Potential Sources of Stormwater Pollutants

Leaching of Metals and Organic Compounds from Roofing Materials

Alexandra Andersson Wikström
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Alexandra Andersson Wikström

Luleå University of Technology
Department of Civil, Environmental and Natural Resources Engineering
Division of Architecture and Water
Urban Water Engineering

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ABSTRACT

Runoff from paved surfaces in the urban environment is recognised as a major contributing source to deteriorated water quality. In stormwater, both various metals and organic compounds can be present and the quality of stormwater is dependent on e.g. the characteristics of the surfaces that the runoff encounters. Diffuse pollution sources, i.e. anthropogenic emissions from e.g. traffic or constructions, has been pointed out by the European Water Framework Directive to significantly contribute to pollution of stormwater receivers. In order to create and obtain a sustainable, liveable and aesthetical urban environment it is critical to be able to mitigate stormwater pollution, not least considering the increasing amount of stormwater due to climate change.

The aim of this master's thesis was to evaluate the potential release of inorganic- and organic stormwater pollutants from conventional roofing materials by laboratory leaching experiments. The study was mainly aimed to serve as a first screening on the roofing materials, in order to be able to select a number of materials for further investigation later on. The organic compounds included in this study were polycyclic aromatic hydrocarbons, nonylphenols and -ethoxylates, phthalates and herbicides. Previous research on stormwater pollution has mainly focused on metals and there is therefore a knowledge gap on organic compounds in urban runoff. The leaching experiments were designed considering previous similar studies. Synthetic rainwater was prepared based on measurements of rainwater quality in Sweden. Duplicates of 16 commonly used roofing materials were prepared and immersed in beakers of synthetic rainwater. The beakers were agitated on an orbital shaking device for 24 hours and pH as well as conductivity was recorded in the leachates before sending the samples to the contracted laboratory for analysis. Metals were analysed on all materials and the organic compound analyses were performed on selected materials based on each material's composition and was limited with the substance's probability to release from each material.

From the analysis results, mean values for the leached concentrations of all duplicates were calculated. The annual potential release of substances from materials was estimated based on the leached concentrations and data on the average annual precipitation in Sweden, in order to get an indication of the order of magnitude of the pollutant release.

The results showed a potential release of a number of the included substances from many of the studied roofing materials, in varying order of magnitude. The shingle roofing was the material that showed the ability to release the largest number of pollutants. Some materials e.g. the clay tile also showed potential to adsorb substances on the material surface. Metals were mainly released in dissolved form from most materials. Phthalates were not present in concentrations above report limits in the leachates from any of the studied materials. The results also indicate a significant different in the release potential from materials that were considered similar in their composition and expected to have similar leaching behaviour prior to the laboratory experiments, e.g. two similar felt roof materials from different manufacturers.

SAMMANFATTNING

Avrinning från hårdgjorda ytor i stadsmiljön har erkänts som en bidragande faktor till försämrad vattenkvalitet. Både en rad olika metaller och organiska ämnen kan finnas i dagvatten och dagvattnets kvalitet beror till stor del på egenskaperna hos de ytor som avrinningen passerar. Diffusa föroreningskällor, alltså antropogena utsläpp från exempelvis trafik eller byggnader, har i EU:s vattendirektiv utpekats som en stor föroreningskälla till dagvattenrecipienter. Att minska problemet med dagvattenföroreningar är absolut nödvändigt för att kunna upprätta och bibehålla en långsiktigt ekologisk hållbar, beboelig samt estetiskt tilltalande stadsmiljö, inte minst med tanke på den ökande mängden ytavrinning till följd av klimatförändringar.

Målet med detta arbete var att utreda det potentiella bidraget av metaller och organiska ämnen till dagvatten från traditionella takmaterial med hjälp av lakförsök i laboratorieskala. Studien ämnade fungera som en första screening av takmaterialen för att kunna välja ut ett antal takmaterial att utreda vidare i kommande studier. De organiska ämnen som ingick i studien var polycykliska aromatiska kolväten, nonylfenoler och –etoxilater, ftalater samt herbicider. Tidigare studier av dagvattenföroreningar har främst fokuserat på metaller och till följd av detta finns en kunskapslucka gällande organiska ämnen i dagvatten. Lakförsöken i denna studie planerades baserat på en litteraturstudie av tidigare liknande experiment inom området. Syntetiskt regnvatten tillverkades baserat på mätningar av regnvattenkvalitet i Sverige. Duplikat av 16 stycken vanligt förekommande takmaterial förbereddes och sänktes ned i bägare med syntetiskt regnvatten. Bägarna placerades på ett skakbord för omrörning i 24 timmar. Konduktivitet och pH mättes och proverna sändes därefter till analyslaboratoriet för analys. Samtliga material analyserades med avseende på metaller, medan de organiska analyserna begränsades till ett antal material beroende på materialens sammansättning och baserades på substansernas sannolikhet att urlakas från de olika materialen.

Medelvärden av de uppmätta koncentrationerna i lakvattnet från duplikaten beräknades. Det potentiella årliga bidraget av metaller och organiska ämnen uppskattades med hjälp av lakade koncentrationer samt data över årsmedelnederbörd i Sverige. Detta gjordes för att få en ungefärlig uppfattning av storleksordningen av eventuella utsläpp från materialen.

Resultaten visar att flera av de studerade takmaterialen potentiellt kan bidra med de olika föroreningarna till dagvatten, i varierande omfattning. Shingeltaket var det material som uppvisade potential att bidra med flest antal substanser till ytavrinningen. Vissa av takmaterialen visade också en förmåga att kunna adsorbera ämnen på ytan av materialen, exempelvis tegelpannorna. Metaller släpptes främst i form av lösta joner från de flesta av materialen. Ftalater fanns inte i koncentrationer över rapporteringsgränsen för något av de analyserade materialen. Resultaten indikerar också en betydande skillnad i utsläpp från material som anses vara likvärdiga och som före studien förväntades uppvisa liknande resultat, såsom två likvärdiga papptak från olika tillverkare.

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1 INTRODUCTION

Stormwater runoff is recognised as a significant source of pollution to receiving water bodies (Clark et al., 2008). Runoff from roofs and other impermeable surfaces has been shown to be the one of the largest contributor of both organic compounds and heavy metals. The occurrence and concentrations of different pollutants in the stormwater are dependent on the characteristics of the surfaces that the water encounters (Eriksson et al., 2007). That includes the structure and composition of urban materials as well as atmospheric deposition of pollutants and additions from anthropogenic activities in the vicinity. A polluted stormwater may cause risks for exposed humans, animals or plants. It can also result in technical and aesthetical problems in the urban environment. The quality of the rainwater that creates roof runoff will affect processes such as corrosion and weathering on the roofs and thus the concentrations of pollutants in the stormwater reaching the receiving waters (Göbel et al., 2007).

The Swedish Government has developed 16 environmental quality objectives meant to serve as a basis for the environmental work in Sweden (Environmental Objectives Council, 2009). Many of these are directly connected to the need for sustainable stormwater management systems. One of these objectives is "A Good Built Environment" with the aim to provide a good living environment and sustainable management of resources such as water and land. The objective "A Non-Toxic Environment" aims at reaching a state where non-naturally occurring substances have a negligible impact on ecosystems and human health. Also, the environmental quality objectives "Flourishing Lakes and Streams" and "Good-Quality Groundwater" are indeed dependent on the stormwater that reaches these water bodies to be of good quality.

The European Water Framework Directive (WFD) - Directive 2000/60/EC (2000) has recognised pollution from nonpoint sources as a contributing factor to deteriorated water quality. In urban environments, nonpoint source pollution is generated from anthropogenic emissions such as constructions or transports (Björklund, 2011). Mitigation of stormwater pollution is in the European WFD considered critical in minimising the effect of nonpoint source pollution (Eriksson et al., 2007). A number of priority pollutants have been identified by the WFD for this purpose, considering occurrence and toxicity in the aquatic environment (Björklund, 2011). This list contains 33 substances of which five are metals and the rest are organic compounds. Despite this, previous research has mainly focused on metals and nutrients. The knowledge about organic pollutants released from construction materials and their impact on stormwater runoff is limited (Burkhardt et al., 2011). Additives such as plasticisers, stabilisers and corrosion inhibitors are widely used in construction materials and paints and only a limited number of studies have been performed on the leaching behaviour of these materials (e.g. Jungnickel et al., 2008; Schoknecht et al., 2009).

Stormwater management has previously mainly focused on transporting the water from the urban environment to the receiving waters in order to avoid flooding (Lidstöm, 2012). This has now evolved to also include the quality of the water and the liveability in the urban environment. Sustainable urban drainage systems need to be implemented in order to tackle the increasing amounts of stormwater due to climate change. To successfully implement these systems and ensure that they improve the water quality, it is important to design systems based on the composition of the stormwater (Gasperi et al., 2014). It is therefore critical to study the quality of stormwater derived from different parts of the urban environment.

2   SCOPE OF THESIS

The overall aim of this master's thesis was to contribute with knowledge on potential sources of diffuse pollution to stormwater. This knowledge can in the future be part of a basis for deciding what type of construction materials to use as well as how to successfully implement sustainable stormwater treatment systems.

More specifically, the aim of this thesis was to evaluate the potential contribution of organic and inorganic pollutants from a range of different conventional roofing materials to stormwater. This study is to be considered as a first screening of the materials, in order to select fewer materials to be investigated further later on.

The thesis work included a literature review of previous studies in the subject as well as laboratory experiments that were designed and performed for a number of selected roofing materials commonly used in the urban environment. Finally, the results were evaluated and interpreted in order to be able to make final conclusions. Metals were included in this study as well as the organic compounds phthalates, PAHs, nonylphenols and pesticides.

The following specific objectives were formulated to cover the scope of this thesis:

- To evaluate if the studied materials could be expected to contribute with specific pollutants to the stormwater quality.

- To evaluate if there was a significant dissimilarity in any pollutant release from different roofing materials of comparable composition.

3   BACKGROUND

Roof runoff is an important contributor of substances to stormwater receivers (Sulaiman et al., 2009). Previous studies have concluded that roof runoff can be a source of various metals (e.g. Quek & Förster, 1993; Davis et al., 2001; Odnevall Wallinder et al., 2009) and a wide range of organic compounds (Jungnickel et al., 2008; e.g. Björklund, 2011; Wangler et al., 2012). The release of certain substances have been reported to be dependent on a number of different parameters, such as pH in the precipitation (Sulaiman et al., 2009), rain intensity (Jungnickel et al., 2008) as well as the characteristics of the roof surface (Eriksson et al., 2007). The knowledge on pollutant release from construction materials is limited and in need of further insight (Burkhardt et al., 2011). Only a few laboratory studies have previously been performed.

3.1   Precipitation in Sweden

The quality of precipitation has been monitored since the year 1955 in Sweden (Granat, 1990). Focus has been on parameters such as SO_4^{2-}, NO_3^-, Cl^-, NH_4^+ and pH. In this time perspective, the deposit of sulphate reached a peak in the end of the 1960's and has been decreasing since then. According to Karlsson et al. (2003) the monitoring has also shown that the pH of precipitation was higher in 2002 than in the 1980's, due to a major decrease of acidic emissions in Europe. Kindbom et al. (2001) stated that the concentrations of different parameters are generally higher in the south of Sweden with decreasing concentrations towards the north, which is correlated to the concentrations in the air. Correspondingly, the pH is generally higher in the north of Sweden than in the south. The lowest pH in precipitation measured in 2002 was below 4.5 for several locations in the south of Sweden and the highest pH the same year was above 5.3, measured in north Sweden (Karlsson et al., 2003). The concentrations of Na as well as other seawater components show large variations in coastal areas and inland. This indicates different contributing input parameters to precipitation in different locations (Granat, 1990).

The annual mean precipitation in Sweden is 720 mm (Lidstöm, 2012). The Swedish Meteorological and Hydrological Institute (SMHI) have nationwide observations of day-to-day precipitation. From this information, a clear connection between the duration of the precipitation event and the precipitation intensity can be seen, where the intensity is generally higher for short durations and vice versa. Shorter and more intense rain events have been shown to be important in an urban hydrology perspective (Wern & German, 2009). Average rain depth in Sweden and the average recurrence interval (ARI) have been calculated from the SMHI measurements by Wern and German (2009) and are presented for some chosen durations in Table 1.

Table 1   Average rain depth (mm) and ARI for 6 – 48 h rain events in Sweden. Data from Wern and German (2009).

Duration (h)	Average Recurrence Interval (ARI)		
	1 year	**2 years**	**5 years**
6	21.0	25.5	31.6
12	26.3	32.0	39.3
24	31.8	38.6	47.2
48	38.1	45.8	55.6

The composition of rainwater in Sweden is comparable with rainwater in other European countries concerning many of the measured parameters. The acidity of rainwater can be

increased by contribution of air masses from industrialised regions, but it can also be decreased by contribution of air masses from the Atlantic Ocean for coastal countries (Pio et al., 1991). Measurements of the rainwater chemistry in the coast of Portugal, in the southwest of Europe, indicated that Portugal is less affected from industrial emissions in the European continent due to the closeness to the coast. Measurements in France performed in the years 1997 – 1999 showed a mean pH in the range of 4.8 – 6.7 for different rain events in the region (Celle-Jeanton et al., 2009). Sanusi et al. (1996) analysed the rainwater quality in eastern France. The average concentrations of rainwater constituents such as SO_4^{2-}, NO_3^-, Cl^- and NH_4^+ were generally higher in the rainwater in eastern France than the corresponding concentrations of rainwater components in the Swedish measurements described by Granat (1990), Kindbom et al. (2001) and Karlsson et al. (2003).

3.2   Conventional Roofing Materials
The most common roofing for both apartment buildings and detached houses in Sweden is concrete tile, followed by clay tile (Boverket, 2010). Concrete tile occupies a roof surface area of about 158 million square meters and clay tile occupies around 80 million square meters (Boverket, 2010). For Swedish apartment buildings felt- and metal roofing exists to some extent, while these roof types are more common for detached houses (SOU, 2007). Larger industrial buildings often have felt roofing or corrugated metal sheet. Felt roofing is usually covered in the asphalt product bitumen (Bolliet et al., 2013) and its durability is more sensitive to changes in temperature compared to the other roofing material (SOU, 2007). Asphalt shingle is a similar product used for pitched roofs. Asphalt shingle very common roofing material in America, mainly due to low costs and easy installation (The House Designers, 2015). There are also various types of wooden shingles and synthetic shingles made from rubber or plastics, designed to look like wood shingles.

Among the metal roofs, steel plates or aluminium plates are most commonly used (SOU, 2007). Cu and Zn are also used, mainly in roof covering or gutters (Göbel et al., 2007). Metal roofs are available in various forms, such as stainless steel or as shingles to imitate classical pan tile roofs (The House Designers, 2015). Metal roofs have up to the double durability compared to asphalt roofing materials.

Flat roofs, especially on larger constructions such as industrial buildings, are now often covered with roofing membranes (Takdukspris.eu, n.d.). These are most often made of reinforced polyvinyl chloride (PVC), but can also be manufactured of other rubber materials (e.g. HDPE or TPE) and are welded to the roof using hot air.

Due to the increasing amount of surface runoff, correlated to the rising level of urbanisation and climate change, green roofs have become an alternative form of roof cladding (Mentens et al., 2006). Green roofs can have various configurations, including everything from vegetated roofing to rooftop gardens. Green roofs generally consist of a vegetative layer followed by a substrate layer, to retain the water and anchor the vegetation, and a drainage layer.

3.3   Stormwater Pollutants
The European WFD recognises that prevention and control needs to be adopted in order to achieve good status of water bodies (Zgheib et al., 2011). Due to this, the accurate knowledge on pollutants in the water cycle and their different sources of contribution is needed. Today, only limited information on the stormwater priority substances is available.

3.3.1   Organic Pollutants

The knowledge on organic pollutants from anthropogenic sources in stormwater is limited, except for the occurrence of polycyclic aromatic hydrocarbons (PAHs) in stormwater (Björklund, 2011). PAHs are generated by sources such as combustion or traffic and are also present in petroleum products and crude oil, bitumen being one of them (Bolliet et al., 2013). Many of the hundreds of existing PAHs are considered as toxic and hazardous.

Other stormwater pollutants of high relevance are phthalates. Phthalates are widely used industrial chemicals used mainly as additives in plastics, especially polyvinyl chlorides (PVCs), but also in paints or lacquers (Clara et al., 2010). Many phthalates are reprotoxic and can enter the environment via leaching or evaporation, since they are not chemically bound to the matrix of the final products (Björklund et al., 2007; Clara et al., 2010). Phthalates are the single most used plasticiser in the world (KemI, 2014). In 2012, 78 % of plasticisers were phthalates and even though this percentage is decreasing, the total use of phthalates is increasing due to a worldwide growing need of plasticisers.

Alkylphenols are also considered as stormwater priority pollutants (Björklund et al., 2007). In this group, nonylphenols are of highest relevance to study, since they are most commonly used. Nonylphenols are used to produce surfactants, mainly nonylphenol ethoxylates (NPEOs), which are widely used in producing products such as lubricants, paints, lacquers, concrete and more. Nonylphenol ethoxylates are biologically degradable, but form stable decomposition products that can be toxic to aquatic organisms (KemI, 2012). Nonylphenols are also added to e.g. rubber and plastics and are very toxic with long-lasting effects on aquatic organisms and their reproduction (Björklund, 2011). Both NPs and phthalates can also be released to the environment in larger particles – through physical impact on the materials, e.g. crack formation in paints and tearing of plastic surfaces.

Roof runoff can contain pesticides and biocides derived from the roofing materials (Schoknecht et al., 2009). They are applied to protect the material from deterioration by organisms and fungi or algae growth. Biocides are present in many surface coatings, including roof paints, and may transfer to roof runoff (Jungnickel et al., 2008). Diuron is a urea-based pesticide, used as a total herbicide (Gasperi et al., 2014). It is often found on urban surfaces and is being increasingly added to facades and paints to protect from fungi- and algae growth. Prior to the year 2008, diuron was responsible for 31 percent of the total urban pesticide use in the scale of the Paris conurbation. Due to this, this substance is also present in stormwater.

3.3.2   Inorganic Pollutants

Heavy metals in stormwater are of great interest to study, due to their potential toxicity and widespread presence in the urban and natural environment (Davis et al., 2001). The metals Zn, Cr, Cu, Cd, Ni and Pb are all included in the selected stormwater priority pollutants (SSPP) proposed by Eriksson et al. (2007) to be used for e.g. risk evaluations.

Steel, Al and Cu are the three most consumed metals in the world (Bielmyer et al., 2012). In the case of lower pH in precipitation, heavy metals can be present in dissolved form in the stormwater (Göbel et al., 2007). Various metals are commonly used in roofing materials; materials based on Cu, Al, Pb and Zn are all used for roof covering and some of these metals are also used in gutters and downpipes. Pb can also be found in different types of paints for e.g. roofs and facades (Davis & Burns, 1999). The dissolution of lead from paints can be enhanced with the presence of complexing agents such as chloride in the water. In Sweden, the use of lead in paints has been reduced to one tenth in the last decade (KemI, 2011). Lead

is now most commonly found in anticorrosion paints. The heavy metals Cu and Zn have previously been detected in leachate from other building materials, e.g. bricks and concrete (Davis et al., 2001). Tile roof has also been shown to act as a sink for metals, due to the porousness of the material (Quek & Förster, 1993). It is known that dissolved Cu is often retained close to the source by natural processes such as complexing with organic matter (Odnevall Wallinder et al., 2009). These processes change the chemical speciation and can thus decrease the bioavailability.

3.4 Previous Research

The contribution of different pollutants to stormwater pollution has been reviewed in a number of previous studies, both by laboratory experiments and field measurements. Zhang et al. (2012) performed leaching tests on galvanised steel plates by gently agitating the samples in synthetic rainwater for different time series (10, 30 and 50 minutes). Edges and backside had been sealed with a metal-free lacquer. The release of zinc and aluminium from the material was analysed and the results showed that the release of zinc was significantly higher than the release of aluminium from the material. Results also showed that the zinc release was increasing with increased leaching time. Clark et al. (2008) performed leaching tests on a number of commercial roofing materials; asphalt shingle, galvanised metal and fiberglass roofing panels to name a few. The analysis of the leachate constituents included heavy metals, pesticides and semi-volatile organics and the results did not display any significant concentrations of the organic compounds. Results for some of the metals analysed are presented in Table 2 below. In similar leaching immersion tests Jungnickel et al. (2008) and Schoknecht et al. (2009) studied the biocide leaching from roof paint. The results showed relatively high release of urea-based biocides such as diuron (Jungnickel et al., 2008; Schoknecht et al., 2009) and also concluded that the structure of the material's surface as well as the chemical composition was of high relevance for the leachability of biocides. The emission rate of biocides from different façade coatings and paints has been shown to be dependent on temperature as well as many other factors (Wangler et al., 2012)

In a leaching study by Sulaiman et al. (2009) the loss of elements from clay roofing tiles was evaluated. The study concluded that brand new tiles showed a different surface composition than weathered tiles, where elements such as Al, P and Mg had been depleted from the material surface. The pH in the leachate was also increased significantly compared to the initial pH in the leachant, which implied leaching of alkaline constituents.

A number of pilot-scaled field studies have also been performed, sometimes in combination with laboratory experiments, as in the case of Odnevall Wallinder et al. (2002) that studied release rates of nickel and chromium from stainless steel with both laboratory- and field exposure. The results from that study confirmed the corrosion resistance of stainless steel and showed significantly lower release of the metals compared to other roofing plates, e.g. zinc. Chang et al. (2004) also performed a pilot scaled study of the leaching of metals from roofs including composite shingle, painted aluminium and galvanised steel. According to that study, copper and zinc were largest contributors of pollution to stormwater.

Aside from the studies reported above, numerous field measurements to evaluate stormwater constituents have been made, both on metals and different organic compounds. Gasperi et al. (2014) evaluated the levels of PAHs, pesticides, nonylphenols and –ethoxylates as well as 14 metals in three urban catchments on different locations in France. Most metals, two urea-based pesticides (diuron and isoproturon), PAHs, NPs and NPEOs were systematically found in the stormwater on all three sites, but in some cases in varying concentrations. Quek and

Förster (1993) performed field measurements on roof runoff from roofs of different materials, exposure, age and inclination. Heavy metals in the roof runoff were analysed and the results showed that the runoff from a zinc sheet roof was most polluted with heavy metals, while a pan tile roof showed ability to adsorb the heavy metals.

Based on a review of the literature, previous concentrations of selected organic and inorganic compounds found in runoff from roofs or from leaching experiments have been summarised in Table 2 below. Since the studies on organic compounds in roof runoff are limited, some measurements from stormwater where other sources of pollution, such as traffic, are present have also been included in this table.

Table 2 Concentrations of selected stormwater pollutants in roof runoff, leachate or stormwater – a summary from literature.

Roof Type	Experiment Type	Pollutant(s) Analysed	Concentration	Reference
Roofing felt	Laboratory leaching	Cu (mg/kg)	0.026	(Clark et al., 2008)
		Zn (mg/kg)	Not detected	
		Pb (mg/kg)	0.11	
Galvanized metal	Laboratory leaching	Cu (mg/kg)	0.44	
		Zn (mg/kg)	16500	
		Pb (mg/kg)	0.16	
Asphalt- / Tar shingle	Laboratory leaching	Cu (mg/kg)	0.66	
		Zn (mg/kg)	0.34	
		Pb (mg/kg)	1.22	
Zinc sheet	Field sampling	Cd (μg m^{-2}/mm rain)	1.16	(Quek & Förster, 1993)
		Cu (μg m^{-2}/mm rain)	23.6	
		Zn (μg m^{-2}/mm rain)	38279	
		Pb (μg m^{-2}/mm rain)	32.3	
Pan tile	Field sampling	Cd (μg m^{-2}/ mm rain)	0.31	
		Cu (μg m^{-2}/ mm rain)	260.7	
		Zn (μg m^{-2}/ mm rain)	39.9	
		Pb (μg m^{-2}/ mm rain)	30.0	
Stormwater	Field sampling	Σ_{16} PAHs (μg/L)	0.89 - 1.69	(Gasperi et al., 2014)
		NPs (μg/L)	0.35	
		NPEOs (μg/L)	0.16 - 0.35	
		Diuron (μg/L)	1.21	

4 MATERIAL AND METHODS

The laboratory work of this thesis was performed in the environmental laboratory at Luleå University of Technology. The planning of the experiment setup included a literature review of previous leaching experiments in similar subjects. This master's thesis was conducted during a limited period of time and it was therefore necessary to have clear boundaries for what to include in the study. In order to delimit the laboratory work, the analysed parameters on each material were limited with probability, which was decided based on the literature review. The quality of the synthetic rainwater as well as the leaching time was also set as fixed parameters by the same reasons.

4.1 Preparation of Synthetic Rainwater

Synthetic rainwater was prepared in the laboratory based on previous measurements of rainwater content in Sweden (Granat, 1990; Kindbom et al., 2001; Karlsson et al., 2003). Relatively high concentrations of rainwater components and low pH were desired in order to simulate a worst-case scenario leaching of the roofing materials. This notion was partly supported by the fact that pH has previously been shown to have a significant effect of the release of various metals (Cu, Cr and Ni), i.e. increasing release with decreasing pH (Odnevall Wallinder et al., 2002; Odnevall Wallinder et al., 2009). Davis and Burns (1999) stated that high chloride content in water could increase the dissolution of Pb from paints, which also supported the assumption to some extent.

Table 3 below shows the annual mean concentration of common substances and pH in rainwater in Svartedalen, Sweden, for reported years during the period 1982 – 2002. The sampling location Svartedalen is located on the west coast of Sweden and was chosen for the preparation of synthetic rainwater due to generally lower pH and higher concentrations of e.g. SO_4^{2-} and Cl^- on this site, compared to other sampling sites in Sweden. The year 1997 was selected for the preparation of synthetic rainwater as it had lower pH than the more recent years, but was still considered more representative of today's rainwater than the earlier years, considering the decrease of acidic emissions in Europe since the 1980's (Karlsson et al., 2003). A similar composition of synthetic rainwater has been used in related studies and has proven to successfully simulate field conditions in Sweden (Odnevall Wallinder et al., 2002).

Table 3   Annual mean rainwater quality for the years 1983-1990, 1997, 1998, 1999 and 2002 in Svartedalen, Sweden.

Parameter	Unit	1983-1990*	1997**	1998**	1999**	2002***
pH	-	4.32	4.42	4.61	4.56	4.66
Cl	mg/L	2.66	3.00	2.61	2.40	1.69
NH_4-N	mg/L	0.64	0.42	0.51	0.52	0.40
NO_3-N	mg/L	0.59	0.49	0.48	0.53	0.44
SO_4-S	mg/L	1.14	0.73	0.67	0.61	0.48
Ca	mg/L	0.19	0.20	0.19	0.14	0.13
Mg	mg/L	0.18	0.21	0.17	0.17	0.12
K	mg/L	0.10	0.09	0.18	0.13	0.11
Na	mg/L	1.40	1.76	1.43	1.49	0.96

*(Granat, 1990), **(Kindbom et al., 2001), *** (Karlsson et al., 2003)

A stock solution was prepared with ultrapure arium® pro water (0.055 µS/cm; Sartorius), 9.45 M hydrochloric acid (HCl) and the following salts: $NaNO_3$, KNO_3, $(NH_4)_2SO_4$, $CaCl_2 \times 2H_2O$,

$MgSO_4 \times 7H_2O$ and NaCl. All salts were of > 99 % purity. The amount of salts and HCl needed was calculated to conform to the year 1997 in Table 3 above. The calculations were performed according to the formulas below. Equation 1 gives the desired molarity of each parameter,

$$M_p / c_p = n_p \qquad (1)$$

where M_p is the molar mass of the parameter (g/mol), c_p is the desired concentration of the parameter from Table 3 (in g/L) and n_p is the molarity (mol/L). The desired concentrations and the available salts were considered to systematically balance the molarity, one parameter at a time. To be able to balance the final parameter, Cl, HCl needed to be included. From the calculated molarity and the molar mass of the salts used for the preparation, the mass of salts and volume of HCl added to the stock solution was calculated according to Equation 2,

$$m_s = n_s \times M_s \qquad (2)$$

where m_s is the mass of salt to be added to the stock solution (g/L), n_s is the molarity of each salt added to the stock solution and M_s is the molar mass of the salt (g/mol). 100 mL of stock solution was prepared and thus the m_s was finally divided by 10. The calculated masses of the salts and the actually added masses of salts are presented in Table 4 below.

Table 4 Preferred and actually added amount of salts, HCl and H_2O in the stock solution.

Parameter	Calculated Molar (M)	Preferred in Stock Solution	Added to Stock Solution
NaNO₃	0.033	0.278 g	0.278 g
KNO₃	0.002	0.023 g	0.028 g
(NH₄)₂SO₄	0.015	0.198 g	0.198 g
MgSO₄×7H2O	0.009	0.213 g	0.214 g
CaCl₂×2H2O	0.005	0.056 g	0.057 g
NaCl	0.044	0.256 g	0.255 g
HCl	0.031	0.325 mL	0.325 mL
H₂O	-	100.0 g	99.98 g

After adding the salts and HCl, the stock solution was agitated on an Adolf Kühner orbital shaking apparatus for 30 minutes in order to ensure that the salts were completely dissolved. After preparation, the stock solution was stored in a glass bottle with a Teflon covered plastic screw cap in the refrigerator. The stock solution was diluted 1:1000 with ultrapure arium® pro water (< 0.055 µS/cm; Sartorius) and stored in 5000 mL glass vessels before performing the leaching tests. Conductivity and pH in the final rainwater solutions were recorded. A pH range of 4.3 – 4.5 was accepted for the leaching tests.

4.2 Roofing Materials

In this study, conventional roofing materials commonly used for residential houses, apartments and industrial buildings were considered. The total number of materials studied was 16, of which six were different metal sheets with or without coatings. Different types of felt roofing materials from different manufacturers and a PVC sheet used for industrial buildings were also included as well as clay- and cement tiles. In addition, metal roof paint and a paste consisting of bitumen used for maintenance of felt roofs were studied. Two different substrates for the construction of green roofs were also included in this study. The

entire list of studied materials, labelling to favour the laboratory work and a short description of each material is presented in Table 5 below. Table 5 also provides information on what type of substances that have been analysed in each material. In Figure 1 below, the appearances of the materials included in the study are presented. All of the materials included in this study were first-hand from factories and had therefore not been exposed to corrosion or atmospheric deposition prior to the leaching tests.

Table 5 The studied materials, labelling to favour the laboratory work and a short description of each material as well as the performed analyses on each material.

| Material	Label	Description	Performed Analyses
Cu-sheet	M1	Pure copper sheet	Elements (total and dissolved)
Zn-sheet	M2	Zinc sheet	Elements (total and dissolved)
Stainless Steel	M3	Stainless steel sheet	Elements (total and dissolved)
Galvanised Steel	M4	Steel sheet, surface treated with zinc	Elements (total and dissolved)
Metal Roof Paint	M5	Paint used for metal roofs in outdoor environments	Elements (total and dissolved), phthalates, NPs/NPEOs, herbicides
Coated Steel Sheet	M6	Corrugated and coated steel sheets commonly used as roofing	Elements (total and dissolved), NPs/NPEOs
Cement Tile	M7	Untreated cement tile	Elements (total and dissolved), NPs/NPEOs
Coated Cement Tile	M8	Cement tile coated with acrylic paint	Elements (total and dissolved), NPs/NPEOs
Clay Tile	M9	Untreated clay tile	Elements (total and dissolved)
PVC Sheet	M10	PVC sheet with polyester reinforcement used for larger industrial buildings	Elements (total and dissolved), phthalates, NPs/NPEOs
Bitumen Felt Roof (1)	M11	Polyester felt covered with bitumen and shale for low-pitch roofs (min 3°)	Elements (total and dissolved), PAHs, phthalates, NPs/NPEOs
Bitumen Felt Roof (2)	M12	Polyester fabric covered with bitumen and shale for low-pitch or flat roofs	Elements (total and dissolved), PAHs, phthalates, NPs/NPEOs
Bitumen Shingle	M13	Fiberglass covered with bitumen and shale for pitched roofs	Elements (total and dissolved), PAHs, phthalates, NPs/NPEOs
Bitumen Paste	M14	Bitumen paste for maintenance of old felt roofs	Elements (total and dissolved), PAHs, herbicides
Green Roof Substrate (1)	M15	Volcanic rocks/gravel used as a plant substrate for green roofs	Elements (only dissolved)
Green Roof Substrate (2)	M16	Soil used as a plant substrate for green roofs	Elements (only dissolved)
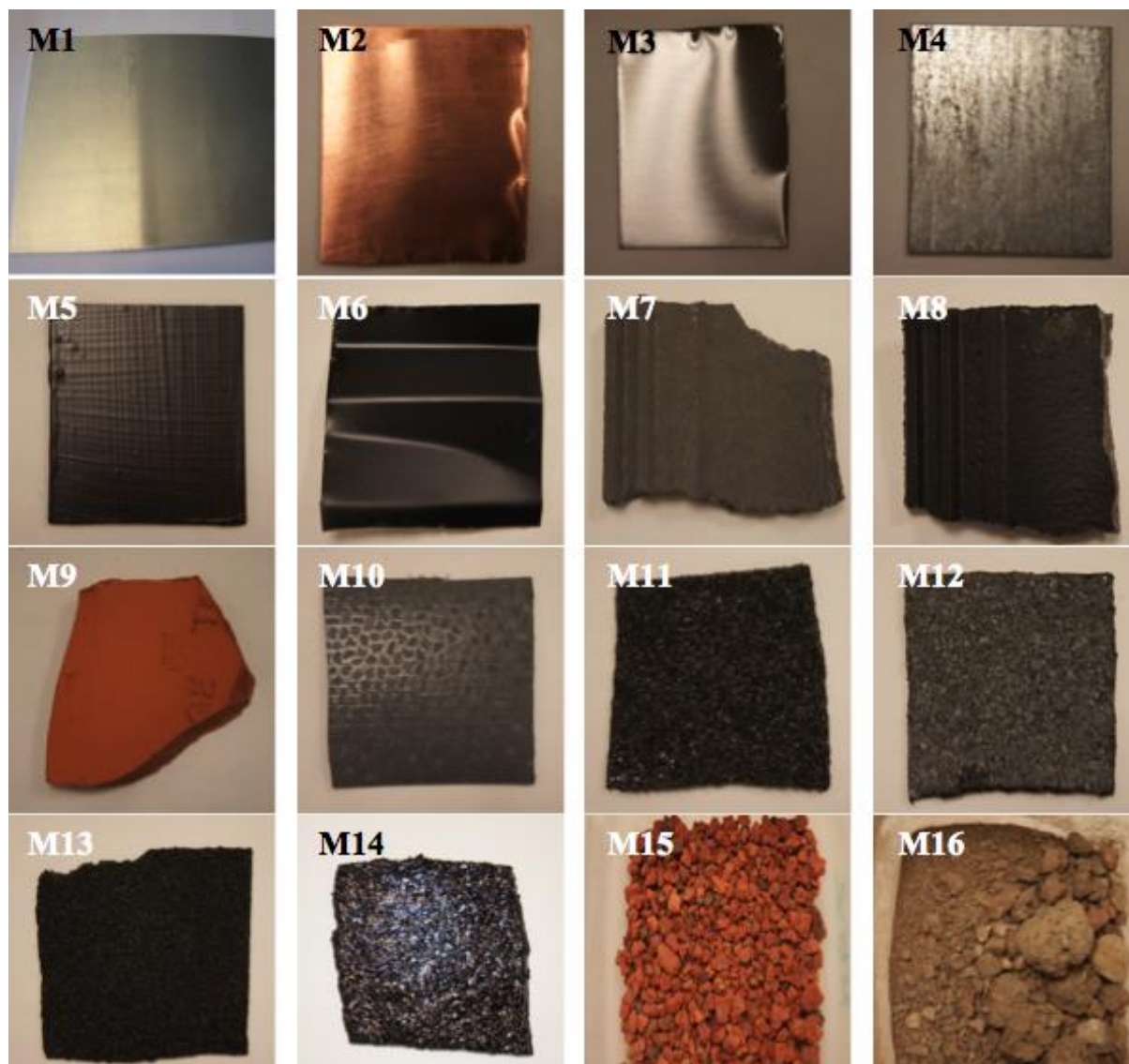
Figure 1 Photos and labelling of the roofing materials included in the study.

Materials M1 – M4 as well as M9, M15 and M16 were only analysed regarding metals. Nonylphenols and nonylphenol ethoxylates were analysed on nearly all of the materials included in the organic compounds leaching, since the usage of NPEOs is referred to as close to universal (Björklund, 2011). PAHs have been shown to be present in bitumen (Bolliet et al., 2013) and was therefore analysed on the bitumen products (M11 – M14). Phthalates were analysed on the felt roofs and shingle (M11 – M13), since phthalates have previously been reported to be present in SBS-bitumen (Lindström, 2007). The PVC (M10) and the roof paint (M5) were also analysed concerning phthalates, as they are known to be present in PVCs and paints (Björklund et al., 2007). Closer descriptions of the performed analyses are presented in Table 6.

4.3 Sample Preparation

Material samples were prepared in duplicates by using appropriate tools for each material. The size of the samples was decided with consideration of the rain depth for a 24 h rain with one year ARI from Table 1 (31.8 mm rain) and the needed amount of leachate for the analyses in the contracted laboratory (ALS Scandinavia). Concerning the green roof substrates, information about the mass needed per square meter was provided from the supplier. For the

metal analysis, cut-edges and backsides of the material samples were sealed with a metal-free lacquer on the materials whose backside did not correspond to its front side, i.e. the coated steel sheet (M6), the cement- and clay tiles (M7 - M9), the PVC (M10) and the felt roof materials, including shingle and the bitumen paste (M11 - M14). Blanks were prepared in the same manner by applying the lacquer on pieces of Plexiglas. The lacquer was applied to each material in three layers. Samples aimed for the organic analysis was prepared by screwing the materials back-to-back using metal screws concerning the coated steel sheet and the bitumen paste. Regarding the PVC-sheet, shingle and felt roofing materials, the materials were rolled alongside the inside of a 3000 mL glass beaker with the materials' backside facing the beakers' walls, in order to minimise the contact between the water and the backsides of the materials. The metal roof paint (M5) was applied in two layers on the front-, backside and cut edges on previously untreated steel sheets using a conventional paintbrush according to guidelines from the manufacturer. To test the bitumen paste used for maintenance of felt roofs (M14), the paste was applied in one layer on one of the bitumen-felt roofs (M12) included in this study, in accordance with the manufacturer's recommendations. The bitumen paste was left to dry for a minimum of 24 hours prior to performing the leaching tests. Blanks aimed for organic analysis consisted of a glass beaker filled with synthetic rainwater.

4.4   Leaching Procedure

Leaching was performed in 500 mL polypropylene containers for metal analysis and 1000 – 3000 mL glass containers for the organic analysis. Prior to the leaching, the plastic containers were acid washed with 1 M HNO_3 and rinsed in deionised water. The glass containers were rinsed with hexane and stored in a fume hood for the hexane residues to evaporate.

Synthetic rainwater was added to the clean beakers in volume corresponding to 31.8 mm water column on the exposed area of each material. The materials were immersed into the synthetic rain and containers were covered with polypropylene lids (plastic containers) or aluminium foil (glass containers) to prevent splashing, evaporation or sample contamination from outside. Thereafter, the beakers were placed on an Adolf Kühner orbital shaking device and left to be agitated in 60 rounds per minute (rpm) for 24 hours. The chosen period of time corresponds to the rain depth of 31.8 mm for a 24-hour rain event with one year ARI in Sweden (Table 1) (Wern & German, 2009). The rainwater depth and the leaching time were also selected due to practical reasons for the execution of the leaching tests, such as ensuring that the materials were entirely covered in water and not diluting the samples below detection limits if the liquid to area-ratio was too high.

After 24 hours of agitating the sample containers, the roofing samples were extracted from the leachate using plastic forceps for the metal analysis and metal forceps for the organic analysis respectively. The forceps were rinsed thoroughly in ultrapure arium[®] pro water (0.055 μS/cm; Sartorius) between each sample in order to avoid cross-contamination. Concerning materials M15 and M16, the leachate was decanted instead of extracting the material from the leachate. The leachate from the soil (M16) was also centrifuged at 4000 rpm for four minutes in order to separate the soil from the leachate. The materials were left to dry in a fume hood for a minimum of 24 hours and then the leaching procedure was repeated. To avoid influence from the first-flush, considering the fact that the materials were brand new, the leachate from the first round of leaching was discarded. The leachate from the second round of leaching was collected in appropriate sample bottles and sent to the contracted laboratory for analysis. Finally, a visual inspection of the materials' appearance after the leaching experiments was performed and any changes were noted.

4.5 Analysis

Conductivity and pH in the leachates from all materials were analysed in the Environmental Laboratory at Luleå University of Technology within 18 h after collecting the samples. The samples were stored cool and dark between the time of collection and the analyses and were systematically shaken before analysis. For the analyses a MeterLab CDM210 conductivity meter (Radiometer Copenhagen) and a pH-meter, WTW pH 330 / SET-1, were used. The conductivity meter was recently calibrated and controlled in deionised water prior to measurements and the pH-meter was calibrated at each measuring occasion. The analyses were performed on unfiltered samples.

ALS Scandinavia Laboratories AB performed all metal- and organic analyses. The samples were delivered to the office located in Luleå and in some cases forwarded for analysis. The office located in Luleå focuses on elements and isotopes while the office in Täby specialises in material analyses and organic compounds. European subcontractors were also used for analysis of organic compounds. The laboratories in Luleå and Täby are accredited by SWEDAC and compliant with the international standard ISO 17025. The accreditations of ALS subcontractors are recognised as equal to SWEDACs accreditations (ALS Scandinavia AB, n.d.a). On the leachates from the materials included in this study, a number of different analysis packages were performed. Table 6 provides information about the analysis packages and methods as well as information on which of the materials each analysis was performed. The analysis V-2 was performed on samples filtered through a 0.45 μm polyethersulfone (PES) membrane filter and the V-3b analysis was performed on unfiltered samples in order to get both the total- and dissolved concentrations of metals. This was done in order to be able to assess the environmental risks of the metal concentrations. The green roof substrates were only analysed regarding dissolved concentrations with the V-2 analysis, as seen in Table 6. Samples aimed for the organic analyses were not filtered. Zgheib et al. (2011) previously pointed out the importance of including the particulate phase concerning analysis of e.g. PAHs.

Table 6   Performed analyses, analysis methods and analysed materials.

Analysis	Description	Analysis Method(s)	Analysed Materials
V-2	Elements in freshwater	ICP-SFMS, ICP-OES	All (M1 – M16)
V-3b	Elements in polluted water (after digestion)	ICP-SFMS, ICP-OES	M1 – M14
OV-1	PAH (EPA-PAH, 16 compounds) in water	GC-MS	M11 – M14
OV-4a	Phthalates (10 compounds) in water	GC-ECD, GC-MS	M5, M10 – M13
OV-18d	Nonylphenols and -ethoxylates (NPs/NPEOs) in water	GC-MS	M5 – M8, M10 – M13
OV-3e-U	Herbicides in water (based on urea, uracil or sulfonyl urea derivates)	LC-MS-MS	M5 and M14

ICP-AES (inductively coupled plasma - optical emission spectrometry) is a multi-element technology that analyses up to 40 different elements (ALS Scandinavia AB, n.d.b). The plasma is formed from argon gas and reaches high temperatures, making the elements emit light of specific wavelengths for each element that is used for determination of element

concentrations. ICP-SFMS (sector-field mass spectrometry) is a technique that can separate isotopes or elements with different masses up to very small differences by magnetic and electrostatic sectors (ALS Scandinavia AB, n.d.b).

GC is a gas chromatograph technique (ALS Scandinavia AB, n.d.b). The sample is vaporised and transported through a column where substances are separated and detected. GC-MS (mass spectrometer) also gives information on the structure of detected substances by ionisation of the substances that elutes from the column. The MS technique is often used for persistent organic pollutants. The ECD (electron capture-detector) means that the substances passing through the column are then conducted through a radioactive foil, emitting β-rays. The method is often used for chlorinated pesticides and PCBs. In this study, the GC-MS technique was used for analysing PAHs, NPs/NPEOs, and phthalates.

LC-MS denotes "liquid chromatography – mass spectrometry" and is a technique that is often used for non-volatile or semi-volatile organic compounds. In this study, the herbicide analysis was performed using this technique.

4.6 Evaluation

The results from the analysis of parameters in the leachates were processed and evaluated in order to be able to present the results comprehensively. The metals of interest were selected and results were consistently only presented for parameters that were reported to exceed report limits for at least one of the analysed roofing materials. Mean values were calculated from all duplicate samples and the reported concentrations are presented in µg/L and µg m^{-2}/mm rain. In order to relate the magnitude of the release of the included substances per year, the mean concentrations were multiplied with the annual mean precipitation in Sweden and presented per 100 m^2 roof surface. For this calculation, 100% of the precipitation was assumed to contribute to the roof runoff.

5 RESULTS

In this section, the results from the leaching experiments are presented. The results from the chemical analyses are not given as a whole, but relevant compounds and measured concentrations are presented for chosen materials with the purpose to fulfil the aim of the study. For relevant substances and materials, the potential annual release was calculated and is presented in the following sections. Results that are below report limits are not always presented and the report limits for each substance are available in Appendix 1. The results for the analysed major elements are not presented in this section, but can be found in Appendix 2.

5.1 Visual Inspection

After the leaching experiments, the visual inspection of the materials showed that the surface of zinc sheet was covered with a light coating different from before the leaching, suggesting that some kind of reaction, e.g. oxidation had occurred. This can be seen in Figure 2. A flake-like structure was observed on the surface of the leachate from the galvanised steel when collecting the samples, but the material itself looked similar to before the leaching experiments. The surface structure of the other materials also appeared similar to prior to the leaching experiments.

Figure 2   The zinc sheet prior to the leaching (left) and after the leaching (right).

5.2 Conductivity and pH

The pH and conductivity were recorded in the leachates from each material duplicates and mean values were calculated. The results are presented in Figure 3 below, where the black line represents conductivity in µS/cm with the scale on the right hand axis and the grey line represents pH with the scale on the left hand axis. Prior to the leaching experiments, the pH in the synthetic rainwater was in the range of $4.3 - 4.5$ and the conductivity was in the range of $25.1 - 30.3$ µS/cm.
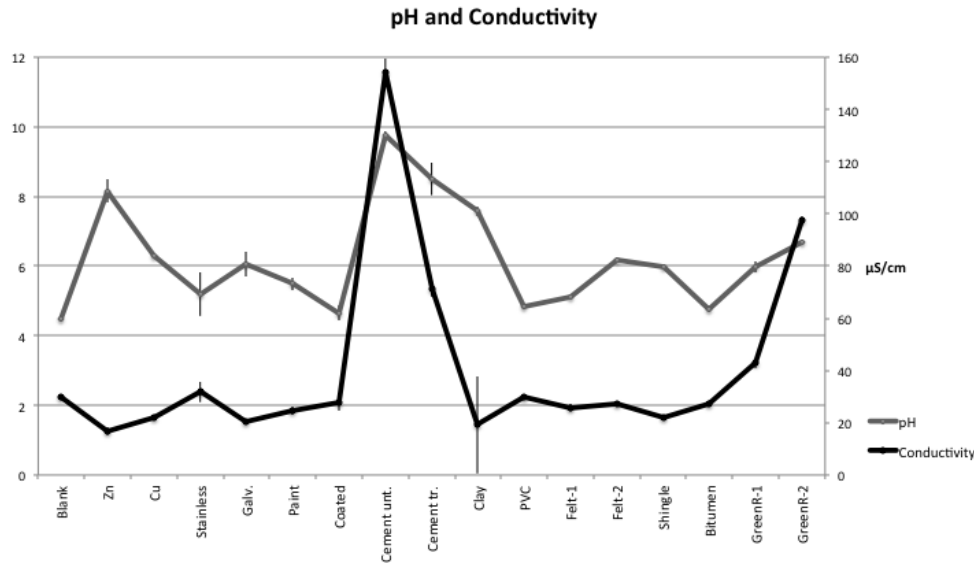
Figure 3 Mean pH and conductivity in the leachate of each material. The uncertainty bars represent the measured pH/conductivity in each duplicate sample.

Figure 3 shows that the pH and conductivity in the leachate from the blank sample was in the same range as for the synthetic rainwater prior to leaching, mentioned above. The leachates from the stainless steel (M3), the coated steel sheet (M6), the PVC (M10) as well as the bitumen paste (M14) did not show any significant changes in pH or conductivity. The most obvious change in pH was for the untreated cement tile (M7), followed by the zinc sheet (M1) as well as the coated cement tile and the clay tile (M8 − M9). The cement tiles also showed a significant increase in conductivity compared to the synthetic rainwater, as did the green roof substrates. There was a large spread in the conductivity values measured in the leachates from the duplicate clay tiles, which made this result unreliable. This is visible in the long uncertainty bar for the clay tile material in Figure 3. Aside from the clay tile, the zinc sheet and the galvanised steel were the only materials that display notably lower conductivity than the synthetic rainwater.

5.3 Metals
Both the total concentrations and the dissolved concentrations were analysed in this study, except for the two green roof substrates (M15 and M16) where only dissolved concentrations were analysed. The results are presented as mean concentrations of the duplicate samples for the metals of interest. The darker bars represent the total concentrations and the lighter bars represent the dissolved concentrations respectively. For the materials where a bar is not visible in the diagrams, the concentrations in the leachates were below the report limit. All specific report limits are found in Appendix 1.

5.3.1 Copper (Cu)
Figure 4 shows the copper concentrations in the leachates from each of the studied materials. The dissolved- and total concentrations were closely conforming to each other for all of the materials. As expected, the Cu concentration in the leachate from the Cu-sheet was significantly higher than concentration in the leachate from any other material. As the entire bar for the Cu-sheet is not visible in the scale for Figure 4, the analysed mean concentrations are presented in the numbers above the bars. Aside from the Cu-sheet, the shingle material

showed high Cu concentrations. None of the other materials showed higher concentrations of copper than the blank sample.
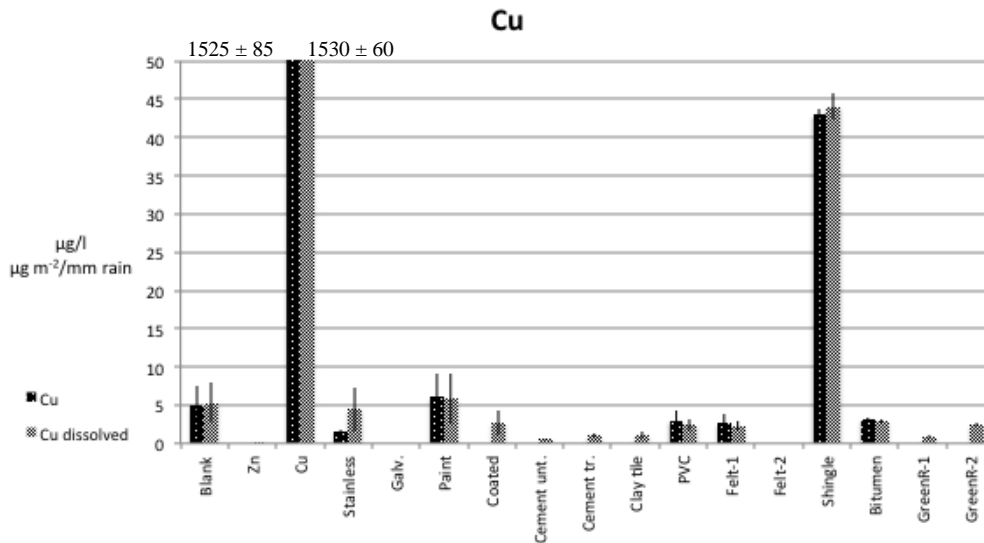

Figure 4   Mean Cu concentrations in the leachates from each roofing material. The uncertainty bars represent the concentration in each duplicate sample.

Table 7 below displays the estimated potential release of Cu in one year from 100 m^2 roof surface of copper sheet and shingle. The release from both materials was mainly in dissolved form and amount to 110 grams and ca. 3 grams respectively.

Table 7   Approximate potential annual releases of Cu from 100 m^2 roofing surface.

Material	Dissolved Cu (g/100 m^2)	Total Cu (g/100 m^2)
Cu sheet	110	110
Shingle	3.2	3.1

5.3.2   Zinc (Zn)

In Figure 5 below, the zinc concentrations for each leachate are presented. There was a strong difference in the total- and dissolved concentrations for the Zn sheet and the galvanised steel, which implied that particulate Zn was released from the materials. The highest concentrations of zinc were found in the leachates from the zinc sheet as well as the galvanised steel. More surprisingly, high concentrations of Zn were also found in the leachate from the metal roof paint and the coated steel. The spread of the concentrations of the duplicate samples concerning the coated steel was relatively high, corresponding to ca. $\pm$ 25 % of the mean total and dissolved concentrations.

Figure 5   Mean Zn concentrations in the leachates from each roofing material. The uncertainty bars represent the concentration in each duplicate sample.

The potential annual release of zinc from chosen roofing materials is presented in Table 8 below. The zinc sheet showed a potential release of almost 900 g zinc per 100 m^2 and year, of which a large part was in particulate form. The galvanised steel showed a significant release of both dissolved and particulate zinc. The roof paint as well as the coated steel seemed to mainly release zinc in dissolved form.

Table 8   Approximate potential annual releases of Zn from 100 m^2 roofing surface.

Material	Dissolved Zn (g/100 m^2)	Total Zn (g/100 m^2)
Zn sheet	6.2	864
Galvanised steel	113	657
Metal roof paint	9.2	8.2
Coated steel	26.6	27.3

5.3.3   Lead (Pb)

The concentrations of lead in the leachates are presented in Figure 6. Relatively equal lead concentrations were observed for the materials that seemed to release lead. Lead was not found in concentrations that were significantly higher than the blank sample in any of the materials. Excluding the galvanised steel, the total- and dissolved concentrations were similar to each other. The result for the galvanised steel showed that the release of Pb was primarily in particulate form. The soil used as a green roof substrate showed the highest release of dissolved Pb. The absence of the total Pb concentrations for many materials was most likely correlated to the higher report limit for the V-3b analysis (0.5 μg/L) than the report limit for V-2 (0.01 μg/L).
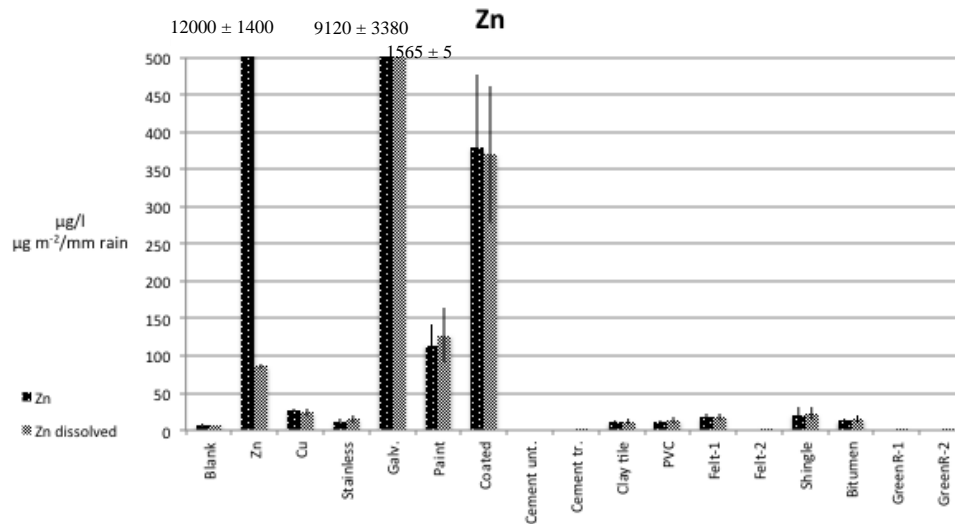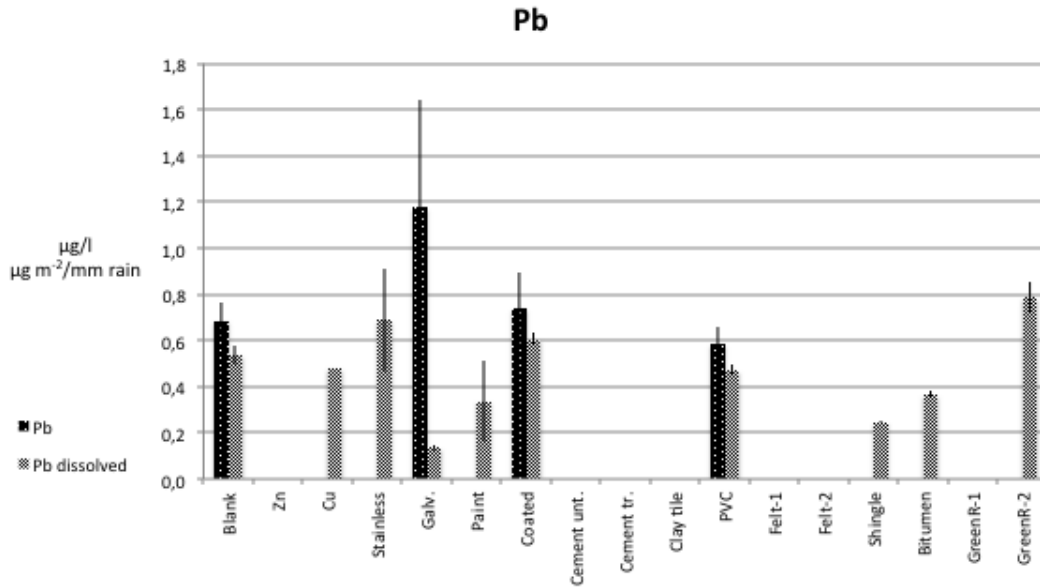
Pb

Figure 6   Mean Pb concentrations in the leachates from each roofing material. The uncertainty bars represent the concentration in each duplicate sample.

The potential annual lead release was only calculated for materials with concentrations that were notably higher than the blank sample, i.e. the galvanised steel and the green roof substrate. The results showed a potential annual release of 84.6 mg total Pb/100 m^2 and 56.6 mg dissolved Pb/100 m^2 respectively.

5.3.4   Nickel (Ni)

The Ni concentrations in the leachates, presented in Figure 7, were below reporting limit for most materials. Small amounts of Ni were released from the roof paint as well as the felt roof materials, while the Ni release from the Shingle was significantly higher. The release of Ni from the shingle was in the same order of magnitude as the release of copper from the same material.
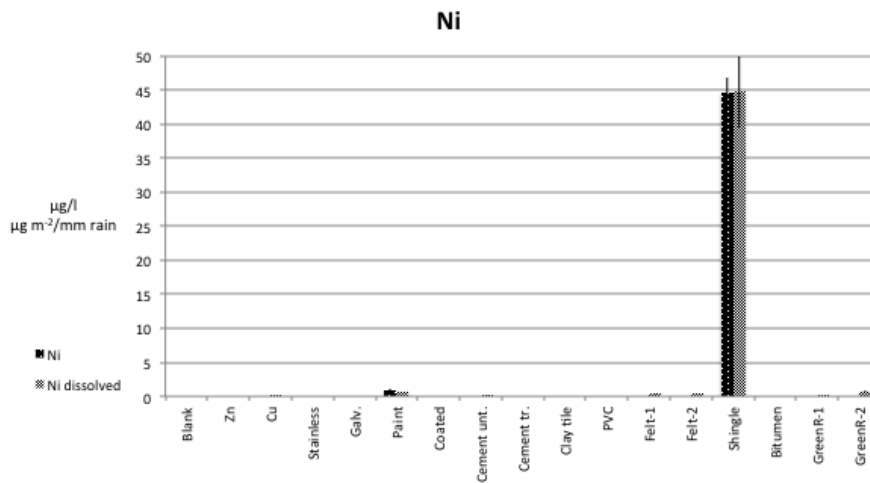
Ni

Figure 7   Mean Ni concentrations in the leachates from each roofing material. The uncertainty bars represent the concentration in each duplicate sample.

The potential annual release of dissolved Ni from 100 m^2 shingle roofing was determined to 3200 mg. Correspondingly, 43.6 mg dissolved Ni could potentially be released from 100 m^2 painted metal roof in one year's amount of precipitation.

5.3.5 Vanadium (V)

From Figure 8 it can be seen that vanadium was mainly released from the untreated cement tile and the clay tile. There was a significant difference in the release of V from the treated- and the untreated cement tile, which implies that the coating on the treated cement tile somehow hindered the surface from releasing V. The conformity between total- and dissolved concentrations was clear concerning the cement tiles as well as the clay tile. There was a large nonconformity both in total- and dissolved concentrations concerning the clay tile duplicates.

Figure 8   Mean V concentrations in the leachates from each roofing material. The uncertainty bars represent the concentration in each duplicate sample.

5.3.6 Cadmium (Cd)

The release of Cadmium from the different roofing materials is presented in Figure 9. The highest concentrations were found in the leachate from the shingle, both concerning particulate and dissolved concentrations. Dissolved Cd was also reported in the leachates from the zinc sheet, the galvanised steel, the copper sheet, the metal roof paint and even the blank sample.

Figure 9   Mean Cd concentrations in the leachates from each roofing material. The uncertainty bars represent the concentration in each duplicate sample.

The potential annual emissions of Cd from a 100 m^2 shingle roof was calculated to approximately 11.0 mg Cd, of which ca. 7.6 mg is in dissolved form.

5.3.7   Chromium (Cr)

The release of chromium from each material is presented in Figure 10. Significant concentrations of Cr were present in the leachates from the untreated cement tile. The dissolved- and total concentrations were equivalent, indicating that the release of Cr is almost exclusively in dissolved form. Noteworthy is also that the Cr release from the treated cement tile was many orders of magnitudes smaller compared to the untreated cement tile. This suggests that the surface treatment on the treated cement tile somehow hindered the release of chromium. Chromium was also present in the leachates from the stainless steel, the clay tile, one felt roof (M11), the shingle and the second green roof substrate (M16).
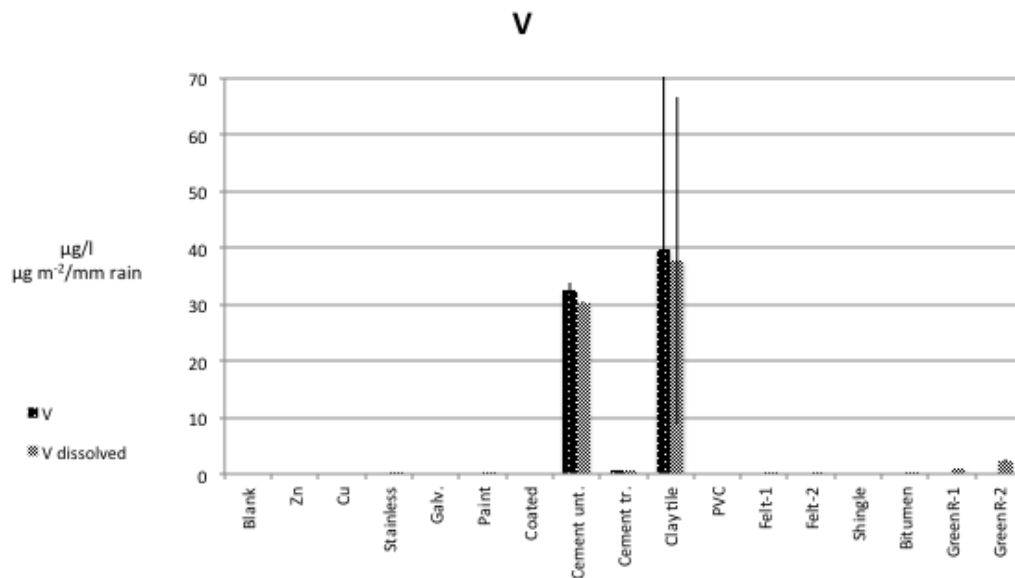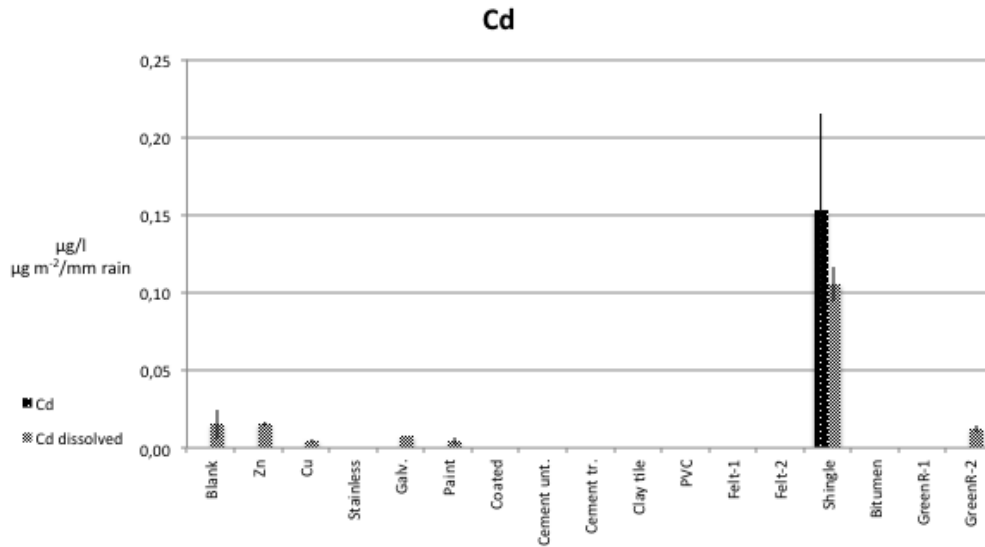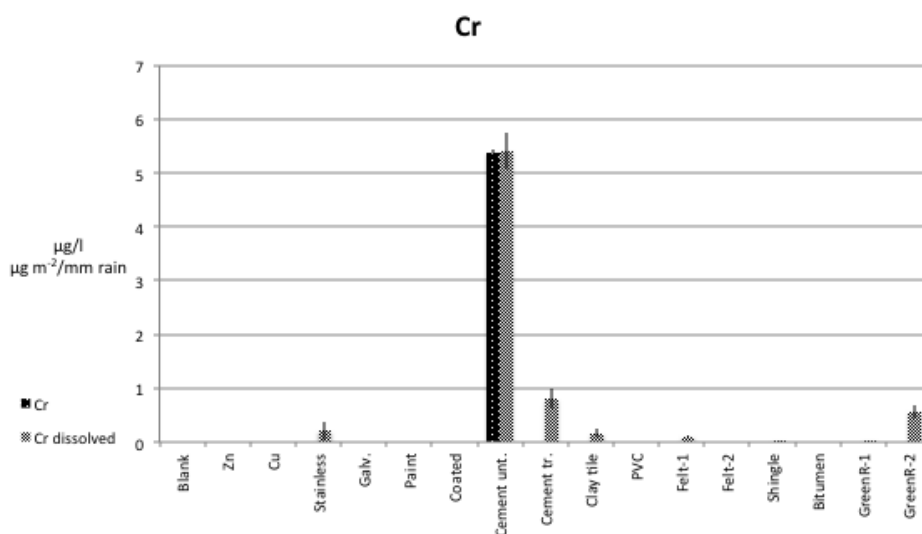

Figure 10   Mean Cr concentrations in the leachates from each roofing material. The uncertainty bars represent the concentration in each duplicate sample.

The results correspond to an annual release of ca. 390 mg dissolved Cr from 100 m^2 roofing of untreated cement tiles and correspondingly ca. 58.1 mg dissolved Cr from the surface treated cement tile.

5.4   Organic Compounds

In the following section, the results from the analyses of organic compounds are presented. All of the presented concentrations were calculated mean values from the duplicate samples. The error bars in the diagrams show the spread of the reported concentrations for each compound. Phthalates were not found in concentrations above the report limits in the leachates from any of the analysed materials and the results from those analyses were therefore not included in this section. The specific report limits for all analyses are available in Appendix 1.

5.4.1   PAHs

The release of PAHs was analysed in the felt roof materials, the shingle and the bitumen paste used for maintenance of felt roofs. 16 common PAHs of low, medium and high molecular weight were analysed. No PAHs were reported in any of the two felt roofs. Figure 11 shows the concentrations of PAHs in the shingle and the bitumen paste. Only the PAHs that were present in the leachates in concentrations above reporting limits was included in the figure. The release of PAHs was significantly larger from the bitumen paste than the shingle. For both materials naphthalene was predominantly released and thus the sum of released PAHs were mainly PAHs of low molecular weight (PAH sum L).
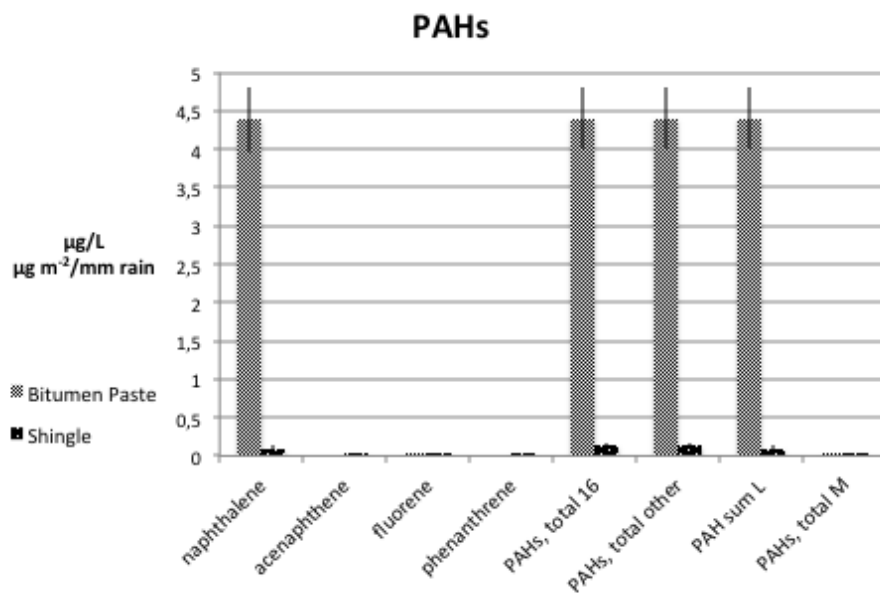
Figure 11   Mean concentrations of reported PAHs in shingle and bitumen paste. The uncertainty bars represent the concentration in each duplicate sample.

Table 9 below displays the estimated annual release of PAHs from 100 m^2 roof surface concerning shingle- and bitumen paste covered roofing. According to this approximation, more than 300 mg naphthalene could be released from 100 m^2 bitumen paste-covered roof in one year's amount of precipitation.

Table 9 Approximate annual releases of PAHs from 100 m^2 bitumen paste- and shingle roofing.

Material	Compound	Annual release (mg / 100 m^2)
Bitumen Paste	naphthalene	316
Shingle	naphthalene	6.2
	phenanthrene	2.6

5.4.2 Nonylphenols and –ethoxylates

In the leachates from the PVC sheet, the shingle roof and one of the felt roof materials (M12), 4-nonylphenols were reported in concentrations above report limits, see Figure 12. The largest release of NPs was from the PVC sheet. NPs and NPEOs were analysed on most materials included in the organic screening (the metal roof paint, the coated steel, both cement tiles, the PVC, both felt roofs and the shingle). No NPs were reported in the other materials. The NPEO-concentrations were below report limits for all materials.
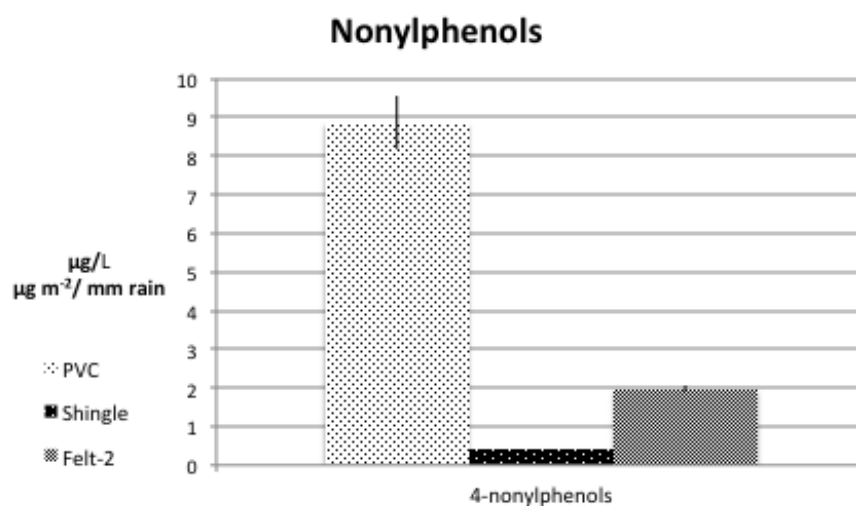

Figure 12 Mean concentrations of nonylphenols in PVC, shingle and one felt roof (M12). The uncertainty bars represent the concentration in each duplicate sample.

The annual release of 4-nonylphenols was approximated, considering the annual mean precipitation in Sweden of 720 mm. The approximation is presented in Table 10 below. This approximation suggested that 100 m^2 of the PVC roofing, which released the largest amount of NPs, would release near 640 mg per year. The release of NPs from the felt roof seemed to be around 140 mg /100 m^2 in one year's precipitation and the corresponding release from the shingle roofing is near 30 mg / 100 m^2.

Table 10 Approximate annual releases of NPs from a 100 m^2 PVC-, shingle- and felt roof.

Material	Annual Release (mg / 100 m^2)
PVC	638
Shingle	29.3
Felt-2	141

5.4.3   Herbicides

The leachates from the metal roof paint as well as the bitumen paste were analysed with respect to urea-based herbicides. In the leachate from the bitumen paste, no herbicides were reported. The result for the metal roof paint is displayed in Figure 13 below. About 0.2 µg/L of diuron was found in the leachate from the paint. Diuron was the only herbicide reported in the leachate and thus the other herbicides are not presented in the figure.
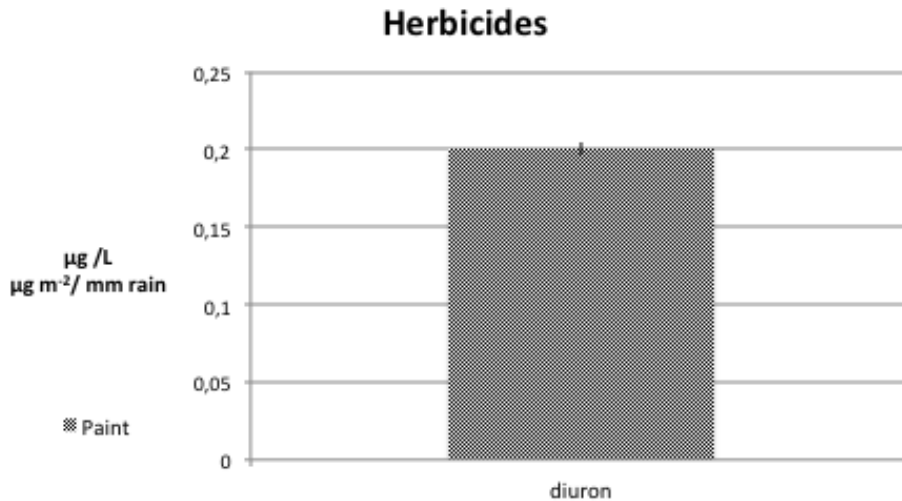

Figure 13   Mean concentration of diuron in the metal roof paint. The uncertainty bar represents the concentration in each duplicate sample.

Considering the annual mean precipitation in Sweden of 720 mm, this corresponded to a release of about 14.4 mg diuron per year for a painted roof surface of 100 m^2.

6 DISCUSSION

The leaching experiments performed in this master's thesis showed that a potential release of many of the included substances exists – of varying magnitude for the different roofing materials. The results from this study were mainly aimed to disclose whether or not a substance was potentially released from the roofing material. The performed leaching experiments are not considered directly comparable with the leaching of substances from a roof in real conditions. As previously stated by Björklund et al. (2007) the leaching of substances in this type of laboratory experiment is significantly faster than the leaching under real conditions. In this case, the same synthetic rainwater surrounds the roofing materials during the entire leaching event, while a roof is exposed to rainwater under a more limited period of time and also constantly fresh rainwater in the case of a real rain event. Parameters that could affect the leaching of substances from the roofing materials, such as temperature (Wangler et al., 2012), leaching time (Zhang et al., 2012) and rain intensity (Jungnickel et al., 2008) were not considered when performing the laboratory experiments in this study. These parameters are therefore proposed to be included in laboratory- or field experiments further on.

Considering the fact that the studied materials were all brand new and had not been exposed to the outside environment prior to the leaching experiments, it was exclusively the materials' contribution to stormwater pollution that was evaluated, without any influence of atmospheric deposition on the roofing materials. Some levels of natural wet or dry deposition of zinc to roofs have previously been confirmed to occur (Bertling et al., 2006). The fact that the materials are new also means that it is difficult to predict the behaviour of the materials in a more long-term perspective based on the present study, considering that processes such as corrosion, weathering or abrasion of the materials might then have affected the potential release of substances. Bertling et al. (2006) also concluded that the formation of corrosion products affects the runoff rates of zinc. This is also a factor to consider in further studies.

Due to the limited number of previous laboratory studies with similar methodology, there are some constraints in the comparability of the results – especially concerning the organic compounds. It is not either completely reasonable to compare the results with previous field measurements of stormwater, since the concentrations found in stormwater are derived from different parts of the urban environment and also most likely diluted compared to concentrations in roof runoff. Field measurements of roof runoff, e.g. by Quek & Förster (1993), were influenced by factors such as atmospheric deposition, corrosion and material abrasion and are therefore not entirely similar to laboratory leaching on brand new roofing materials. However, it can still be useful to make these comparisons in order to get an indication of the order of magnitude on the potential pollutant load from the roofing materials.

6.1 Conductivity and pH

The largest increase of pH from the initial pH of 4.3 – 4.5 in the synthetic rainwater was in the leachates from the cement tiles with a mean pH of 9.8 for the untreated cement tile and 8.5 for the coated cement tile. Due to the alkaline nature of cement – limestone, shell or chalk being a main constituent (Portland Cement Association, n.d.), these results were not unexpected. Since the pH was notably higher in the leachate from the untreated cement tile compared to the surface treated cement tile, one can conclude that the surface treatment was minimising the release of pH-increasing components. Sulaiman et al. (2009) have previously suggested that alkaline compounds were leached from clay tiles, due to a significant increase of pH in their leaching experiments. The initial pH in that study was 4.1 and the final pH in

the leachate from clay tiles varied from 4.9 to 5.3. This presumption was supported by the results from this study, where the pH is elevated in the leachate from the clay tile (mean pH = 7.6) compared to in the initial rainwater solution (pH = 4.3 – 4.5). The reason for the large variations between final pH in leachate solutions in this study and in the study by Sulaiman et al. (2009) was probably due to differences in methods of the experiments as well as the contact time between the synthetic rainwater and the clay tile, which was significantly higher in this study. A noteworthy increase of pH also occurred for the zinc sheet and the galvanised steel. It was visible on the surface of the zinc sheet that some kind of reaction with the leachate had taken place, which can be seen in Figure 2. Bertling et al. (2006) evaluated corrosion-induced zinc runoff rates from zinc-based construction materials and also experienced an increase of pH in runoff from zinc sheets and galvanised steel. They suggested that the increase of the pH was due to formation of basic zinc carbonates with high buffering capacity. This explanation may also be applicable to the increase of pH in the leachates from the zinc sheet and the galvanised steel in this study. The adsorption of metals to roof surfaces is known to increase with increasing pH   (Quek & Förster, 1993). Thus, substances can potentially be adsorbed to some of the roofing materials, depending on the characteristics of the roof surface. The copper sheet also showed an increase of the pH, while the PVC and the stainless steel sheet did not seem to affect the pH of the leachate.

The conductivity of the leachates also showed the most significant change from the synthetic rainwater for the cement tiles, especially the untreated cement. This indicates that a release of constituents occurred, which is supported by the results from the major element analyses (Table A7 in Appendix 2) that showed an elevated release of dissolved Ca, K, Na and Si from both types of cement tiles compared to the blank sample. As the conductivity as well as the concentrations of released major elements were consistently lower in the leachate from the surface treated cement tile, this again implies that the surface treatment significantly decreases the amount of compounds released from the material. This is partly supported by Bertling et al. (2006), who concluded that the presence of a barrier or coating on the material surface decreases the runoff rate of zinc. In this study the zinc sheet and the galvanised steel sheet decreased the conductivity of the synthetic rainwater, indicating that constituents from the synthetic rainwater had been sorbed on the surfaces of the materials. The conductivity in the leachates from the duplicate samples of clay tile showed a spread from close to 0 up to almost 40 μS/cm. The measurement of 0 μS/cm indicates that almost all of the substances present in the synthetic rainwater have been sorbed to the clay tile, while the other sample indicates only a minor change from the initial rainwater conductivity. The green roof substrates showed an increase of the conductivity. The other roofing materials did not seem to have affected the conductivity of the synthetic rainwater remarkably.

6.2   Metals

From the results of the metal analyses, it was clear that the release of most metals from the roofing materials was mainly in the dissolved phase. This may be correlated to the relatively low pH in the synthetic rainwater. It may also result in precipitation or re-adsorption of leached metals to the surface of the roof in case of an increase of the pH. The concentration of dissolved zinc is dependent on changes of pH, with a decrease of dissolved Zn with increasing pH (Stumm & Morgan, 1996), partly supporting the presumption. The results from this study showed that zinc seemed to be released partly in particulate form (Figure 5), concerning the zinc sheet and the galvanised steel. This could be associated to the increased pH in the leachates, especially for the zinc sheet, making the Zn less prone to dissolve. It could also be correlated to the composition of the materials. The change in appearance of the zinc sheet

before and after the leaching procedure, presented in Figure 2, indicates formation of corrosion products. This may also 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 corrosion product formation of basic zinc carbonates and also experienced an increase of pH in runoff from zinc sheets and galvanised steel. Furthermore, the zinc carbonate Hydrozincite is the initial phase of corrosion product and is also the most abundant phase on zinc roofs (He, 2002). Quek & Förster (1993) reported high concentrations of dissolved zinc from a zinc sheet roof, likely due to weathering. The results from this study implied a release of particulate zinc from the zinc sheet instead, but in this case the zinc sheet was not exposed to weathering. The zinc sheet and the galvanised steel were also the materials that exhibited the highest release of Zn. In addition, the coated steel as well as the metal roof paint also showed a significant release of Zn, indicating use of Zn containing additives in the manufacturing process of these products.

Cu was mainly released from the copper sheet, which was expected. Significant concentrations were also present in the leachate from the shingle, making it stand out from the similar felt roofing materials. In Table 2 it can be seen that Cu has also previously been detected to leach from both felt roofing materials and asphalt- and tar shingles in similar laboratory experiments (Clark et al., 2008). The shingle exhibited a higher release of Cu compared to the felt roofing material also in that study. The other studied roofing materials exhibited concentrations in the same order of magnitude or lower than the blank sample. The fact that some materials exhibit Cu-concentrations lower than the blank sample might be correlated to some sort of sorbing process due to changes in pH and porosity of e.g. the cement tiles and the clay tile. Again, the amount of adsorbed metals is a function of pH and also, the materials' roughness can entrap metals (Quek & Förster, 1993).

Pb also exhibited reportable concentrations for several of the materials, but none of the concentrations were significantly higher than the blank and there are therefore some constraints in evaluating the Pb-results. However, the concentrations of lead in the leachates from all of the studied materials were considerably lower than the lead concentrations measured in roof runoff from e.g. a pan tile roof and a zinc roof, presented in Table 2. The results from this study were therefore not considered to indicate any significant contribution of lead pollution from the roofing materials to stormwater quality.

Some metals were only reported in significant concentrations for one or a few of the studied materials. Around 45 μg/L Ni was released from the shingle material, which again distinguished itself from the similar felt roofing materials. Stormwater analyses reported concentrations of 2.9 – 6.6 μg/L Ni in three French catchments (Gasperi et al., 2014). Even though these concentrations are not directly comparable, the potential release of Ni from shingle can be considered as significant. Vanadium concentrations were determined to be between 30 – 40 μg/L for the untreated cement tile and the clay tile. Vanadium is not considered as an environmental pollutant, except for in the cases of e.g. large spills (Scottish EPA, n.d.) and was mainly presented in the results to point out the major difference in substance release between the untreated and the coated cement tiles. The coated cement tile did not seem to release any noteworthy concentrations of V, once again suggesting the fact that the surface treatment can hinder the release of substances from the cement tile. The same observation was made for chromium.

6.3 Organic Compounds

Organic analyses were performed on selected materials included in this study. The selection was done based on the composition of the materials as well as results from previous studies of the materials. Due to this, there is a possibility that one or more of the studied organic compounds could be released from some of the other materials or under other conditions not investigated in this study. Concerning the felt roofing materials, the shingle and the PVC sheet it is also important to notice that edges and backsides of the materials were not completely out of contact with the synthetic rainwater in the leaching experiments and may therefore have contributed to the reported concentrations of the investigated organic compounds to some extent. In a similar leaching study by Clark et al. (2008) some organic compounds were included, but none of them were detected in the leachates from the materials.

Phthalates were not found in concentrations above the report limits for any of the investigated materials. In this study, phthalates were mainly expected to leach from the PVC material, as phthalates are the single most common plasticiser used for PVCs (Björklund et al., 2007; KemI, 2014) and leaching is believed to be the largest source of phthalate-emissions (Björklund et al., 2007). Temperature has previously proven to be an important factor for the emission rate of phthalates (Björklund et al., 2007). This may be a reasonable explanation for the lack of phthalates in the leachate from the PVC sheet, since the temperature in these laboratory experiments were significantly lower (room temperature of ca. 20°C) than the temperature that can be reached on a dark coloured roof surface exposed to sunlight. Phthalates have also been reported to be present in SBS-bitumen (Lindström, 2007) and was therefore analysed in the leachates from the bitumen roofing materials, but no phthalates were reported for neither of these materials. Phthalates can also exist in metal sheets with plastic coatings (Björklund et al., 2007). Due to this, it may be of interest to also study the leaching of phthalates from this type of materials. In further studies of phthalate leaching from roofing materials, temperature dependence is suggested to be an included parameter.

PAHs were released from two of the four analysed materials. All of the PAHs that were found in this study are of low molecular weight with 2-3 aromatic rings. The smaller PAHs are generally more volatile and soluble (Naturvårdsverket, 2007), which may explain why these seemed to be released from the investigated materials. None of the felt roofs seemed to release PAHs, while the shingle roofing released reportable levels of PAHs. This was an interesting discovery, since these three materials are similar in their composition, but from different manufacturers. The concentrations of PAHs in the leachate from the shingle correspond to ca. 7 – 19 % of the measured concentrations of PAHs in stormwater that are presented in Table 2. Correspondingly, the concentrations of PAHs in the leachate from the bitumen paste were ca. 260 – 494 % of the measured concentrations in the stormwater. One has to keep in mind that the bitumen paste is used for maintenance of older roofs and the usage of the product and thus the potential release may therefore be limited to areas where these types of roofs are common. Due to this, the bitumen paste may only influence stormwater quality locally. It is important to recognise that the measured concentrations of PAHs in stormwater are derived from various sources of pollution, such as traffic, and will also be diluted with runoff that does not contain PAHs. The potential long-term release of PAHs from the bitumen paste has not been evaluated in this study and it is therefore not feasible to conclude if the potential annual release of about 316 mg PAHs per 100 m^2 roof surface, calculated in section 5.4.1, is relevant a few years after applying the bitumen paste to the roof.

Of the organic analyses in this study the nonylphenol and –ethoxylates analyses comprised the largest number of materials. NPs were reported in concentrations above report limits concerning three of the materials: shingle, PVC and one felt roofing. PVC has previously been reported to release NPs/NPEOs (Björklund et al., 2007). The concentration in the leachate from the shingle material was in the same order of magnitude as the concentrations reported in stormwater from Table 2, 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 need to be considered with some precaution due to factors such as dilution. It should also be noted that in this study, the edges and backsides of the materials could have contributed to the release of NPs to some extent. This needs to be evaluated in further studies. The felt roof (M12) exhibited a significant potential to release of NPs, while the other felt roof (M11) did not show a similar release. Again, this was an interesting finding considering the similarity in the composition of the two materials. NPEOs were not reported in any of the studied materials.

The herbicide diuron was found in the leachate from the metal roof paint, but in significantly lower concentrations than previous measurements from stormwater presented in Table 2. The concentration of diuron in the leachate corresponded to about 16 % of the concentration measured in stormwater by Gasperi et al. (2014). The stormwater concentration obviously includes other sources of pesticides than one single roofing material and therefore this does not necessarily mean that the contribution from the metal roof paint is negligible. The presence of diuron in the leachate from the metal roof paint is also noteworthy, since the use of diuron has been banned in Sweden since the year 1993 (Naturvårdsverket, 2008). As a temperature dependence of pesticide release has previously been reported for pesticides (Wangler et al., 2012), this is also of interest to study further on. It may also be relevant to include other pesticides aside from the urea-based herbicides in further studies.

7   CONCLUSIONS

Many of the evaluated substances showed a potential to be released from the studied roofing materials and these substances may thereby end up in the stormwater and ultimately stormwater receivers. Of the studied materials, shingle was the material that showed the ability to release the largest number of pollutants. The shingle was shown to potentially release the metals Cu, Ni and Cd as well as the organic compounds PAHs and NPs. One of the felt roof materials (M12) and especially the PVC sheet also showed potential to release NPs. The bitumen paste used for maintenance of felt roofs exhibited the highest probability to release PAHs. Zinc showed potential to be discharged from the zinc sheet, the galvanised steel and also the coated steel as well as the metal roof paint. The metal roof paint also showed the ability to release the herbicide diuron and Ni. The untreated cement tile was indicated to be a potential contributing source of chromium to stormwater. The stainless steel, the treated cement tile, the clay tile and one of the felt roofing materials (M11) were not found to be significant contributors of any of the studied stormwater pollutants under the prevailing laboratory conditions. The same conclusion applied to the green roof substrates.

Phthalates were not found in concentrations above report limits in the leachates from any of the studied materials and were therefore assumed as either reluctant to release from these roofing materials under the prevailing laboratory conditions or simply not present in the studied roofing materials.

There was a clear difference in the release of substances from the untreated cement tile and the surface treated cement tile. The surface treated cement tile showed lower potential to release all of the studied substances and thus the surface coating was indicated to hinder the release of substances to the stormwater quality. The two felt roofs also showed dissimilar release patterns concerning the studied pollutants. M11 did not show the potential to release any of the substances, while M12 showed the ability to release NPs. The shingle was considered to be similar to the felt roofs considering material composition, but demonstrated a higher potential to release pollutants. These observations underlined the potential difference in leaching behaviour of similar roofing materials that had e.g. different surface treatments or was produced by different manufacturers.

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APPENDIX 1: Report Limits

Table A1　Report limits for V-2 Metals in freshwater analysis (ALS Scandinavia AB, n.d.g).

V-2 Metals in freshwater	
Analysis of substance	**Report limit**
Al, aluminium	0.2 µg/L
As, arsenic 1	0.05 µg/L
Ba, barium	0.01 µg/L
Ca, calcium	100 µg/L
Cd, cadmium 2	0.002 µg/L
Co, cobalt	0.005 µg/L
Cr, chromium	0.01 µg/L
Cu, copper	0.1 µg/L
Fe, iron	0.4 µg/L
Hg, mercury	0.002 µg/L
K, potassium	400 µg/L
Mg, magnesium	90 µg/L
Mn, manganese	0.03 µg/L
Mo, molybdenum	0.05 µg/L
Na, sodium	100 µg/L
Ni, nickel	0.05 µg/L
P, phosphorus	1 µg/L
Pb, lead	0.01 µg/L
Si, silicon	30 µg/L
Sr, strontium	2 µg/L
V, vanadium	0.005 µg/L
Zn, zinc	0.2 µg/L

Table A2   Report limits for V-3b Metals in wastewater (after digestion) analysis (ALS Scandinavia AB, n.d.h).

V-3b Metals in wastewater (after digestion)	
Analysis of substance	**Report limit**
Al, aluminium	10 µg/L
As, arsenic 1	0.5 µg/L
Ba, barium	1 µg/L
Ca, calcium	200 µg/L
Cd, cadmium 2	0.05 µg/L
Co, cobalt	0.2 µg/L
Cr, chromium	0.9 µg/L
Cu, copper	1 µg/L
Fe, iron	10 µg/L
Hg, mercury	0.02 µg/L
K, potassium	400 µg/L
Mg, magnesium	140 µg/L
Mn, manganese	0.9 µg/L
Mo, molybdenum	0.5 µg/L
Na, sodium	500 µg/L
Ni, nickel	0.6 µg/L
Pb, lead	0.5 µg/L
V, vanadium	0.2 µg/L
Zn, zinc	4 µg/L

Table A3   Report limits for OV-1 PAH (EPA-PAH 16 compounds) in water analysis (ALS Scandinavia AB, n.d.c).

OV-1 PAH (EPA-PAH 16 compounds) in water	
Analysis of substance	**Report limit**
naphthalene	0.030 μg/L
acenaphthylene	0.010 μg/L
acenaphthene	0.010 μg/L
fluorene	0.010 μg/L
phenanthrene	0.020 μg/L
anthracene	0.010 μg/L
fluoranthene	0.010 μg/L
pyrene	0.010 μg/L
benzo(a)anthracene	0.010 μg/L
chrysene	0.010 μg/L
benzo(b)fluoranthene	0.010 μg/L
benzo(k)fluoranthene	0.010 μg/L
benzo(a)pyrene	0.010 μg/L
dibenzo(ah)anthracene	0.010 μg/L
benzo(ghi)perylene	0.010 μg/L
indeno(123cd)pyrene	0.010 μg/L
sum of 16 PAHs	0.095 μg/L
sum of carcinogenic PAH	0.035 μg/L
sum of other PAHs	0.060 μg/L
sum of PAH L	0.030 μg/L
sum of PAH M	0.030 μg/L
sum of PAH H	0.040 μg/L

Table A4   Report limits for OV-4a Phthalates (10 compounds) in water analysis (ALS Scandinavia AB, n.d.f).

OV-4a Phthalates (10 compounds) in water	
Analysis of substance	**Report limit**
dimethylphthalate	0.6 μg/L
diethylphthalate	0.6 μg/L
di-n-propylphthalate	0.6 μg/L
di-n-butylphthalate	0.6 μg/L
diisobutyl phthalate	0.6 μg/L
di-pentylphthalate	0.6 μg/L
di-n-octylphthalate (DNOP)	0.6 μg/L
di-(2-ethylhexyl)phthalate (DEHP)	1.3 μg/L
butylbenzylphthalate	0.6 μg/L
dicyclohexylphthalate	0.6 μg/L

Table A5   Report limits for OV-18d Nonylphenols and -ethoxylates in water (ALS Scandinavia AB, n.d.d).

OV-18d Nonylphenols and -ethoxylates in water	
Analysis of substance:	**Report limit**
4-nonylphenols (tech. mixture)	0.1 µg/L
4-nonylphenol monoethoxylate	0.1 µg/L
4-nonylphenol diethoxylate	0.1 µg/L
4-nonylphenol triethoxylate	0.1 µg/L

Table A6   Report limits for OV-3e-U Herbicides in water (based on urea, uracil of sulfonyl urea derivates) analysis (ALS Scandinavia AB, n.d.e).

OV-3e-U Herbicides in water (based on urea, uracil of sulfonyl urea derivates)	
Analysis of substance	**Report limit**
diuron	0.05 µg/L
fenuron	0.05 µg/L
foramsulfuron	0.05 µg/L
isoproturon	0.05 µg/L
chlorbromuron	0.05 µg/L
chloroxuron	0.05 µg/L
chlorsulfuron	0.05 µg/L
chlortoluron	0.05 µg/L
linuron	0.05 µg/L
methabenzthiazuron	0.05 µg/L
metobromuron	0.05 µg/L
metoxuron	0.05 µg/L
metsulfuron methyl	0.05 µg/L
monolinuron	0.05 µg/L
monuron	0.05 µg/L
neburon	0.05 µg/L
nicosulfuron	0.05 µg/L
rimsulfuron	0.05 µg/L
sulfosulfuron	0.05 µg/L
thifensulfuron-methyl	0.05 µg/L
triasulfuron	0.05 µg/L
tribenuron methyl	0.05 µg/L
triflusulfuron methyl	0.05 µg/L

APPENDIX 2: Major Elements

Table A7 Mean concentrations of dissolved major elements in the leachates

Element	Unit	Material Blank	Zn	Cu	Stainless	Galv.	Paint	Coated	Cement unt.	Cement tr.	Clay tile	PVC	Felt-1	Felt-2	Shingle	Bitumen	GreenR-1	GreenR-2
Ca	mg/L	0.163	0.182	0.184	0.186	0.177	0.47	0.1535	6.72	3.275	2.52	0.1715	1.0125	1.985	0.7675	0.298	2.535	16.35
Fe	mg/L	0.000785	n.d.	n.d.	0.019805	n.d.	0.0422	0.001155	0.001025	0.00149	0.000755	0.002885	0.07695	n.d.	0.04135	0.002035	0.00231	0.8545
K	mg/L	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	36.85	10.255	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.46	2.445
Mg	mg/L	0.227	0.2295	0.2305	0.2335	0.227	0.425	0.225	0.1785	0.24	0.486	0.227	0.2725	0.3235	0.2475	0.2275	0.994	1.0205
Na	mg/L	1.83	1.895	1.845	1.865	1.865	1.915	1.82	4.35	4.205	2.57	1.805	1.79	1.81	1.87	1.815	3.07	2.74
Si	mg/L	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12.1	0.7305	0.9875	n.d.	n.d.	0.0627	0.0392	n.d.	1.685	1.46