

Determination of Phenols in Runoff

M. Gryniewicz, Ż. Polkowska, A. Kot-Wasik, J. Namieśnik

Technical University of Gdańsk, Chemical Faculty,
11/12 Narutowicz Str, 80-952 Gdańsk, Poland

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Abstract

An analysis of concentrations of phenols in runoff in the area of Gdańsk was performed during one month of heavy rain. Five sampling places localised along streets of heavy traffic were selected. Phenol and 3,4-dimethylphenol were most often found in samples, while concentrations of phenol (120.3 – 911.6 ng/l), chlorophenol (613 ng/l) and p-nitrophenol (469.4 ng/l) were the highest.

Keywords: runoff, analysis of phenols, water sample preparation.

Introduction

In recent years much attention has been paid to analysis of phenols in environmental samples collected in urban areas [1-3]. These compounds originate from several emission sources as presented in Table 1.

Phenols and phenolic compounds are released in many industrial processes. They are present in wastes from coking plants, gas works, and plants producing and repackaging pesticides, and they are intermediates in the production of plastics, drugs, dyes, pesticides. In the atmosphere the presence of phenols is mainly connected with the photochemical reactions of monoaromatic hydrocarbons (benzene, alkyated benzenes) with hydroxyl radicals, ozone and nitrogen dioxides NO_x [1-6]. Phenol and its methylated derivatives are treated as precursors of nitrophenols too. Phenols exhibit strong toxic properties against aquatic organisms, for example the toxic effects of dinitrophenol were observed for algae and fish at concentrations in the range of 1 µM; similar effects but for plant's growth were noticed for dinitrophenol at concentrations of 1-10 µM. In these cases a break in the vegetation growth, nutrient intake, and transpiration was observed [5]. Probably nitrophenols present in the rain

are responsible for the continuous degradation of forests in Central Europe observed already in the 1980s [3, 5]. It is proved that nitrophenols can interrupt human metabolism at 10 µM level. Besides, chlorophenols are supposed to have carcinogenic effects [5]. Phenols also have an adverse effect on the taste and odour of both water and fish, even at concentrations below 1 ppb.

Although some phenols are included in the Environmental Protection Agency's lists of priority pollutants, few data are available on their concentration in runoff. This knowledge is limited to some data for rain, snow and fog [5-9]. Thus, we decided to undertake a study of phenolic compounds in runoff. Five sampling places localised along streets of heavy traffic in Gdańsk were selected and within one rainy month the analysis of phenol content in runoff was performed. This paper presents the results of the study.

Experimental

Sampling

Runoff samples were collected at five locations situated in the centre of Gdańsk City (Figure 1).

Sampling sites were selected so as to be able to estimate the effect of sampling location on the content of the samples. The following locations were chosen:

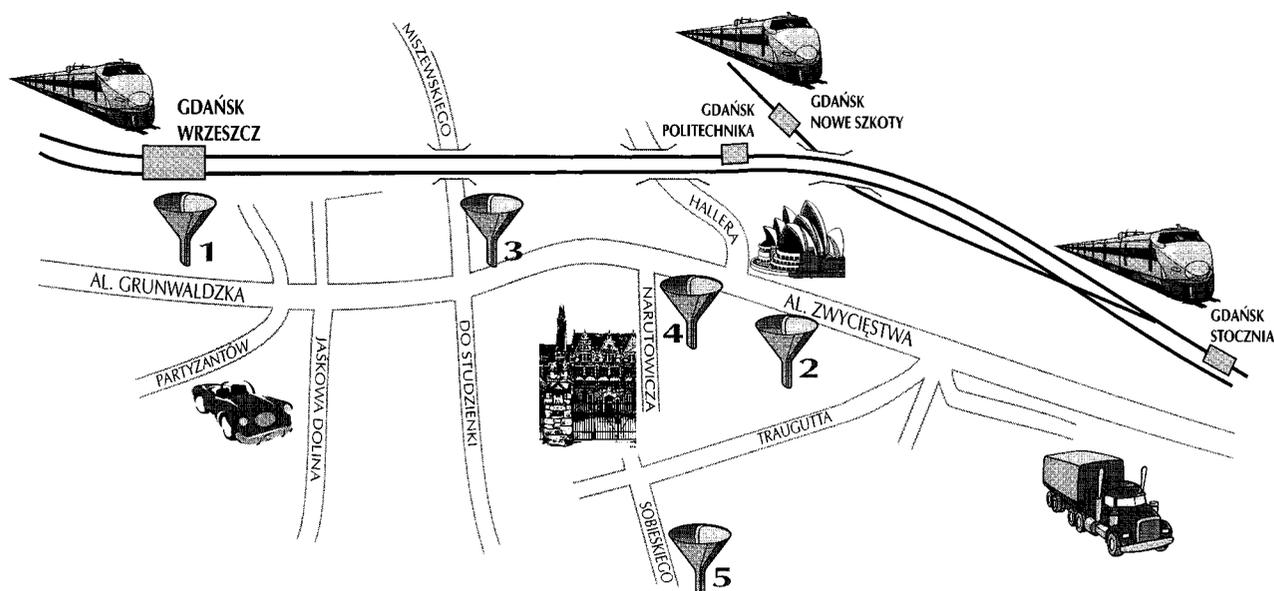


Fig. 1. Locations of the road runoff sampling sites in Gdańsk.

Site 1. Grunwaldzka St. – traffic intensity app. 2500 cars per hour, tram line, parking places, shops along the street.

Site 2. Zwycięstwa St. – traffic intensity app. 2500 cars per hour, tram line, parks and trees along the street, Medical Academy in the neighbourhood.

Site 3. Do Studzienki St. – traffic intensity app. 400 cars per hour.

Site 4 Narutowicza St. – traffic intensity app. 200 cars per hour, the building of Chemical Faculty of Technical University of Gdańsk, printing house, woodworking shop, paper warehouse.

Site 5. Sobieskiego St. – traffic intensity app. 700 cars per hour, the building of Chemical Faculty of the University of Gdańsk.

Samples were collected during rainy period of May, 1999 using a scoop made from polypropylene material and placed in glass amber bottles. After reaching the laboratory sand, a plant's component and insects were filtered off and the samples were prepared according to the procedure described further.

Preconcentration and Isolation of Analytes

Water samples were acidified to pH below 2 using sulphuric acid ($H_2SO_4 > 98\%$ – POCh, Gliwice) and extracted three times with a portion of 4 ml of dichloromethane ($CH_2Cl_2 > 99\%$ – Baker). Then re-extraction was performed using 0.1 M aqueous solution of NaOH

Table 1. Main sources of phenolic compounds in the environment.

Phenolic compounds	Sources	References
phenol	Car exhaust gases	[2, 3]
cresols	Wood impregnation	[4]
nitrophenol	<ul style="list-style-type: none"> – Production of dye-stuffs, pigments, pesticides, medicines; – Herbicides (2,4-dinitro-6-metylophenol – DNOC; 2,4-dinitro-6-secbuthylophenol – <i>dinoseb</i>); – Insecticides — (DNOC); – Evaporation from plants and soil; – Car exhaust gases (2-nitrophenol, 4-nitrophenol, 2,6-dinitrophenol, 2,4-dinitrophenol); – Products of degradation of pesticides 	[5]
metylophenols	Car exhaust gases (metylophenol, dimetylophenol)	[4]
chlorophenols	Wood preservative (pentachlorophenol)	[4]

Table 2. Chromatographic parameters used during analysis of phenols.

Chromatograph	Merck HITACHI La Chrom		
Detector	DAD (L-7450A)		
Column (length x internal diameter x particles)	Li Chrospher 100 RP-18 encapped (125 mm x 4 mm x 5 µm)		
Injection volume	20 µl		
Mobile phase	A: methanol with 0,1% H ₃ PO ₄ B: water with 0,1% H ₃ PO ₄		
Flow rate	1 ml/min		
Gradient elution	time	% A	% B
	0 min.	35	65
	1 min.	35	65
	10 min.	75	25
	15 min.	75	25
	16 min.	35	65
	25 min.	35	65
Temperature	Ambient (24 °C)		
Data collection	Hitachi D-7000 HPLC System Manager (HSM) Software (Version 3.0)		

(NaOH > 98.8% – POCh, Gliwice). Finally, 1 ml extracts were obtained. This sample preparation procedure was chosen because of mechanical and chemical contaminants in runoff collected for analysis. Although contemporary solid-phase extraction (SPE with cartridges and speed disks) is preferred [9-12] we chose the classical liquid-liquid extraction method due to the above mentioned reasons. Thus, problems with clogging of the cartridges in SPE were overcome. In the LLE method used during re-extraction to alkaline aqueous solution only extraction of polar acidic compounds like phenols took place while other organic compounds like PCBs or PAHs remained in the organic solvent layer. In this way we avoided problems of low recovery of phenols during removal of the excess of solvent by evaporation under the stream of nitrogen, which is necessary when using SPE and which causes the loss of nearly 40% of phenol [5].

Chemicals

All studied phenols were purchased from RESTEK CORPORATION (Bellefonte, PA, USA) as standard solutions (1 mg/1 mL) in methanol.

Solvents for HPLC analysis were of HPLC grade and were purchased from Merck. HPLC grade water was obtained from distilled water purified by passing it through the Millipore system (Milli-Q Plus apparatus). For LLE, solvents from J.T. Baker (B.V. Deventer, Holland) were used.

Chromatographic Analysis

Many methods for individual determination of phenols have been proposed, mostly based on chromatographic techniques. Liquid chromatography is a good alternative to gas chromatography [13-16]. The main advantage of HPLC as an analysis technique is that it can

be used without time-consuming derivatisation steps which are often necessary when GC is applied [16]. Therefore, for the determination of phenols in water samples high performance liquid chromatography HPLC coupled with diode-array detection DAD was used. Chromatographic parameters used during analysis are presented in Table 2.

The detection limits were obtained in the range of 2×10^{-4} and 5×10^{-4} µg/µL (0.2 and 0.5 µg/µL) by diluting the standard solution to a signal-to-noise ratio of 3.

External standard calibration was used for quantification of the extracts from runoff after LLE. Calibration curves were obtained by plotting peak area *versus* known injected amount of phenols, using six points ranging from 10^{-1} to 5×10^{-4} µg/µL. The response was linear within this range ($R^2 = 0.9998$ or higher for all studied compounds). The peak area for each point was calculated as an average value of five injections, the relative standard deviation was smaller than 2%.

LLE recovery was determined by spiking tap water with a standard phenols mixture to be between 85 and 95%.

Results and Discussion

Generally, within the examined period (from 05.05.1999 up to 28.05.1999) we collected 25 runoff samples which were analysed for the presence of nine phenols (phenol, o-crezol, p-nitrophenol, dinitrophenol, chlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, 3,4-dimethylphenol, 2,4-dimethylphenol). At the same time pH was measured.

The pH values were in the range of 4,9 and 5,6, with the mean value of 5,2.

Results of determination of total content of phenols in collected runoff are shown in Figure 2.

A distinctly higher content of phenols is observed for runoff collected at Sites 2 and 5, while at Sites 1, 3 and

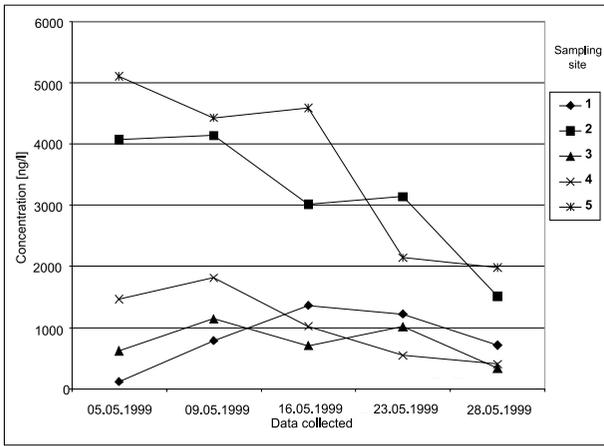


Fig. 2. Results of the determination of the total content of phenols in collected runoff.

4 the total concentration of phenols is at the same level. Figures 3.1 up to 3.5 show the concentration of phenolic compounds founded in runoff collected at different sampling sites.

Phenol and 3,4-dimethylphenol were detected most frequently at sampling site 1 (Fig. 3.1) situated along the main street in Gdańsk with heavy traffic. There the highest concentration found in the period examined were those of phenol (from 120.3 up to 911.6 ng/l), chlorophenol (613 ng/l) and p-nitrophenol (469.4 ng/l). No o-cresol was detected in these samples. At sampling site 2 (Figure 3.2), the concentration of phenol was as high as

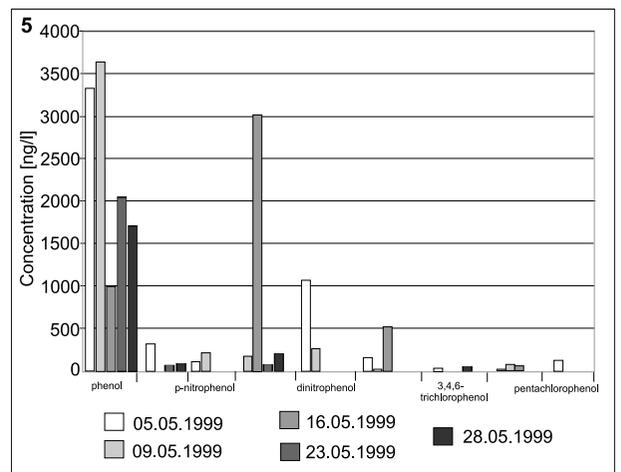
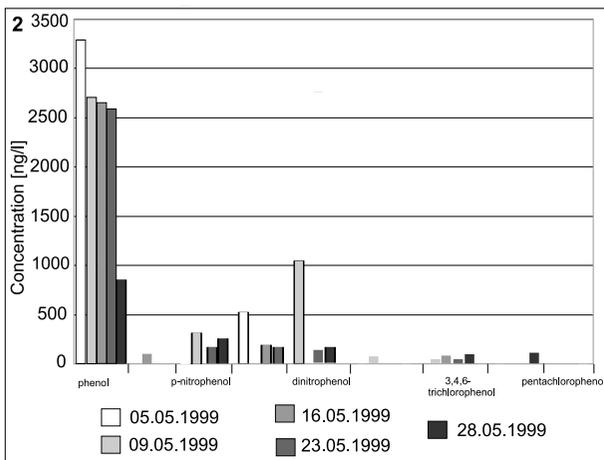
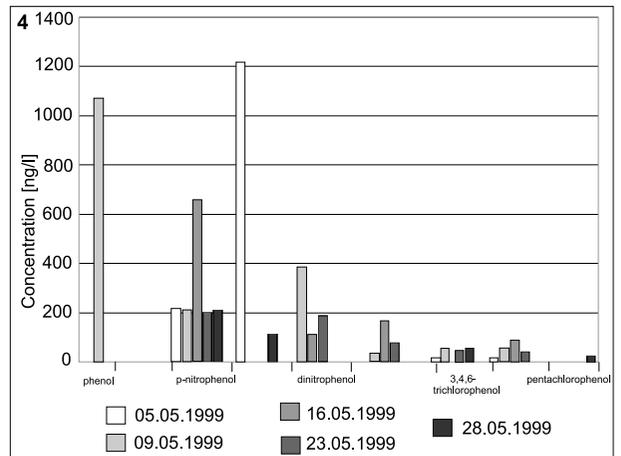
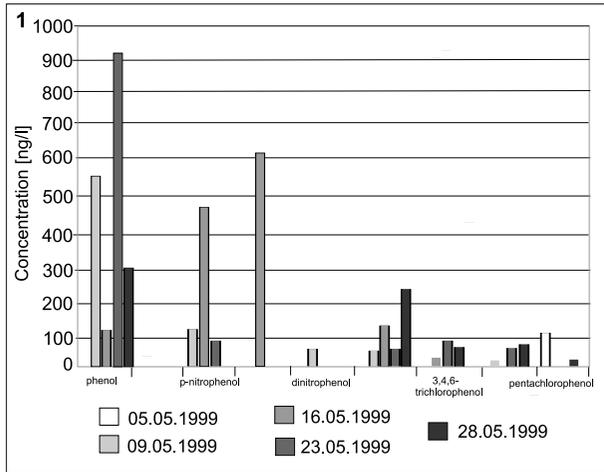
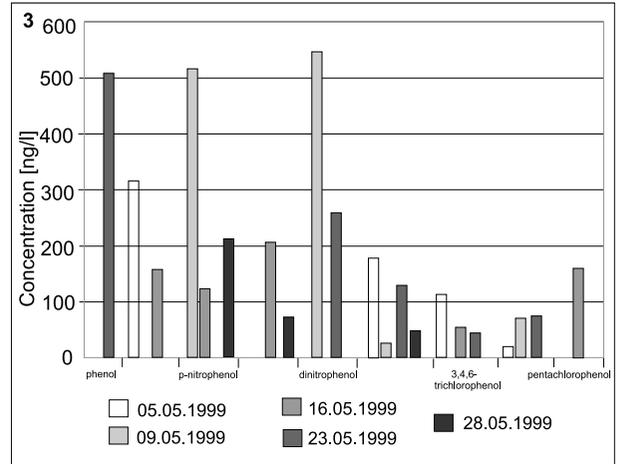


Fig. 3.1-5. Concentration of phenolic compounds found in runoff collected at different sampling sites.

878.1 or even 3651.3 ng/l. This particular compound was detected in all samples analysed. Other phenolic compounds were detected at much lower (from 5 to 10 times) levels. At the same time at sampling site 3 (Figure 3.3) phenol was found only in one sample (23.05.1999 at concentration 506.8 ng/l). Also dinitrophenol (553.7 ng/l) and p-nitrophenol (511.2 n/l) were found. In the runoff collected in that specific site all analysed compounds were presented. At sampling site 4 (Figure 3.4) the most common phenolic compound was p-nitrophenol with a minimum concentration of 197.1 and a maximum concentration of 659.6 ng/l. The highest levels were those of chlorophenol (1215.9 ng/l) and phenol (1069.9 ng/l). Figure 3.5 presents the content of selected phenols at sampling site 5, where phenol was the most often found compound and the highest concentrations were in the range from 994.2 to 3651.3 ng/l. Chlorophenol concentration was also very high (16.05.1999 – 3025.7 ng/l).

Generally, the mean concentrations of phenols in the runoff collected at sampling sites 1, 3 and 4 are in the range of 765.1 and 1049 ng/l, at sampling site 2 and 5 this concentration is even higher and amounts to 3176 ng/l and 3650 ng/l, respectively. The high level of phenol in the runoff collected in the area of the centre of Gdańsk is caused by the high traffic and industrial factories situated in the area of the city. Only the petroleum refinery introduces approximately 118 kg of phenol to the surface waters annually.

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