

Levels of Pollutants in Runoff Water from Roads with High Traffic Intensity in the City of Gdańsk, Poland

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Abstract

Analyses of samples of runoff waters collected from the principal arterial roads in the city of Gdansk at sites characterised by heavy traffic are described in this study. Collection of the samples was carried out over a six month period, during rain events or directly after such events. Concentrations of the following analytes were determined: nitro-, chloro-, and phosphoroorganic pesticides, volatile halogenoorganic compounds, petroleum hydrocarbons, as well as cations (Na^+ , K^+ , NH_4^+ , Ca^{2+}) and anions (F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-}). Additionally, total parameters such as toxicity and pH were also measured. The results permitted us to correlate the presence and concentration of the individual analytes with the pollution sources and evaluating the influence of the local emission sources on the degree of pollution in the area covered by this study. The analyses performed have confirmed the high pollution level in the runoff waters (from the arterial roads) and a necessity to establish a system of continuous monitoring of the concentration levels of toxic chemical compounds present in these waters. A correlation was also found between the toxicity and concentration levels of the aforementioned groups of analytes.

Keywords: atmospheric deposition, runoff waters, toxic substances, correlations

Introduction

The ecological balance has been significantly shifted due to the rapid developments of the contemporary technological civilisation accompanied by a general chemicalization of life. This process has become particularly intense during the second half of the twentieth century. Problems related to pollution are global, with only minor local differences. Emission of hazardous substances into the atmosphere, lithosphere and hydrosphere endangers all the inhabitants of our planet. Among the three elements of the environment, the atmosphere plays the most important role in the ecosystem of the Earth. It constitutes the major path for pollution transport to waters, soils and living organisms, and facilitates

long-range spreading of the toxic substances. Condensation of water, formation of clouds and subsequent precipitation in the form of rain, snow, hail or fog all occur in the atmosphere. Therefore, chemical composition of precipitation depends on the purity of the atmosphere, and on the airborne pollutants of both natural and industrial origin. Their composition is also influenced by such factors as precipitation intensity, cloud altitude, and type (rain, snow, hail, etc.). In the process of recirculation of water in nature, all the airborne pollutants are returned to Earth's surface, where they contribute to the worsening of the quality of water and changes in the chemical composition of soils.

One of the possible forms in which precipitation reaches the ground environment are runoff waters. They are formed when rain or melting snow flushes such surfaces like roofs, roads, and agricultural areas. Both direct precipitation and the runoff finally reach the surface and

subterranean waters which are used as the principal sources of drinking water.

The "Tricity" (a conurbation of three big cities: Gdansk, Gdynia and Sopot), as an industrial agglomeration is characterised by a large number of local emitters, among them heat and power generating plants, an oil refinery, ports, shipyards, and a phosphate fertiliser factory. The continually growing road traffic and the existing system of heating houses, partially based on the utilisation of coal stoves, also contribute to the overall pollution of the Gdansk region. Traffic and road transportation in general are responsible for manufacturing and subsequently introducing into the environment a huge number of toxic substances, including tar and oil products, dioxines, oxygen compounds, halogenofenols, metals and even salts used for de-icing roads in winter [1].

Road Transportation as a Potential Factor in the Pollution of Runoff Waters from the Arterial Roads

A dynamic increase in the number of motor vehicles creates new problems in the field of environmental protection. Road transportation becomes serious trouble, particularly in the densely populated areas, where natural exchange of air is restricted by a compact settlement. Traffic is closely related to the manufacture of thousands of potentially toxic substances which badly influence the human organism, leading to illnesses and mutagenic changes.

Compounds of low molecular weight are present in the air in a dispersed form, while those of high molecular weight form the suspended matter and dust, subsequently deposited in the areas along the roads. The presence and concentration of the toxic components in car exhaust gases depends on many factors including construction and tuning of the engines, types of fuels and lube oils used, as well as use and technical condition.

The compounds present in the runoff from the arterial roads originate not only from the process of burning

gas and Diesel oil, but also as a result of the usual wear and tear of car parts. Lube oils and fuels are responsible for hydrocarbon emissions. Incomplete combustion of fuels introduces to the environment such compounds as CO, NO₂, ketones, aldehydes and polycyclic aromatic hydrocarbons (PAHs), consumption of the oil in the crankcase contributes to the emission of aromatic hydrocarbons (fluoranthene, pyrene, fenanthrene and naphthalene). Composition of the exhaust gases depends on the type and use of the engine. CO and hydrocarbon emissions maxima are usually observed during braking and idle run, while nitrogen oxides are chiefly produced during cruise and acceleration periods. In addition to the petroleum hydrocarbons, traffic pollutes the environment with heavy metals. Consumption of tires is a source of zinc and cadmium, while use of brake shoes creates lead, chromium, cadmium and magnesium. Engines and oil leaks brings about such metals as aluminium, cobalt, nickel and chromium, and consumption of wheels creates iron, aluminium, chromium, and zinc [1]. Other hazardous pollutants produced by motor vehicles are dusts, asbestos dust originating from the brake lining and dust from the abrasion of tires and asphalt pavements. During the winter season, due to the danger of icing, pavements are treated with a salt-sand mixture, which results in introducing to the environment huge amounts of chloride ions, sodium and magnesium, as well as trace amounts of cobalt and chromium [1].

Recent contributions on the negative environmental impact of lead-free gasoline conclude that it may be even worse than that of leaded gasoline (ethyl gasoline). The reason for such conclusions may lay in a fact that both types of gasoline, while containing similar amounts of aromatic compounds, differ significantly in their octane numbers. Chemical composition of both types of gasoline is shown in Table 1.

The octane number of ethyl gasoline is usually higher; therefore, to raise the octane number of the lead-free gasoline, several substitutes of lead tetraethyl are used in refineries, such as:

Table 1. Chemical composition of gasoline, differences between the lead-free and ethyl gasoline [2].

Country	Type of gasoline	Octane number	Lead contents [g/l]	Saturated compounds [%]	Olefins [%]	Aromatic compounds [%]	Oxidants [%]	Benzene [%]
United Kingdom	lead-free	98.3	–	52.4	7.3	38.4	2.1	2.5
	ethyl	97.7	0.126	59.7	13.8	25.7	0.7	1.7
Scandinavian countries	lead-free	96.0	–	55.8	7.3	36.9	4.6	2.7
	ethyl	99.3	0.06	53.5	4.4	42.2	6.5	2.9
Central Europe	lead-free	95.4	–	55.4	6.9	37.7	4.4	1.8
	ethyl	96.9	0.13	60.4	6.8	32.8	2.8	1.6
Germany	lead-free	96.5	–	55.8	7.3	36.9	4.6	2.7
	ethyl	99.2	0.13	54.2	5.8	40.0	2.3	2.3
France	lead-free	98.7	–	50.1	6.5	43.4	2.7	2.6
	ethyl	97.8	0.14	50.5	17.0	32.5	0.7	1.7

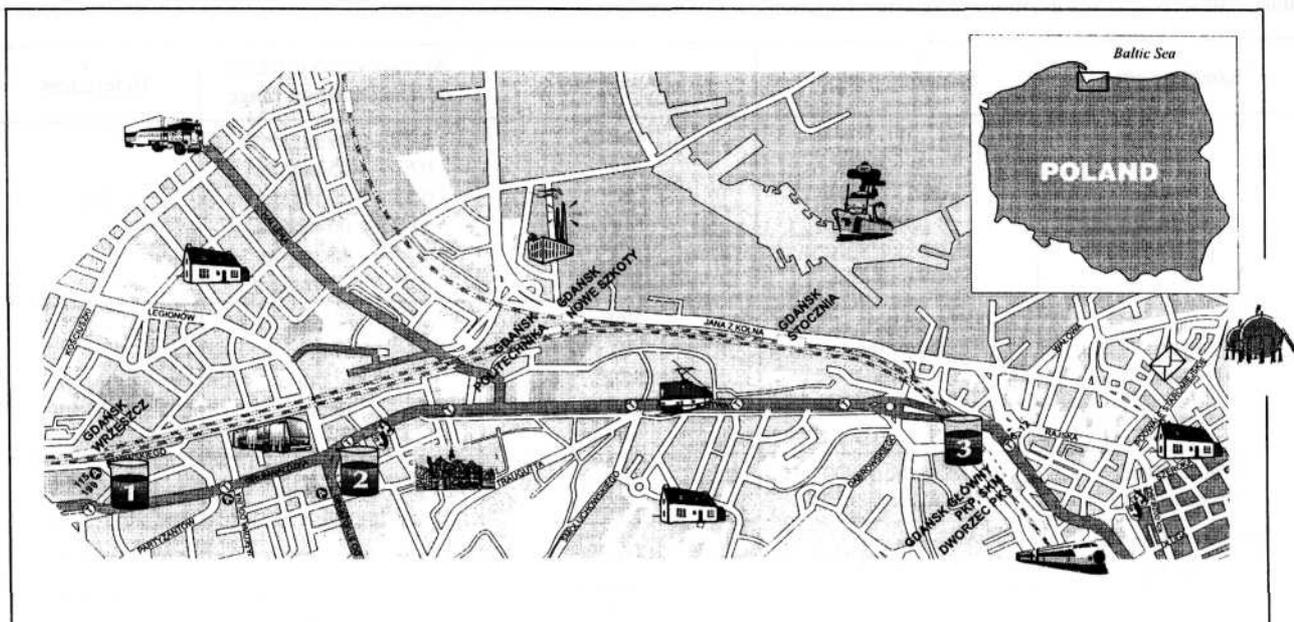


Fig. 1. Locations of road runoff sampling sites in Gdansk.

- aromatic compounds, chiefly the cheap but carcinogenic benzene;
- olefins, combustion of which yields butadiene-1,3, also carcinogenic, as one of its byproducts;
- oxidants - mainly MTBE (methyl,t-butylether) - studies on the influence of this compound on a human organism are currently being performed [2].

Hence, the removal of lead from gasoline has led to its substitution by toxic compounds, dangerous both for the environment and human health. Additional information on the subject is provided by recently published studies, proving the lack of correlation between lead contents in the gasoline and the lead level in the blood. These studies confirm the suppositions that lead from the exhaust gases is poorly bioactive, and that the principal source of this toxic metal found in the blood are lead plumbing, lead-containing solder used in food cans, and, first of all, lead-containing paints [2].

The aforementioned examples illustrate the potential danger to the Earth's ecosystem created by the motorization of society. Pollutants originating from road transportation reach the atmosphere and, subsequently, undergo dry or wet deposition and influence the quality of waters and soils. Runoff from the arterial roads is actually a complex mixture of toxic chemical compounds, which frequently, particularly in Poland, reaches the surface and subterranean waters. The problem is even more significant when the runoff is directed to streams and small rivers, where it can cause damage to the flora and fauna of the aquatic ecosystem, sometimes leading to the complete decline of all forms of life. There are numerous studies proving that the majority of compounds present in road runoff is adsorbed on solid particles, hence, the process of their accumulation in the bottom sediments may be noticed. This is particularly true in the case of metals and PAHs [1]. Table 2 shows the results of deter-

minations of selected pollutants in runoff waters from different geographical regions [1, 3-10].

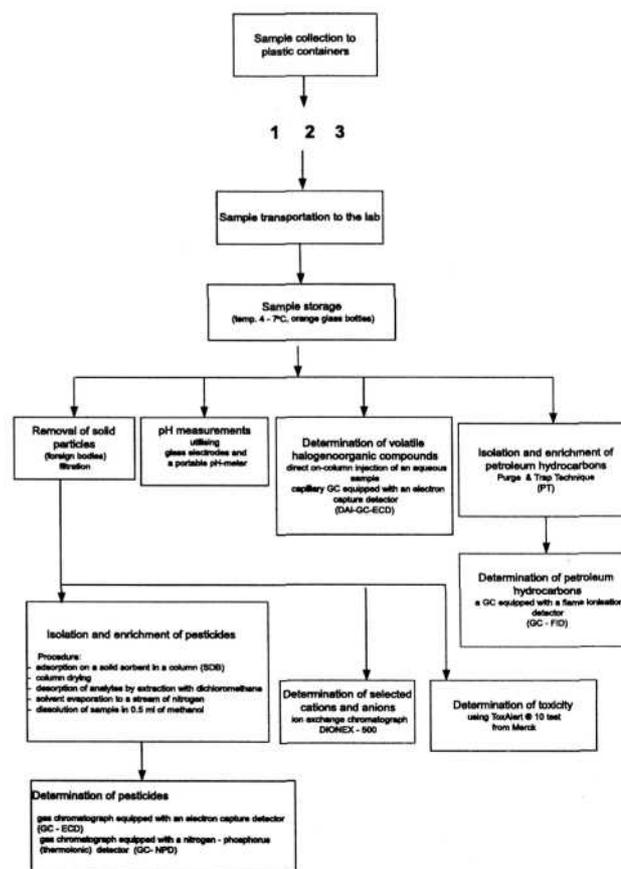


Fig. 2. Schematic diagram of the analytical procedure applied in analyzing the collected road runoff samples.

Table 2. Results of determinations of selected pollutants in runoff waters in different geographical regions.

Sampling site	Sampling period	Analytes	Average concentration or concentration range	References
Urungi (China)	April – May 1991	Ca ²⁺ Na ⁺ K ⁺ Mg ²⁺ Cl ⁻ SO ₄ ²⁻	8.77 – 9.99 mg/dm ³ 0.62 – 1.05 mg/dm ³ 0.13 – 0.20 mg/dm ³ 1.03 – 1.06 mg/dm ³ 0.54 – 1.43 mg/dm ³ 3.37 – 9.79 mg/dm	[3]
Lyon (France)	8 months. 1996	NO ₃ ⁻ Cl ⁻ SO ₄ ²⁻ Pb ²⁺ pH	5.9 mg/dm ³ 23 mg/dm ³ 23 mg/dm ³ 1.1 µg/dm ³ 7.51	[4]
Ergolz. Basel (Switzerland)	December 1993 – April 1994	Pb ²⁺	0.1 – 47 µg/dm ³	[5]
Wichita. Kansas (USA)	November 1997 – November 1998	simazine	0 – 16 µg/dm ³	[6]
Sites along M1 highway (United Kingdom)	October 1990 – July 1991	pH PO ₄ ³⁻ SO ₄ ²⁻ NO ₃ ⁻ Cl ⁻ Mg ²⁺ Ca ²⁺ Pb ²⁺ Aromatic hydrocarbons	7.21 – 8.19 0.16 – 1.47 mg/dm ³ 60.4 – 247.9 mg/dm ³ 20.5 – 66.6 mg/dm ³ 65.1 – 229.1 mg/dm ³ 55.8 – 60.4 mg/dm ³ 131 – 175.5 mg/dm ³ 30 – 42.1 µg/dm ³ 30 – 70 µg/dm ³	[1]
Minneapolis. Minnesota (USA)	Full year	NO ₃ ⁻ + NO ₂ ⁻ Cl ⁻ SO ₄ ²⁻ Na ⁺ PO ₄ ³⁻ pH Pb ²⁺	0.08 – 5 mg/dm ³ 0.96 – 46000 mg/dm ³ 5 – 650 mg/dm ³ 2.23 – 6700 mg/dm ³ 0.16 – 21.9 mg/dm ³ 6.9 – 9.3 11 – 2100 µg/dm ³	[7]
Cumbria (United Kingdom)	Full year 1986	Pb ²⁺ organic Pb	8.0 – 46.5 µg/dm ³ 0.037 – 1.30 µg/dm ³	[8]
Madrid (Spain)	Full year	n-alkanes total aliphatic hydrocarbons total aromatic hydrocarbons	24.8 – 167 µg/dm ³ 412 – 2179 µg/dm ³ 15.1 – 35.5 µg/dm ³	[9]
Aalborg (Denmark)		total N total P Pb ²⁺	1-2 mg/dm ³ 0.2 – 0.5 mg/dm ³ 50 – 150 µg/dm ³	[10]

Experimental

Sampling

Samples of the road runoff were collected at three sites located at the principal arterial roads in Gdansk:

- Site #1 - intersection of Klonowa and Lendziona streets (near the Gdarisk-Wrzeszcz railway station), DW;
- Site #2 - intersection of the Grunwaldzka and Do Studzienki streets (near the Jantar shopping mall), W;
- Site #3 - at the Podwale Grodzkie street (near the Gdansk - Main railway station), DG.

The exact locations of the sampling sites is shown in Figure 1.

Road runoff was collected during or immediately after rain events. Primary samplers were plastic containers from which samples were dispensed to glass bottles (orange glass) prior to their transport to the laboratory, where they were stored at low temperature (4–7°C) in a dark room. No conservants were added, therefore all the analyses were performed within 24 hrs after the sampling, and those of the volatile compounds no later than 2 hrs after collection.

Table 3. Parameters of chromatographic determination of pesticides, volatile halogenoorganic compounds, petroleum hydrocarbons, cations and anions in the collected samples of road runoff waters.

	Chloroorganic pesticides	Nitro- and phosphoroorganic pesticides	Volatile halogenoorganic compounds	Petroleum hydrocarbons	Analysis of cations	Analysis of anions
Chromatograph type and model	GC 6180 VEGA Carlo Erba – Fisons	GC 8000 Fisons	GC 6180 VEGA Carlo Erba – Fisons	GC Hewlett Packard 6890	DIONEX – 500	DIONEX – 500
Detector	ECD	NPD	ECD	FID	conductometric	conductometric
Suppressor	-	-	-	-	autosuppressor DX 500 CSRS® – ULTRA	autosuppressor ASRS ASRS – II™
Detector temperature	350°C	270°C	350°C	280°C		
Column (length x ID x stationary phase film thickness)	30 m x 0.32 mm. AT-5 x 0.25 µm	30 m x 0.25 mm. DB-5 x 0.25 µm	30 m x 0.32, DB-1 x 5 µm. precolumn 2 m x 0.32 mm	30 m x 0.32 mm. DB-1 x 5 µm	IonPac® CS12A	IonPac®AS14
Dosage system	direct (cold on-column)	(splitless)	direct (cold on-column)	direct PT	dosing loop	dosing loop
Carrier gas/effluent (flow rate)	hydrogen	hydrogen	hydrogen	helium	20 mM sulphuric acid. 0.25 cm ³ /min	3.5 mM Na ₂ CO ₃ /1.0 mM NaHCO ₃ , 0.23 cm ³ /min.
Temperature program	60°C → 30°C/min. → 180°C → 10°C/min → 280°C (10 min)	60°C → 30°C/min. → 180°C → 10°C/min → 280°C (5 min)	isothermal 104°C	40°C (1 min.) → 15°C/min → 120°C → 1°C/min. → 220°C (3 min.)	-	-
Injection temperature	60°C	100°C	below 100°C	-	ambient	ambient
Sample volume injected	2 µl	2 µl	2 µl	-	2.5 µl	2.5 µl
Purging gas (flow rate)	-	-	-	nitrogen (38 cm ³ /min. – 10 min.)	-	-
Sorption trap (sorbent)	-	-	-	TENAX TA. Carbotrap	-	-
Desorption temperature	-	-	-	250°C	-	-
Desorption time	-	-	-	5 min.	-	-

Analytical Methods

Due to the high contents of solid particles (sand, dust, etc.) in the road runoff samples, the inclusion of a filtration stage prior to analysis was necessary. Figure 2 presents a schematic diagram of the analytical procedure for such samples [11-13], while Table 3 shows the detailed parameters of chromatographic determination of pesticides, volatile halogenoorganic compounds, petroleum hydrocarbons, as well as the selected cations and anions in the runoff samples. Toxicity bioassays were performed using the ToxAlert 10 system (Merck) which includes freeze-dried bioluminescent bacteria *Vibrio fischeri* [13]. The osmolality of all samples was adjusted to 2 NaCl for optimal reagent performance. The change in bioluminescence was measured after 15 minutes and expressed as a percentage of inhibition. Sample inhibition over 20% will be considered toxic. In Table 4, the limits of determination of the analytical methods employed for the purpose of this study are listed.

Results and Discussion

Road Runoff

Table 5 lists the physico-chemical characteristics and total analyte concentrations in samples of runoff waters from the chosen sampling sites. Table 6 lists the frequency of occurrence, mean concentrations and concentration ranges for the particular groups of analytes.

The character of the salinity and acidity of the studied samples was determined on the basis of definition proposed by J. Baron and A. S. Denning [15]. Table 7 presents the sums of concentrations of the cations: Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , as well as the concentration of H^+ ions, constituting the base for conclusions regarding their salinity and acidity.

All of the analysed samples have been classified as highly saline and weakly acidic. According to the aforementioned authors, in a case when:

$(\text{Na}^+ + \text{K}^+ + \text{NH}_4^+ + \text{Mg}^{2+} + \text{Ca}^{2+}) < 50 \mu\text{eq}/\text{dm}^3$; a sample was characterised as a weakly saline one, and when:

$\text{H}^+ < (\text{Na}^+ + \text{K}^+ + \text{NH}_4^+ + \text{Mg}^{2+} + \text{Ca}^{2+})$; a sample was also treated as weakly acidic. In an opposite case, i.e., when:

$(\text{Na}^+ + \text{K}^+ + \text{NH}_4^+ + \text{Mg}^{2+} + \text{Ca}^{2+}) > 50 \mu\text{eq}/\text{dm}^3$; a sample was considered highly saline, and when: $\text{H}^+ > (\text{Na}^+ + \text{K}^+ + \text{NH}_4^+ + \text{Mg}^{2+} + \text{Ca}^{2+})$; a sample was also labelled as highly acidic [15].

Figures 3-5 present correlation plots being a base for determining dependencies between sample toxicity and the concentration of selected groups of analytes. On the basis of the data obtained, the following conclusions may be drawn:

-- there is a linear dependency of the total toxicity parameter on the sum of concentrations of volatile halogenoorganic compounds and the sum of concentrations of petroleum hydrocarbons. Obtained correla-

Table 4. Estimated limits of determination for particular analytes in road runoff samples.

Group of compounds	Analyte	Limit of determination
Chloroorganic pesticides	γ - HCH (lindane)	0.05 ng/dm ³
	α - HCH	0.05 ng/dm ³
	aldrine	0.05 ng/dm ³
	heptachlore epoxide	0.05 ng/dm ³
	o, p' - DDE	0.05 ng/dm ³
	p, p' - DDD	0.05 ng/dm ³
	o, p' - DDD	0.05 ng/dm ³
	p, p' - DDE	0.05 ng/dm ³
	o, p' - DDT	0.05 ng/dm ³
p, p - metoxychlor	0.05 ng/dm ³	
Nitro- and phosphoroorganic pesticides	antrazine	0.05 ng/dm ³
	propazine	0.05 ng/dm ³
	symazine	0.05 ng/dm ³
	bromfos	0.05 ng/dm ³
	malathion	0.05 ng/dm ³
	tertbutylozine	0.05 ng/dm ³
	chlorfenwinfos	0.05 ng/dm ³
fenitrothion	0.05 ng/dm ³	
Volatile halogenoorganic compounds	CCl ₄	0.01 $\mu\text{g}/\text{dm}^3$
	CHCl ₃	0.01 $\mu\text{g}/\text{dm}^3$
	CHBrCl ₂ + C ₂ HCl ₃	0.01 $\mu\text{g}/\text{dm}^3$
	CHBr ₂ Cl	0.01 $\mu\text{g}/\text{dm}^3$
	CHBr ₃	0.02 $\mu\text{g}/\text{dm}^3$
	CH ₂ Cl ₂	0.01 $\mu\text{g}/\text{dm}^3$
C ₂ Cl ₄	0.01 $\mu\text{g}/\text{dm}^3$	
Petroleum hydrocarbons	benzene	0.03 $\mu\text{g}/\text{dm}^3$
	touene	0.03 $\mu\text{g}/\text{dm}^3$
	ethylbenzene	0.03 $\mu\text{g}/\text{dm}^3$
	p, m - xylene	0.03 $\mu\text{g}/\text{dm}^3$
	o - xylene	0.03 $\mu\text{g}/\text{dm}^3$
	styrene	0.03 $\mu\text{g}/\text{dm}^3$
	cumene	0.03 $\mu\text{g}/\text{dm}^3$
	m - dichlorobenzene	0.03 $\mu\text{g}/\text{dm}^3$
	heptane	0.03 $\mu\text{g}/\text{dm}^3$
	isooctane	0.03 $\mu\text{g}/\text{dm}^3$
	octane	0.03 $\mu\text{g}/\text{dm}^3$
	cyclohexanone	0.03 $\mu\text{g}/\text{dm}^3$
	decane	0.03 $\mu\text{g}/\text{dm}^3$
dodecane	0.03 $\mu\text{g}/\text{dm}^3$	
Cations	Na ⁺	0.01 mg/dm ³
	NH ₄ ⁺	0.01 mg/dm ³
	K ⁺	0.01 mg/dm ³
	Mg ²⁺	0.01 mg/dm ³
	Ca ²⁺	0.01 mg/dm ³
Anions	F ⁻	0.01 mg/dm ³
	Cl ⁻	0.01 mg/dm ³
	NO ₂ ⁻	0.01 mg/dm ³
	NO ₃ ⁻	0.01 mg/dm ³
	PO ₄ ³⁻	0.01 mg/dm ³
	SO ₄ ²⁻	0.01 mg/dm ³

tion coefficients R were equal to 0.58 and 0.69, respectively;

- there is no correlation (R=0.27) between the sum of the chloroorganic pesticides and the total toxicity parameter;

Table 5. Summary of the determined physico-chemical parameters and total concentrations of analytes in the runoff samples from the surfaces of arterial roads.

Sampling date	pH	Toxicity [%]	Total concentration of volatile halogenoorganic compounds [$\mu\text{g}/\text{dm}^3$]	Total concentration of petroleum hydrocarbons [$\mu\text{g}/\text{dm}^3$]	Total concentration of nitro- and phospho-organic pesticides [ng/dm^3]	Total concentration of chloroorganic pesticides [ng/dm^3]	Total concentration of cations [meq/dm^3]	Total concentration of anions [meq/dm^3]	Total concentration of heavy metals [$\mu\text{eq}/\text{dm}^3$]	Total concentration of lead [$\mu\text{eq}/\text{dm}^3$]
The Lendziona St. – Klonowa St. Intersection (DW)										
26.10.99	7.91	29	1.99	16.66	3.39	4.74	1.21	0.01	2.45	0.02
28.10.99	7.59	33	2.33	18.83	7.26	2.85	1.96	0.36	3.84	0.04
15.11.99	6.59	10	5.78	31.76	2.07	3.75	2.45	1.72	12.75	0.01
19.11.99	6.95	10	0.96	ld	4.09	8.19	3.76	2.99	64.90	0.01
25.11.99	7.75	19	0.08	ld	2.73	0.12	0.54	0.13	ld	ld
2.12.99	8.17	68	0.47	ld	3.39	4.57	0.39	0.22	ld	ld
8.12.99	8.13	44	nd	ld	0.39	0.40	0.35	0.13	4.47	0.02
15.12.99	7.31	23	0.30	ld	2.00	2.10	1.36	0.57	9.51	0.03
16.12.99	7.71	22	0.13	ld	2.39	0.08	0.56	0.19	3.48	0.02
7.01.00	7.98	84	ld	ld	2.49	22.96	17.07	25.18	7.70	0.04
27.01.00	7.06	14	ld	ld	3.56	14.47	24.71	40.05	9.58	0.19
28.01.00	6.94	16	ld	ld	3.07	22.76	1.41	0.83	5.18	0.03
31.01.00	7.01	37	ld	79.91	0.97	1.52	1.63	0.83	ld	ld
15.03.00	7.6	15	ld	35.35	6.02	nd	5.64	39.30	ld	ld
31.03.00	8.02	16	ld	ld	4.02	1.78	1.85	0.90	ld	ld
The Grunwaldzka St. – Studzienki St. Intersection (W)										
26.10.99	7.76	50	0.17	20.76	3.16	1.96	1.85	0.32	5.00	0.03
28.10.99	7.57	77	1.61	29.94	3.03	5.94	3.77	1.48	5.01	0.02
15.11.99	6.8	16	16.78	53.74	1.02	0.33	1.32	0.93	3.09	0.04
19.11.99	6.83	41	0.62	ld	1.78	5.87	2.30	0.28	3.20	0.08
25.11.99	7.41	28	0.01	ld	2.97	3.29	9.69	12.66	ld	ld
2.12.99	7.40	63	0.12	ld	3.90	4.01	0.88	0.41	ld	ld
8.12.99	7.63	41	nd	ld	nd	3.93	0.85	0.38	6.35	0.06
15.12.99	7.42	30	0.04	ld	1.73	6.11	3.65	5.22	5.93	0.11

Cont. Table 5.

Sampling date	pH	Toxicity [%]	Total concentration of volatile halogeno-organic compounds [$\mu\text{g}/\text{dm}^3$]	Total concentration of petroleum hydrocarbons [$\mu\text{g}/\text{dm}^3$]	Total concentration of nitro- and phosphoro-organic pesticides [ng/dm^3]	Total concentration of chloroorganic pesticides [ng/dm^3]	Total concentration of cations [meq/dm^3]	Total concentration of anions [meq/dm^3]	Total concentration of heavy metals [14] [$\mu\text{eq}/\text{dm}^3$]	Total concentration of lead [14] [$\mu\text{eq}/\text{dm}^3$]
16.12.99	7.47	24	0.56	ld	4.21	3.85	7.80	1.17	3.32	0.05
7.01.00	7.4	82	ld	ld	3.46	9.10	16.43	19.39	4.88	0.09
27.01.00	7.08	12	ld	ld	19.32	4.38	3.20	18.12	6.44	0.05
28.01.00	7.12	92	ld	ld	1.65	3.87	2.15	1.28	6.72	0.05
31.01.00	7.19	72	ld	22.16	3.97	1.28	1.37	0.82	6.15	0.04
15.03.00	9.06	14	ld	21.31	1.38	8.62	3.88	5.72	ld	ld
31.03.00	7.19	27	ld	ld	0.06	3.06	0.67	14.67	ld	ld
Podwale Grodzkie Street (DG)										
26.10.99	8.01	59	5.17	41.42	6.95	0.04	1.98	0.48	2.62	0.04
15.11.99	7.17	24	9.44	10.03	12.82	23.89	2.01	2.07	4.09	0.08
19.11.99	6.38	16	1.76	ld	2.17	15.32	26.24	35.48	18.18	0.03
25.11.99	7.6	19	0.12	ld	0.56	0.11	6.94	7.56	ld	ld
2.12.99	8.13	46	1.60	ld	2.34	2.41	1.20	0.25	ld	ld
8.12.99	8.18	54	0.03	ld	4.86	0.78	0.50	0.43	3.24	0.03
15.12.99	7.61	37	0.13	ld	3.54	8.74	2.44	1.92	10.81	0.04
16.12.99	7.45	29	0.47	ld	1.81	3.74	2.05	1.20	4.69	0.24
7.01.00	7.83	73	ld	ld	1.16	16.88	29.22	41.32	7.77	0.56
27.01.00	6.96	51	ld	ld	6.06	11.34	3.68	1.82	7.45	0.13
28.01.00	7.15	67	ld	ld	3.46	9.33	5.58	5.26	6.09	0.14
31.01.00	6.95	74	ld	ld	5.35	2.16	2.83	0.99	6.81	0.10
15.03.00	7.55	26	ld	ld	4.84	0.64	10.67	16.91	ld	ld
31.03.00	7.62	19	ld	ld	16.00	2.45	23.47	24.12	ld	ld

ld – lack of data
nd – not detected

Table 6. Mean concentrations and concentration ranges of the analytes in samples of runoff waters from highways and roofs of buildings (numbers in brackets indicate the number of samples in which the analyte was detected).

Analyte	Unit	Minimum conc.	Maximum conc.	Mean concentration	Number of samples analyzed
ANIONS					
F ⁻	meq/dm ³	nd	0.39	0.0094	44 (8)
Cl ⁻		0.04	39.76	4.26	44 (44)
NO ₂ ⁻		nd	0.08 (DW in December)	0.004	44 (1)
NO ₃ ²⁻		nd	0.24	0.03	44 (40)
PO ₄ ³⁻		nd	1.66	0.04	44 (7)
SO ₄ ²⁻		0.04	4.18	0.29	44 (44)
CATIONS					
NH ₄ ⁺	meq/dm ³	nd	0.51	0.06	44 (20)
Na ⁺		0.03	25.24	2.32	44 (44)
K ⁺		0.01	2.17	0.12	44 (44)
Mg ²⁺		nd	8.64	0.24	44 (44)
Ca ²⁺		0.05	5.21	0.80	44 (44)
PETROLEUM HYDROCARBONS					
Benzene	µg/dm ³	0.1	7.41 (DW in January)	2.20	22 (22)
Toluene		nd	14.33 (DW in January)	2.52	22 (20)
Ethylbenzene		nd	7.84 (DG in November)	0.61	22 (8)
p.m-Xylene		nd	5.34	0.96	22 (9)
o-Xylene		nd	6.98	0.99	22 (8)
Styrene		nd	1.27	0.18	22 (7)
Kumene		nd	0.538	0.11	5 (1)
m-Dichlorobenzene		nd	0.724	0.15	5(1)
Heptane		nd	nd	–	17 (0)
Isooctane		nd	4.25	0.50	17 (5)
Octane		nd	2.74	0.23	17 (4)
Cyclohexanone		nd	nd	–	17 (0)
Decane		nd	4.11	1.03	17 (12)
Dodecane	nd	4.19	0.50	17 (7)	
VOLATILE HALOGENOORGANIC COMPOUNDS					
CCl ₄	µg/dm ³	nd	9.23 (W in November)	0.71	29 (16)
CHCl ₃		nd	5.87 (W in November)	0.58	29 (27)
CHBrCl ₂ + C ₂ HCl ₃		nd	1.68	0.5	29 (10)
CHBr ₂ Cl		nd	nd	–	29 (0)
CHBr ₃		nd	nd	–	29 (0)
CH ₂ Cl ₂		nd	0.01	0.001	29 (2)
C ₂ Cl ₄		nd	0.01	0.001	29 (4)

Cont. Table 6.

Analyte	Unit	Minimum conc.	Maximum conc.	Mean concentration	Number of samples analyzed
CHLOROORGANIC PESTICIDES					
γ - HCH (lindane)	ng/dm ³	nd	1.86	0.54	44 (27)
α - HCH		nd	2.22	0.35	44 (18)
Aldrine		nd	1.02	0.34	44 (33)
Heptachlor epoxide		nd	2.77	0.78	44 (30)
o.p' - DDE		nd	7.06	0.30	44 (7)
p.p' - DDD		nd	1.86	0.19	44 (11)
o.p' - DDD		nd	1.12	0.13	44 (8)
p.p' - DDE		nd	1.17	0.11	44 (10)
o.p' - DDT		nd	1.84	0.09	44 (6)
p.p' - DDT		nd	7.04	0.35	44 (9)
p.p - methoxychlor		nd	6.38	0.25	44 (8)
NITRO- AND PHOSPHOROORGANIC PESTICIDES					
Atrazine	ng/dm ³	nd	24.68 (W in January)	1.36	44 (25)
Propazine		nd	22.32 (W in January)	2.90	44 (18)
Simazine		nd	11.31	1.26	44 (25)
Bromfos		nd	4.63	0.29	44 (20)
Malathion		nd	24.68 (DG in March)	0.83	44 (35)
Tertbutylazine		nd	7.64	0.43	44 (13)
Chlorfenvinfos		nd	1.09	0.09	44 (11)
Fenitrothion		nd	2.20	0.11	44 (16)
TOXICITY		%	5	92 (W in January)	36.47
pH	-	6.38 (DG in November)	9.06 (W in March)	7.26	44 (44)

nd - not detected

- correlation exists ($R=0.55$) between the sum of concentrations of the nitroorganic and phosphoroorganic pesticides in the toxicity parameter;
- no correlation is observed on toxicity vs. concentration of the cations ($R=0.06$) and toxicity vs. concentration of the anions ($R=0.06$) plots.

Conclusions

The project was carried out for 6 months, between October 1999 and April 2000. In total, 44 samples of road runoff were analysed. Based on the results obtained, the following conclusions can be drawn:

- Benzene was detected in all samples due to its wide spread use as an octane booster and lead substitute in gasoline.

- Very high concentrations of Cl^- , Na^+ and Ca^{2+} were observed in some samples collected in winter are related to the use of the respective salts to fight icing of roads and pavements.
- The presence of NO_3^- and SO_4^{2-} in almost all samples is related to very high intensity of traffic in the Tricity. Burning of fossil fuels results in emissions of nitrogen and sulphur oxides (as well as petroleum hydrocarbons) to the atmosphere. The problem is aggravated by the large number of heavy transport trucks crossing the Tricity in transit, and by the dynamic development of private transportation, unfortunately based mostly on cars without catalytic converters.
- The analysed samples of the runoff were highly saline and, at the same time, weakly acidic. High concentrations of the cations may be associated with a dynamic economic development of the region, *e.g.*, in the con-

Table 7. Summary of the calculated total concentration levels of the cations (Na^+ , K^+ , NH_4^+ , Mg_2^+ , Ca^{2+}) and H^+ ions and conclusions on samples salinity and acidity.

Sampling date	Sampling site	Σ cations concentration [$\mu\text{eq}/\text{dm}^3$]	H^+ ions concentration $\times 10^{-2}$ [$\mu\text{eq}/\text{dm}^3$]	Conclusions
26.10.99	DW (1)	1210	1.23	Highly saline, weakly acidic
	W (2)	1850	1.74	Highly saline, weakly acidic
	DG (3)	1980	0.98	Highly saline, weakly acidic
28.10.99	DW (1)	1960	2.57	Highly saline, weakly acidic
	W (2)	3770	2.69	Highly saline, weakly acidic
15.11.99	DW (1)	2450	25.7	Highly saline, weakly acidic
	W (2)	1320	15.8	Highly saline, weakly acidic
	DG (3)	2010	6.78	Highly saline, weakly acidic
19.11.99	DW (1)	3760	11.2	Highly saline, weakly acidic
	W (2)	2300	14.8	Highly saline, weakly acidic
	DG (3)	26240	41.7	Highly saline, weakly acidic
25.11.99	DW (1)	540	1.78	Highly saline, weakly acidic
	W (2)	9690	3.89	Highly saline, weakly acidic
	DG (3)	6940	2.51	Highly saline, weakly acidic
2.12.99	DW (1)	390	0.68	Highly saline, weakly acidic
	W (2)	880	3.98	Highly saline, weakly acidic
	DG (3)	1200	0.74	Highly saline, weakly acidic
8.12.99	DW (1)	350	0.74	Highly saline, weakly acidic
	W (2)	850	2.34	Highly saline, weakly acidic
	DG (3)	500	0.66	Highly saline, weakly acidic
15.12.99	DW (1)	1360	4.90	Highly saline, weakly acidic
	W (2)	3650	3.39	Highly saline, weakly acidic
	DG (3)	2440	2.45	Highly saline, weakly acidic
16.12.99	DW (1)	560	1.95	Highly saline, weakly acidic
	W (2)	7800	3.8	Highly saline, weakly acidic
	DG (3)	2050	3.55	Highly saline, weakly acidic
7.01.00	DW (1)	17070	1.05	Highly saline, weakly acidic
	W (2)	16430	3.98	Highly saline, weakly acidic
	DG (3)	29220	1.48	Highly saline, weakly acidic
27.01.00	DW (1)	24710	8.71	Highly saline, weakly acidic
	W (2)	3200	8.32	Highly saline, weakly acidic
	DG (3)	3680	11.0	Highly saline, weakly acidic
28.01.00	DW (1)	1410	11.5	Highly saline, weakly acidic
	W (2)	2150	7.95	Highly saline, weakly acidic
	DG (3)	5580	7.08	Highly saline, weakly acidic
31.01.00	DW (1)	1630	9.77	Highly saline, weakly acidic
	W (2)	1370	6.46	Highly saline, weakly acidic
	DG (3)	2830	1.12	Highly saline, weakly acidic

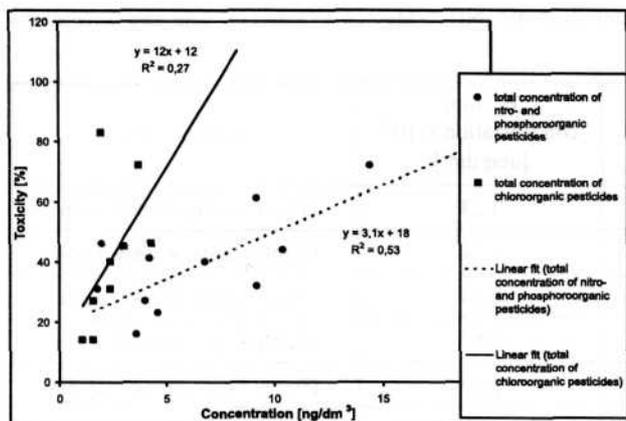


Fig. 3. Dependence of the toxicity on the averaged sums of concentrations of chloroorganic pesticides and on the averaged sums of concentrations of nitro- and phosphoroorganic pesticides.

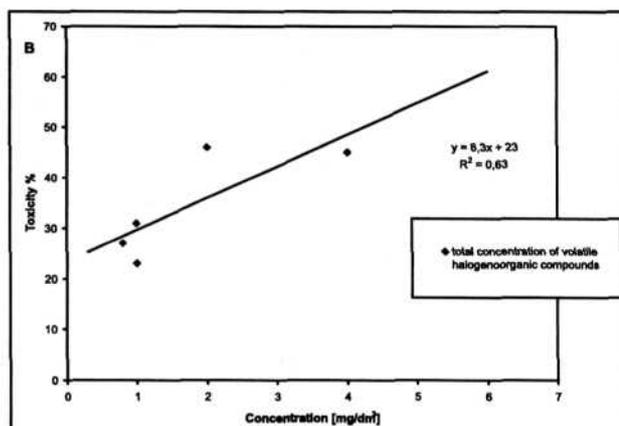
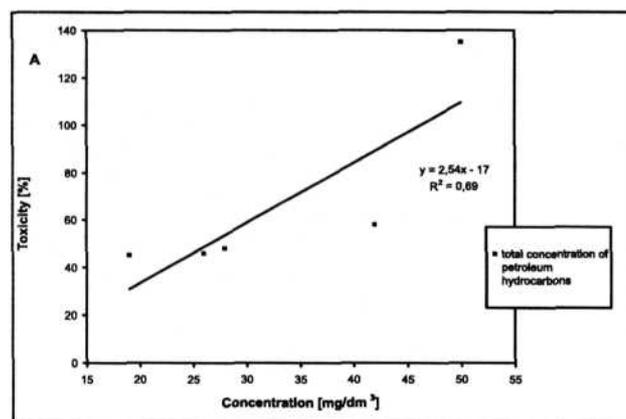


Fig. 4. Dependence of the toxicity on the averaged sums of concentrations of petroleum hydrocarbons and on the averaged sums of concentrations of halogenoorganic compounds.

struction industry, while the dominating neutral and weakly basic pH of the samples may be explained by the decrease in emission of pollutants, enforced by the Ministry of the Environment, strongly penalizing the plants which exceed emission limits. This policy led to the installation of suitable filters in the heat and power plants and the oil refinery.

- The fact that malathion (35 times out of 44 analyses), aldrine (33 out of 44) and heptachlor epoxide (30 out of 44) were detected most frequently can be explained by their widespread use in the past and very long degradation times.
- The presence of volatile organohalogen compounds in runoff waters can be explained by the still widespread use of these compounds as solvents in the industry, as well as automotive shops and dry cleaners.
- The correlation found between the toxicity parameter and the concentration of the volatile chloroorganic compounds indicates that the two quantities depend on each other directly proportionally, *i.e.*, an increase

in the concentration of these analytes leads to an increase in sample toxicity. The same type of correlation was also found in the case of toxicity vs. sum of concentrations of the petroleum hydrocarbons. - On the basis of data available in literature, one can state that similar pollutants in the runoff were also found in samples collected in other geographical regions. Levels of concentration of SO_4^{2-} ions are close to those measured by others. Within the borders of the city of Gdansk, SO_4^{2-} contents varied in the 1.81-200.5 mg/dm^3 range, while in the UK it was 60.4-270.9 mg/dm^3 [1], and in the US - 5-650 mg/dm^3 [7]. Measured pH values remained within 6.38-9.06 range in Gdansk, while the respective ranges were 7.12-8.19 in the UK [1] and 6.9-9.3 in the US [10]. In general, runoff waters are heavily contaminated, which significantly contributes to the degradation of the environment. Runoff waters can contaminate surface and

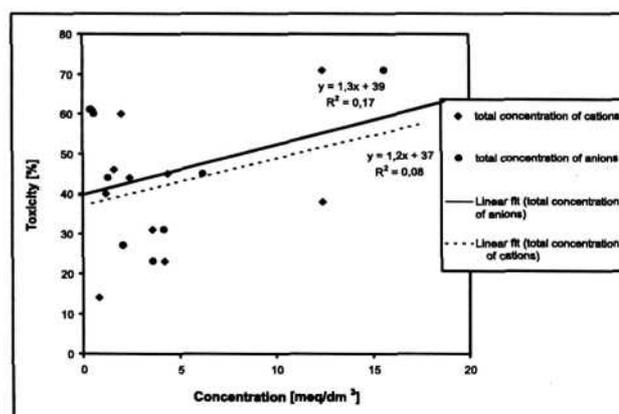


Fig. 5. Dependence of the toxicity on the averaged sums of concentrations of cations and on the averaged sums of concentrations of anions.

subterranean water, potentially endangering drinking water supplies. Thus, they should be collected in sewers and neutralised in sewage treatment plants. Monitoring of runoff water pollution seems to be very important in this context.

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