E-06	3.81E-05	9.00E-07	8.21E-02
DEHP												n/a	3.21E-11	8.80E-07	1.10E-03	6.89E-02	6.54E-02	4.11E-05	6.69E-03
DINP													n/a	2.35E-04	3.19E-02	1.03E-01	3.31E-01	4.21E-04	1.40E-03
DCP														n/a	5.12E-08	2.87E-04	2.89E-04	1.14E-05	3.39E-01
BPA															n/a	1.75E-06	6.53E-06	8.69E-06	1.19E-01
TSS																n/a	1.17E-05	4.19E-03	2.98E-01
pH																	n/a	5.51E-03	9.91E-01
cond.																		n/a	1.97E-04
AADT																			n/a



Sampling locations LU1-LU7 (blue points) and reference site, REF, (red point) in Luleå



Sampling location E4S (purple point) in Stockholm

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Department of Civil, Environmental and Natural Resources Engineering

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