

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

25 that the necessary information for assessing the negative impact of airport activities on the
26 environment can be obtained.

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

29

30 **1. Introduction**

31 In recent years, there has been a massive expansion within the air transport industry. The air
32 transport industry is likely to continue growing in the long term, which leads to increased levels
33 of waste production [1-4]. One of the most important environmental effects associated with
34 airport operations is the large volume of produced polluted airport runoff water (stormwater
35 runoff) [1-3,5-15]. Runoff water, as an effect of the transformation of atmospheric precipitation,
36 is one of the most important routes through which atmospheric pollutants reach the surface of the
37 Earth. In an airport area the rainfall, which contains atmospheric pollutants, additionally washes
38 over highly polluted surfaces such as: de-icing runways, taxiways, maintenance surface, or
39 runways on the airport platform, and rinses off pollutants from them (Table 1) [3-5, 9-20,16-18].
40 The rainfall waters which turn into runoff waters carry various toxic compounds and get into
41 communal sewage systems, and thence to treatment plants, or, if such plants are non-existent or
42 not working properly, into soil, surface water, and even groundwater which can be the source of
43 drinking water [4,19-26]. A special threat to all elements of the environment are compounds from
44 the glycol group, the benzotriazole group (BTs), and the group of polycyclic aromatic
45 hydrocarbons (PAHs), as they are characterized by high toxicity and cancerogenicity
46 [2,5,8,11,16,19,24,27-31]. Aircraft de-icing and anti-icing fluids are used heavily worldwide,
47 with millions of litres of ADAFs entering the environment every year. The Environmental



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

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

59 In view of this, it is important to develop new analytical procedures for determination the
60 most important and probably also the most toxic compounds in samples of airport runoff water
61 and to apply the obtained data to assessment of the threats the contaminants pose to surface water
62 and groundwater [1,2,20,27,35-38]. There is no doubt that the most crucial step of suitable
63 analytical protocols is sample preparation for determination of trace and ultratrace constituents.
64 The preparation of samples of airport runoff water for analysis is not a simple task because of: the
65 diversity of compounds in it (analytes), the diversified content of the matrix of the samples, the
66 possibility of interferences related to the occurrence of compounds, which have similar physical
67 and chemical characteristics, in water, and the lack of references necessary to ensure an
68 appropriate quality control/quality assurance (QA/QC) [39]. Only few data have been published
69 on the results of the sample preparation step in runoff water analysis. In the world literature the
70 solid phase extraction (SPE) and liquid-liquid extraction (LLE) techniques were mainly applied
71 to the determination of target analytes in urban runoff water samples [7,9,12,40,41], and the same

72 two extraction techniques were applied in the sample preparation step in airport runoff water
73 analysis [22,23,29,42]. There have also been some reports on the determination of PAHs, BTs
74 and glycols in properly prepared samples with use of gas chromatography (GC), mass
75 spectrometry (MS), chromatography, tandem mass spectrometry (GC-MS/MS), liquid
76 chromatography (LC)-MS and LC-MS/MS, gas chromatography with flame-ionization detection
77 (GC-FID), and two-dimensional gas chromatography coupled to time-of-flight mass spectrometry
78 (GCxGC-TOF-MS) [4,6,16,22,25,27]. The first pieces of information about runoff water
79 analytics have appeared in literature but the problem is still far from being recognized and
80 popularized [22].

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

93

94



95 2. Materials and methods

96 2.1 Chemicals and materials

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

99 2.2 Sample collection

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

115 2.3 Development of analytical procedures

116 The desire to obtain reliable information about the state of individual elements of the
117 environment and the processes that occur in them very often requires the use of complex, labour-



118 and time-consuming analytical procedures. Therefore, there is a constant need to develop the
119 various stages of the procedures, which will allow to obtain data on the content of trace and ultra-
120 trace components in the samples characterized by complex matrices (such as runoff waters from
121 the area of the airports).

122 *2.3.1 Sample preparation*

123
124 In the case of airport runoff water samples (where there are a variety of processes
125 associated with the ongoing maintenance of the airport) the sample preparation step is crucial in
126 the analytical procedure. The collected samples should be transported to the laboratory and
127 analyzed as soon as possible (interactions between components in the sample). The decision on
128 the way of sample preparation depends on the type of the obtained analytical information. The
129 first step used in the preparation of environmental samples was to remove solid contaminants
130 (e.g., sand, leaves, dust, etc.) by filtration (pore size 0.45 μm).

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

137 For the study of pollutants released to runoff waters in various processes carried out in the
138 areas of airports (fuel combustion products, anti-corrosive and de-icing substances) three groups
139 of compounds: polycyclic aromatic hydrocarbons, benzotriazoles and glycols, were selected. In
140 order to prepare the samples for the determination of organic pollutants, different extraction
141 techniques: liquid-liquid extraction (A1), and solid phase extraction (A2, A3, A4, A5) were

142 applied. Schematic presentation of the analytical procedures used for the determination of
143 compounds from the group of PAHs, BTs and glycols is shown in Figure 1. The recovery and
144 precision for the whole analytical procedure were evaluated by analyzing extracts of runoff water
145 by GC-MS, spiked before extraction with 20 μgL^{-1} to 50 μgL^{-1} of PAH and BT analytes, and 5
146 and 50 mgL^{-1} of the glycol analytes. Table 4 shows the average recoveries together with the
147 standard deviation (RSD) of the procedures and comparison of analytical protocols used for the
148 determination of PAHs, BTs and glycols. In addition, the results of PAH determination were
149 explored using the technique of factor analysis (algorithm using principal component factors and
150 varimax rotation of factor loadings). Prior to factor analysis the raw data were auto-scaled by
151 variables as it is commonly recommended in case of data with serious differences in
152 concentration values or different units [48]. The purpose of such pre-processing step was to scale
153 variance of each variable to unity and to centre mean values. The aim of the FA was to identify a
154 structure of the data including three different extraction techniques (A1, A2, A3). The structure of
155 the data was explored by 4 factors that cumulatively explain nearly 80% of the variance (Table
156 5). The first factor indicate a correlation between the content of fluorene, pyrene and benzo [b]
157 fluoranthene, second one between naphthalene, acenaphthene, anthracene, and dibenzo [a, h]
158 anthracene, third one between benzo [a] anthracene, chrysene and fluoranthene and the fourth one
159 between benzo [k] fluoranthene, benzo [a] pyrene, indeno [1,2,3-c, d] terylene and benzo [g, h, i]
160 terylene. The projection of sample distribution in the space of principal components was made
161 with regard to the type of sample preparation technique for the analysis (Figure 2). On the basis
162 of the information shown in Figure 2, which contained the factorial combination of all the
163 factors, it can be concluded that the results of PAH concentrations obtained by means of
164 extraction techniques (A1, A2 and A3) for analytes forming factors (F1, F3 and F4) are
165 comparable. This is evidenced by the general lack of clearly disjoint groups of points

166 corresponding to the three considered extraction techniques. The exception is the score plot
167 shown in Figure 2a, where the results of the analysis of the samples extracted using A3 technique
168 form (at the top of the chart) the group, which is separated from the results of the analysis of the
169 samples prepared by means of A1 and A2 method. It can be concluded that generally higher
170 concentration levels of compounds such as naphthalene, acenaphthene, anthracene, and dibenzo
171 [a, h] anthracene are achieved by application of extraction method A3, compared with the results
172 obtained for the samples extracted by means of A1 and A2 techniques, regardless of the sampling
173 place.

174 2.3.2 Chromatographic analysis of suitably prepared samples

175 Gas chromatography coupled with mass spectrometry (GC-MS) was used for the determination
176 of PAH compounds, glycols and benzotriazoles in the appropriately prepared extracts. The
177 conditions of final determination of the analytes belonging to these groups of compounds were
178 optimized. As a part of this work calibration step, which is aimed to present the dependence
179 between the analytical signal and the concentration of the analyte in a form of a calibration
180 graph, was also performed. On the basis of the calibration curves, it was possible to determine
181 concentration levels of certain substances in real samples. The curves were prepared immediately
182 prior to each series of analysis by diluting the stock solution. Each solution was analyzed in
183 triplicate. Technical specifications, operating conditions and basic metrological parameters of the
184 optimized analytical procedures are summarized in Table 6. Calibration was performed in the
185 range of 0.04-2 [$\mu\text{g}\cdot\text{L}^{-1}$] for PAHs, 2-300 [$\mu\text{g}\cdot\text{L}^{-1}$] for glycols, and 5-75 [$\mu\text{g}\cdot\text{L}^{-1}$] for BT,
186 respectively. Linear calibration curves were obtained by plotting the peak area against the
187 concentration of the respective standards. Calibrations showed good linearity as indicated by the
188 values of R^2 . The limit of detection (LOD) was determined for glycols, BT, PAHs in quality
189 control samples based on three replicates of measurement. LOD was calculated using the



190 equation $LOD=3.3SD/b$ (b is the slope of the calibration curve; SD is the standard deviation of
191 the curve). The quantification limit (LOQ) was set to three times the LOD. The LODs of the
192 PAHs ranged from 0.0003 to 0.057 [$\mu\text{g}\cdot\text{L}^{-1}$], and from 0.0003 to 0.010 [$\mu\text{g}\cdot\text{L}^{-1}$] for benzotriazoles,
193 and the highest from 0.016 to 0.936 [$\mu\text{g}\cdot\text{L}^{-1}$] for glycols respectively.

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

197

198 3. Results

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

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

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

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



237 **4. Discussion**

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

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

258 In this study, five different versions of sample preparation using extraction techniques,
259 such as: LLE and SPE, were tested. This work also presents complete analytical procedures
260 suitable for the determination of the analytes from the group of PAHs, BTs and glycols present in



261 the airport runoff water samples. The development of the procedure for determining some of the
262 most toxic xenobiotics in runoff waters was used to analyze real samples collected from three
263 airports located on the Polish territory and in the United Kingdom. In all examined runoff water
264 samples collected from the airports, the presence of compounds from the group of PAHs and
265 glycols was confirmed. Moreover, the presence of BTs was observed in the majority of the
266 samples. Runoff water samples collected from the areas of Polish and British international
267 airports as well as local airports had similar qualitative composition, and quantitative
268 composition of the analytes was very diverse, which depends on the emission of pollutants
269 generated by the airport, but also on the meteorological conditions in a given area.

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

274

275 **Acknowledgements**

276 The authors would like to thank the Ministry of Science and Higher Education for the grant
277 awarded within the framework of the Project No. 0528/IP3/2011/71 for financing this
278 investigation. The authors express their gratitude to Eng. Krzysztof Suchomski for his help in
279 preparing the graphic side of this publication.

280 **4. References**

- 281 [1] M. Pitt, A. Smith, *Journal of Air Transport Management*, 9 (2003) 103-111.
282 [2] M. Switzenbaum, S. Veltman, M.D. Wagoner, T. Schoenberg, *Chemosphere*, 43 (2001) 1051-
283 1062.
284 [3] L. Luther, in: S. Environmental Policy Analyst Resources, and Industry Division (Ed.), 2007.
285 [4] S.R. Corsi, G.R. Harwell, S.W. Geis, D. Bergman, *Environmental Toxicology and Chemistry*,
286 25 (2006) 2890-2900.

- 287 [5] S. Barash, J. Covington, C. Tamulonis, in: U.S.E.P. Agency (Ed.), Washington, 2000.
288 [6] A. Kiss, E. Fries, *Environ Sci Pollut Res*, 16 (2009) 702-710.
289 [7] S. Weiss, J. Jacobs, T. Reemtsma, *Environ Sci Technol*, 40 (2006) 7193-7199.
290 [8] M.S. Schwitzenbaum, S. Vetman, T. Schoenberg, C.M. Durand, D. Mericas, B.W. No.173, in,
291 1999.
292 [9] T. Reemtsma, M. Ulf, U. Duennbier, M. Jekel, *Water Res.*, 44 (2010) 596-604.
293 [10] D. Pillard, D. DuFrense, *Arch Environ Contam Toxicol*, 37 (1999) 29-35.
294 [11] D. Pillard, J. Cornell, D. Dufresne, M. Hernandez, *Water Res.*, 35 (2001) 557-560.
295 [12] E. Hoffman, G.L. Mills, J.S. Lamiter, J.G. Quinn, *Environ Sci Technol*, 18 (1984) 580-587.
296 [13] C. Sun, J. Fitzpatrick, S. Goebel, J. Loos, in, University of Missouri—Columbia, 2011.
297 [14] G.A. Burton, R.E. Pitt, *Stormwater Effects Handbook: A CRC/Lewis*, London, 2002.
298 [15] D.M. Revitt, R.B.E. Shutes, N.R. Llewellyn, P. Worrall, *Wat. Sci. Tech*, 36 (1997) 385-390.
299 [16] G.D. Breedveld, R. Roseth, M. Sparrevik, T. Hartnik, L.J. Hem, *Water, Air, Soil Pollut*, 3
300 (2003) 91-101.
301 [17] V. Barcan, E. Kovnatsky, A. Shylina, *Atmospheric Environment* 34 (2000) 1225-1231.
302 [18] D.M. Ramakrishna, T. Viraraghavan, *Water, Air and Soil Pollution*, 166 (2005) 49-63.
303 [19] S. Grant, N. Rekhi, N. Prise, R. Reeves, in: C.D.o. Transportation (Ed.), Caltrans,
304 Sacramento, 2003.
305 [20] A. Sulej, Ż. Polkowska, J. Namieśnik, *Critical Reviews in Science and Technology*, 42
306 (2012) 1691-1734.
307 [21] A.M. Sulej, Ż. Polkowska, J. Namieśnik, *Critical Reviews in Analytical Chemistry*, 41
308 (2011) 190–213.
309 [22] D. Cancilla, J.C. Baird, S.W. Geist, S. Corsi, *Environmental Toxicology and chemistry*, 22
310 (2003) 134-140.
311 [23] D.A. Cancilla, J. Martinez, G.C.v. Aggelen, *Environ. Sci. Technol.*, 32 (1998) 3834–3835.
312 [24] H.K. French, S.E.A.V.d. Zee, A. Leijnse, *J. Contam. Hydrol*, 49 (2001) 23–48.
313 [25] W. Giger, in: E.a. research (Ed.), Swiss Federal Institute of Aquatic Science and
314 Technology, Stresa, 2006.
315 [26] J.M. Strong-Gunderson, S. Wheelis, S.L. Carroll, M.D. Waltz, A.V. Palumbo, in, 1995.
316 [27] S.R. Corsi, S.W. Geis, J.L.-. Rosales, C.P. Rice, R.J. Sheesley, G.G. Failey, D. Cancilla,
317 *Environ. Sci. Technol.*, 40 (2006) 3195-3202.
318 [28] S.R. Corsi, Si Wi Geis, G. Bowman, G.G. Failey, T.D. Rutter, *Environ. Sci. Technol.*, 43
319 (2009) 40-46.
320 [29] S.R. Corsi, D.J. Zitomer, J. Field, D.A. Cancilla, *Environ. Sci. Technol*, 37 (2003) 4031-
321 4037.
322 [30] J.W. Readman, G. Fillmann, I. Tolosa, Ja Bartocci, J.P. Villeneuve, C. Catinni, L.D. Mee,
323 *Marine Pollution Bulletin* 44 (2002) 48–62.
324 [31] P. Baumard, H. Budziński, P. Garrigues, *Marine Pollution Bulletin*, 36 (1998) 577-586.
325 [32] J.A. Leerdam, A.C. Hogenboom, M.M.v.d. Kooi, P.d. Voogt, *International Journal of Mass*
326 *Spectrometry*, 282 (2009) 99-107.
327 [33] Y.-S. Liu, G.-G. Ying, A. Shareef, R.S. Kookana, *Journal of Chromatography A*, 1218
328 (2011) 5328-5335.
329 [34] D.S. Hart, L.C. Davis, L.E. Erickson, T.M. Callender, *Microchem. J.*, 77 (2004).
330 [35] D.H. Zitomer, in, Marquette University, Milwaukee, 2001, pp. 38.
331 [36] U.S.D. Transportation, in, Federal Aviation Administration 2010.
332 [37] P. Popp, C. Baurer, B. Hauser, P. Keil, L. Wennrich, *J. Sep. Sci.*, 26 (2003) 961-967.
333 [38] M. O'Donnell, in: U.S.D.o. Transportation (Ed.), Federal Aviation Administration, 2008.

- 334 [39] J. Pawliszyn, Handbook of sample preparation, A John Wiley & Sons, Inc., Publication,
335 New Yearsy, 2010.
- 336 [40] W. Zhang, S. Zhang, D. Yue, C. Wan, Y. Ye, X. Wang, Environ Toxicol Chem., 27 (2008)
337 31-37.
- 338 [41] K. Lamprea, V. Ruban, Environ Technol., 32 (2011) 1141-1149.
- 339 [42] C. Harris, E. Routledge, C. Schaffner, J. Brian, W. Giger, J. Sumpter, Environ Toxicol
340 Chem. , 26 (2007) 2367-2372.
- 341 [43] Ź. Polkowska, K. Skarżyńska, T. Górecki, J.Namieśnik, Atmospheric Environment, 36
342 (2002) 361-369.
- 343 [44] M. Korhonen, A. Kiviranta, R. Ketola, Toxicological and Environmental Chemistry, 66
344 (1998) 37-45.
- 345 [45] K. Levsen, S. Behnert, B. Prieb, M. Svoboda, H. D.Winkeler, J. Zietlow, Chemosphere, 21
346 (1990) 1037-1061.
- 347 [46] W.F. Rogge, L. Hildemann, M.A. Mazurek, G.R. Cass, B. R.Simoneit, Environmental
348 Science and Technology, 27 (1993) 1892-1904.
- 349 [47] E. Manoli, C. Samara., Trends in Analytical Chemistry, 6 (1999) 417-428.
- 350 [48] D. Massart, B. Vandeginste, S. Deming, Y. Michotte, L. Kaufman, Chemometrics: a
351 textbook, Elsevier, Amsterdam, 1988.
- 352
- 353

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

| Type of pollutant | Origin of pollution | Major toxicants |
|--------------------------------------|--|--|
| Fuel combustion products | <ul style="list-style-type: none"> • combustion of fuels • aircraft, vehicle maintenance operations • fuelling operations • engine testing operations | <ul style="list-style-type: none"> • PAHs • PCB • phenols, formaldehyde • benzene |
| Anti-corrosion pollutants | <ul style="list-style-type: none"> • aircraft de-icing anti-icing fluid additives (ADAFs) • engine coolants and oils in automobiles • industrial cooling systems • plastic stabilizers | <p>Benzotriazoles</p> <ul style="list-style-type: none"> • 4-methyl-1-H-benzotriazole (4-MeBT) • 5-methyl-1-H-benzotriazole (5-MeBT) • 1H-benzotriazole (1-MeBT) |
| De/anti-icing chemical wastes | <ul style="list-style-type: none"> • de/anti-icing operations | <p>Glycols:</p> <ul style="list-style-type: none"> • propylene glycol (PG) • ethylene glycol (EG) • diethylene glycol (DEG) |

2

3 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, <i>n</i> -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) | |

4

5

6

7

8

9

10

11

12

13

14

15

16

17



18
19
20

21 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 |
| 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 | - | - |

22

23
 24
 25
 26 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 | | | | | | |
| H-benzotriazole | C18-SPE | GC-MS | 68 | 12 | High recovery | High RSD Relatively high consumption of solvent |
| ethyl-1H-benzotriazole | | | 102 | 8.1 | | |
| ethyl-1H-benzotriazole | | | 88 | 7.2 | | |
| GLYCOLS | | | | | | |
| propylene 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, R² | LOD [µg·L⁻¹] | LOQ [µg·L⁻¹] |
| Naphthalene | $y=5.00 \cdot 10^6 x - 6.44 \cdot 10^4$ | 0.982 | 0.013 | 0.040 |
| Acenaphthylene | $y=2.00 \cdot 10^6 x + 9.96 \cdot 10^3$ | 0.997 | 0.0003 | 0.001 |
| Acenaphthene | $y=4.00 \cdot 10^6 x + 2.98 \cdot 10^3$ | 0.998 | 0.001 | 0.004 |
| Fluorene | $y=3.00 \cdot 10^6 x - 3.26 \cdot 10^4$ | 0.995 | 0.013 | 0.030 |
| Phenanthrene | $y=6.42 \cdot 10^5 x - 8.31 \cdot 10^3$ | 0.993 | 0.043 | 0.130 |
| Anthracene | $y=4.22 \cdot 10^5 x + 3.83 \cdot 10^4$ | 0.994 | 0.017 | 0.051 |
| Fluoranthene | $y=8.81 \cdot 10^5 x + 6.89 \cdot 10^3$ | 0.996 | 0.001 | 0.004 |
| Piren | $y=8.66 \cdot 10^4 x + 7.57 \cdot 10^4$ | 0.985 | 0.0005 | 0.002 |
| Benz[a]anthracen | $y=8.84 \cdot 10^4 x + 2.86 \cdot 10^3$ | 0.997 | 0.006 | 0.019 |
| Chrysene | $y=8.90 \cdot 10^4 x + 2.01 \cdot 10^3$ | 0.998 | 0.004 | 0.011 |
| Benzo[b]fluoranthene + benzo[k]fluoranthene | $y=2.29 \cdot 10^5 x + 1.11 \cdot 10^4$ | 0.997 | 0.057 | 0.170 |
| Benzo[a]pyrene | $y=1.49 \cdot 10^5 x + 2.10 \cdot 10^3$ | 0.994 | 0.053 | 0.160 |
| Indeno[1.2.3-cd]pyrene | $y=1.53 \cdot 10^5 x + 1.64 \cdot 10^2$ | 0.998 | 0.057 | 0.170 |
| Benzotriazoles | | | | |
| 1H-benzotriazole | $y=2.92 \cdot 10^5 x + 2.84 \cdot 10^4$ | 0.983 | 0.010 | 0.030 |
| 4-Me-1H-benzotriazole | $y=5.98 \cdot 10^5 x - 3.00 \cdot 10^6$ | 0.962 | 0.010 | 0.030 |
| 5-Me-1H-benzotriazole | $y=4.44 \cdot 10^5 x + 1.44 \cdot 10^5$ | 0.942 | 0.0003 | 0.001 |
| Glycols | | | | |

| | | | | |
|-------------------|---|-------|-------|-------|
| Ethylene glycol | $y=4.88 \cdot 10^5 x - 4.00 \cdot 10^6$ | 0.970 | 0.189 | 0.567 |
| Diethylene glycol | $y=1.00 \cdot 10^6 x + 2.41 \cdot 10^5$ | 0.986 | 0.016 | 0.047 |
| Propylene glycol | $y=8.62 \cdot 10^5 x - 5.00 \cdot 10^6$ | 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.

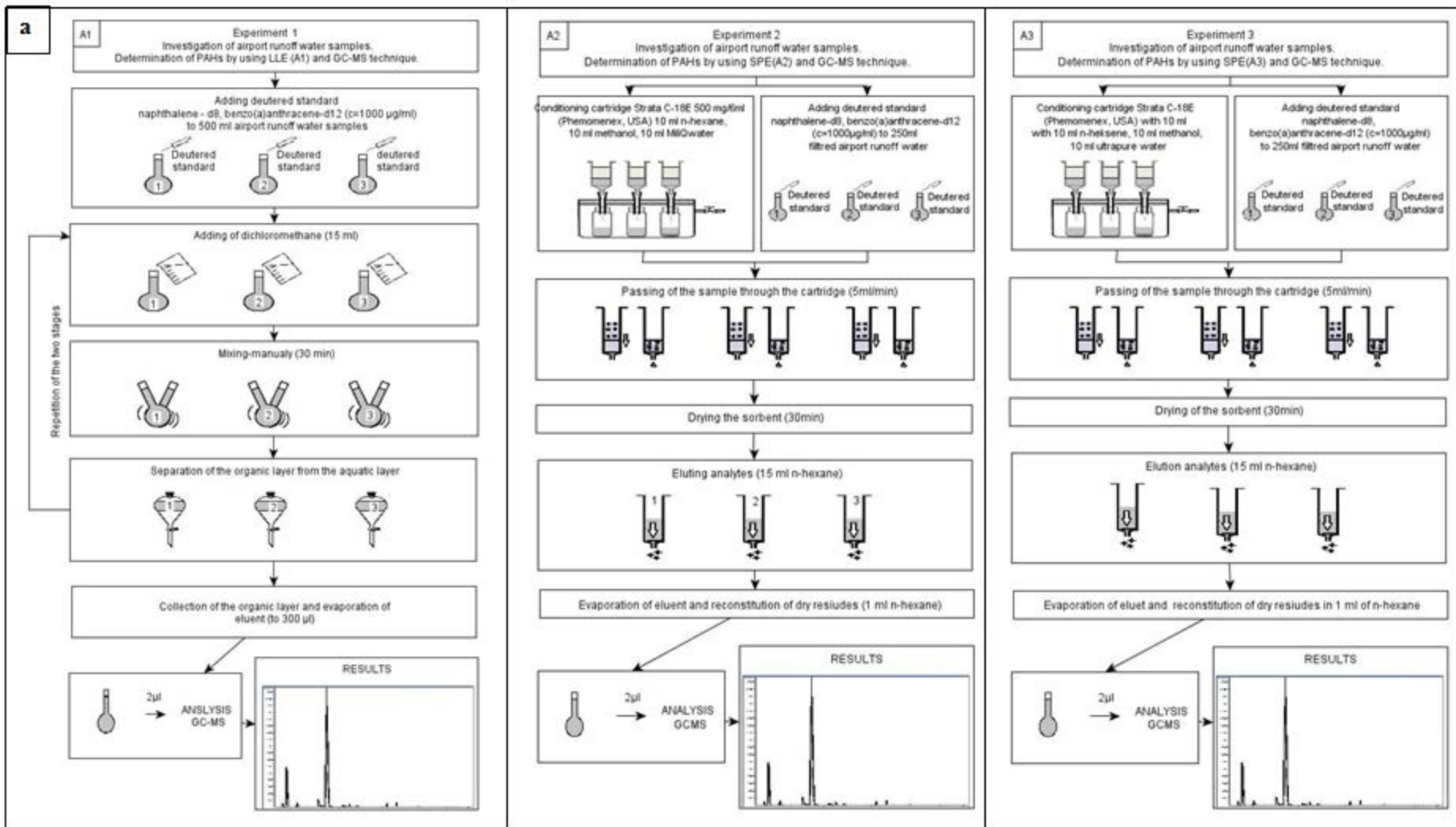


Figure 1b

b

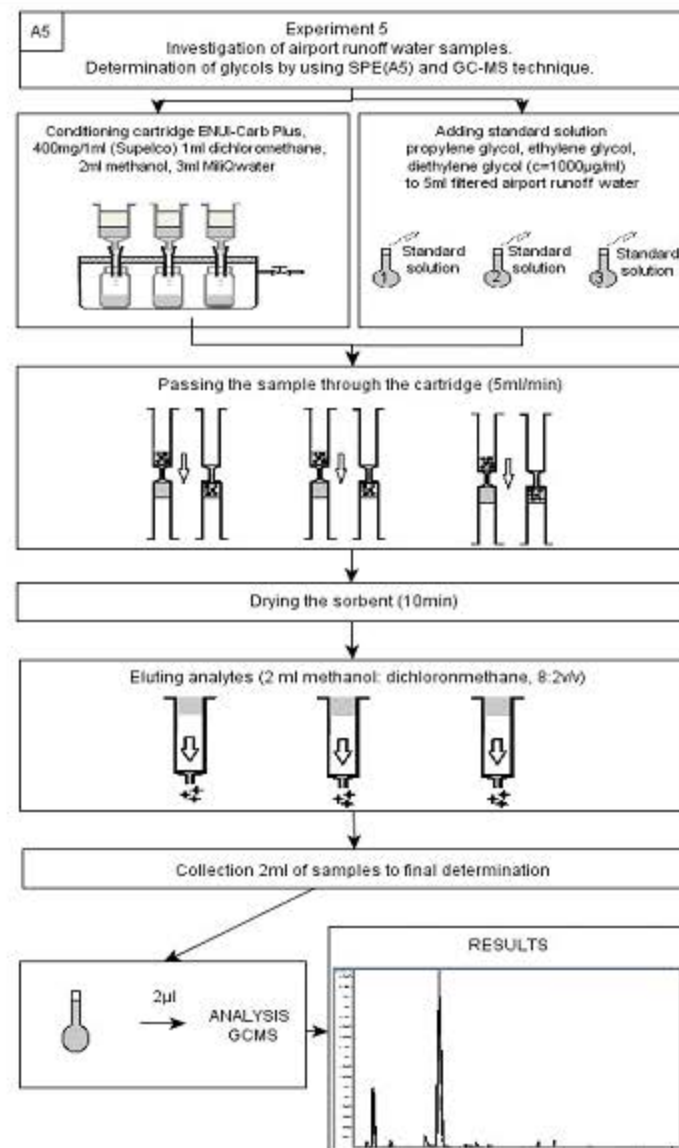
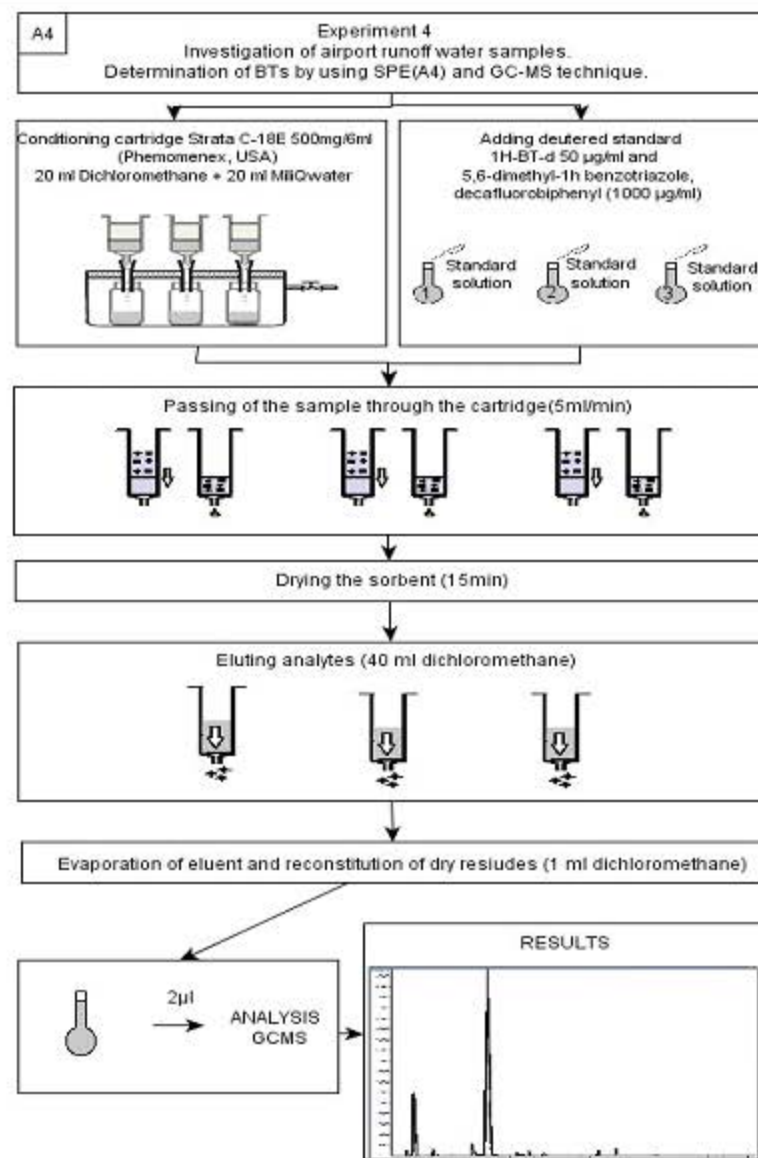


Figure 2
 Plot of sample scores of the first and second factor identified (Figure 2a), the first and third factor identified (Figure 2b), and the first and fourth factor identified (Figure 2c) by principal component analysis with varimax rotation

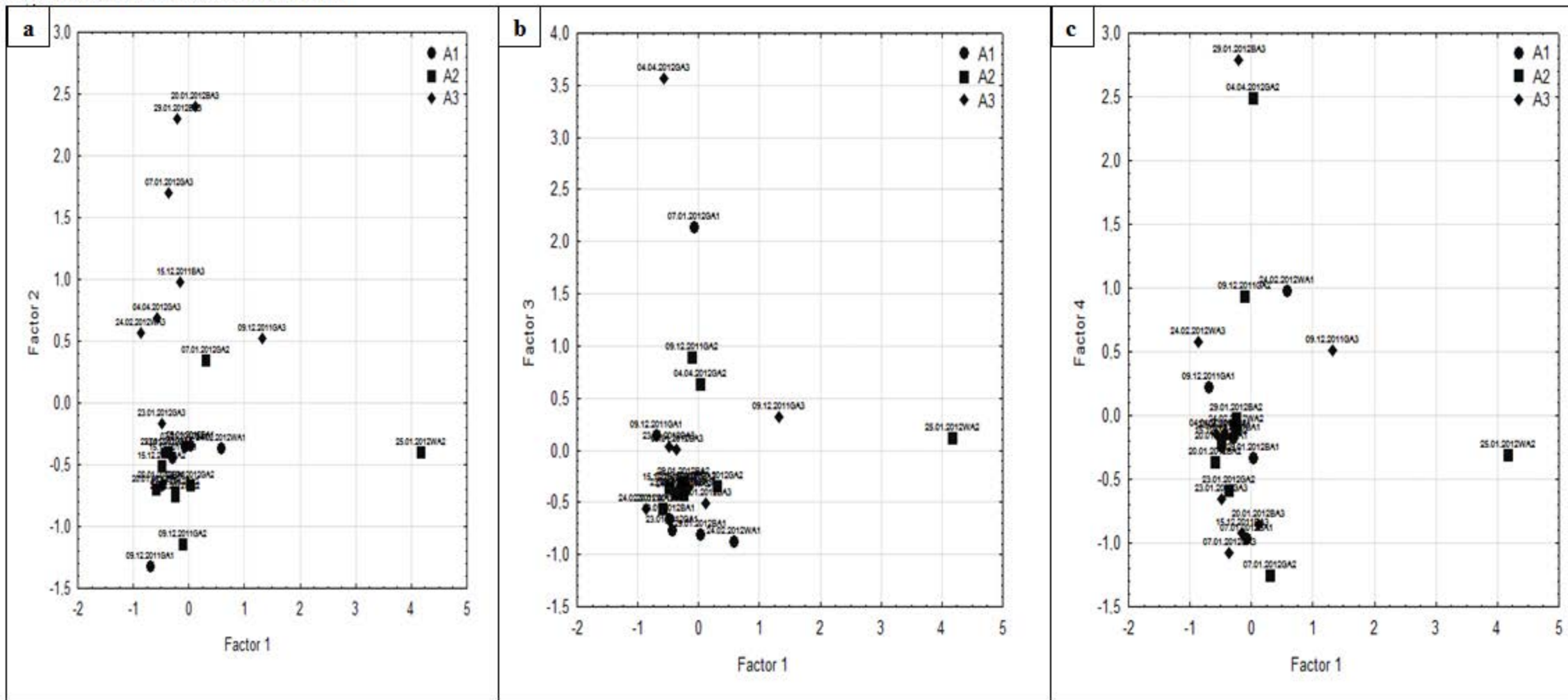


Figure 3
 Chromatograms obtained as a result of the analysis of the airport runoff water samples (samples were prepared by means of A1-A5 (LLE and SPE) techniques).

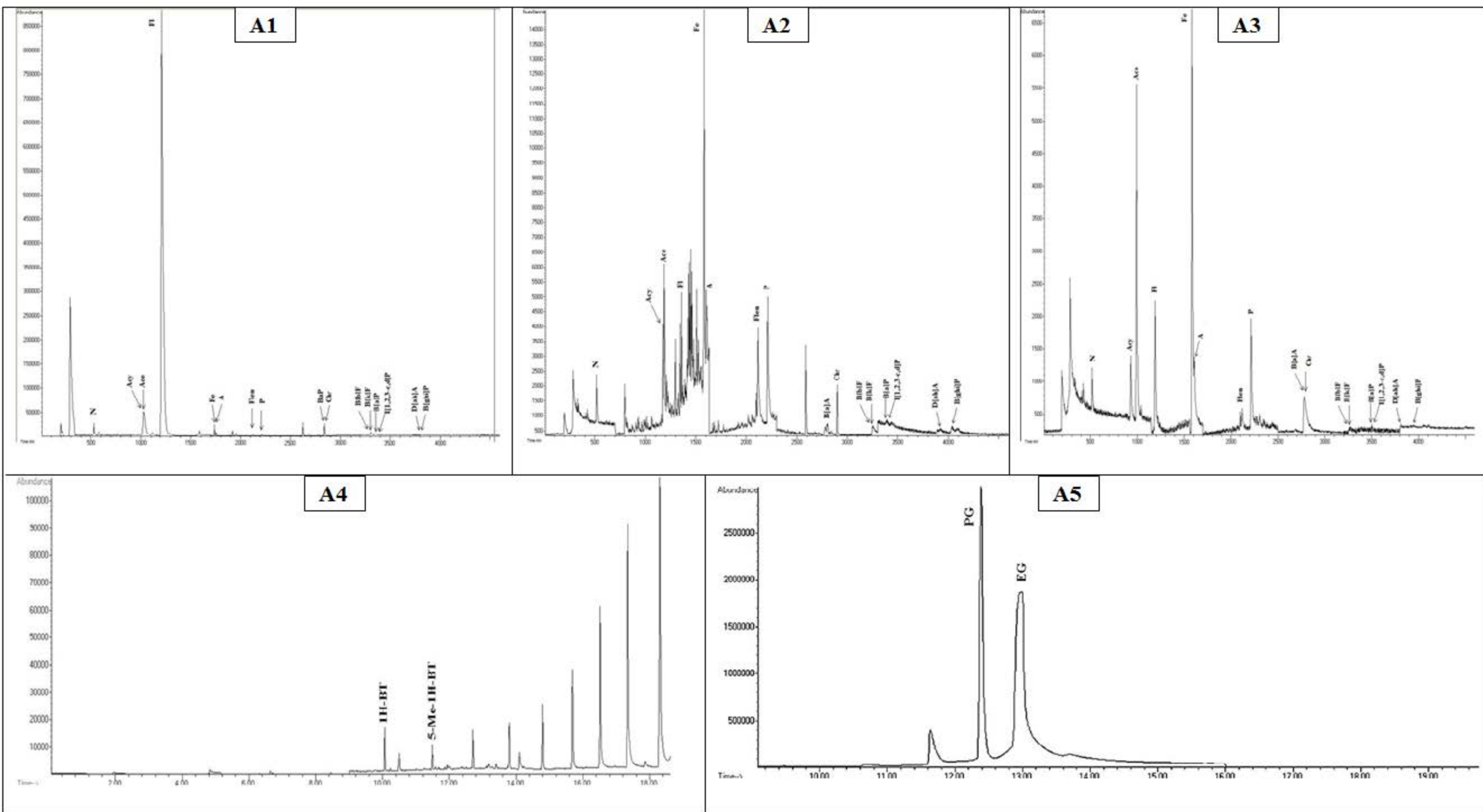


Figure 4
 PAH concentrations determined in runoff water samples collected in the area of airports (international airport PL and local airport PL).

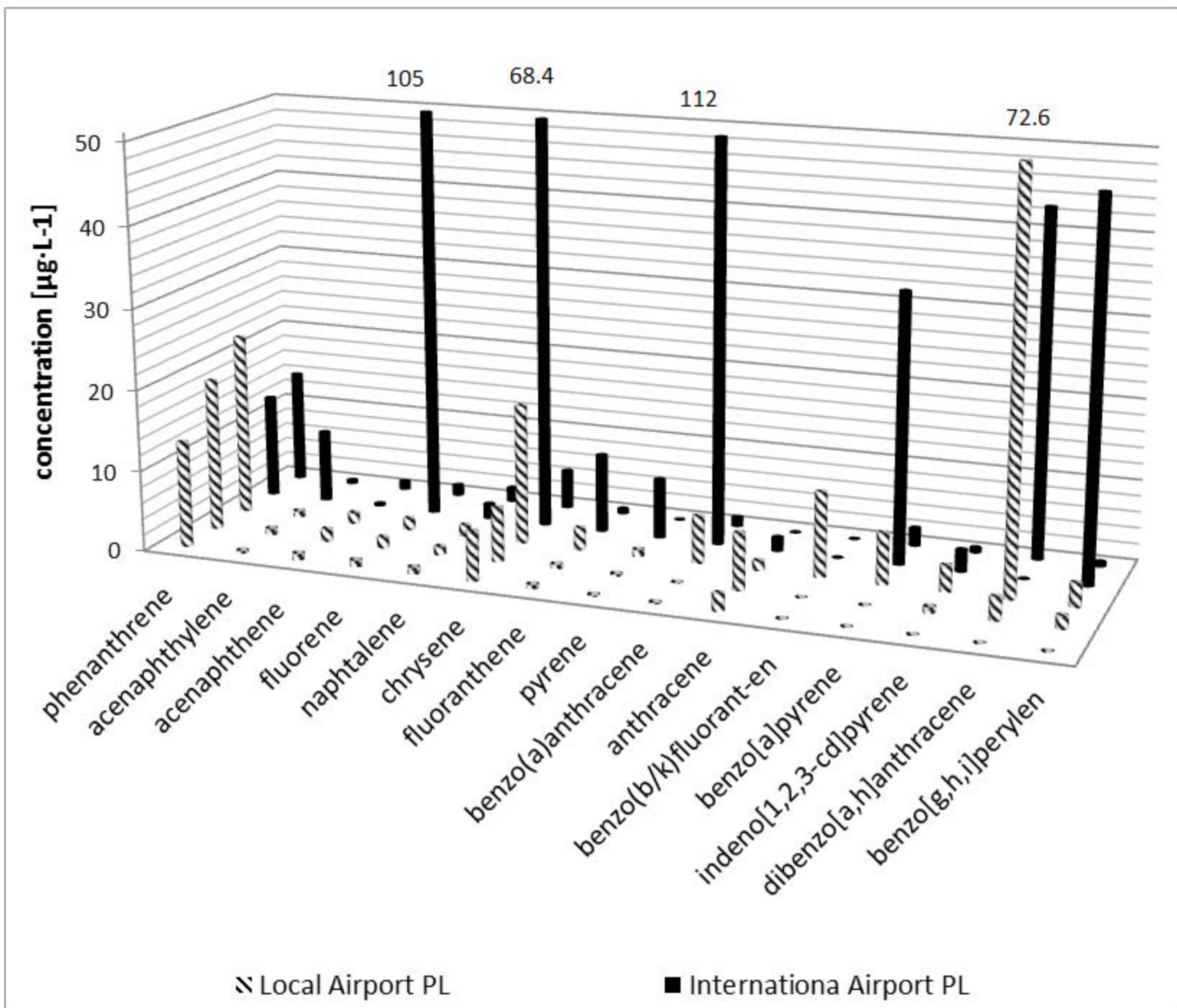


Figure 5

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).

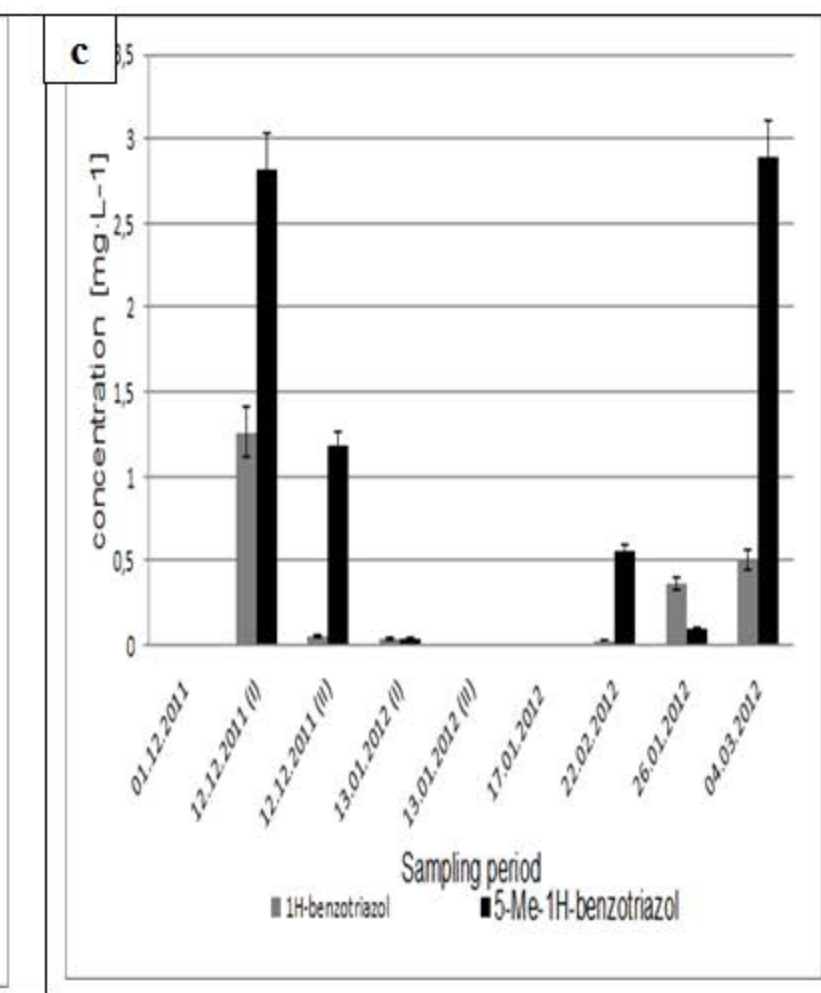
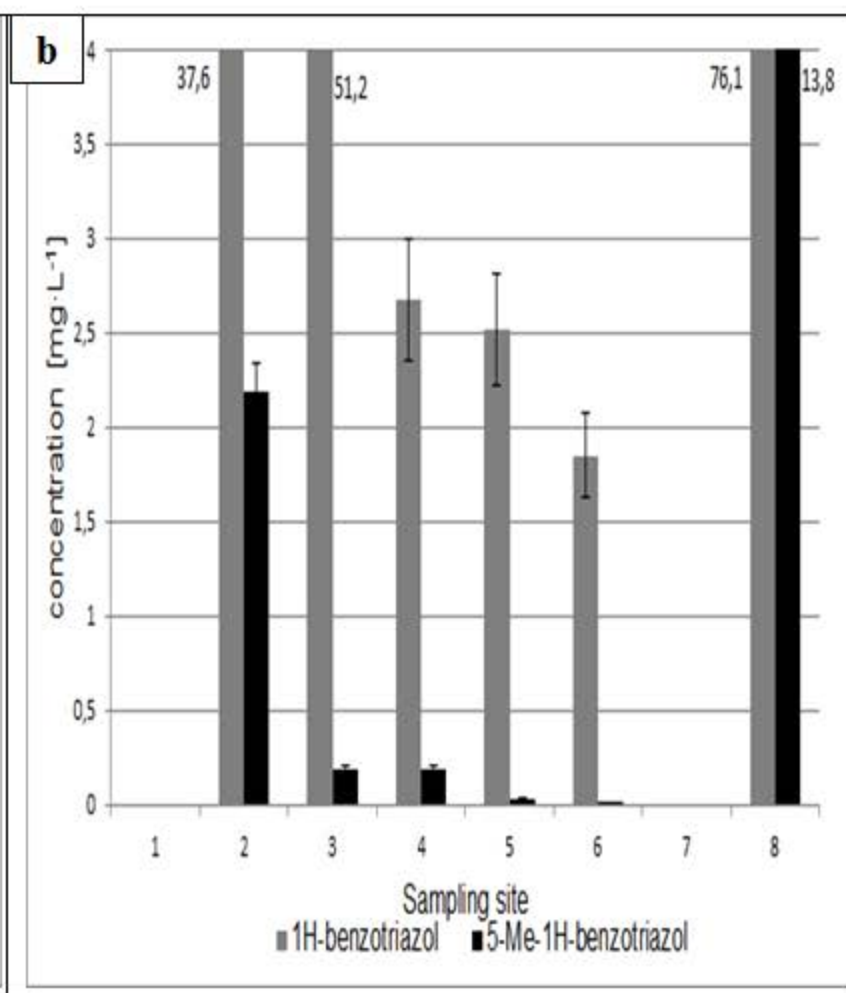
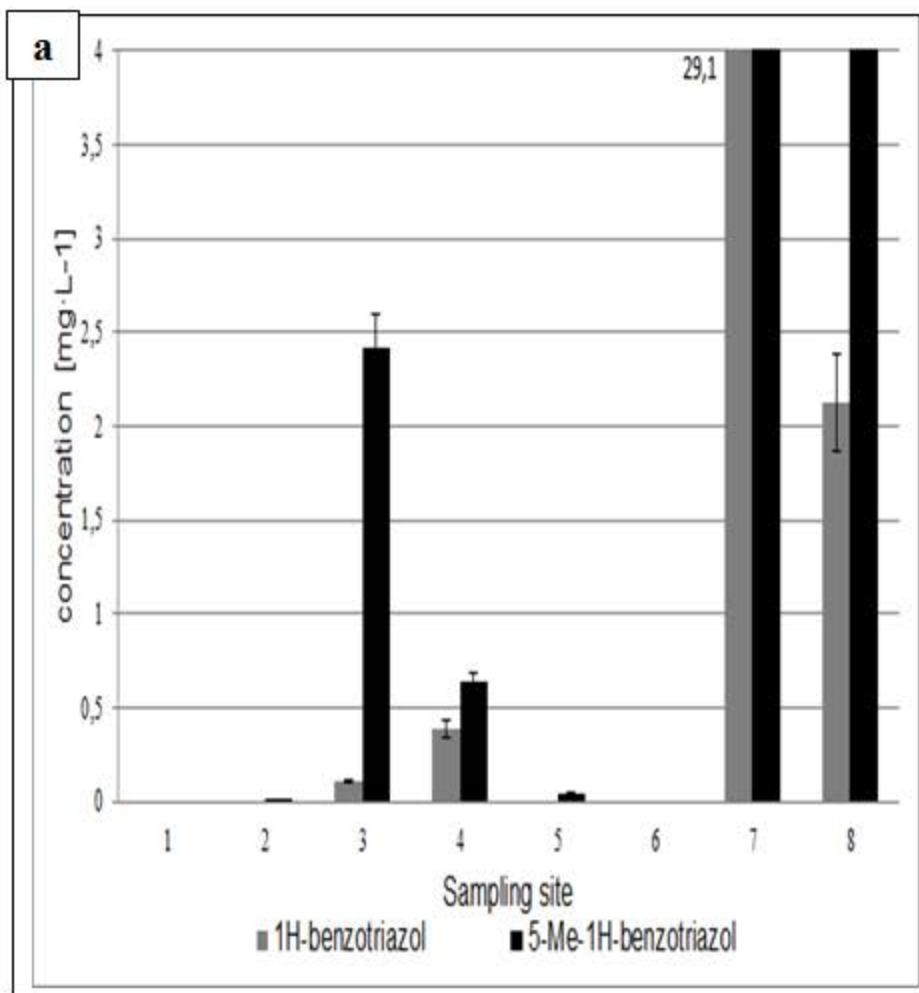


Figure 6

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).

