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**ROAD AND ROOF RUNOFF WATERS AS A SOURCE  
OF POLLUTION IN A BIG URBAN AGGLOMERATION  
(GDANSK, POLAND)**

**WODY SPŁYWNE Z ARTERII KOMUNIKACYJNYCH I DACHÓW  
BUDYNKÓW JAKO ŹRÓDŁO ZANIECZYSZCZENIA W DUŻYCH  
AGLOMERACJACH MIEJSKICH (GDAŃSK, POLSKA)**

**Summary:** Runoff water is an important medium transporting various air pollutants from the air to the soil and surface water. The results of measurement of removal rates of anions and cations, heavy metals and pesticides in the rain, road runoff, and roof runoff near a major urban highway was presented. Samples of road and roof runoff were collected from various sites in the city of Gdansk. Samples were collected during the precipitation events. The analytes determined in the samples included organochlorine, organonitrogen and organophosphorus pesticides, heavy metals, as well as selected anions and cations. Heptachlor epoxide and *o,p'*-DDE (DDT metabolite) were detected the most often among the pesticides. Sulphate ions were found in all samples. Very high concentrations of sodium and chloride ions were measured in road runoff samples collected directly before the winter season. Overall, the results confirmed that road and roof runoff waters are heavily polluted and their quality should be monitored.

**Keywords:** road and roof runoff waters, pesticides, heavy metals, selected anions, urban area

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 rain-water catchment surfaces. The typical roofing materials are metal sheets, ceramic and clay tiles, rock slate and ferro concrete, asbestos cement, gravel, polyester, tar felt.

Runoff water is an important transport medium for various air pollutants from the air to the surface- and ground water, and then indirectly to other environmental compartments (see Figure 1) [1, 2]. Rain water washes dusts away from the atmosphere and the impervious urban surfaces and, in the form of road and roof runoff, carries off dissolved, colloidal and solid constituents in a heterogeneous mixture, which includes organic and

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inorganic compounds, nutrients, oils, greases and heavy metals [3, 4]. The contaminant may remain permanently on the surface, may be removed from the road by resuspension or may be removed in the road runoff waters. The road and roof runoff itself seems to play an important role, both as a pollutant source and a pollutant sorbent [4].

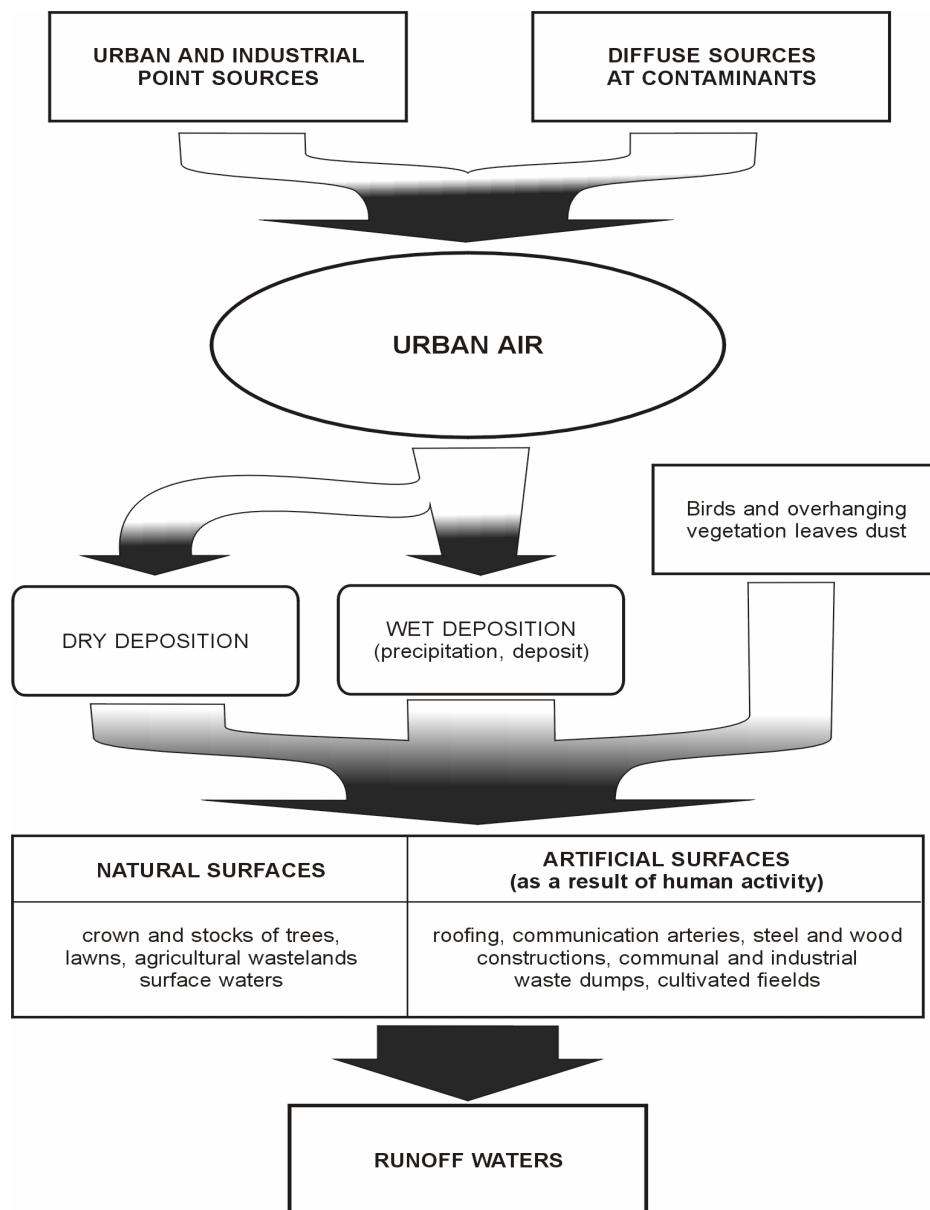


Fig. 1. Sources of pollution and pathways, by which pollutants penetrate into runoff waters

The origin and quantity of pollutants found in highway runoff are site specific and depend on a number of factors, including traffic, highway maintenance, normal depositions on the highway and spillages. Highway surface types (asphalt or concrete) seem to have a minimal effect on the runoff quality [5].

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 [6, 7].

Contamination of runoff water from roads with high traffic intensity and roof runoff waters from different roofing materials in the urban area of Gdańsk district in Poland is discussed in this paper.

## Experimental

### Sampling

Samples of road runoff waters from major highways and roof runoff waters were collected from January 2003 to December 2004. Samples of roof runoff were collected from various sites in the city of Gdansk. Samples were collected during the precipitation events.

The road runoff was collected during or immediately after the rain events. The samplers were plastic containers from which samples were dispensed to amber glass bottles prior to their transportation to the laboratory. Roof runoff samples were collected using smaller, graduated plastic vessels. The individual fractions collected were transferred to dark glass bottles and transported to the laboratory in portable coolers.

The samples were filtered using a glass fiber filter system (Sartorius, Gottingen, Germany) and 0.45  $\mu\text{m}$  membrane filters (Gelman Sciences, USA). Samples were stored at low temperature ( $4\pm 7^\circ\text{C}$ ) in a dark room, with no preservatives added. In general, all analyses were performed within 24 hours of sample collection, with those involving volatile compounds within 2 hours.

### Analytical methods

Samples were collected during or immediately after a precipitation event. They were stored at low temperatures without any chemical preservatives because the analysis was performed either directly on-site or immediately after the samples were delivered to the laboratory. Runoff samples were usually highly contaminated with solids (sand, leaves); therefore, they had to be pre-filtered. The analytical techniques used in this study are summarized in Tables 1 and 2.

Table 1  
Operating conditions of the analytical techniques used in the study (quantified against synthetic rain standards (RAIN-97, CRM 409))

Analyte	Technique	Analytical parameters	Limit of detection	Precision [% RSD]
Anions/ Cations	Ion chromatography IC	Electrical Conductivity, AutoSuppression Recycle Mode ASRC <sup>®</sup> -ULTRA/CSRS <sup>®</sup> -ULTRA, AS9-HC/CS12A column	0.001 meq/dm <sup>3</sup>	1
Metals	Atomic Absorption Spectroscopy (AAS)	AAS, BUCK Scientific model 210-VGP Graphite furnace, BUCK Scientific model 220-GF	0.01 µeq/dm <sup>3</sup>	2

Table 2  
Parameters of the chromatographic determination of the pesticides in the samples

	Organochlorine pesticides	Organonitrogen and organophosphorus pesticides
Chromatograph	GC 6180 Vega, Carlo Erba - Fisons	GC 8000 Fisons
Detector	ECD	NPD
Detector temperature	350°C	280°C
Column (length x ID x stationary phase film thickness)	AT-5, 30 m x 0.32 mm x 0.25 µm	HP-5, 30 m x 0.32 mm x 0.25µm
Injector (injection mode)	Cool on-column	Split/splitless (splitless)
Carrier gas	Hydrogen	Hydrogen
Temperature program	80°C → 15°C/min → 180°C → 15°C/min → 280°C → 15°C/min → 300°C (5 min)	80°C → 15°C/min → 140°C → 10°C/min → 280°C → 20°C/min → 300°C (1 min)
Injector temperature	80°C	80°C
Injected volume	2 mm <sup>3</sup>	2 mm <sup>3</sup>
Data acquisition	Chrom-card	Chrom-card

## Results and discussion

### Major anions

#### Road runoff

Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> were detected in all samples, with the highest concentrations found for Na<sup>+</sup> and Ca<sup>2+</sup>. Among the anions, the highest concentrations were found for Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The highest concentrations were observed for chloride, sulfate and sodium in samples from road runoff. In the case of the chloride ions, the extremely high concentrations (4770 mg/dm<sup>3</sup>) can only be explained by the use of road salt to prevent icing in the area (see Figure 2).

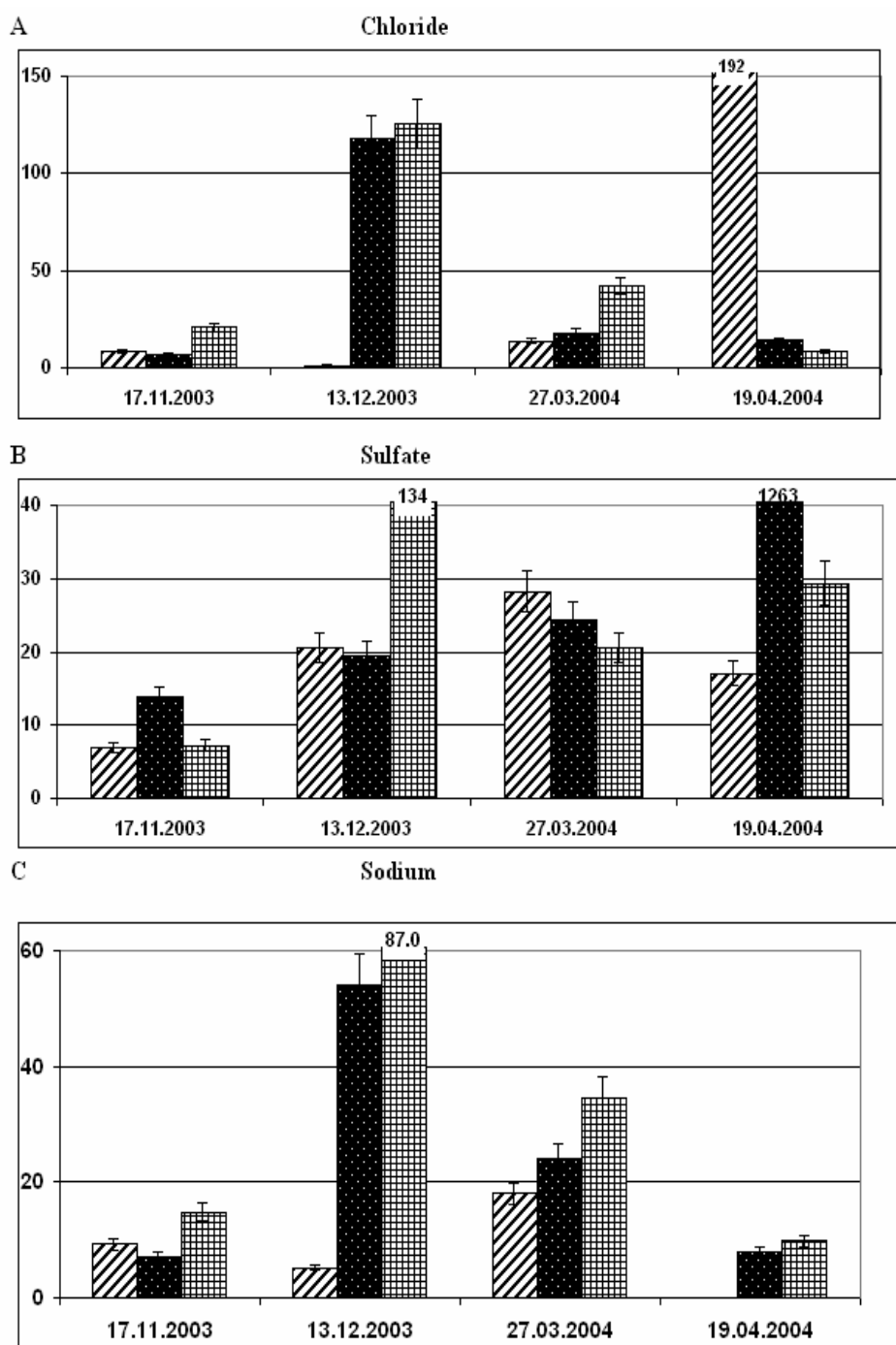


Fig. 2. Anions and cations concentrations [ $\text{mg}/\text{dm}^3$ ] in road runoff waters in different sites in Gdansk

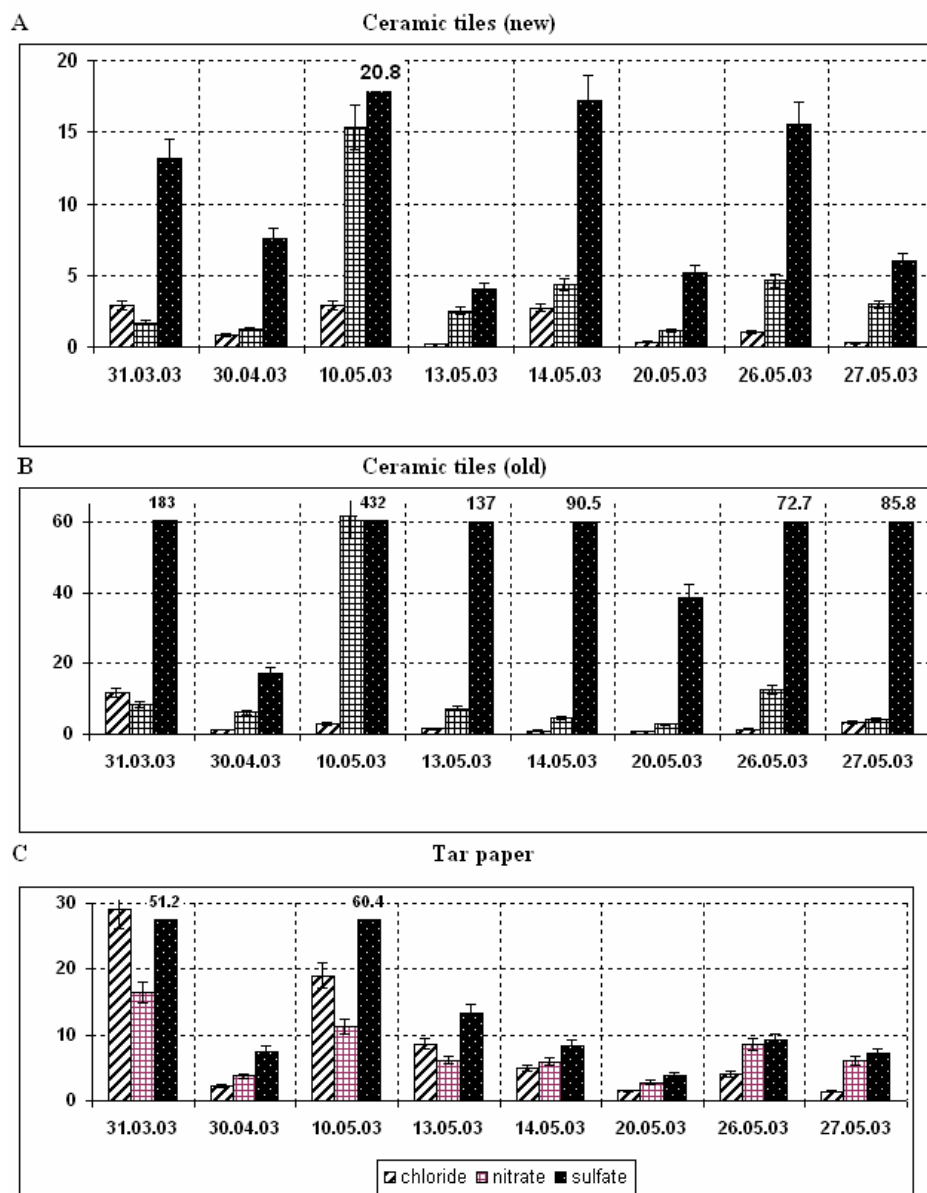


Fig. 3. Anions concentrations [ $\text{mg}/\text{dm}^3$ ] in roof runoff waters in different sites in Gdansk

### Roof runoff

Major ion ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) concentrations in rainwater and roof runoff were determined in all samples (see Figure 3). For rain, the range of concentrations (in  $\text{mg}/\text{dm}^3$ ) of these three ions were contained in the following intervals:  $\text{Cl}^-$  : 0.25÷30;  $\text{NO}_3^-$  :

1.6÷13;  $\text{SO}_4^{2-}$  : 3.0÷1  $\text{dm}^3$ ; while for roof runoff  $\text{Cl}^-$ : 0.05÷31;  $\text{NO}_3^-$  : 0.92÷62;  $\text{SO}_4^{2-}$  : 0.85÷432. Concentration of  $\text{Cl}^-$  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  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ions in runoff from roofs covered with metal roofing tiles was - in all cases - lower than in rainwater. The highest concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were discovered in runoff from a roof covered with ceramic tiles that were several tens of years old.

## Heavy metals

### *Road runoff*

Among heavy metals, Zn and Pb exhibited the highest concentrations, as expected for typical pollutants associated with vehicular traffic. The highest heavy metal concentrations were found in road runoff water. The main source of lead is fuel. However, it appears that only 5% of the lead is removed by runoff water. The largest fraction may, therefore, disperse in the atmosphere or settle on the soil by the roadside. A relatively high level of Zn could be explained by the existence of metallic guardrails. According to Hewitt and Rashed [2], the main sources of zinc are wear and tear from tires and brakes and from the corrosion of galvanized safety barriers, or from an alternative material. As for Pb and Zn, concentrations increase in winter because of the use of chloride-based deicing salts, which generate supply and corrosion phenomena.

The pollution load in highway runoff depends on the average daily traffic, air quality and rainfall intensity and duration. Traffic volume would seem to be an important factor for predicting runoff quality. Prior to storm events, roadways with ADT (Average Daily Traffic) greater than 30,000 vehicles may produce runoff with two to five times the runoff pollutant levels found in that from rural highways. Simple linear regression analysis was performed to evaluate a direct correlation between ADT and the concentration of highway runoff pollutants. The results of this analysis revealed relatively high R values (ranging from 0.49 to 0.70) for all constituents, which may suggest a direct correlation between ADT and pollutant concentrations. However, most of the studies reported in the literature did not confirm strong correlations. For example, Chui et al. [8] found only a weak correlation, and a study conducted by Driscoll et al. [9] suggested that there is no strong and definitive relationship between differences in traffic density and the pollutant concentrations for a site.

### *Roof runoff*

The range of  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  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,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  were found (see Figure 4). The highest concentration of zinc ( $4900 \mu\text{g}/\text{dm}^3$ ) was noted for runoff from a roof covered with asbestos cement sheets. The highest lead content ( $102 \mu\text{g}/\text{dm}^3$ ) was detected in runoff from a flat roof covered with thermally bonded tar paper. While

the highest concentration of cadmium ( $3.70 \mu\text{g}/\text{dm}^3$ ) was noted for runoff from a roof covered with ceramic tiles (old).  $\text{Cu}^{2+}$  was detected only in runoff samples from roofs covered with tar paper or ceramic tiles. The highest concentration of  $\text{Zn}^{2+}$  was in runoff from a flat roof covered with thermally bonded tar paper. However, the source of this pollutant was not the roofing material.  $\text{Zn}^{2+}$  was washed out of the drain pipe, which was made from zinc-coated sheet metal. The highest mean concentration of  $\text{Pb}^{2+}$  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.

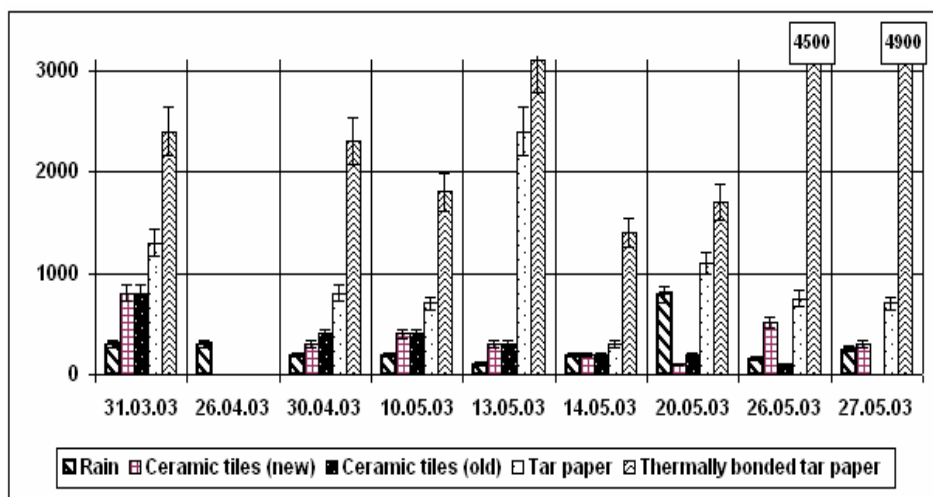


Fig. 4. Zinc concentrations [ $\text{mg}/\text{dm}^3$ ] in roof runoff waters

## Pesticides

### Road runoff

Heptachlor epoxide (metabolite of heptachlor; formed in plants, soil and homeothermic organisms), and *o,p'*-DDE (DDT metabolite) were the most often detected pesticides in the runoff water samples (see Table 3). The highest value for this sum of pesticide was  $1.3 \mu\text{g}/\text{dm}^3$ . Propazine and bromophos, used as selective weed killers, were detected the most often among the pesticides in these groups. The highest value for the sum of the concentrations of organonitrogen and organophosphorus pesticides ( $14 \text{ ng}/\text{dm}^3$ ) was recorded on the same day (October 27) in Gdansk-Oliwa. The concentration of organochlorine pesticides in this sample was also relatively high at  $81 \text{ ng}/\text{dm}^3$ . Elevated pesticide concentrations in runoff waters were also observed for samples collected on October 24. This may have been related to the fact that those were the first precipitation events following a prolonged dry spell. Both sites are characterized by very heavy traffic volume.

Table 3

Pesticides concentrations in roof runoff waters in different sites in Gdańsk [ $\mu\text{g}/\text{dm}^3$ ]

Analyte	Range of concentration	Average concentration
HCH	0.14÷25.9	4.15
Lindane	0.23÷9.04	2.32
Aldrin	0.34÷17.7	3.27
Heptachlor epoxide	0.38÷28.9	8.32
<i>o,p'</i> DDE	0.17÷4.49	1.23
<i>p,p'</i> DDE	0.09÷3.38	1.49
Endrin	0.18÷1.73	0.73
<i>p,p'</i> DDD	0.25÷2.75	1.01
<i>p,p'</i> DDT	0.13÷26.6	3.80
<i>o,p'</i> DDT	0.07÷1.51	0.48
<i>o,p'</i> DDD	0.15÷4.01	1.44
<i>p,p'</i> methoxychlor	0.11÷15.4	2.79
Dichlorovos	1.78÷26.6	9.71
Tertbutyloazine	0.62÷8.05	3.62
Simazine	4.73÷12.5	7.99
Atrazine	0.27÷1.79	0.91
Propazine	0.92÷1.68	1.26
Fenitrothion	0.40÷1.76	1.09
Malathion	1.70÷1.70	1.70
Bromophos	3.04÷46.7	14.0

### Roof runoff

The highest total concentration of the organochlorine pesticides ( $20 \text{ ng}/\text{dm}^3$ ) was found in a sample collected from a roof covered with tar paper in the Gdansk-Przymorze quarter. The sample with the highest concentration of the sum of organonitrogen and organophosphorus pesticides ( $52 \text{ ng}/\text{dm}^3$ ) was collected in the same quarter from a roof covered with metal tiles. Most of the samples contained a few thousand  $\text{ng}/\text{dm}^3$  of organochlorine pesticides, and a few tens to a few hundred  $\text{ng}/\text{dm}^3$  of organonitrogen and organophosphorus pesticides. Precipitation samples collected in the same area between October 2000 and March 2001 contained much lower pesticide levels, ranging from 1 to  $42 \text{ ng}/\text{dm}^3$  for organochlorine pesticides and from 2 to  $14 \text{ ng}/\text{dm}^3$  for organonitrogen and organophosphorus pesticides [10].

Pesticides most often detected in runoff samples included heptachlor epoxide (metabolite of heptachlor, synthesized in plants, soil and warm-blooded organisms), *p,p'*-DDE (DDT metabolite), bromophos, malathion (insecticide/miticide used mostly in agriculture) and terbutylazine (broad-spectrum herbicide used in agriculture and forest management). In the case of precipitation samples collected during the same period, *o,p'*-DDE was detected the most often, followed by *p,p'*-DDE,  $\gamma$ -HCH (lindane; insecticide used mostly in agriculture) and heptachlor epoxide [10].

Table 4 lists the pesticides (and their concentrations) detected the most often for the individual roofing materials studied. The highest concentrations were recorded for heptachlor epoxide (tar paper, galvanized sheet metal, asbestos cement corrugated sheets and bituminous membrane), *p,p'*-DDT (asbestos cement corrugated sheets), *o,p'*-DDD (asbestos cement corrugated sheets), *p,p'*-DDD (ceramic roofing tiles), *o,p'*-DDE (asbestos cement corrugated sheets, ceramic roofing tiles), aldrin (tar paper, galvanized sheet

metal), bromophos (metal and ceramic roofing tiles) and atrazine (metal roofing tiles, asbestos cement corrugated sheets). Pesticides were found the most often in runoff from asbestos cement corrugated sheets, ceramic tiles and metal roofing tiles.

Table 4

Pesticides (and their concentrations) detected the most often for the individual roofing materials studied

Roofing material	Analyte (concentration [ng/dm <sup>3</sup> ])
<b>Tar paper</b>	aldrine (6.020), methoxychlor (430), heptachlor epoxide (19.970), <i>p,p'</i> - DDD (520), <i>o,p'</i> -DDE (540), <i>o,p'</i> - DDD (340), <i>p,p'</i> - DDE (450), <i>o,p'</i> - DDT (190), <i>p,p'</i> -DDT (370), $\alpha$ -HCH (200), $\gamma$ -HCH (400), propazine (1.070), terbutylazine (120)
<b>Ceramic roofing tiles</b>	aldrine (130), methoxychlor (430), heptachlor epoxide (430), <i>p,p'</i> - DDD (4.610), <i>o,p'</i> - DDE (2.800), <i>o,p'</i> - DDD (1.210), <i>p,p'</i> - DDE (1.360), <i>p,p'</i> - DDT (1.080), $\alpha$ -HCH (740), $\gamma$ -HCH (600), propazine (1.110), terbutylazine (120), bromophos (2,720)
<b>Asbestos cement corrugated sheets</b>	aldrine (610), methoxychlor (130), heptachlor epoxide (14.540), <i>p,p'</i> - DDD (500), <i>o,p'</i> - DDE (4.640), <i>o,p'</i> - DDD (7.040), <i>p,p'</i> - DDE (1.040), <i>o,p'</i> - DDT (750), <i>p,p'</i> - DDT (8.460), $\alpha$ -HCH (460), $\gamma$ -HCH (840), atrazine (1.210), terbutylazine (130), bromophos (310)
<b>Metal roofing tiles</b>	Heptachlor epoxide (1.640), <i>o,p'</i> - DDE (920), <i>o,p'</i> - DDD (1,890), <i>p,p'</i> - DDE (680), <i>o,p'</i> - DDT (490), <i>p,p'</i> - DDT (830), $\alpha$ -HCH (320), $\gamma$ -HCH (500), propazine (400), bromophos (4.912), atrazine (2.980), simazine (620), malathion (1.960), fenitrothion (630), chlorfenvinfos (180)
<b>Painted galvanized steel</b>	aldrine (6.020), methoxychlor (430), heptachlor epoxide (19.970), <i>p,p'</i> - DDD (520), <i>o,p'</i> - DDE (540), <i>o,p'</i> - DDD (340), <i>p,p'</i> - DDE (450), <i>o,p'</i> - DDT (190), <i>p,p'</i> - DDT (370), $\alpha$ -HCH (200), $\gamma$ -HCH (400), propazine (1.070), terbutylazine (120)
<b>Bituminous membrane</b>	heptachlor epoxide (1.680), bromophos (50)
<b>PTFE</b>	bromophos (40)

## Conclusions

### Road runoff

The analytes determined in road runoff can originate from many different sources, including road deposition (*eg* from tire wear, break wear, fluid leaks), atmospheric deposition (transport of particulates and gaseous pollutants), road wear (cracks and potholes in asphalt and concrete pavements), road maintenance practices (use of de-icers or pesticides) and accidental spills. Overall, road runoff carries with it a substantial load of toxic substances and can be potentially dangerous to the environment. Consequently, it is our opinion that the quality of road runoff should be monitored, especially in large urban agglomerations with heavy traffic.

### Roof runoff

Roofs can be a source of water pollution. However, results of roof runoff studies have been variable. The variation reflects differences in roofing materials, industrial treatments, care and maintenance, age, climatic conditions, orientation and slope of

roofs, and air quality of the region. The deposition of various pollutants from the atmosphere into roof surfaces during a dry period greatly influences the runoff water quality from roof catchment systems. The amount of the pollutants deposited on the roof surfaces increases with the age of the roofing material, the increase in the length of the dry period between rainfall events, and ambient temperature, as evidenced by the increase in pollutant concentrations in the water samples collected.

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## WODY SPŁYWNE Z ARTERII KOMUNIKACYJNYCH I DACHÓW BUDYNKÓW JAKO ŹRÓDŁO ZANIECZYSZCZENIA W DUŻYCH AGLOMERACJACH MIEJSKICH (GDAŃSK, POLSKA)

**Streszczenie:** Wody spływne są bardzo ważnym medium, transportującym zanieczyszczenia atmosferyczne z powietrza do gleby i wody powierzchniowej. Przedstawiono wyniki dotyczące analizy próbek opadów atmosferycznych oraz wód spływnych z arterii komunikacyjnych i dachów budynków. Wykonano oznaczenia na zawartość anionów, kationów, metali ciężkich i pestycydów. Próbki były pobierane podczas wystąpienia opadu w różnych miejscach na terenie miasta Gdańska. W analizowanych próbkach wykryto i oznaczono pestycydy (*o,p'*-DDE - metabolit DDT), siarczany (we wszystkich) i bardzo duże stężenia jonów sodowych i chlorkowych. Badania potwierdziły, że oba spływy z arterii komunikacyjnych i dachów budynków są bardzo zanieczyszczone i stężenia zanieczyszczeń w nich zawartych powinny być monitorowane.

**Słowa kluczowe:** opady atmosferyczne, wody spływne z arterii komunikacyjnych i dachów budynków, pestycydy, metale ciężkie, wybrane aniony, tereny miejskie