

The release of pollutants from roofing materials in laboratory experiments

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Abstract: Diffuse pollution sources have been recognised by the European Water Framework Directive to significantly contribute to pollution of stormwater receivers. Stormwater runoff is considered to represent diffuse pollution sources. The aim of this study was to clarify the contributions of specific sources in the urban environment to the content of organic and inorganic pollutants in stormwater. This was done by conducting laboratory screening tests of several conventional roofing materials and coatings to determine which pollutants they release and how they might contribute to the deterioration of stormwater quality. The studied pollutants include metals (Cd, Cr, Cu, Ni, Pb, V, Zn) as well as polycyclic aromatic hydrocarbons (PAHs), phthalates, pesticides, nonylphenols and – ethoxylates. Many of the studied roofing materials, e.g. roofing shingle, a PVC sheet and a bitumen paste for felt roof maintenance, exhibited the potential to release several of these substances into stormwater runoff. However, phthalates were not released from any of the studied materials under the tested conditions. In addition, quite similar materials exhibited rather different substance release profiles.

Keywords: Diffuse pollution sources, Micropollutants, Stormwater quality

Introduction

The densification of urban areas due to growing urbanisation may increase the pollutant loads in stormwater and thereby contaminate lakes and watercourses in the urban environment and its surroundings, in contravention of the goals specified in the European Water Framework Directive (WFD) (2000). The sources of this pollution are roads, traffic and building materials in urban areas, which are weathered and exposed to precipitation (e.g. Göbel et al., 2007). The occurrence and concentrations of pollutants in stormwater are dependent on the characteristics of the surfaces that the runoff encounters as well as anthropogenic activities taking place in the vicinity (Eriksson et al., 2007).

The mitigation of stormwater pollution is considered to be essential for minimising the effect of diffuse pollution (Björklund, 2011). Many laboratory studies on this topic have been presented, dealing with a wide range of building materials and structures as well as analysed pollutants (e.g. Davis and Burns, 1999; Davis et al., 2001; Odnevall Wallinder et al., 2004; Clark et al., 2008; Schoknecht et al., 2009; Bielmyer et al., 2012; Wangler et al., 2012). However, a collective overall picture is still missing. Reasons for this include a lack of knowledge of the examined materials' origins as well as the difficulty of comparing results between existing studies due to differences in the parameters that they analysed and the diversity of the laboratory procedures used.

The aim of this study was to investigate the potential contribution of organic and inorganic pollutants from a range of conventional roofing materials to stormwater. This was done by performing laboratory leaching tests with synthetic rainwater. In addition, the variation in the amounts of pollutants released from similar materials of different origin was investigated. The studied pollutants include metals of relevance

(Cd, Cr, Cu, Ni, Pb, V, Zn) as well as polycyclic aromatic hydrocarbons (PAHs), phthalates, urea-based pesticides, nonylphenols and nonylphenol ethoxylates (NPs/NPEOs).

Material and Methods

Roofing Materials

This study focused on conventional roofing materials commonly used in residential houses, apartments and industrial buildings. Table 1 lists the studied materials together with the labels they were assigned to facilitate laboratory work and the substances for which they were analysed. All metal analyses were performed for both total and dissolved ($< 0.45 \mu\text{m}$) concentrations.

Table 1 The materials considered in this study, the labels they were assigned to facilitate laboratory work, and the substances for which they were analysed.

Label	Material Description	Performed Analyses
M1	Pure copper sheet	Metals
M2	Zinc sheet	Metals
M3	Stainless steel sheet	Metals
M4	Galvanised steel: Steel sheet, surface treated with zinc	Metals
M5	Metal roof paint used for metal roofs in outdoor environments	Metals, phthalates, NPs/NPEOs, urea-based pesticides
M6	Corrugated and coated steel sheets commonly used as roofing	Metals, NPs/NPEOs
M7	Untreated cement tile	Metals, NPs/NPEOs
M8	Cement tile coated with acrylic paint	Metals, NPs/NPEOs
M9	Untreated clay tile	Metals
M10	PVC sheet with polyester reinforcement used for larger industrial buildings	Metals, phthalates, NPs/NPEOs
M11	Bitumen Felt Roof (1): Polyester felt covered with bitumen and shale for low-pitch roofs ($\geq 3^\circ$)	Metals, PAHs, phthalates, NPs/NPEOs
M12	Bitumen Felt Roof (2): Polyester fabric covered with bitumen and shale for low-pitch or flat roofs	Metals, PAHs, phthalates, NPs/NPEOs
M13	Bitumen Shingle: Fiberglass covered with bitumen and shale for pitched roofs	Metals, PAHs, phthalates, NPs/NPEOs
M14	Bitumen paste for maintenance of old felt roofs	Metals, PAHs, urea-based pesticides

All substance analyses were performed by an accredited laboratory. Information on the analysed substances and the analytical methods as well as the report limits (LOR) for all analyses can be found in the appendix of a previous publication (Andersson Wikström, 2015).

Sample Preparation

Duplicate samples of each material were prepared. For the metal analysis, three layers of a metal-free lacquer were applied to the cut edges and back faces of materials for which the composition of the back and front faces differed, i.e. the coated steel sheet (M6), the cement and clay tiles (M7 - M9), the PVC (M10), and the bitumen-based materials (M11 - M14). Blank samples were prepared in the same manner by applying the lacquer to pieces of Plexiglas. Organic analyses of the coated steel sheet and the bitumen paste were conducted by first taking two samples of the material to be tested and screwing them together (using metal screws) with their back faces pressed against

one-another. Organic analyses of flexible materials with dual layer structures, namely the PVC sheet, the shingle, and the felt roofing materials were conducted by using the material to be tested to line the walls of a 3000 mL glass beaker, with the 'back' side of the material pressed against the beaker's wall in order to minimise its contact with the water. The metal roof paint (M5) was applied in two layers on the front and rear faces as well as the cut edges of previously untreated steel sheets using a conventional paintbrush according to the manufacturer's guidelines. The bitumen paste used for maintenance of felt roofs (M14) was applied in a single layer to one of the bitumen-felt roofs (M12) included in this study, in accordance with the manufacturer's recommendations. Blanks for organic analysis consisted of a glass beaker filled with synthetic rainwater.

Leaching Procedure

Leaching was performed in 500 mL polypropylene containers for metal analysis and 1000 – 3000 mL glass containers for organic analysis in order to minimise adsorption of analytes to the container walls.

Synthetic rainwater was added to the beakers in a volume corresponding to a 31.8 mm water column on the exposed area of each material. The composition of the synthetic rainwater was based on rainwater quality data reported for Svartedalen, Sweden, by Kindblom et al. (2001). The Svartedalen rainwater had a low pH as well as high sodium chloride and sulphate concentrations compared to typical Swedish rainwater. The synthetic rainwater was prepared from deionised water, HCl and salts such as NaCl, KNO₃, CaCl₂, and MgSO₄. Its composition was adjusted to achieve concentrations of 3.0 mg/L Cl⁻, 0.4 mg/L NH₄⁺-N, 0.5 mg/L NO₃⁻-N, 0.7 mg/L SO₄²⁻-S, 0.2 mg/L Ca²⁺, 0.2 mg/L Mg²⁺, 0.1 mg/L K⁺, 1.76 mg/L Na⁺ and a pH of 4.4 ± 0.1. Synthetic rainwater with a similar composition has previously been used to study the release of Cr and Ni from stainless steel in laboratory and field experiments, and was proven to successfully simulate field conditions in Sweden (Odnevall Wallinder et al., 2002).

The materials to be tested were placed in containers that were then charged with the synthetic rainwater as described above. The containers were then covered with polypropylene lids (plastic containers) or aluminium foil (glass containers) to prevent splashing, evaporation or contamination from outside. Thereafter, the beakers were placed on an orbital shaking device and agitated at 60 revolutions per minute for 24 hours. The chosen rain depth of 31.8 mm corresponds to a 24-hour rain event with a one year ARI in Sweden (Wern and German, 2009). The rainwater depth and leaching time were also chosen for practical reasons: they had to be sufficient to ensure that the tested materials were completely immersed in the water without diluting the extracts to the point that the leached analytes became undetectable.

After agitating the samples, the materials were left to dry in a fume hood for a minimum of 24 hours and then the leaching procedure was repeated. Because brand new materials were used, the leachates from the first leaching cycle were discarded to avoid obtaining unrepresentative results biased by "first-flush" effects. The leachates from the second round of leaching were collected in appropriate sample bottles and their pH was recorded, after which the samples were sent to the contracted laboratory for substance analysis. Finally, the appearance of the leached materials was evaluated visually, and any changes from their initial state were noted.

Results and Discussion

Metals

The metal analyses (Figure 1) showed that most of the metals released from the roofing materials were in the dissolved phase. This may be partly due to the relatively low pH of the synthetic rainwater (pH 4.4). However, the zinc sheet and galvanised steel seemed to release some zinc in particulate form (Figure 1). The leachates from these materials also had substantially higher pH values (pH 8 and 6, respectively) than the original synthetic rainwater (pH 4.4). In addition, a white coating was observed on the surface of the zinc sheet after the conclusion of the leaching experiments. This may indicate the formation of corrosion products, which could explain the release of particulate Zn from the zinc sheet and galvanised steel. Bertling et al. (2006) performed outdoor measurements on different types of zinc-based material panels and suggested that corrosion of these materials resulted in the formation of basic zinc carbonates and also raised the pH of the runoff. Similarly, it has been reported that the zinc carbonate hydrozincite was the initial corrosion product formed on weathered zinc roofs, and was also the most abundant phase on those roofs (He, 2002). The zinc sheet and the galvanised steel were the materials that exhibited the highest release of Zn. However, the coated steel and the metal roof paint also released relatively large amounts of Zn, in keeping with the use of Zn-containing additives during their manufacture.

Cu was, as expected, mainly released from the copper sheet. However, appreciable concentrations of this metal were also present in the leachate from the shingle, in contrast to the otherwise similar felt roofing materials. Cu leaching has previously been observed from both felt roofing materials and asphalt- and tar shingles in similar laboratory experiments (Clark et al., 2008); in that case too, the release of Cu from the shingle exceeded that from felt roofing materials. The Cu concentrations in the leachates from the other studied roofing materials were of the same order of magnitude as the blank samples.

Some metals were only detected in appreciable concentrations in one or a few of the studied materials. The shingle released dissolved Ni at a concentration of ca. 45 µg/L, whereas no such release was observed for the related felt roofing materials. Gasperi et al. (2014) reported Ni concentrations of 2.9 – 6.6 µg/L in stormwater quality measurements conducted in three French catchments. While these concentrations are not directly comparable to those presented here, the potential for Ni release from shingle is noteworthy. The vanadium contents of the leachates from the untreated cement and clay tiles were between 30 and 40 µg/L. In contrast, the coated cement tiles did not seem to release vanadium, suggesting that appropriate surface treatment can hinder the release of certain pollutants from cement tiles. A similar trend was observed for chromium. Cr was also released from one of the felt roofs and the stainless steel. Cd was only released from shingle, with a mean concentration of 0.15 µg/L of which 0.11 µg/L was dissolved.

In general, the leachates' lead concentrations were indistinguishable from those of the blank solutions. All of the measured Pb concentrations were considerably lower than those reported previously for Pb levels in roof runoff from pan tile and zinc roofs (Quek and Förster, 1993). Our results suggest that there is no effect on stormwater quality due to the release of lead from the roofing materials considered in this work.

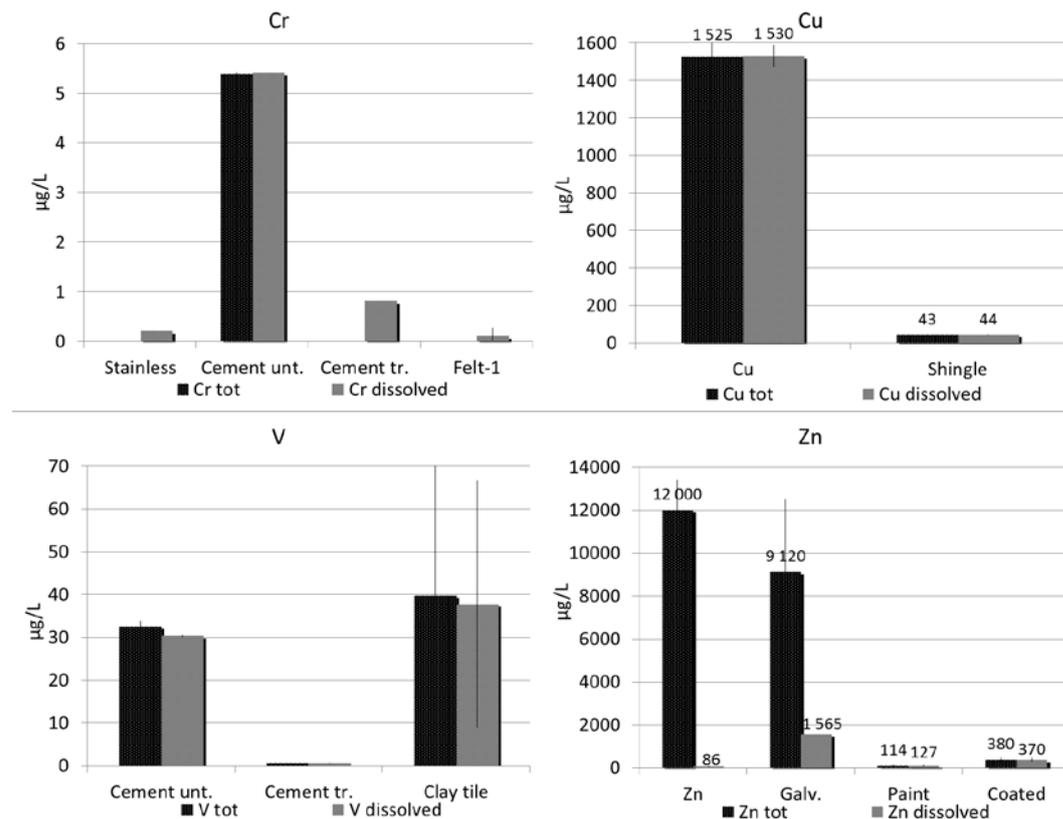


Figure 1 Mean metal concentrations in the leachates from selected roofing materials. The uncertainty bars represent the range of concentrations observed in duplicate samples. The absence of Cr tot. bars for some materials is because in these cases the LOR for the total conc. analysis ($0.9 \mu\text{g/L}$) was greater than that for the dissolved conc. analysis ($0.01 \mu\text{g/L}$).

Organic Compounds

Organic analyses were performed on a subset of the studied materials that were selected on the basis of their composition and the results of earlier studies. It is possible that some of the materials excluded from the organic analyses may release one or more of the studied organic compounds. An earlier leaching study reported by Clark et al. (2008) examined a number of organic compounds but did not detect any of them in the leachates of the included materials.

Phthalates were not detected in the leachates from any of the investigated materials. It was expected that they would mainly leach from the PVC materials, because phthalates are the single most common plasticisers in PVCs (Björklund, 2011) and leaching is believed to be the largest source of phthalate emissions (Björklund et al., 2007). Temperature is known to have important effects on rate of phthalate release (Björklund et al., 2007), which may explain the absence of detectable phthalates in the leachate from the PVC sheet: the laboratory experiments were conducted at a room temperature of ca. 20°C , which is significantly lower than that achieved by solar heating on a dark roof exposed to sunlight. Phthalates have also been reported to be present in SBS-bitumen (Lindström, 2007) and were therefore analysed in the leachates from the bitumen roofing materials, but once again these compounds were not detected. It is therefore suggested that the influence of temperature should be taken into account in future studies on the leaching of phthalates from roofing materials.

PAHs were released from two of the four analysed materials (Figure 2). All of the PAHs that were found in this study were of low molecular weight with 2-3 aromatic rings. The smaller PAHs are generally more volatile and water soluble (Swedish EPA, 2007), which may explain why these seemed to be released from the investigated materials. None of the felt roofing materials released detectable levels of PAHs, but the shingle did. This was an interesting discovery because these materials are similar in composition but originate from different manufacturers. It should be noted that the edges and back sides of the shingle could have contributed to the release of PAHs to some extent. The concentrations of \sum_{16} PAHs in the leachate from the shingle corresponded to ca. 8% – 15% of the measured concentrations of \sum_{16} PAHs in stormwater in the conurbation of Paris (Gasperi et al., 2014). For comparative purposes, the concentrations of \sum_{16} PAHs in the leachate from the bitumen paste corresponded to 260% – 494% of the measured concentrations in the stormwater. It is important to recall that bitumen paste is used to maintain older roofs and so its usage (and potential sites of release) may be limited to areas where such roofs are common. Consequently, the bitumen paste is assumed to mainly influence stormwater quality in a rather localized fashion. It is important to recognise that the measured concentrations of PAHs in stormwater are derived from various sources of pollution, including traffic, and will also be diluted with runoff that does not contain PAHs.

In this study, more materials were subjected to NP/NPEO analysis than to any other organic analysis. NPs were released from three of the tested materials: shingle, PVC and one felt roof material (Figure 2). PVC has previously been reported to release NPs/NPEOs (Björklund et al., 2007). The NP/NPEO concentration in the leachate from the shingle was on the same order of magnitude as the concentrations reported in stormwater in Paris (Gasperi et al., 2014), while the concentrations in the leachates from the felt roofing and especially the PVC sheet were many orders of magnitude higher. As previously stated, these comparisons must be interpreted with care because of factors such as dilution. It should also be noted that the edges and backsides of the materials could have contributed to the release of NPs to some extent. This should be evaluated in further studies. One felt roof (M12) exhibited a potential to release NPs whereas another (M11) did not. This was interesting given the similar compositions of the two materials. NPEOs were not released from any of the studied materials.

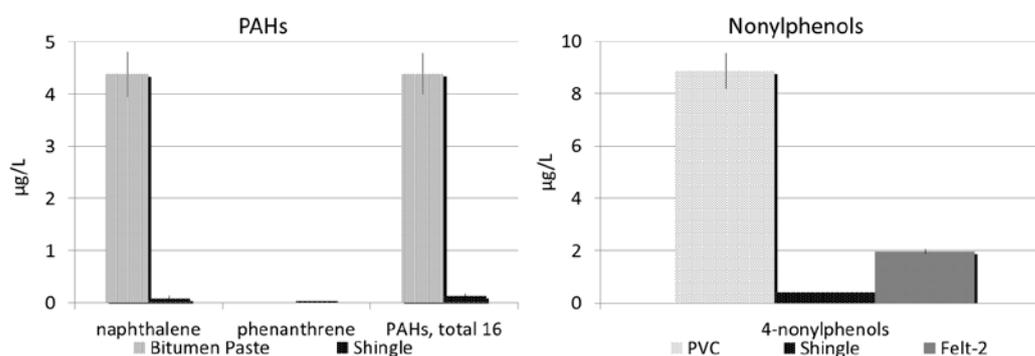


Figure 2 Mean PAH and NP concentrations in the leachates from selected roofing materials. The uncertainty bars represent the range of concentrations observed in duplicate samples.

The herbicide diuron was detected in the leachate from the metal roof paint, but only at a concentration corresponding to around 16% of that reported in previous measurements of stormwater (Gasperi et al., 2014). While it is clear that other pesticide sources contributed to the diuron content of the stormwater, our results indicate that the contribution from the metal roofing paint is not necessarily

negligible. The detected release is also noteworthy because the use of diuron has been banned in Sweden since 1993 (Swedish EPA, 2008). A temperature dependence of pesticide release has previously been reported (Wangler et al., 2012) and may warrant further investigation.

Conclusions

Many of the evaluated substances were detected in the leachates from the studied roofing materials and may thus end up in stormwater. Of the studied materials, shingle released the greatest number of pollutants, including the metals Cu, Ni and Cd as well as two classes of organic pollutants: PAHs and NPs. One of the felt roof materials (M12) and especially the PVC sheet also released NPs. The bitumen paste used for felt roof maintenance released the largest quantities of PAHs. Zinc was released by the zinc sheet, the galvanised steel, the coated steel, and the metal roof paint. The paint also released the herbicide diuron. The untreated cement tile was identified as a potential source of chromium in stormwater. The stainless steel, the treated cement tile, the clay tile and one of the felt roofing materials (M11) did not release any of the studied pollutants in detectable quantities under the experimental conditions.

Phthalates were not detected in the leachates from any of the studied materials so it was assumed that they were either not readily released from these materials under the prevailing laboratory conditions or simply not present in the studied roofing materials.

There were clear differences between the untreated and surface-treated cement tiles with respect to the release of pollutants. The surface-treated tiles released smaller quantities of the studied substances, suggesting that the surface coating was effective at reducing the release of pollutants into stormwater. The two felt roofing materials also showed dissimilar release patterns for the studied pollutants. M11 did not release any of the target substances in detectable quantities whereas M12 released NPs. The shingle was originally assumed to have a similar composition to the felt roofing materials, but released considerably more pollutants in larger quantities. This demonstrates that even quite similar roofing materials can have pronounced differences in their leaching behaviour, possibly as a result of different surface treatments or manufacturing processes.

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