

Roofing Materials as Pollution Emitters – Concentration Changes during Runoff

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Abstract

The influence of roofing material on concentrations of pollutants in roof runoff waters and changes of pollution concentration in time were investigated. In field studies four roofing material types were taken into consideration: ceramic tile, bituminous membrane, asbestos tile, and zinc sheeting. Samples were collected from November 2007 to March 2008. Anions, cations, metals, PAHs, pesticides, and PCBs were determined. The existence of the first flush phenomenon for most pollutants was confirmed, with concentrations up to two orders of magnitude higher in first flush compared to steady state conditions. Time trends of pollutant concentration changes were observed. Additionally, analysis of a series of samples collected from melting snow accumulated on the roof showed an increase of organic pollutant concentrations during thaw.

Keywords: roofing materials, roof runoff, first flush, water quality

Introduction

Roofing material is a significant nonpoint source of pollution of natural waters. Rainwater becomes roof runoff water when it contacts an impervious roof surface [1]. Before contact with such an impervious surface, pollutants present in water originate from wet deposition [2, 3]. The enrichment of pollutants in water occurs because of both flushing the pollutants accumulated due to dry deposition, and release from roofing material. Runoff waters are discharged to surface reservoirs or infiltrated to ground waters, causing their possible pollution.

There are many factors influencing the concentrations of pollutants present in roof runoff waters. The results of previous studies are presented below:

meteorological parameters:

- rainfall intensity – study [4] showed negative correlation with the concentration of pollutants,

- wind speed and direction affect the amount of precipitation hitting the roofing surface [5] and the buildup of dry deposition on the roof surface,
- temperature and insolation both increase the rate of decay of accumulated organic matter and the rates of chemical reactions taking place on the surfaces [4],
- dry period duration before precipitation – positive correlation between duration of antecedent dry period and concentration of pollutants in roof runoff waters was noted [6],
- precipitation volume – during the precipitation event, most pollutants are removed by the initial water volume [7, 8],
- chemical composition of atmosphere – i.e. the presence of marine aerosols may increase corrosion rates, so metals content in roof runoff water can be increased: SO₂ can affect concentration of calcium cations [9].

roofing material parameters:

- type – zinc sheeting [10, 11] and galvanized steel [12] may be a source of zinc ions in runoff waters: copper roofing and roof gutters may release copper ions [13,

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Table 1. Characteristics of main roofing materials used in Poland.

Roofing material	Characteristics
Ceramic tile	The main constituents, fine clay (70%), cement (20%), acryl paints (1.5%), water (8%) and ferric oxides (0.5%) are kilned in high-temperature furnace. The surface is often glazed. The advantages are durability, resistance to atmospheric conditions, fire, UV radiation, good thermal isolation. The disadvantage is large mass.
Zinc sheeting	Consists of zinc-coated iron sheets with prime epoxy-paint, anti-corrosion acryl layer, dyed acryl layer, natural aggregate and transparent acryl coating, often containing anti-fouling agents. Operational parameters vary with roofing quality.
Asbestos – cementic	They contain mainly quartz sand, cement and 10-13% of asbestos. As a building material it is resistant to fire and atmospheric conditions. Old or mechanically damaged eternit materials release asbestos fibers that cause asbestosis.
Bituminous membrane	Consists of three main layers: support layer, influencing mechanical properties (polyester foil, glass fiber, or cardboard) anti-moisture asphalt (bituminous mass) surface layer (slates, quartz sand) may be dyed, protects from mechanical failures and heating. Bituminous membranes are not as durable as other materials, are brittle in low temperatures and soft in high temperatures. The advantage is low cost and ease in formation, allowing it to be used in sophisticated roof shapes.

14] and traces of cadmium and lead [15]. Leaching of herbicides from bituminous and ceramic roofing materials [16] may take place as they are added as anti-vegetation agents [17]. Studies by Clark et al. [18] show that some roofing materials can be a source of nutrients in runoff waters,

- age – some studies showed [19] that older copper and zinc roofing materials have more protective surface films, thus metal corrosion and metal runoff are decreased,
- slope – the amount of precipitation in contact with roofing material and concentration of pollutants increases with decreasing inclination [19].

The first flush phenomenon can be defined as the initial period of water runoff, in which the concentration of pollutants is significantly higher compared to later storm event stages [5]. The occurrence of first flush can also be defined in terms of curve of cumulative fraction of pollution mass versus cumulative total runoff water volume. The first flush is observed when the slope of the curve is greater than 45° [20]. Another definition states that first flush occurs when at least 80% of pollution load is flushed by the first 30% of runoff water volume [21]. For certain pollutants the first flush phenomenon has not been observed. Examples of such compounds may be herbicides leached from roofing material, as their concentration remains relatively constant during the entire roof runoff event. First flush was not observed for γ -HCH (hexachlorocyclohexane) in runoff waters from zinc sheeting, whereas it did occur for a fiber cement roof, the concentration of which decreased 4 times after 1 mm of runoff height [22]. Other studies stated that increased concentration of R- and S-mecoprop (herbicide) in the first volume of runoff took place, after which the concentration slightly decreased and remained constant [17]. Polycyclic aromatic hydrocarbons (PAHs) adsorbed on suspended solids undergo the first flush phenomenon, the concentration was 7 times higher in initial runoff stage than in steady state conditions, which were established after 1 mm of runoff. On the other hand, the concentration of dissolved PAHs remains constant during the entire runoff event on cement fiber roofing. The situation may be opposite when

other roofing types are taken into consideration. Tar felt, as it might be a source of dissolved PAHs in runoff water, caused the first flush of such pollution, whereas adsorbed PAHs remained at relatively constant, low levels [22]. Studies of zinc behavior during 38 runoff events showed that concentration at the beginning of runoff is 2.5 times higher, compared to steady state conditions that were established after one hour of event [21].

In Table 1 the four most common roofing materials used in Poland and their basic properties, possibly influencing the quality of runoff waters, are listed. The data is collected from the producers of roofing materials. Asbestos is used as roofing materials because in the 1970's it gained popularity as a building material, mainly due to low cost. Since 1999 in Poland it is forbidden to use materials containing asbestos, but mainly in rural areas, many buildings are still covered with asbestos-containing roofs.

Since the knowledge about roof runoff is still not sufficient, the aim of our study is to investigate roofing material as a source of pollutants. Different roofing materials (ceramic tile, bituminous membrane, zinc sheeting, asbestos tiles) are compared. The first flush phenomenon for anions and cations, zinc, pesticides, and PAHs is examined and compared with literature data.

Experimental

Sampling

The studies consisted of two major parts: comparison of different roofing materials (four roofs from different parts of Gdańsk), and investigation of pollutant concentration changes during roof runoff (two roofs were chosen – ceramic and metal sheeting). The second ones are located in city suburbs characterized by low traffic density, one roof covered with ceramic tile and another covered with zinc sheeting. They were roofs of neighboring buildings at a distance of 20 meters. All the samples were collected between November 2007 and March 2008.



Table 2. Chromatographic and metrological parameters of anions and cations, PAH and pesticide analysis in roof runoff waters.

ION CHROMATOGRAPHY		
Parameter	Anions	Cations
Column	IonPac® AS9 2 x 250 mm	IonPac® CS14 2 x 250 mm
Eluent	9 mmol Na ₂ CO ₃	20 mmol methanesulfonic acid
Detector	Conductometric	Conductometric
Injection volume [ml]	0.0075	0.0075
Eluent flow rate [ml min ⁻¹]	0.25	0.25
Analysis time [min]	16	17
Sample volume [ml]	2	2
GAS CHROMATOGRAPHY		
	Pesticides and PCB Analysis	PAH Analysis
	<i>GC 6000 Vega Series</i>	<i>Agilent Technologies 7850A</i>
Detector	ECD (chloroorganic pesticides and PCB)/NPD (nitrogen and phosphorus pesticides)	Agilent Technologies 5975C, SIM mode
Column	Rtx-5 (30 m 0.25 mm 0.25 µm)	Rtx – SMS (30 m 0.25 mm 0.25 µm)
Injector	on-column	splitless
Carrier Gas	hydrogen	helium
Temperature Program	80°C → 180°C (15°C min ⁻¹) 180 °C → 300°C (10°C min ⁻¹)	40°C → 120°C (40°C min ⁻¹) 120°C → 280°C (5°C min ⁻¹)
Injector Temperature	80°C	40°C
Detector Temperature	350°C	280°C
Sample Volume	2 µl	2 µl
Metrological Parameters		
	<i>LOD</i>	<i>LOQ</i>
Anions [mg dm ⁻³]	0.009-0.055	0.03-0.16
Cations [mg dm ⁻³]	0.01	0.03
Cadmium [mg dm ⁻³]	0.01	0.03
Lead [mg dm ⁻³]	0.2	0.6
Zinc [mg dm ⁻³]	0.015	0.045
Copper [mg dm ⁻³]	0.05	0.15
Pesticides [µg dm ⁻³]	0.02	0.06
PCB [µg dm ⁻³]	0.02	0.06
PAH [ng dm ⁻³]	0.25-7	0.75-21

The mean annual precipitation amount in Gdańsk is 550 mm. Atmospheric pollutant concentrations were not measured during sample collection. The mean concentrations of pollutants in heating season 2007/08, measured by a nearby monitoring station, were: NO₂ – 14.4 µg/m³, SO₂ – 4.1 µg/m³, and PM-10 – 23 µg/m³ [23].

Samples were collected in 100 ml plastic containers for inorganic compound determination and into 500 ml glass containers for organic pollutant analysis. Samples for organic pollutant determination were collected without headspace volume to avoid losses of volatile compounds. Prior to sample collection, samplers were washed with

detergent, then with distilled water and ultrapure water (Millipore, France). Glass containers also were washed with methanol and dichloromethane and dried at 60°C.

Chemical Analysis

Metals (Zn, Cu, Pb, Cd) were determined using flame atomic absorption spectroscopy SensAA(GBC). Prior to metal content determination, samples were filtered to remove suspended matter. The samples were filtered using a glass fiber filter system (Sartorius, Gottingen, Germany)

Table 3. Ranges of concentrations of pollutants in roof runoff waters collected from different roofing materials.

Pollutant	Units	Bituminous membrane (n = 16)	Ceramic tile (n = 30)	Asbestos tile (n = 14)	Zinc sheeting (n = 23)
		Range of concentration			
Fluorides	mg dm ⁻³	0.01-1.09	0.01-0.38	<LOD	0.01-0.19
Chlorides		0.65-29	0.21-22	0.36-5.7	0.53-7.1
Nitrates		0.04-16.	0.04-15	0.04-9.7	0.05-4.4
Sulphates		0.43-60	0.21-21	0.56-69	0.31-8.5
Sodium		0.03-19	0.27-25	0.03-4.6	0.04-2.5
Ammonium		0.03-3.8	0.1-2.3	0.03-2.5	0.25-2.7
Potassium		0.04-1.5	0.03-2.3	0.03-1.9	0.03-1.9
Magnesium		0.03-1.7	0.03-5.2	0.03-0.85	0.03-0.48
Calcium		0.4-15.6	0.5-19	0.25-38	0.4-5.4
Zinc		5-4900	5-800	5-4200	5-9600
Lead	µg dm ⁻³	1-88	1-40	1-2.3	1-7
Cadmium		0.1-1.9	0.1-3.7	0.1-1.3	0.1-4
Copper		10-300	10-600	<LOD	10-600
Aldrine		0.01-6.1	0.01-2.6	0.01-0.61	0.01-0.6
Methoxychlor		0.01-0.43	0.01-0.43	0.01-0.13	<LOD
Heptachlor epoxide		0.01-20	0.15-0.56	0.01-14.5	0.01-1.6
p,p'-DDD		0.01-2.2	0.01-4.6	0.01-0.5	0.01-0.57
o,p'-DDD		0.01-0.54	0.01-1.2	0.01-7	0.01-1.9
p,p'-DDE		0.01-2.5	0.14-2.9	0.01-1	0.01-0.93
o,p'-DDE		0.01-2.5	0.01-2.8	0.01-4.6	0.01-0.92
p,p'-DDT		0.01-1.9	0.01-2.4	0.01-8.4	0.01-0.8
o,p'-DDT		0.01-1.9	0.01-1.4	0.01-0.75	0.01-0.5
HCH		0.01-0.2	0.01-1.6	0.01-0.46	0.01-0.54
Propazine		0.01-1.1	0.01-1.1	<LOD	0.01-0.4
Terbutylazine		0.01-0.36	0.01-0.28	0.01-0.13	0.01-0.05
Bromophos		0.01-4.9	0.01-2.72	0.01-0.31	<LOD
Atrazine		<LOD	0.01-0.34	0.01-1.21	<LOD
Simazine		0.01-4.4	0.01-5.3	<LOD	0.01-0.62
Malathion		<LOD	0.01-0.29	<LOD	0.01-1.9

and 0.45 µm membrane filters (Gelman Sciences, USA). Blank samples showed that zinc released from samplers and/or filters was not present in water at concentrations above LOD.

Cations (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) and anions (F⁻, Cl⁻, NO₂⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻) were determined using ion chromatography (IC). The parameters of the cations and anion determination are presented in Table 2.

Pesticides and PAHs were isolated and concentrated from runoff samples using solid phase extraction (SPE). Final determination was carried out by gas chromatography, using an electron capture detector or nitrogen phos-

phorus detector (pesticides) and mass spectrometry (PAHs). The volume of the initial sample was 200 mL. The SPE process consisted of several stages. Prior to extraction, LiChrolut RP-18 SPE cartridges (Merck) were conditioned with dichloromethane and methanol. The extraction was carried out by drawing the aqueous samples through the cartridges. The cartridges were then dried with air for 20 min. Next, the analytes were eluted with dichloromethane, and the extracts were evaporated to dryness under nitrogen using a needle evaporator (J.T. Baker, USA). Finally, the dried residue was reconstituted with 0.5 mL methanol (pesticides) or 0.5 mL dichloromethane (PAHs). The extracts

Table 4. Comparison of pollution concentrations in the first flush and steady state conditions of roof runoff waters.

Parameter	Units	First flush concentration	Steady – state conditions concentration	Roofing material	Reference
1	2	3	4	5	6
<i>inorganic compounds</i>					
chlorides	mg dm ⁻³	1.1	0.8	ceramic tile	experimental
		1.9	0.5		
		0.9	0.4	zinc sheeting	
		0.9	1	pan tile	[22]
		1	1.6	concrete	
nitrates		4.8	1.3	ceramic tile	experimental
		5.9	1.4		
		3.8	1	zinc sheeting	
nitrites		0.12	0.09	ceramic tile	
		0.1	0.12		
		0.13	0.12	zinc sheeting	
sulphates		3.2	1.1	ceramic tile	
		5.6	1		
		2.2	0.9	zinc sheeting	
ammonium		1.9	1.3	ceramic tile	
		2.3	1.2		
		2.1	1.2	zinc sheeting	
sodium		0.6	0.3	ceramic tile	
		0.8	0.3		
	0.3	0.3	zinc sheeting		
potassium	0.14	0.11	ceramic tile		
	0.11	0.15			
	0.15	0.09	zinc sheeting		
zinc	0.06	0.01	ceramic tile		
	0.25	0.01	zinc sheeting		
	13.5	~ 5	14-year-old zinc roof	[21]	
copper	3.3	2.6	new zinc panels	[7]	
	4.2	0.13	zinc sheeting	[22]	
	0.5	0.001	concrete tiles		
	0.5	0.004	tar felt roof		
<i>organic compounds</i>					
phenanthrene	ng dm ⁻³	216	161	ceramic tile	experimental
pyrene (particulate)		110	~ 10	cement roof	[22]
		8	6	tar felt	
pyrene (dissolved)		4	4	cement roof	
		5	5	tar felt	

Table 4. Continued.

1	2	3	4	5	6
pyrene (total)	ng dm ⁻³	206	40	ceramic tile	experimental
		133	50		
		105	62	zinc sheeting	
fluoranthene (particulate)		121	~ 10	cement roof	[22]
		14	~ 6	tar felt	
fluoranthene (dissolved)		4	4	cement roof	
		24	~ 18	tar felt	
fluoranthene (total)		250	53	ceramic tile	experimental
		155	71		
		148	72	zinc sheeting	
anthracene		16	8	ceramic tile	
		57	21		
		53	6	zinc sheeting	
fluorene		7	10	ceramic tile	
acenaphtylene		45	8	zinc sheeting	
chrysene	19	2	zinc sheeting		
PCB 52	182	42	ceramic tile		
PCB 180	62	43	ceramic tile		
γ-HCH	130	45	zinc sheet	[22]	
	45	45	fiber cement		
atrazine	210	20	tile	[28]	
	100	50	gravel		

were stored at 2°C prior to analysis [24]. Chromatographic parameters of chloroorganic pesticides and PAH determinations are listed in Table 2.

To determine the limit of quantitation (LOQ) of every analytical method, accuracy versus concentration graph for 5 standard solutions was plotted. The concentration of analyte corresponding to accuracy of 10% was assumed to be LOQ. A lower limit of detection was calculated according to formula $LOD=LOQ/3$. Lower limits of detection and lower limits of quantitation for determined chemicals and for chosen analytical procedures are presented in Table 2.

Results and Discussion

Comparison of Different Roofing Materials

The ranges of concentrations of pollutants in runoff waters collected from four types of roofing materials (bituminous membrane, ceramic tile, asbestos tile, zinc sheeting) are compared in Table 3. The concentrations of pollutants depend mainly on the sorptive parameters of roofing

materials. Comparison of the roof parameters influencing the quality of runoff water by subtracting background rainwater concentrations is difficult. The surface area of roofs included in the study is at least 100 times larger than the surface area of funnels used for rainwater collection. This means that collection of the same volume of sample requires 100 times more time. It is possible that composition of rainwater has changed during that time. It is possible to collect such time-weighted average rainwater samples and treat them as background for several runoff samples collected. Meanwhile, however, it introduces errors. Major ions originate mainly from dry deposition processes. Their presence in runoff waters from metal roofs was observed at lower concentrations than on other roof types. Metal species were present at the highest concentrations in waters collected from metal roofs, so they probably originated from dissolved corrosion by-products, corrosion by-products released upon wear, or electrochemical release from bulk metal. Because zinc is only double as high as in samples collected from zinc sheeting compared to other roofing material, and copper was found in ceramic tile and bituminous membranes while it was not detected in

Table 5. Changes of chosen pollutant concentrations in water samples collected during two roof runoff events.

Parameter	Units	Runoff height [mm] (<i>time [hours]</i>)			
		<i>initial (1)</i>	<i>1 (4)</i>	<i>2 (5)</i>	
first storm event					
<i>ceramic tile</i>					
specific conductivity	[$\mu\text{S cm}^{-1}$]	44.6	31.2	29.8	
chlorides	[mg dm^{-3}]	2.07	1.23	0.03	
nitrites		0.19	0.12	0.1	
nitrates		2.76	1.83	1.55	
sulphates		1.71	1.3	1.04	
sodium		1.22	0.67	0.61	
potassium		0.19	0.07	0.08	
ammonium		1.02	1.11	0.43	
zinc		0.09	0.09	0.09	
fluoranthene		[ng dm^{-3}]	94.1	31.4	73
pyrene	79.7		11.4	52.1	
PCB 52	303		131	200	
PCB 180	124		19	84.7	
		<i>1 (1)</i>	<i>3 (4)</i>	<i>4 (5)</i>	<i>5 (6)</i>
second storm event					
<i>ceramic tile</i>					
specific conductivity	[$\mu\text{S cm}^{-1}$]	76.2	42	29.8	33.2
chlorides	[mg dm^{-3}]	0.36	3.61	1.95	2.16
nitrites		0.12	<LOD	0.08	0.06
nitrates		0.26	<LOD	0.11	0.88
sulphates		0.73	1.01	0.68	0.73
sodium		0.29	1.69	0.72	1.18
potassium		0.14	0.22	0.08	0.22
ammonium		0.01	<LOD	0.48	0.49
calcium		0.38	0.36	0.52	0.58
zinc		0.09	0.05	0.05	0.09
acenaphthylene	[ng dm^{-3}]	22.9	8.3	4.2	4.2
phenanthrene		84.3	86.3	81.2	129
fluoranthene		47.4	32	53.7	41.7
pyrene		19.4	32.3	47.1	83.2
PCB 52		1327	565	365	<LOD
PCB 180		268	91	211	340
<i>zinc sheeting</i>					
specific conductivity	[$\mu\text{S cm}^{-1}$]	30.4	24.7	22.5	
chlorides	[mg dm^{-3}]	1.01	2.11	2.06	
nitrites		0.15	0.12	0.07	
nitrates		0.51	0.07	0.04	
sulphates		1.82	0.66	0.61	
sodium		0.54	0.86	0.94	
potassium		0.15	0.13	0.08	
ammonium		0.36	0.5	0.35	
calcium		0.54	0.26	<LOD	
zinc		0.068	0.079	0.062	
acenaphthylene	[ng dm^{-3}]	12.1	17.5	8.5	
phenanthrene		131	88.3	70.8	
fluoranthene		56.1	32.4	73.3	
pyrene		49.5	33.5	94.8	

Table 6. Changes of pollutant concentrations during snow melt accumulated on the roof.

Parameter	Units	Day		
		1	2	3
chlorides	[mg dm ⁻³]	1.42	0.86	1.82
nitrites		0.08	0.08	0.07
nitrates		1.59	1.46	1.23
sulphates		1.21	1.36	1.11
sodium		0.84	0.73	0.87
potassium		0.11	0.08	0.29
ammonium		0.44	0.38	0.39
calcium		0.63	0.21	0.36
zinc		0.07	0.11	0.08
naphthalene		[ng dm ⁻³]	1.7	1.5
phenanthrene	52.1		130	100
fluoranthene	33.3		84	124
pyrene	23.4		66.1	78.9
chryzene	<LOD		15.5	31
benzo[k]fluoranthene			6.2	20.5
benzo[b]fluoranthene			6.5	22.7
benzo[a]anthracene			6.5	13.1

asbestos tile, it might be expected that the metal come not only from roofing material but also from other sources (probably particulates accumulated due to dry deposition). Pesticides can be leached from roofing material or can originate from deposition processes. As they may be added to some ceramic tile types as anti-vegetation agents, their concentrations are higher in runoff from ceramic tile. Their concentrations are also high in runoff water collected from asbestos tile and tar paper, probably because of preferable sorption of pesticides on the surfaces of these materials.

Long-term effects of zinc on aquatic algae and bacteria are observed at a concentration of 0.027 mg/L [25]. Mixtures of pesticides have acute and chronic toxicity to zooplankton [26]. The sensitivity of zooplankton to lindane highly depends on the kind of species: *Acartia tonsa* (96 h LC₅₀=17 µg/L) and *Cypridopsis vidua* (96 h LC₅₀=3.2 µg/L) are more sensitive than *Daphnia carinata* (48 h LC₅₀=100 µg/L) or *Brachionus calyciflorus* (24 h LC₅₀=13 mg/L) [27]. The data show that roof runoff water might be a threat to sensitive aquatic organisms.

The First Flush

The first flush samples were collected at the very beginning of the storm event as soon as the precipitation event was noted. After at least 30% volume [15] of stormwater

during each event passed, it was assumed that collected samples could represent steady state conditions, with relatively constant levels of concentrations of chemical species. The comparison of pollutants levels for the first flush and for steady state conditions is presented in Table 4. Both experimental and literature data are compared.

The data collected in Table 3 confirm the existence of the first flush phenomenon for most chemical species. The first flush event was not observed for potassium cations, nitrites, and PAHs in their dissolved forms. There were few time difference in concentrations in the first flush and steady state conditions for chlorides, nitrates, sulphates, sodium, copper, and PCBs. For total chryzene and PAHs adsorbed on particulates, the difference was ten orders of magnitude and hundreds of orders of magnitude for zinc in water samples collected from concrete tiles. The first flush is an unfavorable phenomenon as the great load of pollutants is released into water in relatively short time and is washed with small water volume.

Concentration Changes during Storm Runoff

Two experiments were performed, both during precipitation of very low intensity. During this study only zinc sheeting and ceramic tile were investigated. Height and time of precipitation during the sample collection give basic information about drizzle intensity. Total height of first precipitation was two millimeters and it continued for 5 hours. During the second rain event the concentrations were measured in runoff waters for both roofing types: zinc sheeting and ceramic tile. The height of precipitation was 5 mm and the event lasted for six hours, but the first measurements were taken at a height of 1 mm. The dry period before rain events in both cases were about one day. Both roofs were gabled in eastern and western directions. Samples were collected from western sides of both buildings. The results of the experiments are presented in Table 5.

During the first runoff event the decrease in concentrations of chlorides, nitrates, sulphates, and sodium was observed, while the concentrations of zinc, nitrites and potassium remained constant during the storm event. The minimum in PAHs (fluoranthene and pyrene) and PCB (PCB 52 and PCB 180) concentrations was at 1 mm of precipitation height (fourth hour). This could occur due to the change in the intensity of rain event.

During the second runoff event the specific conductivity decreased in time of storm event for both roofing types, and the values were smaller in runoff samples collected from zinc sheeting. Similar to the first investigated drizzle event, concentrations of nitrites, potassium, and zinc were low and constant or slightly decreasing in time for both sampling sites. Some fluctuations were present in tracks of other parameters, but general trends could be noted. An increase of sodium and chlorides (in both roof types), calcium and ammonium (in ceramic tile only) concentrations were remarkable. Strong correlation between chlorides and sodium concentrations ($r^2=0.93$ for ceramic tile; $r^2=0.95$ for zinc sheeting) may indicate that fluctuations did not originate from error but from other reasons (presence of sea

aerosols or road salts). Decrease of sulphates, ammonium, and calcium concentrations were observed in samples collected from zinc sheeting roof. What is interesting is that similar concentrations of zinc were observed on both roofing materials. This might be expected due to the short time period before runoff event. Despite the fluctuations, a decreasing trend of PAH concentrations was noted during a storm event for both sampling sites. PCBs were determined only in ceramic tile runoff, PCB 52 concentration was sharply decreasing, whereas PCB 180 concentration was fluctuating in time. Unclear trends in concentration changes during runoff may indicate that the main factor influencing quality of runoff during these events was rainwater quality. This explanation is supported by the short dry periods before events (short time for dry deposition or accumulation of corrosion products). What is more, some compounds change similarly during the second event in both roofing materials (i.e. chlorides, nitrates, sodium, pyrene, fluoranthene).

Changes in Concentration during Thaw

When roofs are covered with the snow layer, another runoff system is formed. Samples were collected to investigate the concentrations of pollutants in roof runoff waters originating from melting snow. Such samples were collected from ceramic tile roof at midday from 13 to 15 November 2007. There was no precipitation at that time, the snow was frozen during the night and was melting during the day. The results are presented in Table 6.

The concentrations of PAHs were increasing in water samples collected in successive days of melting snow event. The probable reason of increase of PAHs concentration was the accumulation of particulate matter, which PAHs are usually bound to. PAHs are combustion by-products, so their release is enhanced in winter, when house heating systems are in operation. Particles can easily settle on the snow accumulated on the roof. PAHs, apart from being deposited on the snow, are released to runoff water and the smaller the volume of remaining snow, the higher the rate of their release. No particular trends in changes of inorganic compound concentrations were observed.

Conclusions

Roofing is an important source of variable pollutants, originating from material accumulated on the roof as well as roofing material itself. The experiment and literature data indicate that loads of most pollutants are much higher during the first flush event than in other stages of roof runoff. Metals, PAHs, cations and anions are the most common first flush pollutants. Some solutions have to be proposed to deal with the first flush existence problem. These might include the installation of special filters in the gutters or leading the first flush water to the sewage system. The role of roofing material is complex and can act as a source of pollutants: a temporary sink when pollutants are adsorbed on its surface, and a re-emitter when adsorbed pollutants are flushed by runoff waters.

The experiments confirm the general trend of decreasing the concentration of pollutants in roof runoff water during the runoff event. Since the runoff phenomenon is dependent on many parameters, some divergences from expected slopes were observed. During the roof runoff originating from rainwater, concentration of inorganic pollution distinctly decreased, whereas concentrations of PAHs did not follow any definite trend. On the other hand, during roof runoff originating from snow meltdown, the distinct increase of PAH concentration was observed and inorganic species did not follow any particular trend. Further investigation of roof runoff water quality is needed for better understanding of the contamination pathways of natural waters and the role of roofing materials in this phenomenon.

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References

1. POLKOWSKA Ż., GRYNKIEWICZ M., ZABIEGAŁA B., NAMIEŚNIK J. Levels of Pollutants in Runoff Water from Roads with High Traffic Intensity in the City of Gdańsk, Poland. *Polish J. Environ. Stud.* **10**, 351, **2001**.
2. KLIMASZEWSKA K., POLKOWSKA Ż., NAMIEŚNIK J. Influence of Mobile Sources on Pollution of Runoff Waters from Roads with High Traffic Intensity. *Polish J. Environ. Stud.* **16**, 889, **2007**.
3. POLKOWSKA Ż., ZABIEGAŁA B., GÓRECKI T., NAMIEŚNIK J. Contamination of Runoff Waters from Roads with High Traffic Intensity in the Urban Region of Gdańsk, Poland. *Polish J. Environ. Stud.* **14**, 799, **2005**.
4. CHANG M., McBROOM M.W., BEASLEY R.S. Roofing as a source of nonpoint water pollution. *J. Environ. Manag.* **73**, 307, **2004**.
5. WALLINDER I.O., VERBIEST P., HE W., LEYGRAF C. Effects of exposure direction and inclination on the runoff rates of zinc and copper roofs. *Corr. Sci.* **42**, 1471, **2000**.
6. EVANS C.A., COOMBES P.J., DUNSTAN R.H. Wind, rain and bacteria: The effect of weather on the microbial composition of roof-harvested rainwater. *Wat. Res.* **40**, 37, **2006**.
7. HE W., WALLINDER I.O., LEYGRAF C. A laboratory study of copper and zinc runoff during first flush and steady-state conditions. *Corr. Sci.* **43**, 127, **2001**.
8. BARCO J., PAPIRI S., STENSTROM M.K. First flush in a combined sewer system. *Chemosphere* **71**, 827, **2008**.
9. SULAIMAN F.R., BRIMBLECOMBE P., GROSSI C.M. Mobilization and loss of elements from roofing tiles. *Environ. Geol.* **58**, 795, **2009**.
10. HEIJERICK D.G., JANSSEN C.R., KERLEN C., WALLINDER I.O., LEYGRAF C. Bioavailability of zinc in runoff water from roofing materials. *Chemosphere* **47**, 1073, **2002**.



11. BERTLING S., WALLINDER I.O., LEYGRAF C., KLEJA D.B. Occurrence and fate of corrosion induced zinc in runoff water from external structures. *Sci. Total Environ.* **367**, 908, **2006**.
12. BELGHAZI A., BOHM S., SULLIVAN J.H., WORSLEY D.A. Zinc runoff from organically coated galvanized architectural steel. *Corr. Sci.* **44**, 1639, **2002**.
13. KARLEN C.R., WALLINDER I.O., HEIJERICK D., LEYGRAF C. Runoff rates, chemical speciation and bioavailability of copper released from naturally patinated copper. *Environ. Pollut.* **120**, 691, **2002**.
14. SORME L., LAGERKVIST R. Sources of heavy metals in urban wastewater in Stockholm. *Sci. Total Environ.* **298**, 131, **2002**.
15. DAVIS A.P., SHOKOUHIAN M., NI S. Loading estimates of lead, copper, cadmium and zinc in urban runoff from specific sources. *Chemosphere* **44**, 997, **2001**.
16. POLKOWSKA Ż. Examining the Effect of the Type of Roofing on Pollutant Content in Roof Runoff Waters from Buildings in Selected Districts of the City of Gdańsk Polish J. Environ. Stud. **13**, 191, **2004**.
17. BUCHELI T.D., MULLER S., VOEGELIN A., SCHWARZENBACH R. Bituminous roof sealing membranes as major sources of the herbicide (R,S)-mecoprop in roof runoff waters: potential contamination of groundwater and surface waters. *Environ. Sci. Technol.* **32**, 3465, **1998**.
18. CLARK S.E., STEELE K.A., SPICHER J., SIU C.Y., LALOR M.M., PITT R., KIRBY J.T. Roofing Materials' Contributions to Storm-Water Runoff Pollution, *J. Irrig. Drain. Eng.* **134**, 638, **2008**.
19. WALLINDER I.O., LEYGRAF C., KARLEN C., HEIJERICK D., JANSENN C.R. Atmospheric corrosion of zinc based materials: runoff rates, chemical speciation and ecotoxicity effects. *Corr. Sci.* **43**, 809, **2001**.
20. DELETIC A. The first flush load of urban surface runoff. *Wat. Res.* **32**, 2462, **1998**.
21. SCHRIEVER A., HORN H., HELMEREICH B. Time focused measurements of roof runoff quality. *Corr. Sci.* **50**, 384, **2008**.
22. FORSTER J. Variability of roof runoff quality. *Wat. Sci. Technol.* **39**, 137, **1999**.
23. ARMAAG Annual Report, **2008**.
24. POLKOWSKA Ż., KOT A., WIERGOWSKI M., WOLSKA L., WOŁOWSKA K., NAMIEŚNIK J. Organic pollutants in precipitation: determination of pesticides and polycyclic aromatic hydrocarbons in Gdansk, Poland. *Atm. Environ.* **34**, 1233, **2000**.
25. PAULSSON M., NYSTROM B., BLANCK H. Long-term toxicity of zinc to bacteria and algae in periphyton communities from the river Gota Alv, based on a microcosm study. *Aquat. Toxicol.* **47**, 243, **2000**.
26. HANAZATO T. Pesticide effects on freshwater zooplankton: an ecological perspective. *Environ. Pollut.* **112**, 1, **2001**.
27. VAN DEN BRINK P., CRUM S., GYLSTRA R., BRANSEN F., CUPPEN J., BROCK T. Effects of a herbicide-insecticide mixture in freshwater microcosms: Risk assessment and ecological effect chain, *Environmental Pollution* **157**, 237, **2009**.
28. BUCHELI T.D., MULLER S.R., HEBERLE S., SCHWARZENBACH R.P. Occurrence and behavior of pesticides in rainwater, roof runoff and artificial stormwater infiltration. *Environ. Sci. Technol.* **32**, 3457, **1998**.