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ACIDITY MAJOR ANIONS, AND TRACE METALS IN URBAN RAIN AND ROOF RUNOFF FROM SELECTED ROOF COVERINGS

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Abstract: *The paper presents results of research regarding the concentration levels of selected pollutants in rain samples and roof runoff waters from buildings. The concentrations of the following analytes were determined: pH value, the anions: Cl^-, NO_3^-, SO_4^{2-} and heavy metals: Zn^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+} were performed. Two samples were collected in the Tricity, the third in D brówka Tczewska near Gda½sk with old and modern-type buildings with various types of roofing. Samples were collected for a period of two months (from April to June 2006) always during rainfall. The results obtained allowed us to assess the presence and concentration of the given analytes contained in roof runoff waters from buildings, and so, their contribution to the total pollution of runoff waters. A correlation between the type of roofing and the level of concentration of particular analyte groups was noted, which shows that the materials which roofs are made from (as surfaces and as materials) can be an additional factor influencing the pollution of waters running off them.*
Keywords: *Precipitation chemistry; Roof runoff; Acidity Major Anions; Trace metals; Roof coverings.*

1. INTRODUCTION

In urban environments, most impervious surfaces are sources of stormwater. The three principal categories of impervious area within urban environments are roads, roofs and other paved areas. Roofs are made of a variety of materials and most, with the exception of those made from grass/reed and potentially toxic materials, are suitable as rainwater catchment surfaces. The typical roofing materials are metal sheets, ceramic and clay tiles, rock slate and ferro cement, asbestos cement, gravel, polyester, tar felt.

Roof runoff is considered a potential source of pollution for two primary reasons. First, compounds contained in roofing materials (the material used for the roof cover, the guttering, the downpipes and paints, sealants and cleaners) may be leached into runoff (physical washing off or erosion), and airborne pollutants and organic substances, such as leaves, dead insects, and birds' wastes, are added to roofs by interception and deposition. During storms, rainwater not only adds a variety of chemicals and contaminants to the roof watershed, the acidic nature of rainwater will react with compounds retained in or by the roof and cause many elements in the roof runoff to leach out [1,2].

Roofing materials are potentially a source of alkalinity, dissolved ions, suspended solids and some trace metals [1,3-19]. There is a clear indication that roofs made of metal elevate the concentrations of that metal in the runoff, and that the pH of the incident rainfall also influences metal concentrations [1,2,16]. The literature available indicates several other factors including roof slope, time between rainfall events and material age impact on the leaching potential of metals into roof runoff [7,13,17,19,20]. For heavy metals, unlike the other parameters of pollution, the highest runoff concentrations were measured in the roof runoff samples. This is especially striking for lead and zinc, for which concentrations in roof runoff are 4-6 times higher than in other runoff samples [5,12]. The corrosion rates of copper and zinc (from roofs) were earlier proven to be largely influenced by, e.g., wind direction, degree of sheltering, orientation and inclination on a building [15].

Runoff waters often contain pollutants, therefore they can be a potential danger to aquatic ecosystems [3,20,21]. Both precipitation and runoff waters end up in surface and/or groundwater, which are the primary sources of drinking water. It is necessary, therefore, to monitor the pollution of runoff waters.

This paper presents results of research regarding concentration levels of selected pollutants in samples of precipitation and roof runoff waters from different roof surfaces (ceramic tiles-old and new, metal roofing tiles, thermally bonded tar paper, tar paper with quartz gravel surfacing, asbestos cement corrugated sheets). These study evaluated the pH and temperature dependence of washoff of pollutants (heavy metals and anions) from various roofing material types. The concentrations of the following analytes were determined: the heavy metals Zn, Cu, Pb, Cd and the anions: F^-, Br^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, furthermore, measurements of pH value were performed. Environmental samples were collected in several districts of the city of Gda½sk (1) and Gdynia (2) with old and modern-type buildings with various types of roofing. The third point was localized in a country area, 10 kilometers from Gda½sk.

2. EXPERIMENTAL PART

2.1 Sampling

Samples of runoff water were initially collected from roofs of buildings located in three places. Two of them were localized in the Tricity, the third in D brówka Tczewska near Gda½sk. Samples of runoff and precipitation waters were collected for a period of two months (from April to June 2006). Table 1 presents localization of sampling sites of runoff and precipitation water and type of roof covering. They were collected during a precipitation event, defined as steady precipitation lasting for at least 5 hrs. Sample collection usually took place within 1 hr from the beginning of the precipitation event. The samples were collected with a plastic scoop, transferred to dark glass bottles and transported to the laboratory (usually within less than 1 hour from collection). No chemicals were added to preserve the samples, therefore the determinations were typically initiated immediately after the samples arrived at the laboratory. In order to protect the samples from changes in composition, they were cooled to a temperature of 4 – 7°C [22,23].

2.2 Analytical Methods

Samples of precipitation and roof runoff water were transported to the laboratory at best immediately after collection. pH was measured directly after collection, while determination of heavy metals and anions as soon as possible. Methods of chemical analyses and their detection limits and precision are given in Table 2. Selected anions and cations were determined using quantified against synthetic rain standards (RAIN-97, CRM 409). Analytical methods and techniques developed and verified in previous studies [22,23] were employed.

Tabela 1
The Localization of the Sampling Sites for Sampling Rainwater and Roof Runoff Water

Sampling location	*Description*	*Type of roofing*	*Material of guttering and downpipes*
Gda½sk Technical University (GTU)	right part of main building	ceramic tiles-old	zinc sheet
	left part of main building	ceramic tiles-new	PVC (polyvinyl-chloride)
	maintenance division building	tar paper with quartz gravel surfacing	zinc
	Auditorium maximum building	thermally bonded tar paper	zinc
Gdynia Chwarzno	detached house	metal roofing tiles Balex-Metal	PVC
D brówka Tczewska (near Gda½sk)	detached house	asbestos cement corrugated sheets	zinc
		metal roofing tiles Plannja	mild steel coating

Table 2
General Characteristics of Analytical Techniques Used during Studies

Para-meter	*Analysis method*	*Detection limits*	*Intermediate precision RSD [%]*	*Expanded uncertainty K=22 [%]*
pH	CX-315 pH-meter (Elmetron) equipped with an ESAg-301 combination electrode	0–14 pH units	5	7
Heavy metals Zn, Cu, Pb, Cd	Atomic Absorption Spectrophotometr Model 210 VGP from BUCK Scientific Electrothermic graphite furnaces Buck M 220; autosampler Buck A 220– AS;	0.1–5 $\mu g l^{-1}$	1	3
Anions SO_4^{2-}, NO_3^-, NO_2^-, PO_4^{3-}, Cl^-, F^-, Br^-	Ion Chromatography DIONEX-500AS9-HC column (2 x 250 mm), AutoSuppression Recycle Mode ASRC® -ULTRA (2 mm), conductivity detection, eluent 9.0 m M Na_2CO_3, flow rate 0.25 ml/min	0.01–0.1 $mg l^{-1}$	1	4

3. RESULTS AND DISCUSSION

The analyses performed yielded large amounts of data regarding the content of various analytes in precipitation and roof runoff from buildings.

3.1 pH

Rainwater pH is an important factor in assessing roof runoff quality as acidic rainwater has the potential to dissolve a larger proportion of trace contaminants on rooftops. Rainwater is naturally acidic due to the dissolution of carbon dioxide in the atmosphere, forming carbonic acid. Besides, NO_x and SO_x in the air dissolve into the rainwater and result in the formation of strong acids. Depending on the composition of the roofing material, these particles can alter the pH of the runoff. The available data demonstrates that the pH of roof runoff is typically more alkaline [8,12,14,16] than rainwater [1,24]. In some areas, the presence of alkaline soil particles (where the soils are alkaline) on the roofs from deposition and wind erosion can also increase the pH [24].

The research program included 9 rain samples, 8 runoff samples for each roof whose coverage was two types of ceramic tiles, two types of tar paper and 4 runoff samples for each roof whose coverage was asbestos cement sheets and two types of metal roofing tiles. For rain samples, pH ranged from 5.9 to 6.9 (which is taken as alkaline), while for roof runoff from 5.4 to 7.4. Frequency distribution of pH found in runoff water for all roof coverings is shown in Figure 1.

The most frequently observed pH is between 6.0 and 7.4. In a clean atmosphere the pH is between 5.0 and 5.6 due to the dissolution of CO_2 in rain and cloud droplets and the existence of background SO_2 [25,26]. Considering this criterion, the rain and roof runoff in Gda½sk and Gdynia was not acidic. Figure 1 shows that in more than about 93% of cases, the pH was more alkaline (>5.6). About 20% of roof runoff samples had a pH above 7.0, suggesting inputs of alkaline from roof coverings (adsorbed on rainless days). The neutral or alkaline pH means that acids (basically of nitrogen and sulphur) were neutralized by alkaline components, such as calcium and ammonium. The lowest pH value (5.4) was recorded for a runoff water sample collected on May, 2006 from a roof covered with metal roofing tiles. The highest pH value was 7.4; it was for a sample of runoff water collected on the same day from a roof coated with asbestos cement sheets. Thomas and Greene measured a pH of 6.9 in rainwater and 6.8 to 8.1 in roof runoff, Chang *et al.* measured pH in rainwater 4.2 to 7.0 and 3.6 to 7.4 in roof runoff [1,24]. Roofs containing cement (concrete tile, asbestos cement and gravel) can significantly elevate the pH as the alkaline cement particles (containing $CaCO_3$) are picked up and dissolved in the rainwater [16]. Table 3 illustrates the general trend of pH in roof runoff samples.

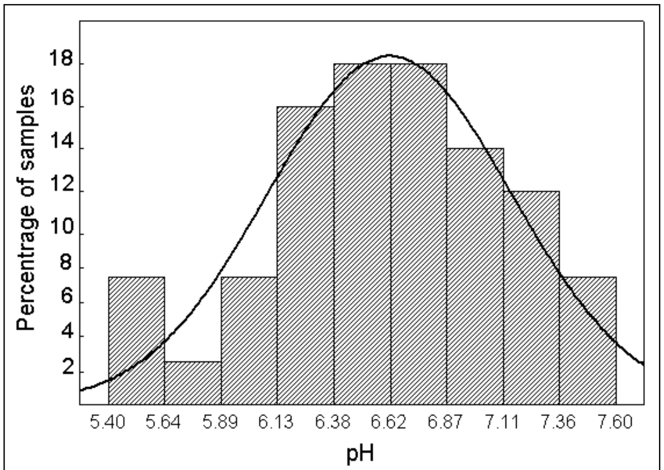

Figure 1: Frequency Distribution of pH.

The length of time between rain events affects the pH of runoff, as a longer dry period allows more deposition of solids and further weathering of the roof surface [16]. Unlike contaminant concentrations, pH appears to remain stable throughout a rainfall event [9].

3.2 Acidity Major Anions

Major ion (Cl^-, NO_3^-, SO_4^{2-}) concentrations in rainwater and roof runoff were determined in all samples. For rain, the range of concentrations (in mgl^{-1}) of these three ions were contained in the following intervals: Cl^-: 0.25 – 30.8; NO_3^-: 1.61 - 13.0; SO_4^{2-}: 3.03 – 10.6; while for roof runoff Cl^-: 0.05 – 30.8; NO_3^-: 0.92 – 61.6; SO_4^{2-}: 0.85–432. Concentration of Cl^- in rainwater samples was usually higher than in runoff samples, and only in runoff water from a flat roof covered with thermally bonded tar paper, it was slightly higher. On the other hand, concentrations of Cl^-, NO_3^- and SO_4^{2-} ions in runoff from roofs covered with metal roofing tiles was–in all cases–lower than in rainwater. The highest concentrations of SO_4^{2-} and NO_3^- were discovered in runoff from a roof covered with ceramic tiles that were several tens of years old. Somewhat lower ranges of concentrations are presented by Karlen *et al.*: Cl^-: 0 – 6; NO_3^-: 0.4 - 3.1; SO_4^{2-}: 0 – 34 i Mason *et al.*: Cl^-: 2.13 – 7.81; NO_3^-: 18.0 - 39.7; SO_4^{2-}: 9.6–19.2 [14,27]. However, in the Gda½sk area, the ionic composition of rainwater and roof runoff are largely influenced by sea-salt component (Bay of Gda½sk, Baltic Sea).

Table 3
Comparison of Roof Runoff pH from Different Roof Surfaces

Roof type	*Site*	*Minimum*	*Maximum*	*No. of samples*	*Reference*
Tar felt	Urban	5.8	6.3	11	[8]
Tar felt	Urban	3.8	4.6	2	[16]
Pantiles	No data	4.6	5.5	2	
Thermally bonded tar paper	Urban	6.2	6.8	8	This work
Tar paper with	Urban	6.0	6.7	8	This work
Tar board	Urban	6.3	7.8	13	[22]
Pantiles	Urban	5.3	6.5	18	[8]
Zinc sheet	Urban	7.0	7.8	11	
Zinc sheet	No data	6.5	6.8	2	[16]
Zinc sheet	Urban	5.1	6.3	16	[13]
Zinc sheet coated with paint	Urban	6.6	7.4	8	[22]
Zinc sheet coated	Urban	7.3	7.4	2	
Aluminum	Rural	4.8	7.3	31	[1]
Galvanized iron	Rural	3.6	7.4	31	
Metal roofing tiles	Urban	5.4	6.7	8	This work
Metal roofing tiles	Urban	6.1	7.0	12	[22]
Flat Gravel	No data	6.8	7.1	2	[16]
Flat Gravel	Industrial	7.0	7.6	No data	[14]
Concrete Tiles	Urban	7.3	7.5	11	[8]
Asbestos cement sheets	Urban	6.7	7.9	18	[22]
Asbestos Cement	No data	7.3	8.2	2	[16]
Asbestos cement sheets	Urban	7.1	7.4	4	This work
Ceramic tiles	Urban	6.6	7.5	22	[22]
Ceramic tiles (new)	Urban	6.2	7.1	8	This work
Ceramic tiles (old)	Urban	6.9	7.6	8	This work
Wood shingle	Rural	3.3	6.9	31	[1]
Composition shingle	Rural	4.1	8.3	31	
Teflon	Urban	-	6.8	1	[22]

The type of roofing material influences the quality and quantity of anions to be found in runoff waters. The highest sum of anion concentrations was noted for a runoff sample from a roof covered with old ceramic tiles. The change in the content of precipitation water is–to the least degree–influenced by contact with roofing made from metal roof tiles. This depended on the large slope and the smooth surface of this kind of roofing. Such an arrangement is beneficial to fast removal of pollutants settling as a result of dry deposition by wind or the first drops of rain. On such roofing as ceramic or cement tiles, asbestos cement sheets or tar paper, many pollutants settle due to dry deposition, and penetrate deep into the rough surface.

The studies on selected anions in precipitation and runoff waters were also conducted by German researchers supervised by J. Forster. They analysed samples of rain and water collected from roofs of the University of Bayereuth. The data obtained by German and Polish researchers are presented in Figure 2. In both cases chloride, nitrate and sulphate concentrations in roof runoff were higher (in most cases, Germany approximately twice) than found in rainwater. Little difference in concentration between the five roof types suggests that the major source of these ions is dry deposition, rather than an input from weathering of the roof surface. Nitrate concentrations in roof runoff are generally not affected by the roof type, but by the environment. Bird faeces and agricultural activities were direct sources of nitrates into roof runoff [9,24].

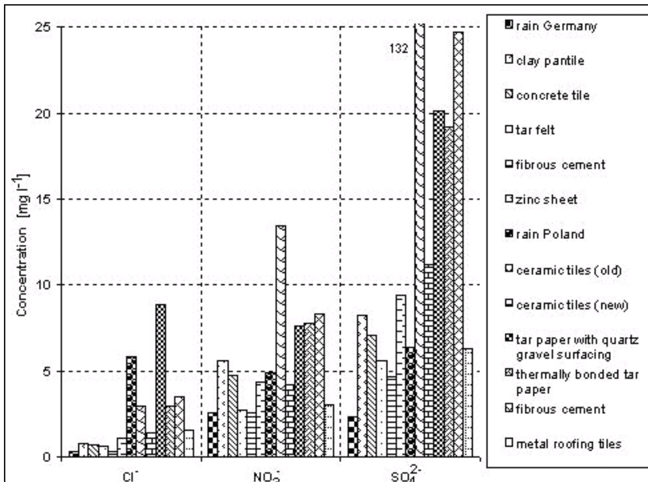

Figure 2: **Comparison of Anion Concentration in Rain and Roof Runoff Samples from Selected Roof Coverings**

Variation of pH with SO_4^{2-} and NO_3^-

The ratio of NO_3^-/SO_4^{2-} which indicates their relative importance in acidification [28] was calculated. A ratio above 1.0 indicates that HNO_3 influences acidity and that below 1.0 indicates the influence of H_2SO_4 is more. The NO_3^-/SO_4^{2-} ratio for rain and roof runoff water samples are given in Table 4.

Table 4
The NO_3^-/SO_4^{2-} Ratio for Rain and Runoff Water Samples Collected from Selected Roof Coverings

Roof type	*Range of ratio NO_3/SO_4^2*
rain	0.40 – 0.67
ceramic tiles (new)	0.098 – 0.57
ceramic tiles (old)	0.036 – 0.28
tar paper with quartz gravel surfacing	0.14 – 0.72
thermally bonded tar paper	0.15 – 0.55
metal roofing tiles *Balex Metal*	0.31 – 0.51
metal roofing tiles *Plannja*	0.16 – 0.94
asbestos cement corrugated sheets	0.19 – 0.42

The NO_3^-/SO_4^{2-} ratio for rain and roof runoff water was less than 1.0 which indicates that acidity is influenced more by SO_4^{2-}. This trend is also observed in other places [29]. Figure 3 shows the variation of pH and SO_4^{2-} (A) or NO_3^- (B) in all roof runoff samples. The figure 3 A i B shows that when the NO_3^- or SO_4^{2-} is higher, pH becomes lower. Only for samples from 8 to14 there is no clear indication of this relationship. This is caused by washing out of NO_3^- and SO_4^{2-} adsorbed on the surface of a very old roof (ceramic tiles–old) by the rain.

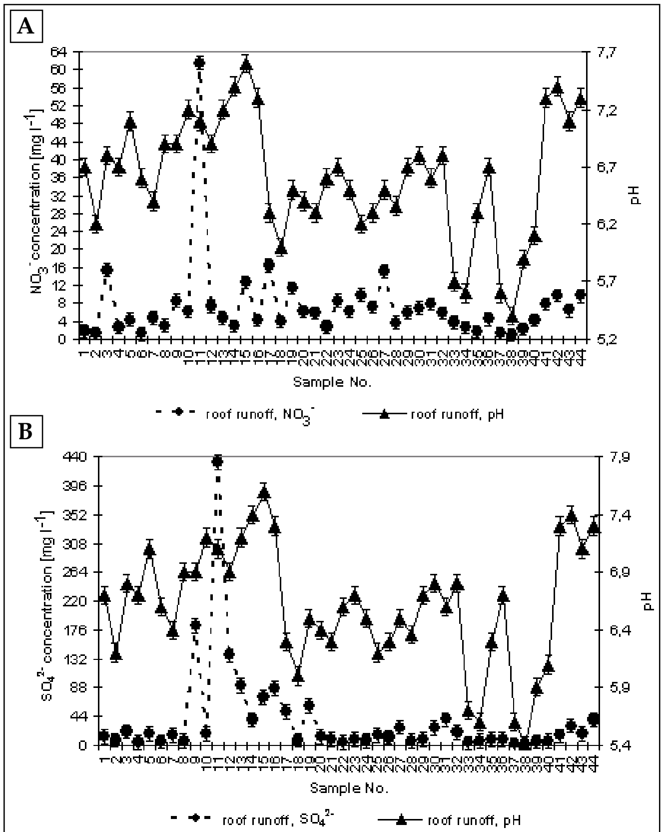

Figure 3: Variation of pH and SO_4^{2-} (A) or NO_3^- (B) in all Roof Runoff Samples

3.3 Trace Metals

The range of Zn^{2+}, Pb^{2+}, Cu^{2+} and Cd^{2+} concentrations measured in rain samples and runoff water from different roofs. Concentration of heavy metals in roof runoff was mostly higher than in rain. In all rain and roof runoff samples, Zn^{2+} and Pb^{2+} were found. The highest concentration of zinc (4900 μgl^{-1}) was noted for runoff from a roof covered with asbestos cement sheets. The highest lead content (102 mgl^{-1}) was detected in runoff from a flat roof covered with thermally bonded tar paper. While the highest concentration of cadmium (3,70 μgl^{-1}) was noted for runoff from a roof covered with ceramic tiles (old). Cu^{2+} was detected only in runoff samples from roofs covered with tar paper or ceramic tiles (no copper content was detected in any rainwater sample).

The highest concentration of Zn^{2+} was in runoff from a flat roof covered with thermally bonded tar paper. However, the source of this pollutant was not the roofing material. Zn^{2+} was washed out of the drain pipe, which was made from zinc-coated sheet metal. The highest mean concentration of Pb^{2+} was noted for runoff samples from a roof covered with thermally bonded tar paper. The source of this metal in runoff water is dry deposition, while the low inclination of the roof helps it to accumulate pollutants, which are subsequently washed off by the rain. Approximate values of Cd^{2+} concentrations in rainwater and runoff samples from rooftops allow us to claim that the source of this metal is atmospheric deposition. Cu^{2+} was detected only in runoff samples from roofs in the area of the Gda½sk University of Technology. Most probably, Cu^{2+} was washed out from the brass elements decorating the drainpipe baskets.

The pollution of rain and roof runoff samples by heavy metals is widely discussed in literature [3,4,7,13,14]. Metals such as copper, lead or zinc are very often found in runoff from rooftops. Roofing material is the main factor influencing the concentration level of these pollutants in water. Metals are the product of corrosion of roofing and drainpipe materials, which is why runoff waters from roofs covered with zinc-coated sheet metal contain a large amount of zinc and trace amounts of cadmium, while copper roofs are a source of copper [2]. However, metals found in runoff waters do not find their way only as a result of washing out, since their large content was noted in sewage from non-metal materials (eg. ceramic roof tiles, polyester, tar-paper). This depends on the location of the sampling site [27]. The highest heavy metal contents were noted in runoff waters from the roofs of homes located in industrial and urban areas. Table 5 presents results of research which was performed in many countries all over the world.

The quantity of metal released from roofs is determined by a number of interacting parameters, including current environmental and precipitation characteristics (rain quantity, intensity, pH, occurrence of dry and wet periods, corrosion layer characteristics, patina composition, age, inclination of the roof surface) [2].

3.4 Variation of Various Analytes with Temperature

Figure 4 presents an exemplary graph illustrating the dependence of concentrations of pollutants present

Table 5
Metal Concentrations in Runoff Water Samples Collected from Different Roof Surfaces

[$\mu g l^{-1}$]

Roof Type	*Site*	*Zn^{2+}*	*Pb^{2+}*	*Cu^{2+}*	*Cd^{2+}*	*Reference*
Zinc sheet	Urban	490	230	n.d.	630	[18]
Ceramic tiles		52	183	n.d.	630	
Rusty galvanised	Industrial	12200	302	20	630	[21]
Old metal roof		1980	10	11	n.d.	
Plywoodw/tar paper		877	11	166	n.d.	
Tar roof aluminium paint		297	10	25	n.d.	
Anodised aluminium		101	15	16	n.d.	
Galvanised iron	Industrial	~3600	~100	n.d.	n.d.	[24]
Concrete tile		~1600	~90	n.d.	n.d.	
Galvanised iron	Urban	~50	~10	n.d.	n.d.	
Concrete tile		~200	~50	n.d.	n.d.	
Tar felt	Urban	112	38.7	7.6	1.1	[16]
Pantiles		49,58	62.0	475	0.63	
Asbestos cement		33.3	41.2	8.3, 12.7	0.22	
Zinc sheet		44000	57.6	32.4	1.7	
Gravel		9500	4.6	7.6	0.10	
Tile	Urban	360	172	1905	2.1	[4]
Polyester		2076	510	6817	3.1	
Flat gravel		36	22	140	0.2	
Tile	Various	48	41	304	0.40	[19]
Polyester		115	24	842	0.30	
Gravel		9	2.7	18	0.11	
Zinc sheet	No data	6400	n.d.	n.d.	n.d.	[3]
Galvanized steel		6200	n.d.	n.d.	n.d.	
Wood shingle	Rural	16317	0.045	0.029	n.d.	[1]
Composition shingle		1372	0.038	0.025	n.d.	
Aluminum		3230	0.037	0.026	n.d.	
Galvanized iron		11788	0.049	0.028	n.d.	
Ceramic tiles (old)	Urban	343	4.83	222	1.58	This work
Ceramic tiles (new)		364	2.40	227	0.45	
Metal roofing tiles		300	4.75	n.d	n.d.	
Asbestos cement sheets		3075	1.63	n.d.	1.30	
Thermally bonded tar paper		2762	35.2	250	0.97	
Tar paper with quartz gravel surfacing		1006	3.71	150	0.70	

n.d.- not detected

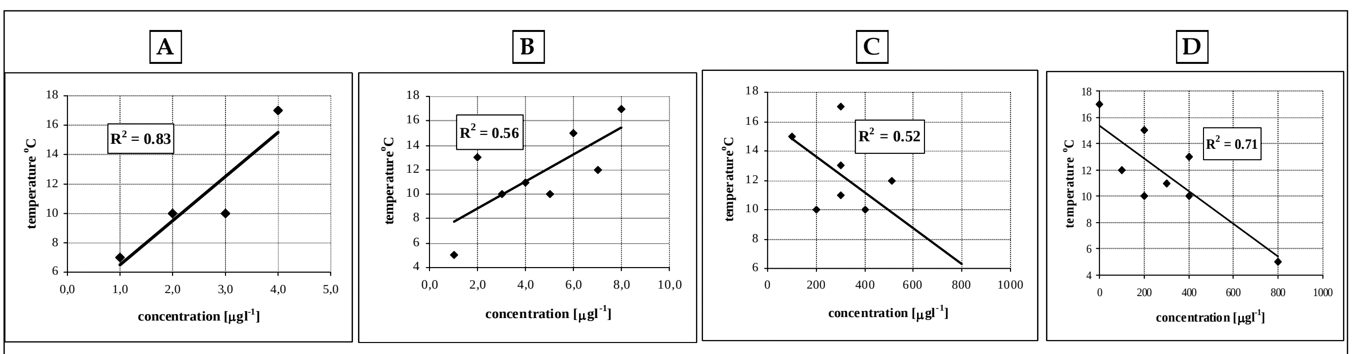

Figure 4: Wp»yw Temperatury Otoczenia na st"óenie Pb^{2+} (A,B) and Zn^{2+} (C,D) w próbkach Roof Runoff Water: A-**asbestos Cement Sheets;** B-**tar Paper with Quartz Gravel Surfacing;** C-**ceramic tiles (new);** D-**ceramic tiles (old)**

in roof runoff on ambient temperature during sample taking. An influence of ambient temperature on Cl^- concentration was observed in runoff samples from roofs covered with ceramic tiles, eternit and tar paper with quartz gravel surfacing. A linear dependence of SO_4^{2-} concentration in runoff waters from roofs covered with metal roofing tiles and asbestos cement sheets was also noted. A correlation between NO_3^- concentration in runoff samples and ambient temperature was noted only in two cases: for tar paper with quartz gravel surfacing and metal roofing tiles *BalexMetal*. Ambient temperature had an effect on Pb^{2+}

concentration in runoff samples from roofs covered with asbestos cement sheets or tar paper with quartz gravel surfacing (Figure 4). A reverse influence of ambient temperature was noted for Zn^{2+} concentration in runoff samples from roofs covered with new and old ceramic tiles.

4. CONCLUSIONS

Roofs can be a source of water pollution. However, the results of studies on roof runoff published thus far in the literature vary widely. The variation reflects differences in roofing materials, industrial treatments, care and maintenance, age, climatic conditions, orientation and slope of the roof and air quality of the region. The deposition of various pollutants from the atmosphere onto roof surfaces during a dry period greatly influences the runoff water quality from roof catchment systems. The amounts of pollutants deposited on roof surfaces increase with the age of the roofing material (see ceramic tiles–new and old in Figure 2), the length of the dry period between rainfall events, as well as ambient temperature, as evidenced by the observed increase in pollutant concentrations in the water samples collected.

In general, studies of this type carried out on real specimen collected from roofs that might have been exposed to the atmosphere for dozens of years are difficult. For example, the choice of roofing materials to be included in the study might often be quite accidental. More often than not, they are selected based on the experience of the researchers and local conditions. Consequently, it is important to carry out studies of this type on as broad a spectrum of analytes as possible, to better characterize the pollutants that might enter the environment via this route. Studies published thus far in the literature were mostly limited to the United States, Australia, Malaysia and a few countries in Europe [1,3-19]. The majority of the published data pertain to heavy metals [1,2,5,7,12,13,15-17,20].

The research presented in this paper is a continuation of the preliminary studies on the chemistry of runoff waters in Poland described in two earlier papers [22,23]. These papers focused on the determination of pollutant levels in roof runoff [22] and on the correlations between the toxicity of runoff waters and the concentrations of selected organic and inorganic pollutants (pesticides, volatile organohalogen compounds, petroleum hydrocarbons, cations and anions) [23]. In this paper, correlations were examined between rain and roof runoff acidity, as well as between acidity and concentrations of selected pollutants. All six roof types caused runoff pH to be significantly different than rainwater pH. The pH exceeded 5.6 for 93% of the samples (Figure 3). This effect may have been due to the presence of basic particles such as organic debris, clay and mineral particles, which had accumulated on the roof surfaces [18]. Concrete tiles and other roofs containing cement have the potential to raise the pH of runoff waters. As the rainwater flows over the roof surface, small alkaline particles of weathered cement (containing $CaCO_3$) are picked up and dissolved in the water, increasing its pH.

Roof runoff from most roofs has ionic composition different from that of the rain falling onto it. The changes are predominantly related to the dissolution of particulate matter deposited on the roofs and the dissolution of the roofing material itself. Cement-based products tend to release more calcium to the runoff than other roof types due to the interaction of the acidic rainwater with the cement. This, in turn, increases the pH of the runoff.

The most common metals in roof runoff are copper and zinc. Higher concentrations of these metals were observed in roof runoff whenever the rainfall encountered metallic zinc or copper on the roof. The concentrations of most other metals in roof runoff appear to be related to the particulate matter derived from atmospheric deposition.

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