Analytical procedures for the determination of fuel combustion products, anti-corrosive compounds, and de-icing compounds in airport runoff water samples

Anna Sulej[*], Żaneta Polkowska[*], Aleksander Astel [**], Jacek Namieśnik[*]

[*]Gdańsk University of Technology, Chemical Faculty, Department of Analytical Chemistry, 11/12 G. Narutowicza Str., 80- 233 Gdańsk, Poland, phone: +48 58 347 1010, fax: +48 58 347 2694

[**]Pomeranian Academy, Biology and Environmental Protection Institute, Environmental Chemistry Research Unit, 22a Arciszewskiego Str., 76-200 Słupsk, Poland

Author to whom correspondence should be addressed; e-mail: anna.maria.sulej@gmail.com;

Tel.: +48-58-347-1010; Fax: +48-58-347-2694.

Abstract

The purpose of this study is to propose and evaluate new procedures for determination of fuel combustion products, anti-corrosive and de-icing compounds in runoff water samples collected from the airports located in different regions and characterized by different level of the activity expressed by the number of flights and the number of passengers (per year). The most difficult step in the analytical procedure used for the determination of PAHs, benzotriazoles and glycols is sample preparation stage, due to diverse matrix composition, the possibility of interference associated with the presence of components with similar physicochemical properties. In this study, five different versions of sample preparation using extraction techniques, such as: LLE and SPE, were tested. In all examined runoff water samples collected from the airports, the presence of PAH compounds and glycols was observed. In the majority of the samples, BT compounds were determined. Runoff water samples collected from the areas of Polish and British international airports as well as local airports had similar qualitative composition, but quantitative composition of the analytes was very diverse. New and validated analytical methodologies ensure that the necessary information for assessing the negative impact of airport activities on the environment can be obtained.

Key words: sample preparation techniques, analytical procedures, airport runoff water, polycyclic aromatic hydrocarbons, benzotriazoles, glycols

1. Introduction

In recent years, there has been a massive expansion within the air transport industry. The air transport industry is likely to continue growing in the long term, which leads to increased levels of waste production [1-4]. One of the most important environmental effects associated with airport operations is the large volume of produced polluted airport runoff water (stormwater runoff) [1-3,5-15]. Runoff water, as an effect of the transformation of atmospheric precipitation, is one of the most important routes through which atmospheric pollutants reach the surface of the Earth. In an airport area the rainfall, which contains atmospheric pollutants, additionally washes over highly polluted surfaces such as: de-icing runways, taxiways, maintenance surface, or runways on the airport platform, and rinses off pollutants from them (Table 1) [3-5, 9-20,16-18]. The rainfall waters which turn into runoff waters carry various toxic compounds and get into communal sewage systems, and thence to treatment plants, or, if such plants are non-existent or not working properly, into soil, surface water, and even groundwater which can be the source of drinking water [4,19-26]. A special threat to all elements of the environment are compounds from the glycol group, the benzotriazole group (BTs), and the group of polycyclic aromatic hydrocarbons (PAHs), as they are characterized by high toxicity and cancerogenicity [2,5,8,11,16,19,24,27-31]. Aircraft de-icing and anti-icing fluids are used heavily worldwide, with millions of litres of ADAFs entering the environment every year. The Environmental

Protection Agency (U.S EPA) has estimated that approximately 80 million litres of ethylene or propylene glycol-based ADAF-contaminated runoff is discharged directly to surface waters in the United States annually [5,22]. Compounds from the group of benzotriazoles are commonly added to aircraft de-icing fluids as corrosion inhibitors. e.g., in engine coolants, aircraft de-icers, or anti-freezing liquids [2,6,7,32].

The annual usage of BTs has been estimated to be about 9000 tons/year in the United States, and global usage is much greater [11,33,34]. Benzotriazoles is the fourth most abundant individual aquatic contaminant (after ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and linear alkylbenzene sulfonates (LAS) [25]. According to Directive 67/548/EWG, those compounds are classified as dangerous to the environment and can cause long-term adverse effects in the aquatic environment [4,6,10,22,27-29,33,34].

In view of this, it is important to develop new analytical procedures for determination the most important and probably also the most toxic compounds in samples of airport runoff water and to apply the obtained data to assessment of the threats the contaminants pose to surface water and groundwater [1,2,20,27,35-38]. There is no doubt that the most crucial step of suitable analytical protocols is sample preparation for determination of trace and ultratrace constituents. The preparation of samples of airport runoff water for analysis is not a simple task because of: the diversity of compounds in it (analytes), the diversified content of the matrix of the samples, the possibility of interferences related to the occurrence of compounds, which have similar physical and chemical characteristics, in water, and the lack of references necessary to ensure an appropriate quality control/quality assurance (QA/QC) [39]. Only few data have been published on the results of the sample preparation step in runoff water analysis. In the world literature the solid phase extraction (SPE) and liquid-liquid extraction (LLE) techniques were mainly applied to the determination of target analytes in urban runoff water samples [7,9,12,40,41], and the same two extraction techniques were applied in the sample preparation step in airport runoff water analysis [22,23,29,42]. There have also been some reports on the determination of PAHs, BTs and glycols in properly prepared samples with use of gas chromatography (GC), mass spectrometry (MS), chromatography, tandem mass spectrometry (GC-MS/MS), liquid chromatography (LC)-MS and LC-MS/MS, gas chromatography with flame-ionization detection (GC-FID), and two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GCxGC-TOF-MS) [4,6,16,22,25,27]. The first pieces of information about runoff water analytics have appeared in literature but the problem is still far from being recognized and popularized [22].

The purpose of this study is to propose and evaluate new procedures for determination of trace amounts of wide spectrum of xenobiotics in runoff water samples collected from the airports located in different regions and characterized by different level of the activity expressed by the number of flights and the number of passengers (per year). At the step of isolation and preconcentration of analytes from the above-mentioned samples, different versions of LLE and SPE techniques have been applied. The developed analytical methods were used for the determination of PAH compounds, benzotriazoles and glycols, which are the main pollutants at the airports. It seems to be the first work on such a large scale regarding the wide spectrum of analytes and the diversity of places, from which runoff water samples were collected. Multidimensional data have been explored with use of chemometric techniques (Factor Analysis, FA) in order to gain additional information and find correlations between different analytes and parameters of the analyzed samples.

2. Materials and methods

2.1 Chemicals and materials

Reagents and apparatus used during development of the analytical procedures for the determination of selected compounds (PAHs, BTs, glycols) are shown in Table 2.

2.2 Sample collection

Runoff water samples were collected during or shortly after the rainfall from the areas of three airports (international airport in Poland, local airport in Poland, and international airport in the United Kingdom). The samples were collected from the areas of the airports in three seasons: autumn, winter, and spring, from 2011 to 2012. During this period 189 runoff water samples were collected from places in which runoff water was lying on lower ground and from airport drainage areas. The places of sample collection were located where the most maintenance work was carried out: fuelling, loading and unloading (of transport airplanes), spraying the airplanes with de-icing substances, parking and servicing of maintenance cars, i.e. the places from which the greatest number of contaminants gets into the runoff waters which later flow into drainage ditches and further into the environment (Table 3). Airport runoff water samples were collected in 1,000 mL bottles of dark glass using a syringe (100 ml) with Teflon tubes. The samples were transported to the laboratory (usually within 1 h after collection). Prior to use, the syringes and tubing were rinsed with MilliQ water and then with the water to be sampled. The runoff samples were usually contaminated with solids (sand, leaves, *etc*.) which had to be pre-filtered (0.45 µm, Millex®-HV). Bottles were stored at 4 °C in the dark until extraction [43-47].

2.3 Development of analytical procedures

The desire to obtain reliable information about the state of individual elements of the environment and the processes that occur in them very often requires the use of complex, labourand time-consuming analytical procedures. Therefore, there is a constant need to develop the various stages of the procedures, which will allow to obtain data on the content of trace and ultra-trace components in the samples characterized by complex matrices (such as runoff waters from the area of the airports).

2.3.1 Sample preparation

In the case of airport runoff water samples (where there are a variety of processes associated with the ongoing maintenance of the airport) the sample preparation step is crucial in the analytical procedure. The collected samples should be transported to the laboratory and analyzed as soon as possible (interactions between components in the sample). The decision on the way of sample preparation depends on the type of the obtained analytical information. The first step used in the preparation of environmental samples was to remove solid contaminants (e.g., sand, leaves, dust, etc.) by filtration (pore size 0.45 µm).

Due to the complex composition of the matrix and a large number of interfering compounds, selecting the appropriate extraction method can contribute to optimal (required for further steps in the procedure) sample enrichment, removal of the interfering components and shorter exploitation of apparatus used to perform the final determination. The extraction step is important in view of the fact that errors made at this stage may significantly affect the results of the final determination.

For the study of pollutants released to runoff waters in various processes carried out in the areas of airports (fuel combustion products, anti-corrosive and de-icing substances) three groups of compounds: polycyclic aromatic hydrocarbons, benzotriazoles and glycols, were selected. In order to prepare the samples for the determination of organic pollutants, different extraction techniques: liquid-liquid extraction (A1), and solid phase extraction (A2, A3, A4, A5) were applied. Schematic presentation of the analytical procedures used for the determination of compounds from the group of PAHs, BTs and glycols is shown in Figure 1. The recovery and precision for the whole analytical procedure were evaluated by analyzing extracts of runoff water by GC-MS, spiked before extraction with 20 μgL-1 to 50 μgL-1 of PAH and BT analytes, and 5 and 50 mgL-1 of the glycol analytes. Table 4 shows the average recoveries together with the standard deviation (RSD) of the procedures and comparison of analytical protocols used for the determination of PAHs, BTs and glycols. In addition, the results of PAH determination were explored using the technique of factor analysis (algorithm using principal component factors and varimax rotation of factor loadings). Prior to factor analysis the raw data were auto-scaled by variables as it is commonly recommended in case of data with serious differences in concentration values or different units [48]. The purpose of such pre-processing step was to scale variance of each variable to unity and to centre mean values. The aim of the FA was to identify a structure of the data including three different extraction techniques (A1, A2, A3). The structure of the data was explored by 4 factors that cumulatively explain nearly 80% of the variance (Table 5). The first factor indicate a correlation between the content of fluorene, pyrene and benzo [b] fluoranthene, second one between naphthalene, acenaphthene, anthracene, and dibenzo [a, h] anthracene, third one between benzo [a] anthracene, chrysene and fluoranthene and the fourth one between benzo [k] fluoranthene, benzo [a] pyrene, indeno [1,2,3-c, d] terylene and benzo [g, h, i] terylene. The projection of sample distribution in the space of principal components was made with regard to the type of sample preparation technique for the analysis (Figure 2). On the basis of the information shown in Figure 2, which contained the factorial combination of all the factors, it can be concluded that the results of PAH concentrations obtained by means of extraction techniques (A1, A2 and A3) for analytes forming factors (F1, F3 and F4) are comparable. This is evidenced by the general lack of clearly disjoint groups of points corresponding to the three considered extraction techniques. The exception is the score plot shown in Figure 2a, where the results of the analysis of the samples extracted using A3 technique form (at the top of the chart) the group, which is separated from the results of the analysis of the samples prepared by means of A1 and A2 method. It can be concluded that generally higher concentration levels of compounds such as naphthalene, acenaphthene, anthracene, and dibenzo [a, h] anthracene are achieved by application of extraction method A3, compared with the results obtained for the samples extracted by means of A1 and A2 techniques, regardless of the sampling place.

2.3.2 Chromatographic analysis of suitably prepared samples

Gas chromatography coupled with mass spectrometry (GC-MS) was used for the determination of PAH compounds, glycols and benzotriazoles in the appropriately prepared extracts. The conditions of final determination of the analytes belonging to these groups of compounds were optimized. As a part of this work calibration step, which is aimed to present the dependence between the analytical signal and the concentration of the analyte in a form of a calibration graph, was also performed. On the basis of the calibration curves, it was possible to determine concentration levels of certain substances in real samples. The curves were prepared immediately prior to each series of analysis by diluting the stock solution. Each solution was analyzed in triplicate. Technical specifications, operating conditions and basic metrological parameters of the optimized analytical procedures are summarized in Table 6. Calibration was performed in the range of 0.04-2 [$\mu g \cdot L^{-1}$] for PAHs, 2-300 [$\mu g \cdot L^{-1}$] for glycols, and 5-75 [$\mu g \cdot L^{-1}$] for BT, respectively. Linear calibration curves were obtained by plotting the peak area against the concentration of the respective standards. Calibrations showed good linearity as indicated by the values of R^2. The limit of detection (LOD) was determined for glycols, BT, PAHs in quality control samples based on three replicates of measurement. LOD was calculated using the equation LOD=3.3SD/b (b is the slope of the calibration curve; SD is the standard deviation of the curve). The quantification limit (LOQ) was set to three times the LOD. The LODs of the PAHs ranged from 0.0003 to 0.057[$\mu g \cdot L^{-1}$], and from 0.0003 to 0.010 [$\mu g \cdot L^{-1}$] for benzotriazoles, and the highest from 0.016 to 0.936 [$\mu g \cdot L^{-1}$] for glycols respectively.

Figure 3 provides an example of the chromatograms obtained from the analysis of runoff water samples collected from local and international airport in Poland and from international airport in the United Kingdom, using extraction techniques A1-A5.

3. Results

In order to illustrate the possibilities of using five different extraction techniques (A1-A5), which are the main stage of the developed analytical procedures for the determination of PAHs, BTs and glycols, the results of the research on airport runoff water samples collected in the areas of three airports (international airport, local airport in Poland and international airport in United Kingdom) were presented. During the period from autumn 2011 to spring 2012, 207 runoff water samples were collected (125 samples -national airport PL, 55 samples-local airport PL, 27 samples-international airport UK).

In the samples collected in the areas of three airports, which are the subject of this research, compounds, which represent a group of pollutants originated from fuel combustion (PAHs), were detected and analyzed. Figure 4 presents the results of the concentration levels of individual PAH analytes determined in runoff water samples collected in the areas of airports (international airport PL, local airport PL). The highest concentrations of PAH analytes were noted in the samples collected from the international airport PL. Compounds whose concentrations were the highest, regardless of the airport, were chrysene and phenanthrene.

Histograms presented in the Figure 5 are the source of information on the concentrations of individual analytes from the group of benzotriazoles determined in runoff water samples collected in the area of the airports (Polish international, local airport and British international airport). The quantitative analysis showed that the concentration levels of BTs in runoff water samples collected from international and national Polish airports were significantly greater compared with other locations. The highest concentrations of 5-Me-1H-1H-BT and BT were determined in the sample taken from Polish international airport from the measuring point, where de-icing operations are performed (89.3 μg·L-1 and 29.1 μg·L-1 respectively). In general, the highest concentration levels of compounds that represent a group of pollutants originated from anti-corrosive substances (e.g. BTs) were determined in the samples taken from aircraft de-icing places, machinery parks and technical roads in the airports. Relatively low concentration levels of BTs were determined in the samples taken from the area of British international airport.

At all airports under investigation, compounds, which represent a group of pollutants originated from anti-icing substances (e.g. glycols) were detected and analyzed. This is illustrated by the data shown in Figure 6 concerning the concentrations of glycols in runoff water samples collected from the area of airports (international and local polish airport and also British international airport). Generally, the concentration levels of glycols in the samples collected from international British airport were much higher (254 mgL-1) compared with other locations. Among the compounds from the group of glycols, the highest concentrations were reported for ethylene glycol in all cases. High concentration levels of the compounds from the group of glycols were determined mainly in the samples collected from the areas, where aircraft de-icing processes are performed, as well as within the parking places (where de-icing operations are carried out in the smaller airports) and airport technical roads (transmission and scattering of de-icing fluids by maintenance vehicles).

4. Discussion

Intensification of air transport, i.e. the increase in air traffic at the airports and the development of airport network, causes that anthropogenic impact on the environment is more and more significant. There is no doubt that it is necessary to conduct a comprehensive control of the composition of the airport runoff water samples. The study of pollutants present in specific environmental samples, such as runoff water samples from the area of the airports, allows a better understanding and characterization of the occurrence of xenobiotics in the environment. Only widely spread monitoring of such samples can allow to obtain data, which will be the basis for evaluating the intensity of the airport activity on the inanimate nature and living organisms and subsequently to prepare strong foundations for the management of waste produced by the airports.

In order to estimate the amount of individual xenobiotics released to runoff waters and to investigate their environmental fate appropriate analytical procedures are required. The most difficult step in the analytical procedure (during which significant errors can be made) used for the determination of the described in this work groups of compounds that represent the pollution from fuel combustion products, anti-corrosive compounds, and de-icing compounds in airport runoff waters is the sample preparation step. It is due to the diversity of the compounds present in the samples collected from the airport platform, a diverse matrix composition, the possibility of interference associated with the presence of components with similar physico-chemical properties, the lack of the reference materials necessary to ensure an adequate level of assurance and quality control of the analytical measurements).

In this study, five different versions of sample preparation using extraction techniques, such as: LLE and SPE, were tested. This work also presents complete analytical procedures suitable for the determination of the analytes from the group of PAHs, BTs and glycols present in the airport runoff water samples. The development of the procedure for determining some of the most toxic xenobiotics in runoff waters was used to analyze real samples collected from three airports located on the Polish territory and in the United Kingdom. In all examined runoff water samples collected from the airports, the presence of compounds from the group of PAHs and glycols was confirmed. Moreover, the presence of BTs was observed in the majority of the samples. Runoff water samples collected from the areas of Polish and British international airports as well as local airports had similar qualitative composition, and quantitative composition of the analytes was very diverse, which depends on the emission of pollutants generated by the airport, but also on the meteorological conditions in a given area.

This type of research is conducted in only a few reputable scientific institutions. However, it can be confidently stated that runoff waters from the area of the airports are attracting greater interest as a source of information about the potentially negative impact of the rapidly increasing airport activity on the state of the environment.

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Table 1 Major sources of emission and xenobiotics generated during airport operations

Type of pollutant	Origin of pollution	Major toxicants
Fuel combustion products	• combustion of fuels • aircraft, vehicle maintenance operations • fuelling operations • engine testing operations	• **PAHs** • PCB • phenols, formaldehyde • benzene
Anti-corrosion pollutants	• aircraft de-icing anti-icing fluid additives (ADAFs) • engine coolants and oils in automobiles • industrial cooling systems • plastic stabilizers	**Benzotriazoles** • 4-methyl-1-H-benzotriazole (4-MeBT) • 5-methyl-1-H-benzotriazole (5-MeBT) • 1H-benzotriazole (1-MeBT)
De/anti-icing chemical wastes	• de/anti-icing operations	**Glycols**: • propylene glycol (PG) • ethylene glycol (EG) • diethylene glycol (DEG)

Table 2 Reagents and apparatus used in this research study

Apparatus and reagents		
Apparatus	Sample preparation	Centrifuge shaker (Conbest, ELMI, Poland), Vacuum set of SPE-12G™ (J.T. Baker, Poland),
	Finally determination	Agilent 7890A gas chromatograph coupled with mass spectrometer Agilent 5975C,
Solvents	Methanol, *n*-heksane, Dichloromethane (Lichrosolv, Merck, Germany);	
SPE columns	Strata C-18E (Phenomenex, USA), ENVI-Carb Plus (Sigma-Aldrich, USA),	
Standard solutions	Mix of 16 PAHs (2000 μg·mL^{-1} in dichloromethane, Supelco, USA), Mix of benzotriazoles (1000 μg·mL^{-1} in methanol, Sigma-Aldrich, Germany), Mix of glycols (1000 μg·mL^{-1} in methanol, Sigma-Aldrich, Germany)	
Other	Deionized water Milli-Q (Millipore Corporation, USA), Nitrogen (purity 99,99%, Poland)	

Table 3 The characteristics of the places of sample collection of airport runoff waters

Sample number	Locations of sample collection		
Airport	**International PL**	**Local PL**	**International UK**
1	influent of a river	vicinity of an airport terminal	de-icing area (1)
2	effluent of a river	de-icing area	a river in the vicinity of the airport
3	municipal water catchment area	machinery stock, parking places	de-icing area (2)
4	CARGO water catchment area	runway	de-icing area (3)
5	airport ramp	parking places	de-icing area (4)
6	car park	the periphery of an airport	a road near the airport
7	de-icing area	car park	-
8	airport ramp	-	-

Table 4 Comparison of analytical procedures used for the determination of PAHs, BTs and glycols.

Analytical procedures/Analytes	Pre-treatment method	Analytical method	Recovery (%)	RSD (%)	Advantages	Disadvantages
A1-A3 PAHs (16analytes from PAHs group)						
A1	LLE	GC-MS	60 – 80	6 – 12	Simplicity of the used apparatus Suitability for highly contaminated samples	Large amounts of solvent needed Large amounts of a sample needed Time-consuming and labor-intensive
A2	C18-SPE		72 – 101	1.8 – 5.2	Smaller amount of a sample needed	Time-consuming
A3	C18-SPE		78 – 102	1.5 – 5.5	High LODs	Time-consuming
A4 BENZOTRIAZOLES						
1-H-benzotriazole	C18-SPE	GC-MS	68	12	High recovery	High RSD Relatively high consumption of solvent
ethyl-1H-benzotraizole			102	8.1		
ethyl-1H-benzotraizole			88	7.2		
GLYCOLS						
opylene glycol	Envi-CarbPlus-	GC-MS	86 - 94	2.5 – 3.1	Small amount of a sample	Mechanical clogging of the pores by

Ethylene glycol	SPE		70 -78	6.7 – 7.7	High recovery	runoff water samples
Diethylene glycol			89 - 96	8.6 – 8.9		

Table 5 Factor loadings and explained variance of varimax rotated factors

	Factor 1	**Factor 2**	**Factor 3**	**Factor 4**
Naphthalene	-0.12	***0.75***	0.25	0.20
Acenaphthylene	0.39	0.45	-0.10	0.53
Acenaphthene	0.03	***0.90***	0.08	0.09
Fluorene	***0.91***	0.06	0.06	-0.11
Phenanthrene	0.28	0.43	0.45	0.36
Anthracene	0.11	***0.63***	0.11	-0.14
Fluoranthene	0.52	-0.09	***0.69***	0.37
Pyrene	***0.90***	-0.04	0.35	0.18
Benz[a]anthracene	0.08	0.03	***0.85***	0.01
Chrysene	0.10	0.18	***0.92***	0.21
Benzo[b]fluoranthene	***0.86***	0.02	0.03	0.31
Benzo[k]fluoranthene	0.59	-0.00	0.03	***0.72***
Benzo[a]pyrene	0.21	0.06	0.47	***0.75***
Indeno[1,2,3-c,d]pyrene	0.06	0.16	0.29	***0.86***
Dibenz[a,h]anthracene	-0.12	***0.62***	-0.13	0.56
Benzo[g,h,i]perylene	0.13	0.42	0.51	***0.61***
Eigenvalue	3.34	2.79	3.06	3.30
Variance explained [%]	21	17	19	21

Table 6 Basic parameters of the analytical procedure for PAH determination in airport runoff water samples based on the application of LLE, SPE and GC-MS techniques (obtained from the analysis of the samples of standard solutions).

Conditions of the analysis			
Analyte	**PAHs**	**Benzotriazoles**	**Glycols**
Sample preparation technique	LLE and SPE	SPE	SPE
Element of the measurement system	GC-EI-MS	GC-EI-MS	GC-EI-MS
Gas chromatograph	Agilent 7980A	Agilent 7980A	Agilent 7980A
Detector	Agilent 5975C	Agilent 5975C	Agilent 5975C
Detector working mode	monitoring of selected ions	monitoring of selected ions	monitoring of selected ions
Temperature of the source of ionization	230 °C		
Quadrupole temperature	150 °C		
Energy of the electron stream	70eV		
Chromatographic column	ZB-5MS; 30m x 0,25mm; 0,25µm stationary phase		SPB-1000 30m x 0,25mm; 0,25µm
Stationary phase	5/95 phenyl/polydimethylsiloxane		modified polyethylene glycol
Pressure of the carrier gas (He)	7,07 psi	8,80 psi	7,65 psi
Flow rate of the carrier gas	1 ml·min^{-1}		
Temperature of injection port	295°C	260 °C	220 °C
Connection temperature	295°C	260 °C	220 °C
Working mode of injection port	splitless		
Temperature programme	40-120 °C (40 °C/min) 120-280 °C (5°C/min)	70°C (2 min) 70-275°C (14 °C/min)	50-200 °C (8 °C/min) 200 °C (1min)

		275°C (2 min)	
Volume of injection	2 µl	1 µl	
Time of the analysis	46 minutes	19 minutes	20 minutes
Number of the analytes	16	3	

Metrological characteristics				
Polycyclic aromatic hydrocarbons				
Analyte	**Calibration curve equation**	**Regression coefficient, R^2**	**LOD $[\mu g\cdot L^{-1}]$**	**LOQ $[\mu g\cdot L^{-1}]$**
Naphthalene	$y=5.00\cdot10^{6}x-6.44\cdot10^{4}$	0.982	0.013	0.040
Acenaphthylene	$y=2.00\cdot10^{6}x+9.96\cdot10^{3}$	0.997	0.0003	0.001
Acenaphthene	$y=4.00\cdot10^{6}x+2.98\cdot10^{3}$	0.998	0.001	0.004
Fluorene	$y=3.00\cdot10^{6}x-3.26\cdot10^{4}$	0.995	0.013	0.030
Phenanthrene	$y=6.42\cdot10^{5}x-8.31\cdot10^{3}$	0.993	0.043	0.130
Anthracene	$y=4.22\cdot10^{5}x+3.83\cdot10^{4}$	0.994	0.017	0.051
Fluoranthene	$y=8.81\cdot10^{5}x+6.89\cdot10^{3}$	0.996	0.001	0.004
Piren	$y=8.66\cdot10^{4}x+7.57\cdot10^{4}$	0.985	0.0005	0.002
Benz[a]anthracen	$y=8.84\cdot10^{4}x+2.86\cdot10^{3}$	0.997	0.006	0.019
Chrysene	$y=8.90\cdot10^{4}x+2.01\cdot10^{3}$	0.998	0.004	0.011
Benzo[b]fluoranthene + benzo[k]fluoranthene	$y=2.29\cdot10^{5}x+1.11\cdot10^{4}$	0.997	0.057	0.170
Benzo[a]pyrene	$y=1.49\cdot10^{5}x+2.10\cdot10^{3}$	0.994	0.053	0.160
Indeno[1.2.3-cd]pyrene	$y=1.53\cdot10^{5}x+1.64\cdot10^{2}$	0.998	0.057	0.170
Benzotriazoles				
1H-benzotriazole	$y=2.92\cdot10^{5}x+2.84\cdot10^{4}$	0.983	0.010	0.030
4-Me-1H-benzotriazole	$y=5.98\cdot10^{5}x-3.00\cdot10^{6}$	0.962	0.010	0.030
5-Me-1H-benzotriazole	$y=4.44\cdot10^{5}x+1.44\cdot10^{5}$	0.942	0.0003	0.001
Glycols				

Ethylene glycol	$y=4.88\cdot10^5x-4.00\cdot10^6$	0.970	0.189	0.567
Diethylene glycol	$y=1.00\cdot10^6x+2.41\cdot10^5$	0.986	0.016	0.047
Propylene glycol	$y=8.62\cdot10^5x-5.00\cdot10^6$	0.977	0.936	2.81

Figure 1a

The schematic presentation of the analytical procedures for the determination of PAHs in the airport runoff water samples by means of : LLE (A1), SPE (A2), and SPE (A3) (Figure 1 a) and SPE (A4), SPE (A5) techniques (Figure 1b) at the step of sample preparation.

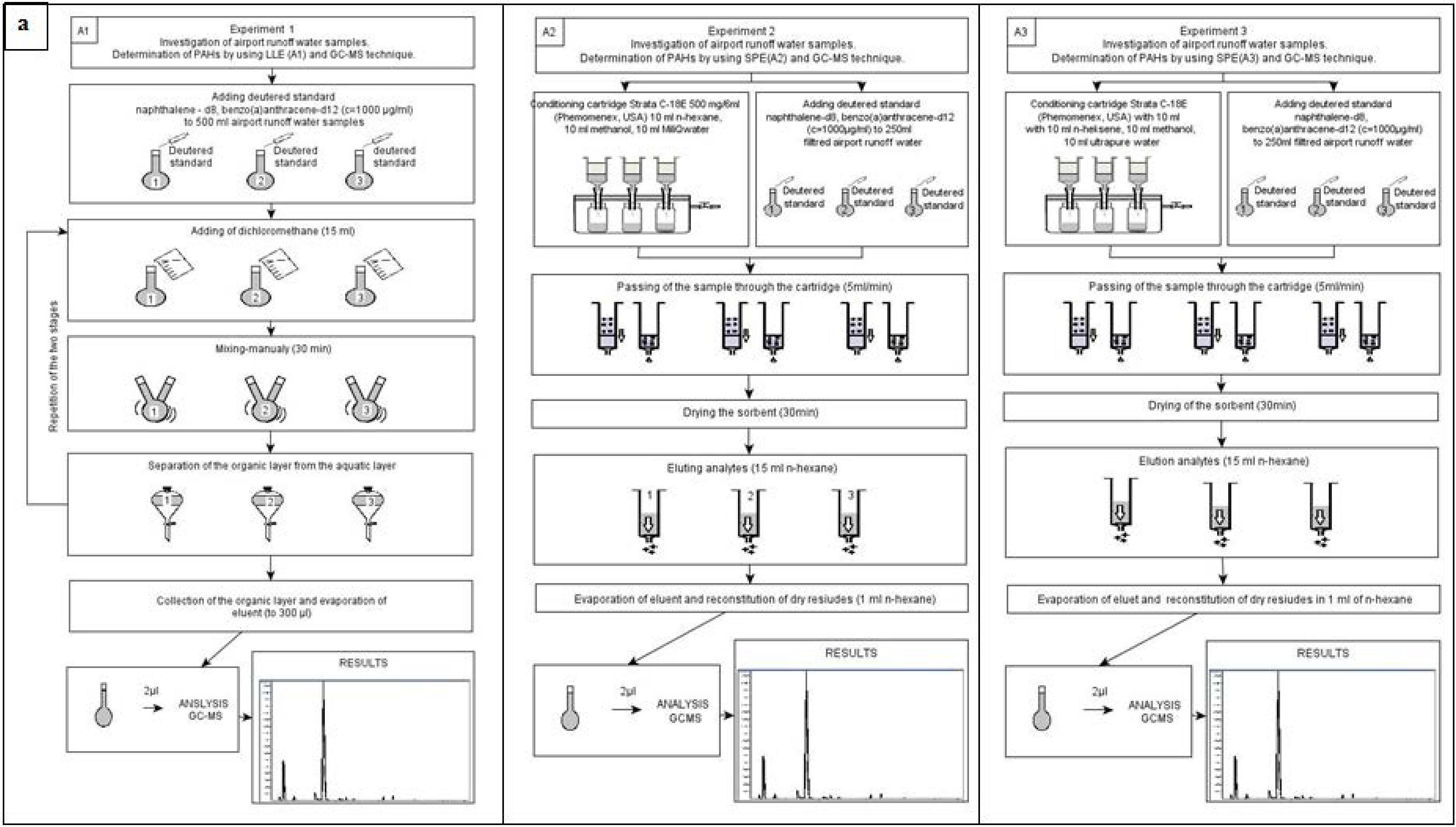

Figure 1b

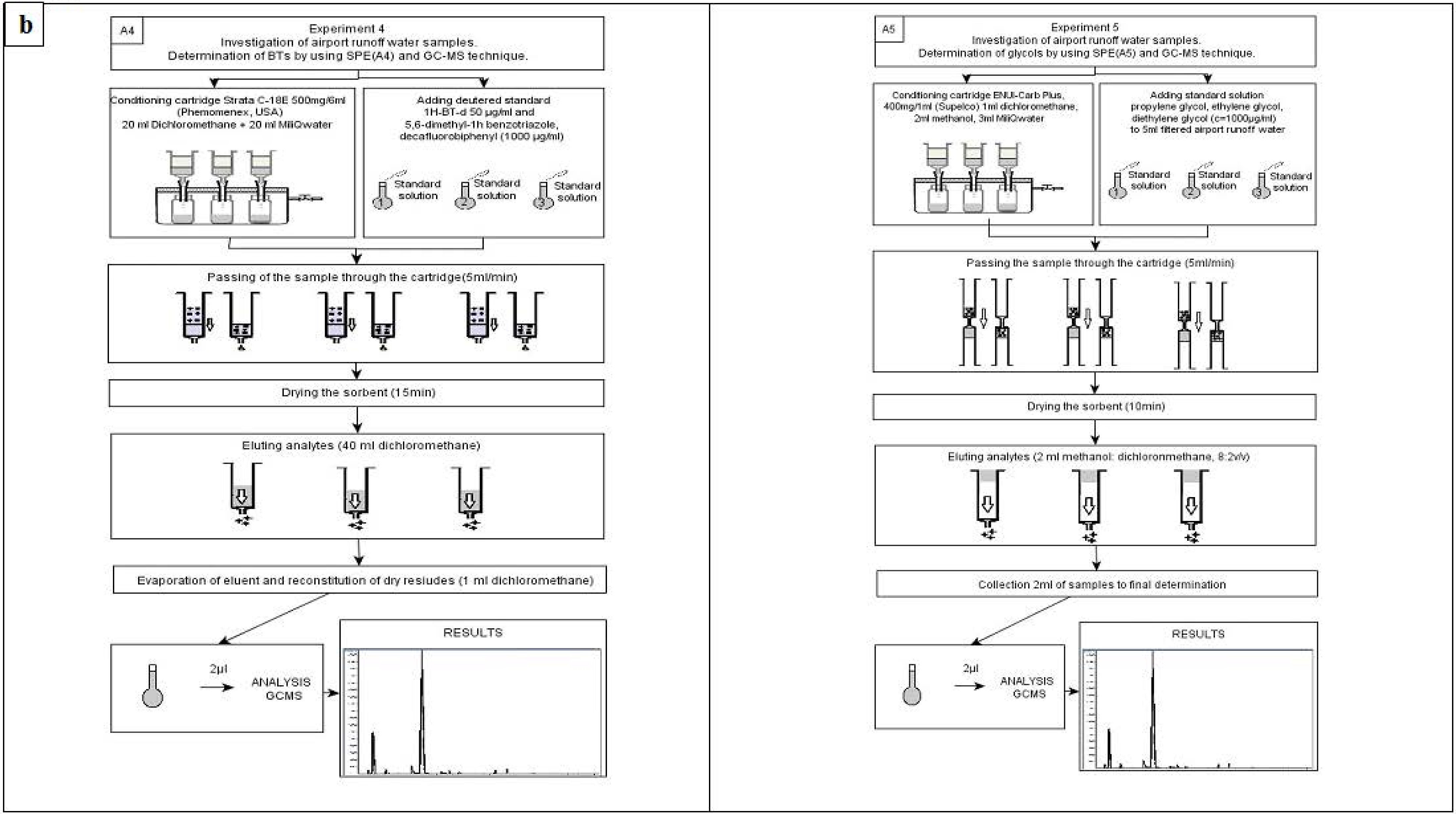
b
A4
Experiment 4
Investigation of airport runoff water samples.
Determination of BTs by using SPE(A4) and GC-MS technique.
Conditioning cartridge Strata C-18E 500mg/6ml
(Phemomenex, USA)
20 ml Dichloromethane + 20 ml MiliQwater
Adding deutered standard
1H-BT-d 50 µg/ml and
5,6-dimethyl-1h benzotriazole,
decafluorobiphenyl (1000 µg/ml)
1 Standard solution
2 Standard solution
3 Standard solution
Passing of the sample through the cartridge(5ml/min)
Drying the sorbent (15min)
Eluting analytes (40 ml dichloromethane)
Evaporation of eluent and reconstitution of dry residues (1 ml dichloromethane)
2µl
ANALYSIS
GCMS
RESULTS
A5
Experiment 5
Investigation of airport runoff water samples.
Determination of glycols by using SPE(A5) and GC-MS technique.
Conditioning cartridge ENUI-Carb Plus,
400mg/1ml (Supelco) 1ml dichloromethane,
2ml methanol, 3ml MiliQwater
Adding standard solution
propylene glycol, ethylene glycol,
diethylene glycol (c=1000µg/ml)
to 5ml filtered airport runoff water
1 Standard solution
2 Standard solution
3 Standard solution
Passing the sample through the cartridge (5ml/min)
Drying the sorbent (10min)
Eluting analytes (2 ml methanol: dichloronmethane, 8:2v/v)
Collection 2ml of samples to final determination
2µl
ANALYSIS
GCMS
RESULTS

Figure 2

Plot of sample scores of the first and second factor identified (Figure 2a), the first and third factor identified (Figure 2b), and the first and fourth factor identified (Figure 2c) by principal component analysis with varimax rotation

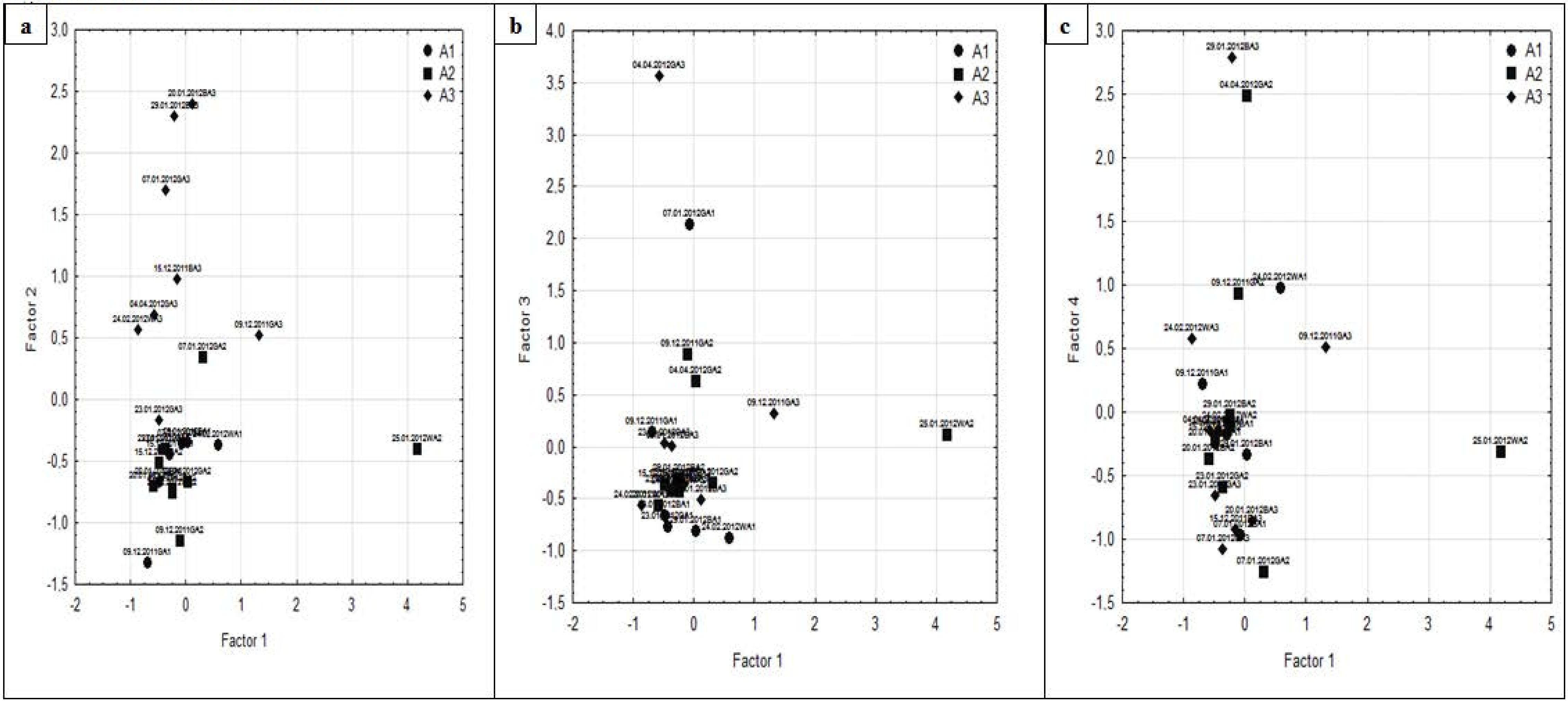

Figure 3
Chromatograms obtained as a result of the analysis of the airport runoff water samples (samples were prepared by means of A1-A5 (LLE and SPE) techniques).

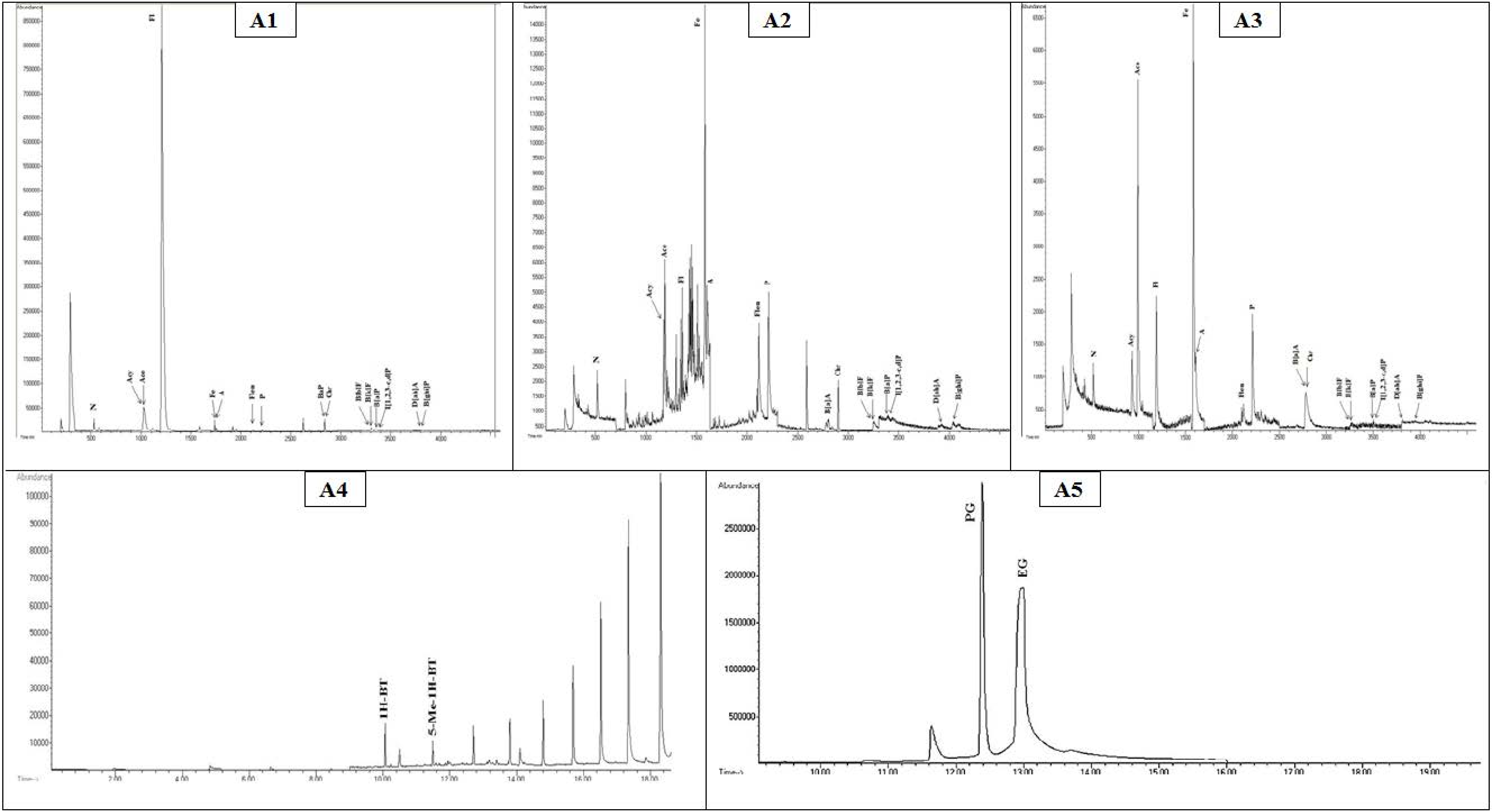

Figure 4
PAH concentrations determined in runoff water samples collected in the area of airports (international airport PL and local airport PL).

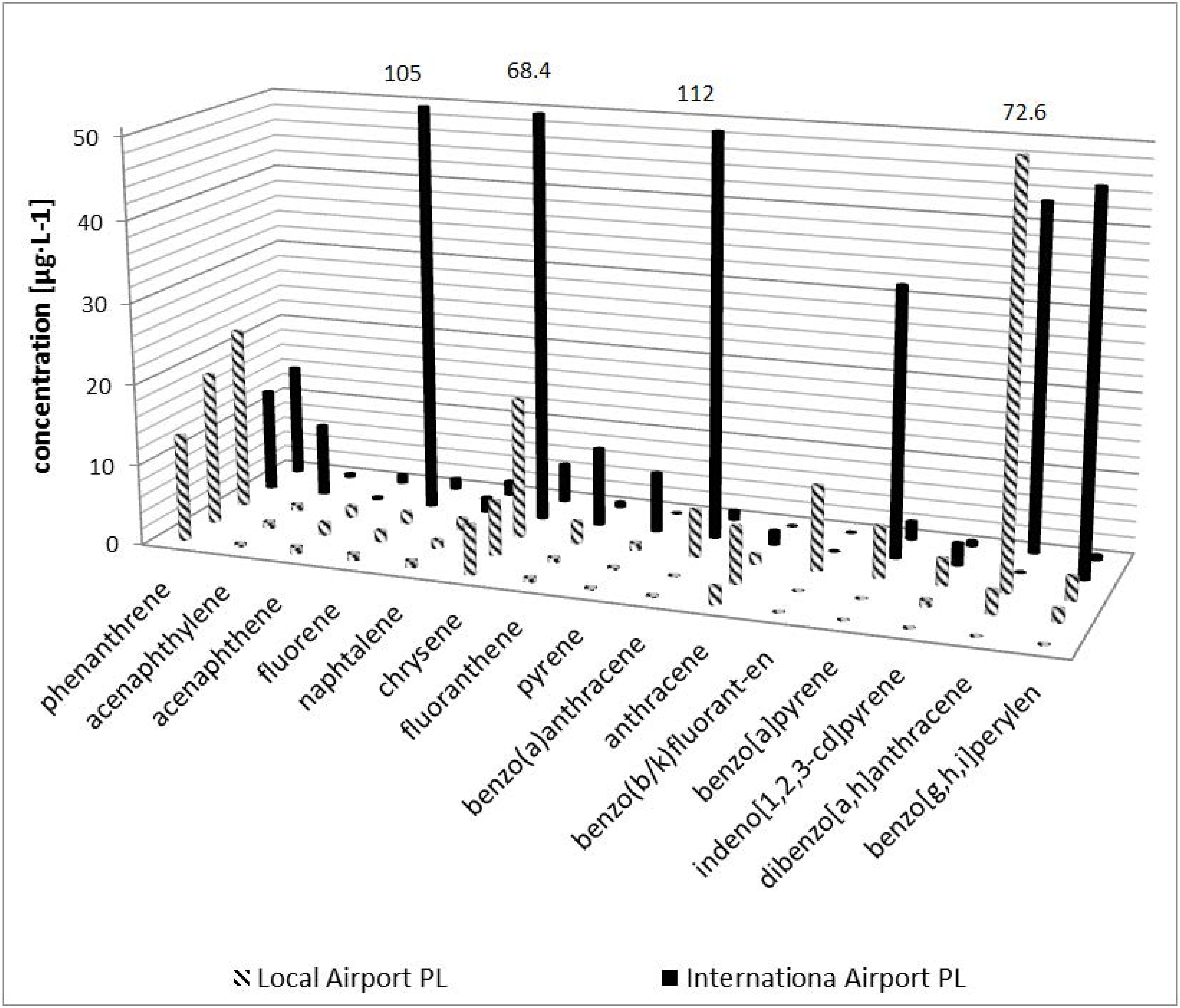

Figure 5

Concentration levels of benzotriazoles determined in airport runoff water samples collected from international airport PL (Figure 5a), local airport PL (Figure 5b), and international airport UK (Figure 5c).

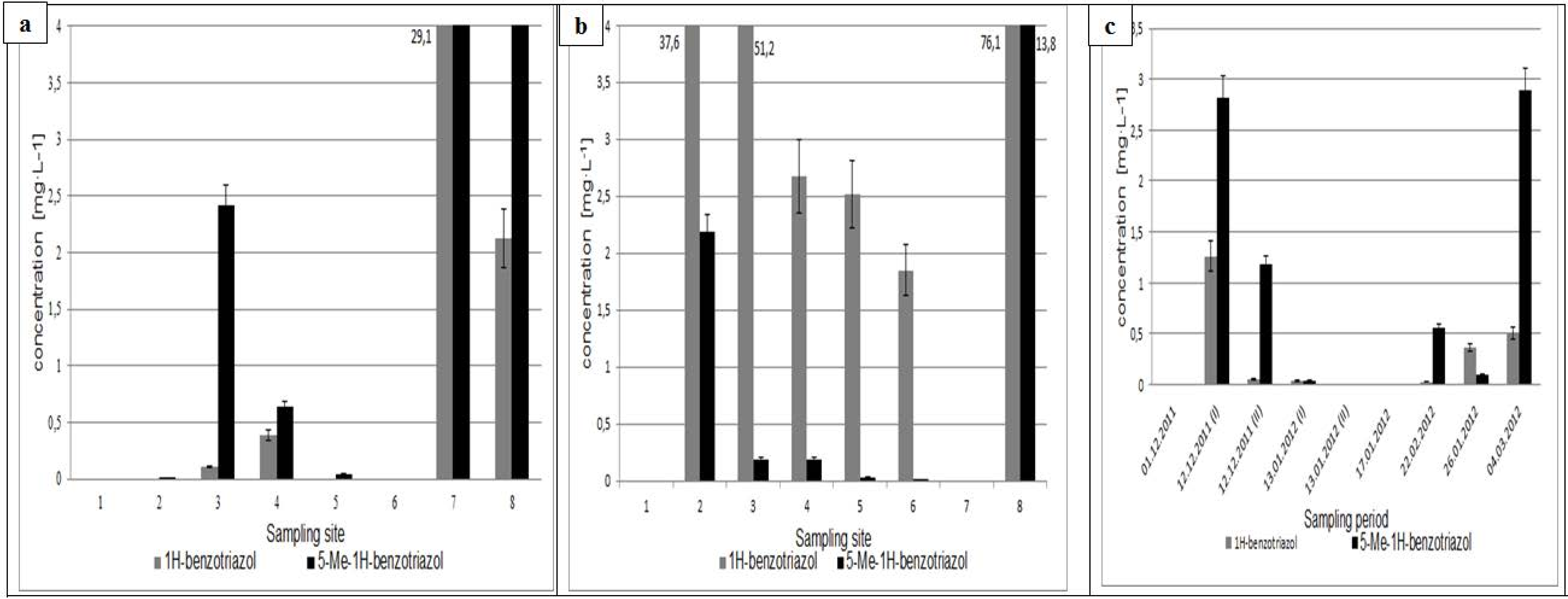

Figure 6
Concentration levels of individual glycols determined in the airport runoff water samples collected from international airport PL (Figure 6a), local airport PL (Figure 6b), and international airport UK (Figure 6c).