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Determination of fuel combustion product in airport runoff water samples using liquid–liquid extraction with gas chromatography–spectrometry

A. M. Sulej-Suchomska[1,2] · Ż. Polkowska[1] · A. Przyjazny[3] · Z. J. Kokot[2] · J. Namieśnik[1]

Abstract Determination of xenobiotics in samples of airport runoff water is both a complex and indispensable task due to an increasing threat resulting from the activities of numerous airports. The aim of this study was to develop, optimize, and validate a procedure based on liquid–liquid extraction (LLE) coupled with gas chromatography–mass spectrometry (GC–MS) for the determination of polycyclic aromatic hydrocarbons (PAHs). So far, no procedure was available that would ensure reliable data about concentration levels of these toxic pollutants in a new type of environmental samples, such as airport stormwater. The most difficult step in the analytical procedure used for the determination of fuel combustion products in airport stormwater samples is sample preparation. In this work, eight different protocols of sample preparation were tested. The evaluation of the LLE demonstrated that the best extraction conditions were as follows: dichloromethane (extraction solvent), solvent volume of 15 mL and sample volume of 250 mL. The percent recovery values ranged from 66 to 106 %, which shows that the LLE technique is a powerful method for extracting PAHs from airport runoff water samples with a complex matrix composition. Moreover, the developed procedure was characterized by satisfactory selectivity and a relatively low LOQ (0.17–0.52 μg/L). The procedure has been successfully applied to the analysis of stormwater samples collected from different sites at international airport in Poland. The procedure can thus be used as a tool for tracking the environmental fate of these compounds and for assessing the environmental effect of airports.

Keywords Airport stormwater · Runoff water · PAHs · Analytical procedures · LLE · GC–MS

Introduction

Airport runoff water (stormwater) can contain a wide variety of contaminants, such as polychlorinated biphenyls, benzotriazoles, glycols, metals, detergents, phenols, and formaldehyde at various concentration levels (Barash et al. 2000; Corsi et al. 2003, 2006; Luther 2007; Sulej-Suchomska et al. 2016; Sulej et al. 2012b, 2014; Transportation 2010). Among the identified contaminants are polycyclic aromatic hydrocarbons (PAHs), which constitute one of the most important and toxic components of samples of airport runoff water (Barash et al. 2000; Ray et al. 2008; Sulej et al. 2011b, 2012a, 2013; Yunker et al. 2002; Zhang et al. 2011). The content of PAHs in airport runoff water samples depends on various factors, including type and size of airport, capacities of passengers movement, geographical location of airports, meteorological conditions, and the presence of their own wastewater pretreatment and treatment plants. In general, most samples contain individual PAHs at levels up to 50 ng/L, but highly contaminated samples have concentrations of up to 6000 ng/L, while permissible levels of concentrations for the individual PAHs range from 100 to 400 ng/L according

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Springer

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to the available EPA standards and regulations for PAHs in drinking water (Prabhukumar and Pagilla 2010). Moreover, literature data reveal that approximately 4400 metric tons of PAHs are discharged from wastewater to the aquatic environment per annum as a result of human activity (Pazwash 2011; Prabhukumar and Pagilla 2010). Within airports, PAH analytes are emitted primarily during fuel combustion in airplane engines, and as a result of uncontrolled spillage of aviation fuel (during refuelling, fuel transportation, airplane repairs, and fuel storage), airplane tire wear and runways paved with bitumen (Fatoki et al. 2010; Grynkiewicz et al. 2002; Luther 2007; Prabhukumar and Pagilla 2010; Zhang et al. 2008a).

The determination of xenobiotics content in runoff water collected at the airport is a complex task due to a diverse and variable composition of the matrix, the presence of suspension, and interferents with similar physical–chemical properties but sometimes occurring at higher concentration levels than the analytes as well as the lack of reference materials necessary for quality assurance/quality control (QA/QC) (Barash et al. 2000; Reddy et al. 2013). Consequently, sample preparation step, involving mainly analyte isolation and enrichment, is an important step of analytical procedures for the determination of these analytes. This can be accomplished by the selection of an appropriate extraction technique. Selection of optimum extraction conditions has a decisive effect on the result of the entire analysis (Mechlińska et al. 2010; Sulej et al. 2013). Although the available literature provides first reports on this subject, the information contained therein does not allow full recognition of the impact of the problem, the development of an appropriate analytical procedure, and proposing the optimum remediation technologies (Barash et al. 2000; Breedveld et al. 2003; Latimer et al. 1990; Luther 2007; Zitomer 2001).

Few literature reports provide the data and information on the analysis of runoff water. So far, sample preparation procedures in the determination of PAHs in various types of runoff waters involved liquid–liquid extraction (LLE), solid phase extraction (SPE), and solid phase microextraction (SPME) (Garcia-Falcon et al. 2004; Lamprea and Ruban 2011; Zhang et al. 2008b), while gas chromatography–mass spectrometry (GC–MS) (Grynkiewicz et al. 2002; Zhang et al. 2008a) and high-performance liquid chromatography (HPLC) with UV/Vis or fluorescence detection (Barash et al. 2000; Brown and Peake 2006; Garcia-Falcon et al. 2004; Mahvi and Mardani 2005) were used for the final determination. The inspection of literature data available revealed the lack of appropriate procedures providing reliable information on the level of contamination by PAHs in new types of environmental samples—airport runoff water.

Liquid–liquid extraction is a common laboratory technique. In this case, mechanical shaking of samples results in easier penetration of the porous structure of organic matter present in airport runoff water by organic solvent molecules and the release of analytes adsorbed in it compared with other sample preparation methods (Rawa-Adkonis et al. 2006). Several important LLE conditions such as type of solvent, solvent volume, and sample volume should be evaluated to achieve the optimal procedure performance for the analysis of target analytes. The extraction solvent should be selective, insoluble in water and capable of dissolving (extracting) analytes. It should also be compatible with the final determination method (GC–MS), enabling direct on-column injection and ensuring rapid separation of mixtures (Zgoła-Grześkowiak 2010). The difference in densities of sample and extraction solvents is an important parameter affecting the effectiveness of separation of phases. Additional criteria for selection of the extraction solvent include relative volatility of the solvent and solutes (analytes), toxicity, flammability, and cost. Optimization of solvent and sample volumes is also an important step of method development. The amount of extracted analyte is directly proportional to the volume of organic solvent used; hence, an increase in solvent volume improves analyte recovery from the aqueous phase. If the solubility of analytes in the extraction solvent is high, even small volumes of the solvent are sufficient to extract the required amount of the analytes (Müller et al. 2008). As a result, solvent consumption and operational cost are decreased. Sample volume is another parameter that should be optimized to perform quantitative extraction and obtain appropriate recovery of the analytes from samples of runoff water while considering the fact that one trend in modern analytics is to determine smaller and smaller amounts of analytes in increasingly smaller sample volumes (Stepnowski et al. 2010).

Only common laboratory equipment is required in LLE; the technique is very simple, and analyte recovery is high in comparison with the techniques based on solid phase extraction (Wolska et al. 2005). The disadvantages of LLE include the use of large volumes of high-purity solvents, long time of extraction, and the possibility of formation of emulsions which are difficult to break (Konieczka et al. 2010; Pino et al. 2002). Despite these drawbacks, the International Organization for Standardization (ISO) recommends LLE in the standard procedure for the determination of PAHs (ISO17993:2002) (ISO 2002).

The aim of the present research is to demonstrate the feasibility of combining LLE and GC–MS for the determination of polycyclic aromatic hydrocarbons in new type of environmental samples, such as airport stormwater samples. LLE used for isolation/enrichment of PAHs from airport runoff water was optimized by studying the effect of solvent type, solvent volume, and sample volume. The developed and validated procedure was successfully used for the determination of PAHs in runoff water samples collected from the sites at a Polish international airport.

Materials and methods

Chemicals and materials

Deuterated aromatic compounds (naphthalene-d8, benzo(a)anthracene-d12) and standard mixtures of 16 PAHs [naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Ph), anthracene (An), fluoranthene (Flt), pyrene (Py), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(a)anthracene (BaA), indeno(1,2,3-cd)pyrene (InPy), dibenz(a,h)anthracene (DBahA), benzo(g,h,i)perylene (BghiP)] at a concentration of 2000 µg/mL in dichloromethane from Supelco (Bellefonte, PA, USA) and Restek Corporation (Bellefonte, PA, USA), respectively, were used as internal standards and analytes. Stock solutions of 16 PAHs and an internal standard were prepared in methanol for each compound. All solutions were stored in the dark at 4 °C. Working solutions were prepared daily by appropriate dilution of stock solutions. Deionized water was obtained from Milli-Q water purification system (Millipore, Bedford, MA, USA). Dichloromethane (DCM) and methanol used for sample processing and analyses were GC-pure quality and were purchased from Merck (Darmstadt, Germany). Nitrogen (purity 99.99 %) was supplied by Oxygen (Gdansk, Poland). Glass bottles used to prepare model solutions were from Labart, Poland, and Perlan Technologies (Poland). The glassware used in this study was washed with a detergent and with distilled water followed by placing them in a cleaning solution overnight to remove trace amounts of interferences from the surface of vials. The glassware was then rinsed successively with MilliQ water, methanol, acetone, and hexane. The bottles were dried at 150° C for 4 h.

Sample collection

Stormwater samples were collected during or shortly after the rainfall from the sites at an international airport in Poland. The samples were collected from the areas of the airport during the period from fall 2011 to spring 2012. The runoff samples were collected from places in which runoff water was laying on lower ground (depressions in the terrain). The sites of sample collection were located where the most maintenance work was carried out: the vicinity of an airport terminal, de-icing area, machinery storage area, parking places, runway, the periphery of an airport, and the car park. Airport stormwater samples were collected in 1000-mL bottles of dark glass using a syringe (100 mL) with Teflon tubes. Samples were transported to the laboratory (within 0.5 h after collection). Bottles were stored at 4 °C in the dark until extraction.

Determination of PAHs

The key step in the analytical procedure used for the detection, identification and determination of PAH analytes in samples of this kind is sample preparation (Płotka et al. 2013; Sulej et al. 2011a). Application of various extraction techniques to prepare samples of airport runoff water for the determination of PAHs can affect the final result (Abolfazl Saleh et al. 2009; Ozcan et al. 2010; Sulej et al. 2013). This research made use of liquid–liquid extraction (LLE) to isolate/enrich analytes. Mechanical agitation used in this technique causes easier penetration of molecules of an organic solvent into the porous structure of organic matter present in airport runoff water and better release of the analytes adsorbed inside it.

Optimization of the extraction process is intended to effectively remove interferences, improve detection limits, and facilitate analyte separation during chromatographic analysis. An important role is played by the extraction solvent, which should be immiscible with water and have a density different from water. In addition, it should have a high affinity for target analytes and an excellent gas chromatographic behaviour (Ozcan et al. 2010). Considering these factors, the investigated solvents differ mostly with respect to boiling point, polarity and elution strength. In order to prepare samples for the determination of PAH analytes, different variants of liquid–liquid extraction techniques (L1–L8) were used (Fig. 1). The optimized LLE procedure was tested on samples of the airport runoff

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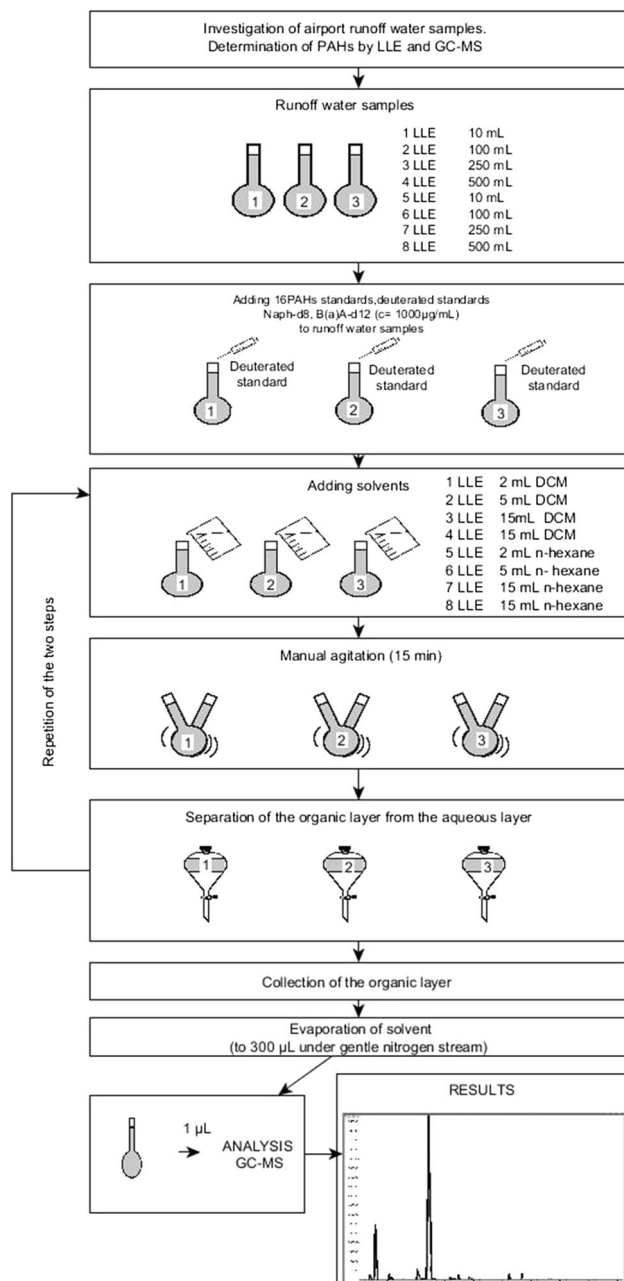
Fig. 1 Schematic diagram of the analytical procedure for PAHs determination using LLE and GC–MS system

water spiked with an appropriate amount of a mixture of 16 PAHs and deuterated standards (naphthalene-d8, benzo(a)anthracene-d12). The following parameters were optimized in the LLE procedure of determination of PAHs in airport runoff water:

- Kind of solvent (hexane, dichloromethane),
- Solvent volume (2–15 mL),
- Sample volume (10–500 mL).

All analyses were carried out in triplicate. The final extracts were analyzed by gas chromatography coupled with MS. The operating conditions of GC–MS were optimized in order to separate PAH analytes with high resolution in the minimum time. The optimized GC–MS conditions are compiled in Table 1. Identification and quantitation of the analytes were carried out by the internal standard method using appropriate standard solutions of PAHs and deuterated standards. Ions monitored for quantitation and confirmation of the presence of PAHs and the corresponding retention time of each peak are given in Table 3.

Data analysis

Analysis of variance (ANOVA) was used as a procedure for assigning sample variance to different sources and deciding whether the variation arises within or among different population groups. Samples were described in terms of variation around group means and variation of group means around an overall mean. In this case, one-way analysis of variance was performed to test differences between the mean values of each of the investigated protocols (L1–L8) used for the determination of PAHs in airport runoff water. If variations within groups are small relative to variations between groups, a difference in group means may be inferred. Hypothesis tests were used to quantify decisions.

The ANOVA results presented in Sect. 3.1.3 show the between-group variation (extraction methods) and within-group variation (error). SS is the sum of squares, and df is the degree of freedom. The total degree of freedom is the total number of observations minus one. The between-group degree of freedom is the number of groups minus one. The within-group degree of freedom is the total degree of freedom minus the between-group degree of freedom. MS is the mean-squared error, which is SS/df for each source of variation.

The F statistic is the ratio of the mean-squared errors. The p value is the probability that the test statistic can take a value greater than or equal to the value of the test statistic. The small p value indicates that differences between column means are significant. ANOVA returns box plots of the observations in y, by group. Additionally, "Box plots" were presented to provide a visual comparison

Table 1 Operating conditions of GC–MS analysis of PAHs extracts

Conditions of the analysis	
Sample preparation technique	LLE
Final determination method	GC–EI–MS
Gas chromatograph	Agilent 7980A
Detector	Agilent 5975C
Detector working mode	Selected ion monitoring (SIM)
Ionization source temperature	230 °C
Quadrupole temperature	150 °C
Electron beam energy	70 eV
Chromatographic column	ZB-5MS; 30 m × 0.25 mm; 0.25 μm film thickness
Stationary phase	5/95 phenyl/polydimethylsiloxane
Type of carrier gas	Helium
Carrier gas pressure	7.07 psi
Carrier gas flow rate	1 mL/min
Injection port temperature	295 °C
Interface temperature	295 °C
Injection mode	Splitless
Temperature program	40–120 °C (40 °C/min); 120–280 °C (5 °C/min)
Injection volume	1 μL
Analysis time	46 min
Number of analytes	16

of the group location parameters. On each box, the central mark is the median and the edges of the box are the 25th and 75th percentiles (1st and 3rd quantiles). The whiskers extend to the most extreme data points that are not considered outliers. The outliers are plotted individually. The interval endpoints are the extremes of the notches. The extremes correspond to $q2 - 1.57(q3 - q1)/\sqrt{n}$ and $q2 + 1.57(q3 - q1)/\sqrt{n}$, where q2 is the median (50th percentile), q1 and q3 are the 25th and 75th percentiles, respectively, and n is the number of observations without any NaN (not a number). Two medians are significantly different at the 5 % significance level if their intervals do not overlap. This test is different from the F test that ANOVA performs, but large differences in the center lines of the boxes correspond to large F statistic values and correspondingly small p values (Hogg and Ledolter 1987).

Analysis of variance compares the means of several groups to test the hypothesis that they are all equal, against the general alternative that they are not all equal. Sometimes this alternative may be too general. Therefore, multiple comparison tests were performed and presented in the graph form. Multiple comparison procedures are commonly used in an analysis of variance after obtaining a significant omnibus test result, like the ANOVA F test. The significant ANOVA result suggests rejecting the global null hypothesis H0 that the means are the same across the groups being compared. Multiple comparison procedures are designed to provide an upper bound on the probability that any comparison will be incorrectly found significant. Errors in inference, including confidence intervals that fail to include their corresponding population parameters or hypothesis tests that incorrectly reject the null hypothesis, are more likely to occur when one considers the set as a whole. In this case, we are using the Bonferroni multi-comparison test (Hochberg and Tamhane 1987).

All statistical calculations were performed using MATLAB 2013a, version 8.1.0.604.

Results and discussion

Optimization of LLE technique

Selection of solvent

Preliminary investigations were carried out using model solutions of 16 PAHs and isotopically labeled standards prepared in an environmental sample resembling a complex composition of the airport wastewater matrix. A comparison of the results of extraction of PAHs by the two

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(a)

(b)
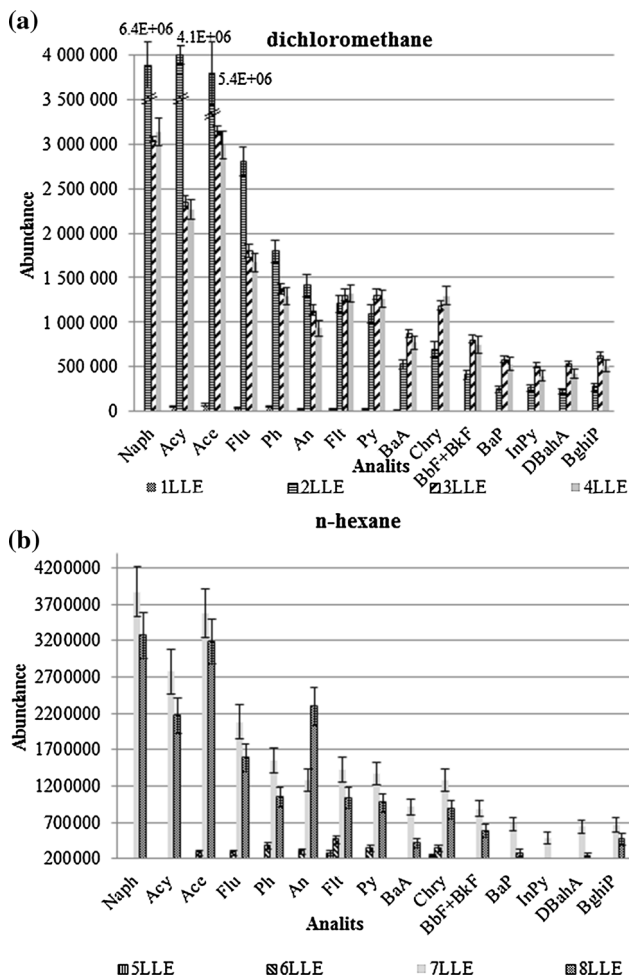
Fig. 2 Comparison of extraction efficiency of 16 PAHs in eight different variants of LLE technique using dichloromethane (**a**) and *n*-hexane (**b**) as the extraction solvents. The *error bars* were taken as the relative standard deviation of three measurements

solvents is shown in Fig. 2. The extraction efficiencies of PAHs by using extraction variants L1–L4 which utilized dichloromethane as a solvent (Fig. 2a) are generally higher in comparison with extraction variants L5–L8 which made use of *n*-hexane (Fig. 2b). The results suggest that the best solvent for the isolation of PAHs is dichloromethane. This solvent is characterized by higher polarity and therefore has higher elution strength. Consequently, it can effectively extract PAHs from aqueous matrices. The additional comparison between investigated type of solvent was performed by applying ANOVA. The data obtained in the application of ANOVA indicated that there is statistically significant difference between means of abundance of individual compounds. The results of statistical analysis confirmed that the type of solvent has an effect on the procedure.

(a)

(b)

(c)
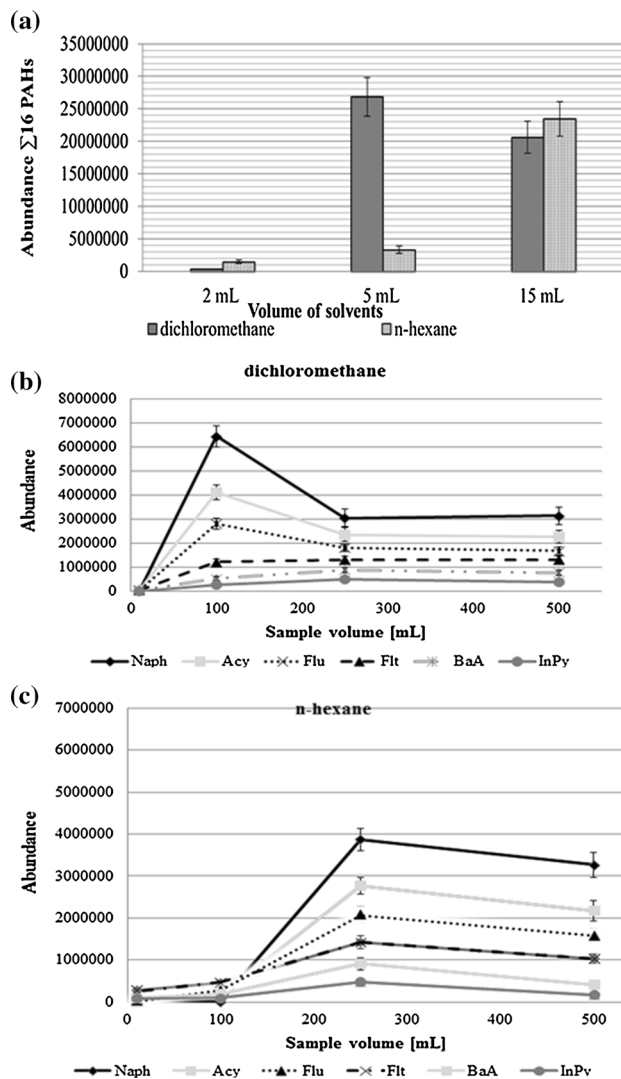
Fig. 3 Effect of mean solvent volume on total peak area of 16 PAHs (**a**) and sample volume on peak area of PAHs extracted with dichloromethane (**b**) and *n*-hexane (**c**). The *error bars* were taken as the relative standard deviation of three measurements

Effect of solvent and sample volume

The next step of the LLE optimization investigations involved studies of the effect of extraction solvent volume on the PAH recovery in model samples. Samples of stormwater fortified with a stock solution of 16 PAHs, including isotopically labeled standards were extracted using 2–15 mL of each solvent. When 15 mL of the solvent was used, the extraction was performed in three steps using 5-mL aliquots during each step. It follows from our previous work that a three-step extraction allows the recovery of 98 % of the analytes. The effect of extraction
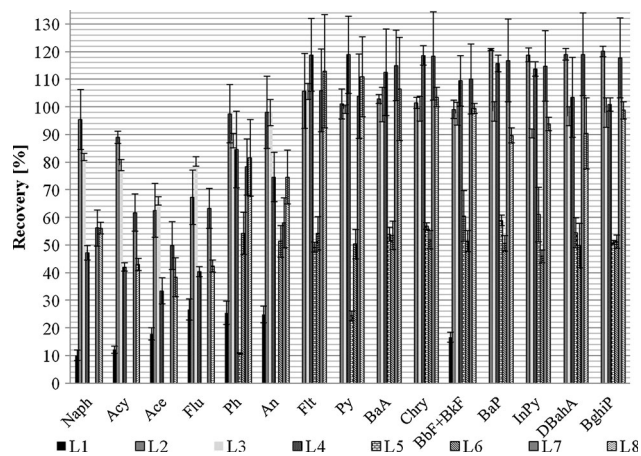
Fig. 4 Average recoveries of PAHs from extracts of model solutions obtained with eight variants of LLE. The *error bars* were taken as the relative standard deviation of three measurements

solvent volume on total peak area of the 16 PAHs is illustrated in Fig. 3a. Inspection of the experimental data reveals that the optimum extraction volumes for dichloromethane and *n*-hexane are 5 and 15 mL, respectively.

To obtain reliable analytical results and, at the same time, to reduce the required volume of samples collected from the airport area, four different sample volumes (10, 100, 250, and 500 mL) were examined. The experimental results reveal that the optimum sample volumes are 100 and 250 mL when using dichloromethane and *n*-hexane, respectively (Fig. 3b, c).

Recovery of PAHs by LLE

Recovery is a very important quality characteristic of LLE. The recoveries of PAH analytes depend primarily on the type of solvent, sample volume, and extraction solvent volume. The results of determination of PAH content in the investigated samples obtained using eight different variants of LLE technique are shown in Fig. 4. A comparison of the efficiency of all the examined variants of LLE reveals that the highest average recovery 66.0–106 % (where RSD was lower than 6.1 % for all the tested compounds) was obtained when variant L3 of LLE was used. When variant L7 of LLE was adapted to analysis of PAHs, in which sample and solvent volumes were the same as in variant L3, except for the type of solvent, the average analyte recovery was lower by about 10 % (49.9–118.9 %) than in case of L3. Relatively high average recoveries were also observed for extraction variant L2 of LLE. The experimental data and their interpretation allow the selection of optimum conditions of LLE prior to the determination of PAHs. Recoveries as high as 66.0–106 % and good reproducibility of the results (1.3–6.1 % RSD) are possible along with a good separation of chromatographic peaks.

The amount of solvent used (per one analytical cycle) was also reduced in accordance with principles of green analytical chemistry.

Moreover, by applying ANOVA, it was possible to compare the means of eight different sample preparation protocols and verify the significance ($p < 0.05$) of the experimental data. The obtained small p value (8.21476E−08) indicates that differences between means of eight investigated methods for the determination of PAHs are statistically significant (Fig. 5a). Box plot in Fig. 5a showed the results of ANOVA with kind of protocols as a treatment. The results obtained reveal that methods L2, L3, L4, L7, and L8 have a similar value of median. Furthermore, method L2 indicates significantly higher extremes of the notches spread. In case of method L4 and L7, the occurrence of an outlier was also observed. In addition, the performed multiple comparison test proved that the differences in means of the above-mentioned protocols (L2, L3, L4, L7 and L8) are insignificant statistically (Fig. 5b). Therefore, a second multiple comparison test was carried out with the recovery as an input data (Fig. 5c). The performed test proved that among the investigated protocols only the means of procedure L3 was significant statistically. As a result of the analysis, protocol L3 was selected as the optimal procedure for the determination of PAHs in airport runoff water samples.

Based on the results of an additional ANOVA test, it can also be noticed that the choice of a proper variant of analytical protocol (L1–L8) is particularly important in case of determination of naphthalene, acenaphthylene, and acenaphthene (Fig. 5d), while the choice of an analytical protocol had the smallest impact on compounds such as benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene, when we take into consideration the range of the extremes of the notches.

In this study, eight different versions of sample preparation using liquid–liquid extraction technique were tested. A summary of the results of optimization of the LLE procedure is compiled in Table 2. Inspection of the data in Table 2 and performed statistical analysis reveals that the optimum extraction procedure for the determination of PAHs in airport runoff water is L3-solvent: dichloromethane, solvent volume: 15 mL, sample volume: 250 mL, and agitation time: 15 min. A typical chromatogram of the extract from a sample of airport runoff water by variant L3 of the LLE procedure is shown in Fig. 6.

Analytical performance

After the optimization tests, the methodology for the determination of fuel combustion products in the airport stormwater samples was validated to ensure an appropriate

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(a)

(b)

(c)

(d)
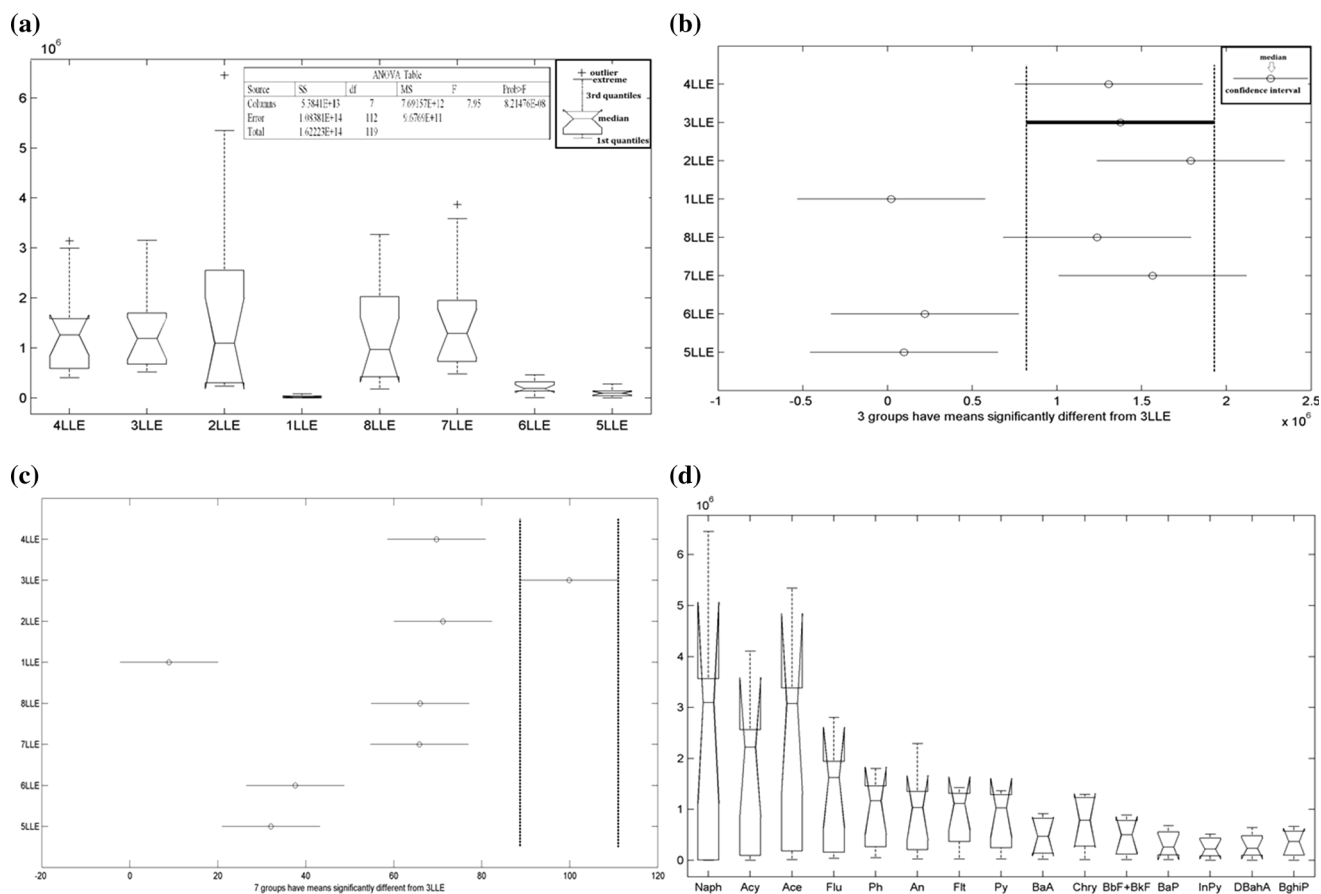
Fig. 5 ANOVA results for indicating differences between means of investigated protocols with kind of protocols as a treatment and peak areas *box plot* of protocols as a treatment (**a**), multiple comparison test of protocols for peak area (**b**), multiple comparison test of protocols for recovery data (**c**) and peaks area *box plot* of compounds as a treatment (**d**)

level of control and quality of the results obtained. Validation process was carried out by establishing the limit of detection (LOD), limit of quantification (LOQ), linearity, range, accuracy, intra-day (within-run) and inter-day (between-run) precision. The values of validation parameters of the optimized analytical procedure are summarized in Table 3. Calibration curves were prepared using five standard solutions with increasing concentrations (1.0, 25, 50, 75, and 100 µg/L) for individual PAHs. Linear calibration curves were obtained by plotting the peak area against the concentration of the respective standards. Each sample was analyzed in triplicate. Calibrations showed good linearity as indicated by the values of coefficients of determination (R^2). On the basis of the calibration curves, it was possible to determine concentration levels of analytes in real samples. Limits of detection were calculated using the equation LOD = 3.3 SD/b (b is the slope of the calibration curve and SD is the standard deviation of the curve). LODs were determined for PAHs in control

samples based on three replicates of the analysis. The LODs for PAH analytes ranged from 0.055 to 0.16 µg/L. The limit of quantification was set to three times the LOD value. During the analysis of samples, procedure blanks were prepared for every five samples to check the instrument background. Duplicate samples and calibration check standards were run after every five samples to assure the precision of each run. The precision of the developed methodology was expressed as the coefficient of variation (CV) calculated for five replicates ($n = 5$) according to the following equation CV = SD/$\overline{X}$ × 100 % (SD is the standard deviation of the peak area and $\overline{X}$ is the average area of the chromatographic peak). Precision was subdivided into intra-day and inter-day precision. The intra-day precision was obtained by preparing all samples individually three times and then analyzing them in a single batch during 1 day, while the inter-day precision was evaluated by preparation and analysis of quality control samples in triplicate on separate days over a period of 5 days. An

Table 2 Comparison of the LLE procedures for analysis of PAH compounds

| Techniques	Recovery (%)	RSD (%)	Peak area $\sum$PAHs-S*	Peak area $\sum$PAHs-R**	Separation of PAHs-S	Separation of PAHs-R	Advantages	Disadvantages
L1	10.0–26.6	11.0–17.2	3.29E+05	6.30E+05	−	+	Very small solvent volume required (2 mL)	Low effectiveness of analyte extraction from standard solutions (4 PAH compounds <LOQ)
							Very small sample volume required (10 mL)	Low effectiveness of analyte extraction from real samples (7 PAH compounds <LOD)
								High noise level on a chromatogram of real samples
								Low recoveries
								Insufficient repeatability
L2	62.5–121	1.9–16.2	2.68E+07	1.20E+04	+	−	Small solvent volume required (5 mL)	Insufficient repeatability
							Small sample volume required (100 mL)	Low effectiveness of analyte extraction from real samples (determination of 3 PAHs)
							High recoveries	
							Very good peak resolution on chromatogram (for both standard and real sample solutions)	
L3	66.0–106	1.3–6.10	2.06E+07	2.50E+07	+	+	High recoveries	Large solvent volume required (15 mL)
							Very good repeatability	Large sample volume required (250 mL)
							Best peak resolution on chromatogram (for both standard and real sample solutions)	
L4	33.4–119	2.3–18.9	1.96E+07	8.30E+05	+	+	High recoveries	Large solvent volume required (15 mL)
							Very good peak resolution on chromatogram (for both standard and real sample solutions)	Large sample volume required (500 mL)
								Insufficient repeatability
L5	10.8–61.0	1.5–16.2	1.46E+06	8.09E+04	±	±	Very small solvent volume required (2 mL)	Low recoveries
							Very small sample volume required (10 mL)	Napht, Ace LOQ (analysis of standard solutions)
							Relatively good repeatability	Low effectiveness of analyte extraction from real samples (7 PAH compounds <LOD)
								High noise level on a chromatogram of real samples

Table 2 continued

| Techniques	Recovery (%)	RSD (%)	Peak area $\sum$PAHs-S*	Peak area $\sum$PAHs-R**	Separation of PAHs-S	Separation of PAHs-R	Advantages	Disadvantages
L6	45.9–54.2	4.8–14.1	3.31E+06	9.27E+04	±	±	Small solvent volume required (5 mL) Small sample volume required (100 mL)	Low recoveries Insufficient repeatability Naphthalene <LOQ (chromatogram of standard solutions) Low effectiveness of analyte extraction from real samples (7 PAH compounds <LOD)
L7	49.8–119	11.2–17.2	2.34E+07	9.48E+05	+	+	High recoveries Very good peak resolution on chromatogram (for both standard and real sample solutions)	Large solvent volume required (15 mL) Large sample volume required (250 mL) Insufficient repeatability
L8	38.4–112.8	1.90–18.2	1.85E+07	7.20E+05	+	±	Relatively high recoveries	Large solvent volume required (15 mL) Large sample volume required (500 mL) Insufficient repeatability High noise level on a chromatogram of real samples

S*—Standard solutions, R**—real samples

Fig. 6 Chromatogram of airport runoff water spiked with Naph-d8 and BaA-d12 using variant L3 of LLE during the sample preparation step. *1* Naph + Naph-8d; *2* Acy; *3* Ace; *4* Flu; *5* Ph; *6* An; *7* Flt; *8* Py; *9* BaA + BaA-d12; *10* Chry; *11* BbF + BkF; *12* BaP; *13* InPy; *14* DBahA; *15* BghiP
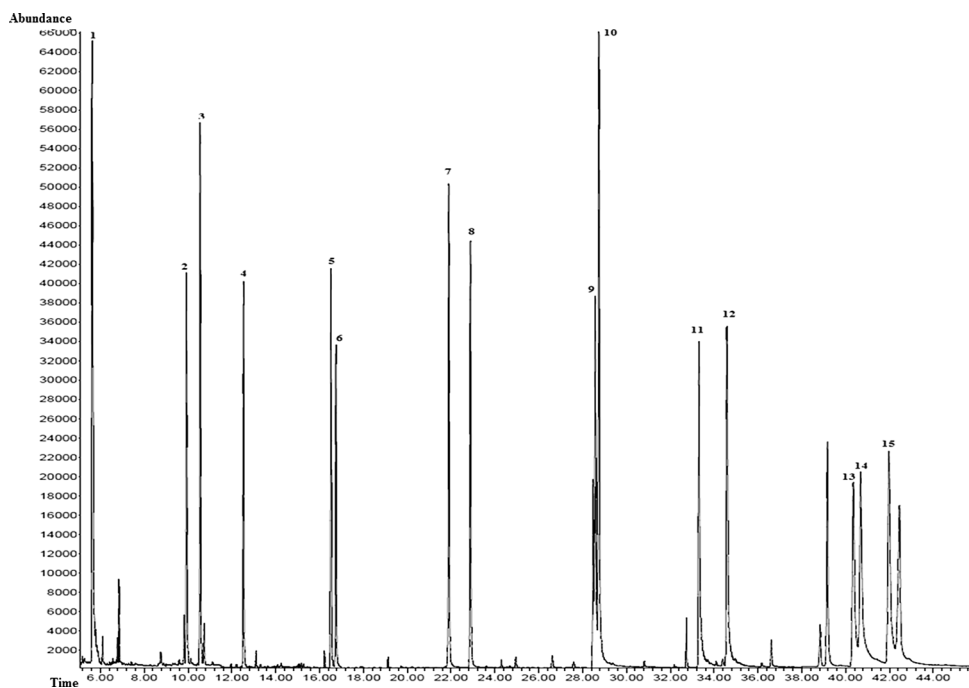
Table 3 Analytical characteristics of the developed procedure

No.	Analytes	Diagnostic ions (m/z)		Retention time (min)	Range (µg/L)	Coefficients of calibration curve (y = ax + b)[a]		R^2	LOD (µg/L)	LOQ (µg/L)	Inter-day precision (%)
						a	b				
1	Naph	127	128	5.7	1.0–100	24,737	27,873	0.994	0.071	0.214	0.721
2	Acy	151	152	9.9		20,068	73,861	0.989	0.095	0.284	4.21
3	Ace	153	154	10.5		31,927	104,532	0.990	0.090	0.269	8.25
4	Flu	165	166	12.5		15,044	52,563	0.990	0.089	0.267	6.40
5	Ph	176	178	16.5		5421	−12,910	0.996	0.055	0.166	1.31
6	An	176	178	16.7		4260	73,586	0.995	0.063	0.189	0.94
7	Flt	202	203	21.9		2585	−30,927	0.980	0.124	0.371	1.22
8	Py	202	203	22.8		2433	−7398	0.987	0.100	0.301	4.73
9	BaA	226	228	28.6		750	−11,512	0.981	0.155	0.464	0.831
10	Chry	226	228	28.7		809	−5223	0.983	0.113	0.339	0.530
11	BbF + BkF	250	252	33.3		347	−3784	0.981	0.120	0.36	1.82
12	BaP	250	252	34.5		274	−4377	0.98	0.172	0.516	1.05
13	InPy	276	277	40.3		247	−2624	0.976	0.135	0.404	4.37
14	DBahA	278	279	40.7		337	−4911	0.977	0.150	0.45	2.81
15	BghiP	276	277	41.9		310	−4455	0.975	0.164	0.491	3.22

[a] $n = 15$; five levels in the range analyzed in triplicate
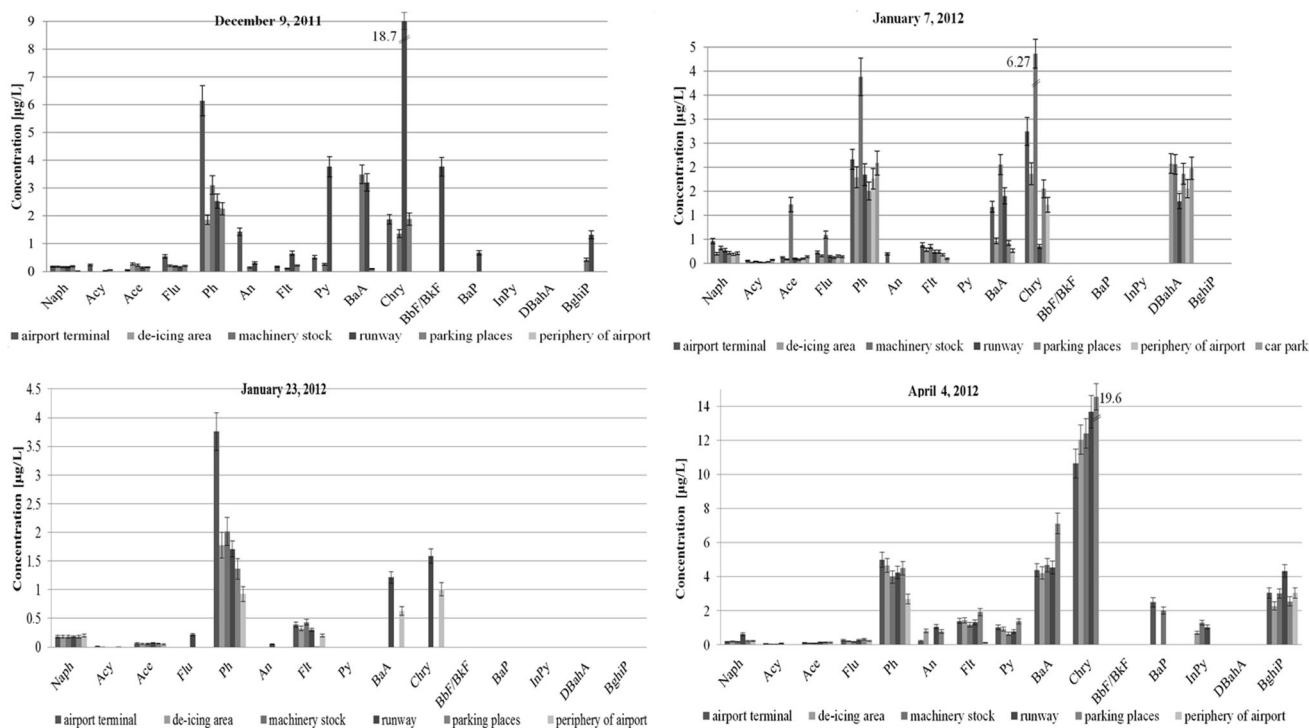
Fig. 7 Concentration levels of individual PAHs determined in runoff water samples collected from the areas of an international airport in Poland. The *error bars* were taken as the relative standard deviation of three measurements

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acceptance limit of $\leq 15\%$ was applied for all quality control (QC) samples. The values of the intra-day precision for stormwater samples were between 0.44 and 7.12 %, while the values of inter-assay precision ranged from 0.530 to 8.25 %. Accuracy studies were performed by analyzing stormwater samples containing low, medium and high concentration levels of PAHs. The recovery values calculated for all concentrations of PAHs met the requirements for the analytical procedures, wherein the recovery should range from 70 to 120 % depending on matrix complexity (Chmiel et al. 2014). The obtained recoveries indicate the suitability of LLE technique for efficient extraction of PAHs from airport runoff water samples. The obtained results are generally better in comparison with those reported from our previous study, where also the LLE/GC–MS procedure was applied to determine PAH in stormwater (Sulej et al. 2013). The results of recovery experiments by means of the developed procedure were higher in comparison with the recoveries achieved by using the previous LLE/GC–MS procedure (60–80 %) for the determination of PAHs. The developed procedure is characterized by a significantly higher precision relative to precision determined by the previous LLE/GC–MS method (RSD = 6–12 %). In addition, in the developed procedure the required volume of sample was significantly reduced from 500 mL to a final volume of 250 mL. Moreover, the time of manual agitation was reduced by a factor of two.

Application to real samples

In samples collected at the sites of a Polish international airport, which are the subject of this work, fuel spills and fuel combustion products were detected and analyzed. An example of concentration levels of individual PAHs determined in stormwater collected at the airport is shown in Fig. 7. Inspection of the data obtained reveals that the PAH analytes were present at relatively high concentration levels in samples of airport runoff waters. Generally, the levels of 16 PAHs in the samples collected from the Polish international airport were in the range of 19.4 ± 1.4 to 164.0 ± 7.5 µg/L.

Conclusion

The paper describes a new, complete analytical procedure, which is based on LLE and GC–MS for the determination of PAHs present in the airport stormwater samples. The results from this study indicate that the developed LLE method could be effectively used as a sample preparation technique for the determination of EPA 16 PAHs in airport runoff waters. The developed procedure is precise, accurate, relatively rapid, inexpensive, and easy for the analyses

of airport sludge. It also requires relatively small volumes of the extraction solvent and the sample and additionally reduces the labor and time intensity compared with the other procedures described in the literature. The elaborated and validated analytical protocol has been applied for the determination of fuel combustion and fuel spill products in real samples collected from the areas of an airport in Poland. The established procedure is innovative in the field of determination of one of the most toxic analytes in a new type of environmental samples such as runoff water samples from the area of the airports, development of detailed metrological characteristics and the diversity of places from which runoff water samples were collected. This procedure can be used as a tool for tracking the environmental fate of these toxic and mutagenic pollutants and for assessing the environmental effect of airports. Subsequently, these data will provide a sound basis for airport infrastructure management.

Acknowledgments We gratefully acknowledge financial support from the National Science Center, Krakow, Poland (Decision No. DEC-2011/01/N/ST4/01913). The authors express their gratitude for the grant awarded within the framework of the Development of Interdisciplinary PhD Studies in Modern Technologies project at the Gdansk University of Technology (V edition), co-funded by the European Union. We are highly indebted to Dr. Piotr Nowicki from Department of Inorganic and Analytical Chemistry, Medical University in Poznan for the performed statistical analysis of the obtained experimental data. The authors express their gratitude to MSc, Eng. Krzysztof Suchomski for his help in preparing the graphic side of this publication.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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