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

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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 levels 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 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.

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 liters of ADAFs entering the environment every year. The Environmental Protection Agency (U.S. EPA) has estimated that approximately 80 million L 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 t/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

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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 • fueling 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 Finally determination	Centrifuge shaker (Conbest, ELMI, Poland), Vacuum set of SPE-12G™ (J.T. Baker, Poland) Agilent 7890A gas chromatograph coupled with mass spectrometer Agilent 5975C
Solvents	Methanol, n-hexane, 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	–	–

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 [1,2,20,2735–38]. 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 (GC × GC–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].