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Toxicity and chemical analyses of airport runoff waters in Poland.

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Abstract

The aim of this study was to assess the ecotoxicological effect of various compounds in complex airport effluents using a chemical and ecotoxicological integrated stategy. The present work deals with the determination of PCBs sum, PAHs, pesticides, cations, anions, phenols, anionic, cationic, non-ionic detergents, formaldehyde and metals– as well as TOC and conductivity in runoff water samples collected from 2009 to 2011 at several locations on two Polish international airports. Two microbiotests (*Vibrio fischeri* bacteria and the crustacean *Thamnocephalus platyurus*) have been used to determine the ecotoxicity of airport runoff waters. The levels of many compounds exceeded several or even several tens of times the maximum permissible levels. Analysis of the obtained data shows that samples that displayed maximum toxicity towards the bioindicators *Vibrio fischeri* were not toxic towards *Thamnocephalus platyurus.* Levels of toxicity towards *T. platyurus* are strongly correlated with pollutants that originate from the technological operations related to the maintenance of airport infrastructure. The integrated (chemical-ecotoxicological) approach to environmental contamination assessment in and around airports yields extensive information on quality of the environment. These methodologies can be then used as tools for tracking the environmental fate of these compounds and for assessing the environmental effect of airports. Subsequently, these data will provide a basis for airport infrastructure management.

Key words: airport; runoff water; stormwater; pollutants; toxicity; *Vibrio fischeri*; *Thamnocephalus platyurus*;

1. Introduction

Despite the positive aspects of the intensive development of aviation, airports are large-scale polluters [1-6], and various kinds of pressure on the environment are a consequence of the activities of airports and air traffic. In this regard runoff waters (stormwater), formed while precipitation or atmospheric deposits flush the airport surface during everyday activities e.g.: fuelling operations, cleaning of aircrafts, ground vehicles and airport aprons, de/anti-icing operations, combustion of aviation and engine fuels, aircraft and vehicle maintenance and repairs (including painting and metalwork), removing weeds, other vegetation and microorganisms from the airport apron and aircraft surface pose a serious problem [1-20]. The most toxic cancerogenic and mutagenic pollutants identified on airport premises include: polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides phenols, formaldehyde, detergents, glycols, benzotriazoles and metals [1, 6, 15, 16, 21-30]. These contaminants penetrate into all components of the environment. In most cases airports do not possess their own waste water treatment plants (WWTPs) so all effluents carrying metals, petroleum compounds, surfactants, de-icing agents used in winter and other organic and inorganic pollutants run off together with rain water or melted snow into drainage ditches, from where they enter mainly to the soil and coastal water bodies [31 32]. The pollutants present in runoff water have different effects on humans and the environment [2, 5-7, 12, 33].

In order to assess the extent to which surface waters are endangered by these pollutants, it is crucial to identify and quantitatively determine the chemical compounds in airport stormwater [2, 6, 17, 34-36]. Determining all various harmful chemicals in such runoff water is a demanding task, because this kind of research is expensive and time-consuming. Although chemical analysis enables the identification and quantification of organic and inorganic pollutants, it does not provide sufficient information to assess environmental hazards, since it is not possible to investigate all the possible substances and their interactions in ecosystems [37]. Effective risk assessment requires finding a relationship between water chemistry and toxicity endpoints. At the present state of the art one common approach is to link chemical concentrations to toxicity data [38-43]. However, it is difficult to extrapolate between chemical concentrations and potential biological effects for the purpose of risk assessment. Only a relatively small amount of data is currently available for the analysis and ecotoxicological assessment of airport runoff waters [1, 15, 16, 28, 44-48].

The aim of this study was to assess the ecotoxicological effect of various compounds in complex airport effluents by means of an integrated chemical and ecotoxicological strategy. The present study focused on the determination of pH, conductivity, total organic carbon (TOC), metals, detergents and formaldehyde, the sum of phenols, PAHs, PCBs, pesticides, cations and anions found in airport stormwater, as well as measuring toxicity of samples using Microtox® and Thamnotoxkit F™ tests. Microtox® test which was employed in this paper is very popular whilst Thamnotoxkit F™ test for the airport runoff toxicity has been mentioned in the literature only once [48]. The relationship between water chemistry and toxicity data can be used to identify the potential toxic impact of airport storm water runoff discharges on recipient waters. Chemical and toxicity testing represents a relatively recent and powerful tool for the management of storm water pollution and protection of the aquatic ecosystem. The results of this type of study will provide essential information for assessing the threat to surface and groundwaters in the vicinity of airports.

2. Experimental

In view of the difficulties with toxicity in-situ testing, various chemical analyses were performed on samples brought to the laboratory. The procedures used for sample collection, handling, chemical and toxicity measurements in the laboratory are described in the following sections.

2.1 Storm water sampling, collection and handling

The samples of runoff water were collected during precipitation, defined as steady lasting for at least 5 h. Samples were collected usually within 30 min from the beginning of the precipitation event (first flush). During the research period the amount of the precipitation ranged from 2 to 10 mm and the events lasted from 3 to 5 h.

The samples of runoff water were collected at the international Polish airports with high and low capacity of passenger movement, in three seasons- winter, spring and summer- from 2009 to 2011. The runoff samples were collected from depressions in the terrain where rainwater accumulated and from the airport drainage system. The sampling locations at the airports were areas with the highest concentration of technical service operations, where the largest amounts of pollutants enter drainage ditches with runoff and may be released into the environment.

Runoff waters at each location at the airport with low capacity of passenger movement were collected manually with a plastic scoop (100 ml) and tubing, while at the airport with high capacity of passenger movement, they were scooped from the drainage system with a bucket. The material for analysis was then poured into 500 ml water-tight plastic bottles (for the determination of inorganics) or into 1000 ml dark glass bottles (analysis of organics) and transported to the laboratory (usually within less than 1h after collection). Prior to use, the syringes, tubing and bucket were rinsed with MilliQ water and then with the water to be sampled. No chemicals were added to preserve the samples, therefore the determinations were typically initiated immediately after the samples arrived at the laboratory. Prepared extract of runoff water samples were stored at 4 °C in the dark until final determination [49-53].

2.2 Chemical analysis

Chemical analysis of the samples included various instrumental methods compliant with different chemical and ecotoxicity variables. Technical specifications, reagents for determining selected parameters and analyte contents in samples and basic validation parameters of the proposed analytical procedures are summarized in Table 1.

Milli-Q deionized water was used during the determination of the various target analyte groups. The concentrations of organic and inorganic compounds, metals, cations and anions in water runoff samples were determined by ion chromatography (IC), gas chromatography coupled with mass spectrometry (GC-MS), inductively conjugated plasma mass spectrometry (ICP/MS) and spectrophotometric methods.

2.3 Test organisms and test methods

For toxicity assessment small-scale aquatic tests known as microbiotests were used [54]. These bioassays do not require maintaining continuous culture of organisms and are based on immobilized or dormant (cryptobiotic) stages of selected aquatic species set free or hatched when needed [41, 42]. The following bioassays for freshwater were applied:

- Thamnotoxkit F™ is a test using the crustacean *Thamnocephalus platyurus*. The test reaction is the mortality of the organism. The test was carried out in accordance with the manufacturer's standard procedure (Tigret, Poland).
- Microtox® is a test using the luminescent bacteria *Vibrio fischeri*. The test reaction is the attenuation of the sample luminescence after 30 minutes' incubation. The test was carried out according to procedure PN-EN ISO 1138-3:2002 [55] using the Microtox model 500 instrument (Strategic Diagnostic Inc., Newark, NJ, USA) for freeze-dried bacteria. The results were calculated using the manufacturer's MicrotoxOmni programme.

2.4 Quality assurance/ quality control (QA/QC)

All data were subjected to strict quality control procedures. The analytical procedures applied for the determination of individual components in varius environmental matrix compositions should be validated against certified reference materials. In this study Reference Material No. 409 (BCR-409, Institute for Reference Materials and Measurements, Belgium); Inorganic ventures ANALITYK-CAL-8 (10 mg/L: Ag, Al., As, B, Ba, Ca, Cd, Co, Cr3, Cu, Fe, Mg, Na, Ni, Pb, Sb, Se, Sr,V, Zn) and Analytical Reference Material TM-DWS.2, Envronnment Canada Al: 58.3 μg/L, Sb: 3.20 μg/L, As: 4.20 μg/L, Ba: 146 μg/L, Be: 13.4 μg/L, Bi: 14 μg/L, B: 81.0 μg/L, Cd: 4.20 μg/L, Cr: 44.4 μg/L, Co: 64.2 μg/L, Cu: 167 μg/L, Ga: 0.04 μg/L, Fe: 223 μg/L, Pb: 7.82 μg/L, Li: 20.1 μg/L, Mg: 47.2 μg/L, Mo: 66.7 μg/L, Ni: 82.3 μg/L, Rb: 0.42 μg/L, Se: 8.69 μg/L, Ag: 9.91 μg/L, Sr: 243 μg/L, Tl: 8.32 μg/L, Sn: 12.1 μg/L, Ti: 15.1 μg/L, U: 14.1 μg/L, V: 44.3 μg/L, Zn: 379 μg/L) were applied. The sensitivity of the applied methods was tested by injecting standard mixtures of the analytes in the measurement range concentration. Linear calibration curves obtained by plotting the peak area against concentration of the respective standards and the correlation coefficients (R^2) were in the range of 0.898-0.999 for all standards. On the basis of the calibration curves, it was possible to determine concentration levels of certain substances in real samples. Each sample was analyzed in triplicate. During the samples analysis, procedural blanks were prepared for every six samples to check the instrumental background. Duplicate samples and calibration check standards were run after every five samples to assure the precision of each run. The limit of detection (LOD) was determined for the analytes 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 [56-58]. The numerical values of the all mentioned validation parameters determined for researched analytes, using particular analytical methods, were presented in Table 1.

Quality control for biotests is a real challenge as the tests operate with a 'living reagent' and thus many factors may affect the results. Therefore, the laboratory which carries out the measurements is involved in the comparative and calibration tests for interlaboratory results check. Moreover, in the case of Microtox® test with *Vibrio fischeri* bacteria the laboratory ran the internal quality control with the reference toxicant $ZnSO_4$ $7H_2O$ to confirm the quality of bacteria guaranteed by producer. EC_{50} values fell into the accepted range of 0.6-2.2 mg/L. Other parameters that interfere with the test results such as turbidity, colour, pH and temperature were also checked and controlled. In the laboratory the repeatability of the results is constantly checked, coefficient of variation (CV) falls in the range of ±10%.

3. Results and discussion

Table 2 lists the results of target analyte groups, physicochemical parameters determination as well as toxicity towards the *Vibrio fischeri* bacteria and the freshwater crustaceans *Thamnocephalus platyurus* in runoff water samples collected from 2009 to 2011 at various characteristic sites of two Polish international airports (*airports with low and high capacity of passenger movement*).

In the majority of the analysed runoff waters samples the levels of examined analytes did not exceed the maximum permissible levels of concentrations according to the available standard for conditions which should be met while discharging sewage to waters or ground and for substances particularly harmful for aquatic environment [59]. This standard is cited due to the fact that in case of a lack or inadequate work of a waste water treatment plant, a significant amount of airfield effluents get to the surface water or to the soil with runoff waters. However, the contents of some studied analytes and measured parameters exceeded considerably permissible concentration levels of pollutants introduced into the environment. For example, the numerical value of the determined parameter of total organic carbon (TOC) exceeded extremely the permissible level of the total organic compound content introduced into surface waters and soil both in case of the airport with high capacity of passenger movement and the airport with low capacity of passenger movement. Such a high value of the TOC parameter in the airport runoff water samples can be associated with a seriuos ground and water pollution first of all with oil derivatives and substances from the polycyclic aromatic hydrocarbon group emitted in particular during combustion and uncontrolled aviation fuel overflows. Exceeding the permissible standard (0,1 mg/L) was also noticed for the determined total phenol content in the runoff water samples from the airport with both high and low capacity of passenger movement. It is acknowledged that phenolic compounds (at mg/L level) are extremely toxic for aquatic organisms [60]. Moreover damages following exposure to substantial doses of phenols affect the nervous and circulatory systems, with a reduction in the number and growth of blood cells (for example erythrocytes, total proteins and cholesterol) [61]. Precise assessment of phenolic compound sources of emission into runoff waters at the airport areas is relatively difficult; the detergents, containing phenolic compounds, used at the airports have been recognized as their main source. The detergents are employed at the airport areas in large amounts to keep airplanes, the airport platform and infrastructure clean. As a result, the increased content level of these types of analytes in the tested airrport runoff water samples can be observed.

Table 1 Validation parameters, technical specifications, reagents used in the proposed analytical procedures.

Analytical techniques	Measure-ment range	LOD	LOQ	CV (%)	Measurement instrumentation	Reagents/Standards
Sum of phenols*	0.15-4.00	0.05	0.15	3.9	**UV/VIS spectrophotometer 6300** (Jenway, Felsted, Essex, UK)	Sodium hydroxide solution 1mol/L, Sulphonic acid 0.5mol/L, Chloroform, Phenol (Merck, Darmstadt, Germany);
Formaldehyde*	0.03-5.00	0.01	0.030	3.8		Formaldehyde solution min.37% (Merck, Darmstadt, Germany);
Cationic detergents*	0.01-2.00	0.003	0.010	4.5		Sodium hydroxide solution 1mol/L, Sulphonic acid 0.5mol/L, N-Cetyl-N,N,N-trimethylammonium bromide (CTBA), Hydrochloric acid 25%, Methanol (Merck,Darmstadt, Germany);
Anionic detergents*	0.05-15.00	0.017	0.050	4.0		Sodium hydroxide solution 1mol/L, Hydrochloric acid 1mol, Sodium 1-dodecanesulphonate, Hydrochloric acid 25%,Methanol (Merck, Darmstadt, Germany);
Non-ionic detergents*	0.01-7.50	0.003	0.010	4.9		Sodium hydroxide solution 1mol/L, Sulphonic acid 0.5mol/L, Triton X-100, Hydrochloric acid 25%,Methanol (Merck,Sarmstadt,Germany);
Cations*a	0.03-500	0.01	0.030	0.9	**DIONEX 3000 chromatograph (DIONEX, Sunnyvale, CA,USA)**: column: Ion Pac® CS14 (3x250mm); suppressor: CSRS-300, 2mm, mobile phase: 38 mM metasulfonic acid, flow rate: 0.36 ml/min, detection: conductivity	Cation Standards (Na^{+} , NH_4^{+} , K^{+}, Ca^{2+}, Mg^{2+}) 1000±5 mg/dm^3; (Merck, Darmstadt, Germany);
Anions*a	0.06-500	0.055-0.09	0.027-0.17	0.6	column: Ion Pac®AS22 (2x250 mm); suppressor: ASRS-300, 2mm, mobile phase: 4.5 mM CO_3^{2-}, 1.4 mM HCO^{3-}, flow rate: 0.38ml/min, detection: conductivity	Anion Standards (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) 1003±5 mg/dm^3; (Merck, Darmstadt,Germany);
TOC*a	0.5-500	0.17	0.50	5.0	**Total Organic Carbon Analyzer TOC-V$_{CSH/CSN}$ (**Shimadzu, Kyoto, Japan) Method of catalytic combustion (oxidation) with using of NDIR detector	Potassium Biphthalate, C_6H_4(COOH) FW204.23, purity 99,9%, (Kanto CO., INC, Tokyo, Japan)
PAHs**	0.15-9.00	0.05-1.40	0.15-4.20	1.5 – 5.5	**Gas chromatograph 7890A** (Agilent Technologies, Santa Clara, CA, USA) coupled with a mass spectrometer (5975C inert MSD – Agilent Technologies), detector (Agilent Technologies 5975C) with electron ionization (SIM mode), Autosampler (7683B – Agilent Technologies), column: ZB – 5MS (30 m;0.25mm;0.25µm); temperature program: 40-120 °C (40 °C/min),120-280 °C (5 °C/min), carried gas: helium, gas flow: 1 ml·min^{-1}, injection volume: 2µl (splitless), inlet temperature 295°C,	Dichloromethane, Methanol (Merck, Darmstadt, Germany); Naphthalene-d8, Benzo(a)anthracene-d12, Supelco, St. Louis, MO, USA; Mixtures of 16 PAHs (2000 µg/mL), Restek Corporation, Bellefonte, PA, USA;
PCBs**	0.05-2.00	0.017	0.050	2.0 – 6.0		Dichloromethane, Methanol (Merck, Darmstadt, Germany); PCB standards, IUPAC Nos. 28,52,101,118,153,138,180 (10µg/mL in isooctane) Restek Corporation, Bellefonte, PA, USA;Certified standards of ^{13}C- labelled PCB 28 and PCB 180 (40µg/mL in nonane), Cambridge Isotope Laboratories, Tewksbury, MA, USA;
Pesticides	0,05-2,00	0,022	0,066	0.5-6.0	**Gas chromatograph 6000 Vega Series 2 (**Carlo Erban,Milan, Italy) coupled with electron capture detector (Finnigan, Waltham, MA, USA); column: ZB-5MS, 30m;0,25mm;0,25µm, Phenomenex, Torrance, USA, temperature program: 80 ºC -180 (15 ºC/min), 180-300 ºC (10 ºC/min), 300 ºC (3 min) carried gas: hydrogen, gas flow: 1 ml·min^{-1}, injection volume: 2µl (splitless), inlet temperature 80°C,	Dichloromethane, Methanol, n-hexane MERCK, Germany; Pesticide standards, Hexachlorobenzene, γ-HCH, Acetochlor, Vinclozolin, Alachlor, Metolachlor ,Aldrin, captan, α-endosulfan, 4,4-DDE, Endrin, 4,4-DDT, Mirex (100 µg/mL in isooctane), LGC Standards, London, UK
Metals**	0.002-1000	0.0007	0.002	0.5 – 1.5	**Elan DRC** (PerkinElmer, Waltham, MA, USA) gas fed to the atomizer→ Ar:0,98 l/min, plasma gas→ Ar: 15 l/min	Mix of ICP standards, Analityk-Cal-8, Inorganic Ventures Christiansburg, VA, USA.

*[mg/L] ** [µg/L] **a** the measurement range can be expanded towards the greater range of concentrations

Table 2 Minimum, maximum and median concentrations of different compounds determined in airport runoff water.

Target analytes	Units		c_{min}	c_{max}	Median	c_{min}	c_{max}	Median
		n	*Airport with low capacity of passenger movement*			*Airport with high capacity of passenger movement*		
∑PCB	[µg/L]	79	ND[a]	1.49	0.04	NT[b]		
∑PAH	[µg/L]	111	0.01	5.69	0.25	0.05	8.55	0.31
∑Pesticides	[µg/L]	50	0.02	8.29	0.26	NT		
Conductivity	[µS]	107	0.01	40. 5	0.33	0.12	1.52	0.65
∑Anions	[mg/L]	100	0.15	10527	5.59	0.56	47.0	9.43
∑Cations	[mg/L]	81	8.38	15339	114	26.6	49.5	36,5
∑ Anionic detergents	[mg/L]	107	0.20	14.9	0.55	0.23	1.08	0.42
∑Cationic detergents	[mg/L]	107	0.03	0.90	0.29	0.29	0.78	0.34
∑Non-ionic detergents	[mg/L]	105	0.07	7.50	0.83	0.28	7.50	2.49
Formaldehyde	[mg/L]	106	0.01	2.90	0.25	0.28	1.63	0.39
∑Phenols	[mg/L]	106	ND	1.59	0.14	0.16	3.33	0.26
TOC	[mg/L]	106	0.96	5510	141	3.89	21999	46.7
Metals	[µg/L]							
Li		33	0.50	10.4	2.31	3.00	363	7.60
Be		1	ND			0.06	0.06	0.06
B		33	2.86	48.8	12.0	16.0	165	128
Al		45	12.0	938	32.5	5.30	289	25.0
V		45	3.50	120	24.8	8.30	171	16.0
Cr		45	1.40	42.7	18.8	7.40	50.2	8.50
Mn		45	1.40	94.1	12.4	0.60	680	12.9
Co		36	0.07	1.88	0.24	0.28	0.81	0.59
Ni		44	0.50	6.95	2.03	0.60	2.80	1.60
Cu		45	3.20	67.6	12,3	1.10	25.8	4.35
Zn		45	10.2	106	38.2	23.2	162	46.3
As		45	0.30	5.70	2.12	1.20	4.20	1.80
Se		33	0.01	1.09	0.28	0.46	1.39	1.03
Rb		45	1.92	287	40.6	6.86	684	12.0
Sr		45	3.80	105	25.6	5.20	1953	373
Mo		45	0.18	16.1	2.09	0.91	41.4	1.51
Ag		24	0.01	1.37	0.07	ND		
Cd		37	0.04	0.42	0.14	0.08	5.28	0.40
Sn		31	0.10	1.00	0.42	0.30	0.50	0.40
Sb		45	0.19	2.82	0.87	0.50	4.17	1.14
Cs		43	0.01	0.59	0.16	0.03	5.64	0.05
Ba		45	2.90	90.9	12,1	4.20	285	61.1
Tl		0	ND			ND		
[illegible]b		135	0.02	7.86	0.67	ND	13.1	0.19
[illegible]		135	0.02	0.61	0.25	0.04	2.81	1.87
[illegible]oxicity	[%]							
[illegible]ibrio fischeri	↓Luminescence	108	4.90	50.8	20.0	20.0	96.0	20.0
[illegible]hamnocephalus platyurus	Mortality	68	0.00	100	25.0	NT		

[a] ND- not detected; [b] NT- not tested; ∑Anions: PO_4^{3-}, F^-, $HCOO^-$, Cl^-, NO_2^-, NO_3^-, Br^-, SO_4^{2-}; ∑Cations: Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}

In the case of PCBs and pesticide compound determination, the concentration levels of these analytes which were found in runoff waters from the airport with low capacity of passenger movement were also too high, according to the standard mentioned above. The concentration values of PCBs, pesticides in effluents discharged into water or ground should be zero [59]. Compounds from the PCB group can be emitted to airport runoff waters during aircraft maintenance operations (heat exchanger fluids, chemical stabilizers and from hydraulic systems) and overflows of lubricants, paints, and oil varnishes at airports. Pesticides can be emitted to runoff water from airport infrastructure during daily washing and maintenance of the crop spraying aircrafts. They can also originate from combustion of fuel process and leakage of fuel, lubricants, oils which contain an addtiton of biocides which are applied to reduce the growth of microorganisms in fuels and lubricating oils. The content of particular metals in the analyzed samples did not exceed permissible concentration levels according to the standard. However, some high metal concentrations, in particular of strontium, boron, barium and zink, whose median numerical values were 373, 128, 61.1 and 46.3 μg/L respectively, were observed in the runoff water samples collected from the area of the airport with high capacity of passenger movement. The metal content, especially heavy metals, in the airport runoff water samples can be connected mostly with the combustion of the large amount of aviation fuel (the emission may be a result of releasing analytes contained in the fuel) and the corrosion of different protective coatings (e.g. galvanized) of the fuselage and other parts of the aircraft. The analytes from the metal group can be also emitted to the airport runoff waters during the take-off and landing abrasion of the aircraft tyres, varnishing or painting of aircrafts and the airport platform, also after welding waste or lead batteries and accumulators. Heavy metals from these sources can be dispersed into the environment and pollute water, soil and air or get directly or through the plants into animal and human organisms [62].

While analyzing available measurement data the surprising differences in analytes determined in the samples collected from the airports which differ in capacity of passenger movement significantly content can be observed. The airports with high capacity of passenger movement do not always emit considerable amount of pollutants because in most cases huge international airports have larger budgets to create a reliable infrastructure management system (own waste water pre-treatment and treatment plants, the system of waste recirculation, ecological detergents and de-icing agents etc.) which enables to reduce considerably the sources of pollutants emission. To illustrate this, the maximum TOC level in runoff waters from Newark International Airport (one of the busiest international airports in the United States, 33.8 million passengers/year), was 1120 mg/L, whereas the equivalent level at *Polish airport with high capacity of passenger movement* (9.4 million passengers/year) was twice as high. This difference is significant since the Polish airport serves a three times smaller number of passengers than Newark (USA) [6]. Again, the mean phenol content in samples from Kansas City International Airport, USA (10 million passengers/year) was 93 mg/L, but at Bradley (ca 5.6 million passengers/year) it was three times higher [6]. For instance, the runoff water collected from monitored *airport with high capacity of passenger movement* showed the ca. 1,8 times higher contents of total metals (501 μg/L) in comparison with the monitored *airport with low capacity of passenger movement*. These examples show that the level of environmental pollution at an airport is not always directly correlated with either its size or its capacity.

Assessing the contamination level of runoff waters from airports requires monitoring of many parameters, which is time-consuming and expensive. Moreover, the results of chemical analyses do not take into account interactions between the compounds present (synergism and antagonism). Therefore it is essential to set up a system integrating selected chemical parameters and ecotoxicological tests [1, 16, 22, 25].

Table 3 lists the sites at the Polish airports, with high and low capacity of passenger movement, with the most toxic runoff waters. It also points the chemical parameters and the target analyte groups with the highest concentrations in accordance with the Polish law 169/27 [59]. Two microbiotests (*Vibrio fischeri* bacteria and the crustacean *Thamnocephalus platyurus*) have been used to determine the ecotoxicity of airport runoff waters. The sample taken at the aircraft refuelling point of *the airport with high capacity of passenger movement* was most toxic towards *Vibrio fischeri* bacteria. This sample contained high levels of the following parameters and target analyte groups: TOC, metals, anions, phenols, detergents, formaldehyde. More than a dozen of samples were highly toxic towards *Thamnocephalus platyurus*: all of them had high concentrations of sodium ions and formate ions. *Thamnocephalus platyurus* is mentioned by Kiss [63], to show a real specificity to some substances and may be used for detection of high Na and Cd concentrations. A considerable effect of sodium, chloride and formate ions on aquatic invertebrates was mentioned by Corsi et al. [16]. Sodium formate is included in pavement de-icer materials while sodium itself is a constituent of road salt which is used to clear snow and ice from paved airport surfaces such as roads, parking lots and sidewalks. Both compounds have a potential to impact aquatic toxicity. In the study no correlation between toxicity tests results and pesticide content/concentration was observed. From conducted research it was also noticed that runoff water samples collected during the winter and early spring season were of the highest toxicity (Table 3). During these seasons the highest number of operations such as de-icing of both aircrafts and the airport area is made, the biggest amount of aviation fuel is burnt (especially during take-offs when the aircraft engines require more energy and time to warm up and start the vehicle because of the reduced ambient temperature) in comparison with the other seasons, which may account for the above characteristic relation. Figure 1 shows the additional exemplary graph presenting the correlation between the season of the sample collection (from the airport with low capacity of passangen movement in 2009) and determined toxicity towards indicator organisms *Thamnocephalus platyurus* and *Vibrio fischeri*. The presented graph confirms the thesis that especially during the winter season the determined toxicity (connected directly with quantity and the specific character of emitted pollutants) of samples is significantly higher in comparison with the toxicity determined for the samples collected in the other seasons of the year when intensity of everyday operations referred to the airport maitenance is much lower than the amount of operations carried out during the winter season.

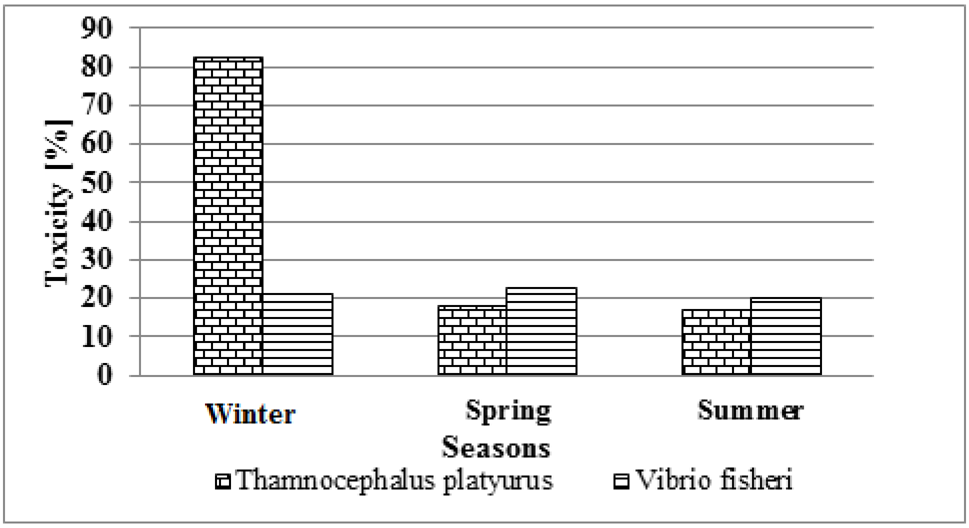

Figure 1 Toxicity determined in runoff water samples collected in airport area in different season in year 2009.

Principal components analysis (PCA) was used to explore the data and explain the relationships between the analysed parameters. The results the PCA analysis of are presented in Table 4 and Figure 2. Pesticides were not included in the PCA analysis due to gaps in the database. Principal component 1 (PC1) included 47.2% of the overall variance and was influenced by eight variables: TOC, anions, cations, EC, toxicity towards *Thamnocephalus platyurus*, the sum of detergents, anionic and non-ionic detergents. These parameters are clustered in the plane PC1 and PC2 at the area II (Figure 2). PC1 represents pollutants associated with technological processes carried out during airport operations and related to the maintenance of airport infrastructure, such as cleaning and washing aircraft and airport aprons. The results show that toxicity towards *Thamnocephalus platyurus* is correlated with the other variables forming cluster II, and that this organism can be successfully used as a screening parameter. The number of necessary chemical determinations could be reduced by measurement of toxicity towards *Thamnocephalus platyurus* instead.

PC2 explained 15.0% of the total variance in the data, and was determined primarily by phenols, formaldehyde, PCBs and PAHs. These variables created the cluster denoted as I with positive values of PC2 (Fig.2). They may be referred to as environmental pollutants included in the airport runoff water samples commonly occurring as a result of combustion processes, transportation, etc. The variation of parameters included in the cluster I differs from the variation of toxicity towards *Vibrio fisheri* and *Thamnocephalus platyrus.* This may suggest the presence in the samples of compounds that were not determined during the research. Many compounds which are not determined in this study are mentioned in the literature as capable of influencing aquatic toxicity of airport runoff waters: urea, glycols, benzotriazole, tolyltriazole, alkylphenols ethoxylates, de-icer and anti-icer additives and other constituents [1, 15, 47 22, 23, 45].

The toxicity towards *Vibrio fischeri* appears in third and fourth principal components (PC3 and PC4). The variation of the toxicity towards the *Vibrio fischeri* parameter is positively correlated with the variation of non-ionic (PC3) and cationic detergents (PC4) and negatively correlated with cationic detergents in PC3 (Table 4).

Anionic detergents and the sum of detergents data show the similar variation on the first five PCs, which may indicate that these detergents occur mainly in anionic form (Table 4).

In contrast, the cationic detergent loadings suggest that the variation of the cationic detergents data differs from the variation of the data for all other parameters in the PC1 (Figure 2). This could be attributed to the fact that these compounds are used occasionally.

The results of the PCA of the measurement data revealed that the crustacean *Thamnocephalus platyurus* and bacteria *Vibrio fischeri*, two organisms from different trophic levels, respond differently to the target analytes. This study revealed that *Thamnocephalus* *platyurus* is more sensitive to some of the pollutants (cluster II) determined in the samples than *Vibrio fischeri* bacteria. However, toxicity to *Vibrio fischeri* bacteria may be important to indicate other parameters which were either not determined at all or not included in the monitoring study. For example Pillard et al. in studies on toxicity of benzotriazole and benzotriazole derivatives mentioned that Microtox® test is more sensitive that tests on invertebrates (*Ceriodaphnia dubia*) and vertebrates (*P. Promelas*) [64].

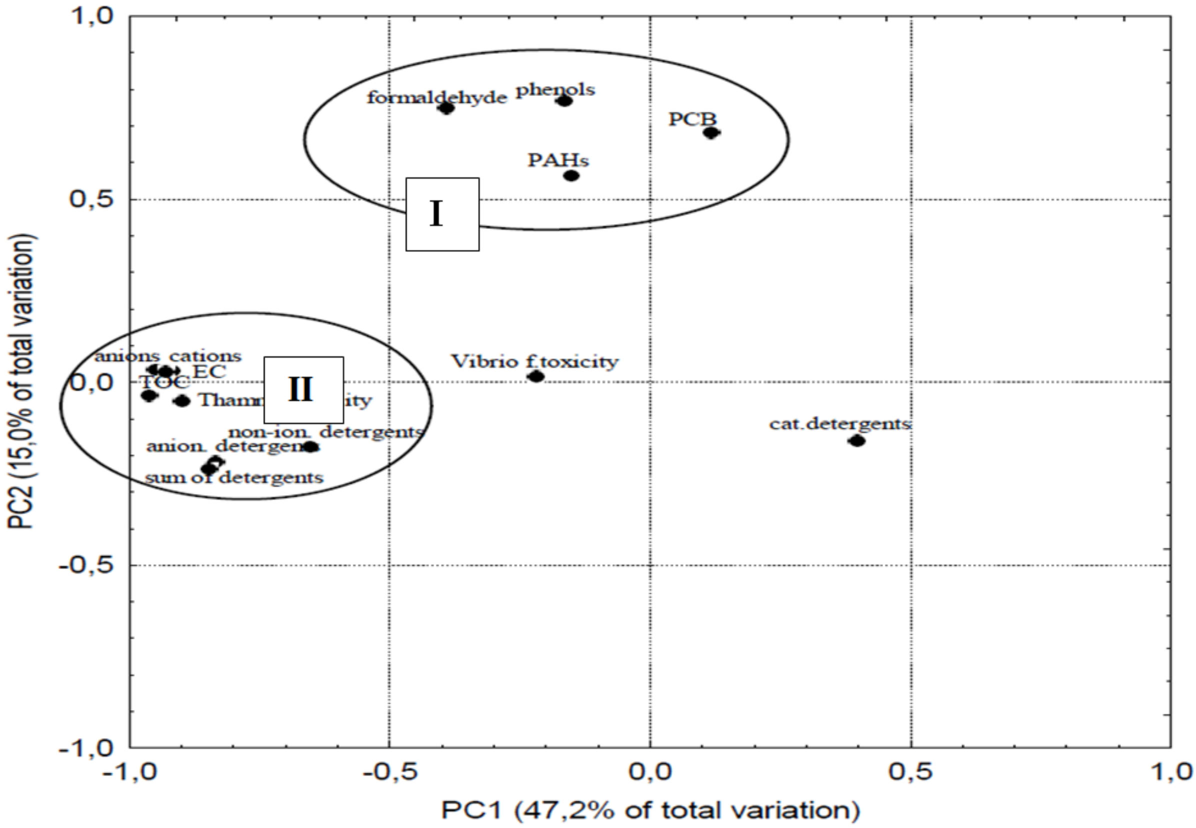

Figure 2 Loadings of the parameters in the plane defined by PC1 and PC2.

Figure 3 features the research results (covering the research period from 2009 to 2011) referring to determined concentrations of particular organic analytes from detergent and phenol groups, formaldehyde and TOC in the samples of runoff waters collected from the area of the monitored airport with low capacity of passenger movement. On the graph the clear increasing tendency of the content level of analytes in airport effluents was observed, beginning with the year 2009. The successive increase of the pollutant concentration levels in the airport runoff waters from 2008 to 2011 can be associated with the increased aviation activity at this airport during the research period, which was also presented in Figure 4. Figure 4 shows the concentration level of the total amount of emitted pollutants while taking into accout the number of passengers handled at the monitored airport with low capacity of passenger movement from 2009 to 2011. The amount of pollutants present in runoff waters is influenced mainly by two parameters: aircraft traffic intensity (connected with the increased number of passengers) and the effort, undertaken by managers of this airport, to reduce the sources of pollutants emission related to the airport exploitation started in 2010. The documented fundamental increase of aviation activity at the monitored airports seems to confirm the prediction of the global growth in the air transport, which is likely to be doubled within the next 15-20 years, and expected therefore considerable growth of the environment pollution being the result of the airport operations [1]. The results from this study show that it is important to carry out both chemical analyses and toxicity tests to be able to correctly evaluate the potential impact of airport stormwater on the environment.

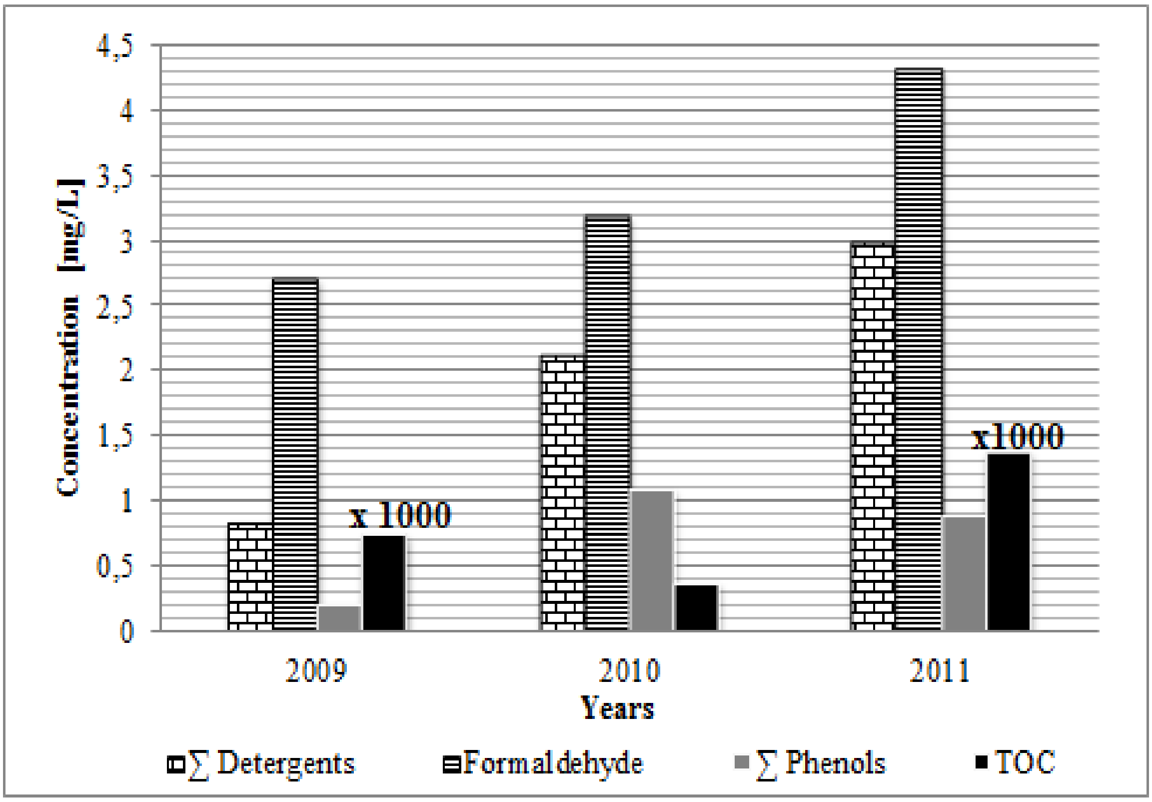

Figure 3 Concentration levels of some selected organic pollutants and TOC parameter in airport runoff water samples.

Table 3. The sites at airports with high/low capacity of passenger movement with the most toxic runoff waters.

Site / Date		Analysis of results	Number of times permissible norms exceeded	Toxicity %
Vibrio fischeri				
Airport with high capacity of passenger movement	Municipal water catchment area14.01.11*	Naphthalene= 0.125 [µg/L]; G_{Napth}** = 0.015 F^-= 0.278[mg/L]; G_{F^-}= 33.1 ∑metals= 1817 [µg/L]; $G_{\sum metals}$= 216 Zn= 162[µg/L]; Al= 209 [µg/L]; G_{Zn}=19.3; G_{Al}=24.9 TOC= 21999 [mg/L]; $G_{TOC}=2.61*10^6$ Formaldehyde=1.63 [mg/L]; $G_{Formaldehyde}$= 194 ∑Phenols= 3.33 [mg/L]; $G_{\sum Phenols}$ = 396 Non-ionic detergents= 7.50[mg/L]; $G_{Non\text{-}ionic\ d.}$= 893 Cationic detergents= 0.78[mg/L]; $G_{Cationic\ d.}$= 92.8	TOC- permissible norm exceeded 733 times ∑Phenols - permissible norm exceeded 33. 3 times	96
Airport with low capacity of passenger movement	Vicinity of an airport passenger terminal 24.03.2009	PO_4^{3-}= 4.99 [mg/L] ∑ Phenols= 0.302 [mg/L] Non-ionic detergents= 2.01 [mg/L] TOC= 289 [mg/L] ∑PCB= 0.13 [µg/L] γ-HCH= 0.149 [µg/L] Aldrin= 0.131 [µg/L] Endrin= 0.123 [µg/L] DDT= 0.00076 [µg/L]	TOC- permissible norm exceeded 9.6 times ∑Phenols- permissible norm exceeded 3 times PCB exceeded by 0.13 µg/L γ-HCH, Aldrin, Endrin, DDT permissible norm exceeded by 0.149 µg/L, 0.131 µg/L, 0.123 µg/L, 0.00076 µg/L respectively.	51
	Vicinity of an airport passenger terminal 07.01.11	∑ Phenols= 0.45 [mg/L] ∑ PCB= 0.14 [µg/l] ∑ PAH= 5.70[µg/l]	∑Phenols- permissible norm exceeded 4.5 times PCB- permissible norm exceeded by 0.14 [µg/L]	44
	Parking places 24.03.2009	TOC= 231 [mg/L] ∑ Phenols= 0.29 [mg/L] ∑ PCB=1.02 [µg/L] γ-HCH=0,039 [µg/L] Aldrin= 0,0018 [µg/L] Endrin=0,0017 [µg/L] DDT=0,0028 [µg/L]	TOC- permissible norm exceeded 7.7 times ∑Phenols - permissible norm exceeded 2.9 times PCB - permissible norm exceeded by 1.02 [µg/L] γ-HCH, Aldrin, Endrin, DDT permissible norm exceeded by 0,039 µg/L, 0,0018 µg/L, 0,0017 µg/L, 0,0028 µg/L respectively.	42
Thamnocephalus platyurus				
Airport with low capacity of passenger movement	Vicinity of an airport passenger terminal 19.01.2009	$HCOO^-$=8701 [mg/L]; Na^+= 4765[mg/L] Anionic detergents=13.5[mg/L] Non-ionic detergents=1.85[mg/L] TOC=3260 [mg/L]	TOC- permissible norm exceeded 109 times Anionic detergents permissible norm exceeded 2.7 times	100
	Machinery park 19.01.2011	$HCOO^-$=10505 [mg/L] Na^+= 5031 [mg/L] TOC=3435 [mg/L]	TOC- permissible norm exceeded 115 times	100
	The periphery of an airport 19.01.2011	∑WWA=2.01 [µg/l] Na^+= 56501[mg/L]; $HCOO^-$=9415 [mg/L] TOC=5510 [mg/L]	TOC- permissible norm exceeded 184 times	100

*Only data about flow of this site was available, Runoff water flow=119 [L/s] **Mass yield (G)= flow∗concentration [mg/s]

Table 4. PCA results obtained for airport runoff water. The table lists variable loadings, eigenvalues and the proportion of the variance explained for the first five PCs. Boldfaced values represent parameters with significant loadings (p=0.05).

Variables	PC1	PC2	PC3	PC4	PC5
PCB	0.12	**0.68**	0.35	-0.19	-0.20
PAHs	-0.15	**0.56**	-0.49	0.33	-0.09
EC	**-0.92**	0.03	-0.25	-0.07	-0.23
ANIONS	**-0.95**	0.03	-0.19	-0.07	-0.07
CATIONS	**-0.93**	0.03	-0.21	-0.06	-0.21
ANIONIC DETERGENTS	**-0.83**	-0.22	0.13	0.15	0.26
CATIONIC DETERGENTS	0.40	-0.16	**-0.50**	**0.55**	0.12
NON-IONIC DETERGENTS	**-0.65**	-0.18	**0.52**	0.08	0.18
SUM OF DETERGENTS	**-0.85**	-0.24	0.18	0.19	0.28
FORMALDEHYDE	-0.39	**0.75**	-0.11	0.11	0.11
∑PHENOLS	-0.17	**0.77**	0.26	0.04	0.39
TOC	**-0.96**	-0.04	-0.12	-0.03	-0.15
VIBRIO FISCHERI TOXICITY	-0.22	0.02	**0.67**	**0.51**	-0.45
THAMNOCEPHALUS PLATYURUS TOXICITY	**-0.90**	-0.05	-0.12	-0.16	0.09
Eigenvalues	6.6	2.1	1.6	0.8	0.7
% of variance explained	47.2	15.0	11.8	6.0	5.3
% of cumul. variance	47.2	62.2	74.0	80.0	85.3

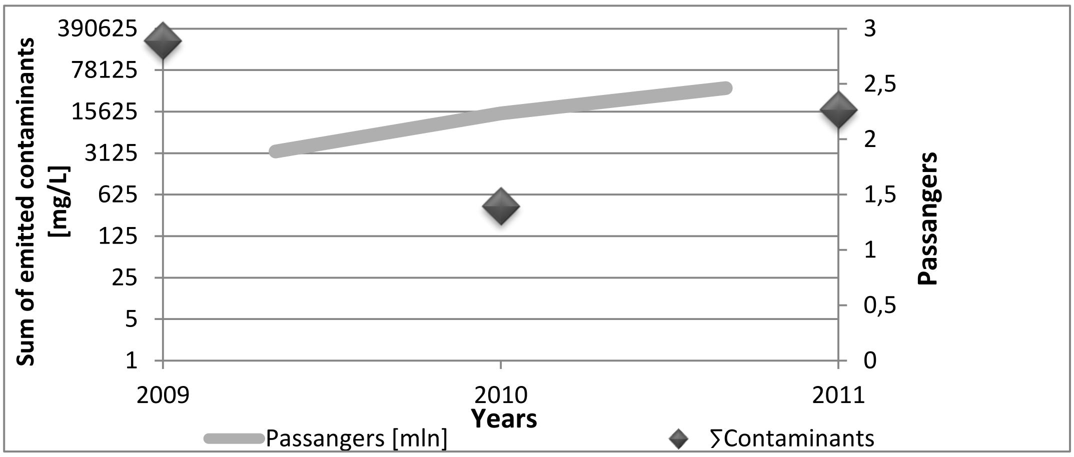

Figure 4 Concentration levels of summary amount of emitted contaminants determined in airport stormwater in correlation with passengers movement during period 2009-2011.

5. Conclusions

Contaminants generated from different sources of airport infrastructure; including leakage of fuel, paint materials, tire debris, use the brakes at high speeds especially during of sharp turns, small fragments of road surfaces and metals, peeled off rust and varnish, vehicle components, dissolved agents against glazed frost and detergent remains; are washed off the airport platform into drainage system by rain water, sometimes retained in the drainage system for a while, and finally transported mainly to the receiving water. Airport runoff water is considered to be an important source of environmental contamination, because runoff not only gets into surface waters, but also to soil, and even to ground water sources of drinking water, and organisms living in this soil and waters as final receptors.

The results of this airport runoff waters analysis confirmed that this type of environmental samples has a complex chemical composition. Commonly occurring environmental pollutants emitted from fuel combustion processes, leakage of fuel and the maintenance operations were detected and determined in the samples: PAHs, PCBs, pesticides, formaldehyde, metals; parameters such as TOC, conductivity; pollutants principally associated with the technological operations related to the cleaning of airport infrastructure (washing of aircraft and airport aprons) like detergents, cations, anions, phenols. The levels of some compounds exceeded several or even several tens of times the maximum permissible levels stipulated by Polish legislation for treated effluents, which can be discharged into surface waters. In the light of these figures, it is imperative that monitoring of airport runoff waters is implemented as soon as possible.

Analysis of the measurement data obtained shows that *Vibrio fischeri* and *Thamnocephalus platyurus*, the two organisms from different trophic levels respond differently to the studied parameters. Levels of toxicity towards *T. platyurus* are correlated with like anionic and non-ionic detergents, anions and cations, pollutants originating from the technological operations related to the maintenance of airport infrastructure (such as cleaning and washing of aircraft and airport aprons).

The results presented here point the usefulness of biotests in assessing the quality of the runoff waters. The integrated chemical-ecotoxicological approach to assessing environmental contamination in and around airports yields more complete information on environmental quality, thereby enabling the better management of runoff waters and to limiting their effects on the environment.

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