

1 **Toxicity and chemical analyses of airport runoff waters in Poland.**

2 **Anna Maria Sulej^a, Żaneta Polkowska^a, Lidia Wolska^{a,b}, Monika Cieszyńska^b, Jacek**

3 **Namieśnik^a**

4 ^aGdańsk University of Technology, Chemical Faculty, Department of Analytical Chemistry, Narutowicza

5 11/12 Street, 80-233 Gdańsk, Poland, phone: +48 58 347 1010, fax: +48 58 347 2694

6 ^b Medical University of Gdansk, Faculty of Health Sciences, Department of Environmental Toxicology,

7 Powstania Styczniowego 9b Street, 81-519 Gdynia, Poland, phone/fax: +48 58 622 33 54

8 e-mail: anna.maria.sulej@gmail.com

9 **Abstract**

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

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

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31

32 1. Introduction

33 Despite the positive aspects of the intensive development of aviation, airports are large-scale
34 polluters ¹⁻⁶, and various kinds of pressure on the environment are a consequence of the
35 activities of airports and air traffic. In this regard runoff waters (stormwater), formed while
36 precipitation or atmospheric deposits flush the airport surface during everyday activities e.g.:
37 fuelling operations, cleaning of aircrafts, ground vehicles and airport aprons, de/anti-icing
38 operations, combustion of aviation and engine fuels, aircraft and vehicle maintenance and
39 repairs (including painting and metalwork), removing weeds, other vegetation and
40 microorganisms from the airport apron and aircraft surface pose a serious problem ¹⁻²⁰. The
41 most toxic cancerogenic and mutagenic pollutants identified on airport premises include:
42 polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides
43 phenols, formaldehyde, detergents, glycols, benzotriazoles and metals ^{1, 6, 15, 16, 21-30}. These
44 contaminants penetrate into all components of the environment. In most cases airports do
45 not possess their own waste water treatment plants (WWTPs) so all effluents carrying
46 metals, petroleum compounds, surfactants, de-icing agents used in winter and other organic
47 and inorganic pollutants run off together with rain water or melted snow into drainage
48 ditches, from where they enter mainly to the soil and coastal water bodies ^{31 32}. The
49 pollutants present in runoff water have different effects on humans and the environment ^{2, 5-7,}
50 ^{12, 33}.

51 In order to assess the extent to which surface waters are endangered by these
52 pollutants, it is crucial to identify and quantitatively determine the chemical compounds in
53 airport stormwater ^{2, 6, 17, 34-36}. Determining all various harmful chemicals in such runoff
54 water is a demanding task, because this kind of research is expensive and time-consuming.
55 Although chemical analysis enables the identification and quantification of organic and
56 inorganic pollutants, it does not provide sufficient information to assess environmental



57 hazards, since it is not possible to investigate all the possible substances and their
58 interactions in ecosystems ³⁷. Effective risk assessment requires finding a relationship
59 between water chemistry and toxicity endpoints. At the present state of the art one common
60 approach is to link chemical concentrations to toxicity data ³⁸⁻⁴³. However, it is difficult to
61 extrapolate between chemical concentrations and potential biological effects for the purpose
62 of risk assessment. Only a relatively small amount of data is currently available for the
63 analysis and ecotoxicological assessment of airport runoff waters ^{1, 15, 16, 28, 44-48}.

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

77 **2. Experimental**

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

82 **2.1 Storm water sampling, collection and handling**

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

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

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

105 **2.2 Chemical analysis**



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

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

115 **2.3 Test organisms and test methods**

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

120 • Thamnotoxkit FTM is a test using the crustacean *Thamnocephalus platyurus*. The test
121 reaction is the mortality of the organism. The test was carried out in accordance with the
122 manufacturer's standard procedure (Tigret, Poland).

123 • Microtox® is a test using the luminescent bacteria *Vibrio fischeri*. The test reaction is
124 the attenuation of the sample luminescence after 30 minutes' incubation. The test was
125 carried out according to procedure PN-EN ISO 1138-3:2002 ⁵⁵ using the Microtox model
126 500 instrument (Strategic Diagnostic Inc., Newark, NJ, USA) for freeze-dried bacteria.

127 The results were calculated using the manufacturer's MicrotoxOmni programme.

128

129 **2.4 Quality assurance/ quality control (QA/QC)**

130 All data were subjected to strict quality control procedures. The analytical
131 procedures applied for the determination of individual components in various environmental
132 matrix compositions should be validated against certified reference materials. In this study
133 Reference Material No. 409 (BCR-409, Institute for Reference Materials and Measurements,
134 Belgium); Inorganic ventures ANALITYK-CAL-8 (10 mg/L: Ag, Al., As, B, Ba, Ca, Cd,
135 Co, Cr₃, Cu, Fe, Mg, Na, Ni, Pb, Sb, Se, Sr, V, Zn) and Analytical Reference Material TM-
136 DWS.2, Environment Canada Al: 58.3 µg/L, Sb: 3.20 µg/L, As: 4.20 µg/L, Ba: 146 µg/L,
137 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:
138 167 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:
139 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:
140 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
141 applied. The sensitivity of the applied methods was tested by injecting standard mixtures of
142 the analytes in the measurement range concentration. Linear calibration curves obtained by
143 plotting the peak area against concentration of the respective standards and the correlation
144 coefficients (R^2) were in the range of 0.898-0.999 for all standards. On the basis of the
145 calibration curves, it was possible to determine concentration levels of certain substances in
146 real samples. Each sample was analyzed in triplicate. During the samples analysis,
147 procedural blanks were prepared for every six samples to check the instrumental
148 background. Duplicate samples and calibration check standards were run after every five
149 samples to assure the precision of each run. The limit of detection (LOD) was determined
150 for the analytes in quality control samples based on three replicates of measurement. LOD
151 was calculated using the equation $LOD=3.3SD/b$ (b is the slope of the calibration curve; SD
152 is the standard deviation of the curve). The quantification limit (LOQ) was set to three times



153 the LOD⁵⁶⁻⁵⁸. The numerical values of the all mentioned validation parameters determined
154 for researched analytes, using particular analytical methods, were presented in Table 1.

155 Quality control for biotests is a real challenge as the tests operate with a ‘living
156 reagent’ and thus many factors may affect the results. Therefore, the laboratory which
157 carries out the measurements is involved in the comparative and calibration tests for
158 interlaboratory results check. Moreover, in the case of Microtox® test with *Vibrio fischeri*
159 bacteria the laboratory ran the internal quality control with the reference toxicant ZnSO₄
160 7H₂O to confirm the quality of bacteria guaranteed by producer. EC₅₀ values fell into the
161 accepted range of 0.6-2.2 mg/L. Other parameters that interfere with the test results such as
162 turbidity, colour, pH and temperature were also checked and controlled. In the laboratory the
163 repeatability of the results is constantly checked, coefficient of variation (CV) falls in the
164 range of ±10%.

165 3. Results and discussion

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

171 In the majority of the analysed runoff waters samples the levels of examined analytes
172 did not exceed the maximum permissible levels of concentrations according to the available
173 standard for conditions which should be met while discharging sewage to waters or ground
174 and for substances particularly harmful for aquatic environment⁵⁹. This standard is cited due
175 to the fact that in case of a lack or inadequate work of a waste water treatment plant, a
176 significant amount of airfield effluents get to the surface water or to the soil with runoff
177 waters. However, the contents of some studied analytes and measured parameters exceeded

178 considerably permissible concentration levels of pollutants introduced into the environment.
179 For example, the numerical value of the determined parameter of total organic carbon
180 (TOC) exceeded extremely the permissible level of the total organic compound content
181 introduced into surface waters and soil both in case of the airport with high capacity of
182 passenger movement and the airport with low capacity of passenger movement. Such a high
183 value of the TOC parameter in the airport runoff water samples can be associated with a
184 serious ground and water pollution first of all with oil derivatives and substances from the
185 polycyclic aromatic hydrocarbon group emitted in particular during combustion and
186 uncontrolled aviation fuel overflows. Exceeding the permissible standard (0,1 mg/L) was
187 also noticed for the determined total phenol content in the runoff water samples from the
188 airport with both high and low capacity of passenger movement. It is acknowledged that
189 phenolic compounds (at mg/L level) are extremely toxic for aquatic organisms ⁶⁰. Moreover
190 damages following exposure to substantial doses of phenols affect the nervous and
191 circulatory systems, with a reduction in the number and growth of blood cells (for example
192 erythrocytes, total proteins and cholesterol) ⁶¹. Precise assessment of phenolic compound
193 sources of emission into runoff waters at the airport areas is relatively difficult; the
194 detergents, containing phenolic compounds, used at the airports have been recognized as
195 their main source. The detergents are employed at the airport areas in large amounts to keep
196 airplanes, the airport platform and infrastructure clean. As a result, the increased content
197 level of these types of analytes in the tested airport runoff water samples can be observed.

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

| Analytical techniques | Measurement 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) | 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 | | 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 ₆ H 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 °C -180 (15 °C/min), 180-300 °C (10 °C/min), 300 °C (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, Analytk-Cal-8, Inorganic Ventures Christiansburg, VA, USA. |

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

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

| Target analytes | Units | n | C _{min} | C _{max} | Median | C _{min} | C _{max} | Median |
|---------------------------------|---------------|-----|---|------------------|--------|--|------------------|--------|
| | | | 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 | | |
| b | | 135 | 0.02 | 7.86 | 0.67 | ND | 13.1 | 0.19 |
| | | 135 | 0.02 | 0.61 | 0.25 | 0.04 | 2.81 | 1.87 |
| toxicity | [%] | | | | | | | |
| <i>Vibrio fischeri</i> | ↓Luminescence | 108 | 4.90 | 50.8 | 20.0 | 20.0 | 96.0 | 20.0 |
| <i>Chamnocephalus platyurus</i> | Mortality | 68 | 0.00 | 100 | 25.0 | NT | | |

^a ND- not detected; ^b NT- not tested; ∑Anions: PO₄³⁻, F⁻, HCOO⁻, Cl⁻, NO₂⁻, NO₃⁻, Br⁻, SO₄²⁻; ∑Cations: Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺

2

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



227 While analyzing available measurement data the surprising differences in analytes
228 determined in the samples collected from the airports which differ in capacity of passenger
229 movement significantly content can be observed. The airports with high capacity of passenger
230 movement do not always emit considerable amount of pollutants because in most cases huge
231 international airports have larger budgets to create a reliable infrastructure management system
232 (own waste water pre-treatment and treatment plants, the system of waste recirculation,
233 ecological detergents and de-icing agents etc.) which enables to reduce considerably the
234 sources of pollutants emission. To illustrate this, the maximum TOC level in runoff waters
235 from Newark International Airport (one of the busiest international airports in the United
236 States, 33.8 million passengers/year), was 1120 mg/L, whereas the equivalent level at *Polish*
237 *airport with high capacity of passenger movement* (9.4 million passengers/year) was twice as
238 high. This difference is significant since the Polish airport serves a three times smaller number
239 of passengers than Newark (USA) ⁶. Again, the mean phenol content in samples from Kansas
240 City International Airport, USA (10 million passengers/year) was 93 mg/L, but at Bradley (ca
241 5.6 million passengers/year) it was three times higher ⁶. For instance, the runoff water collected
242 from monitored *airport with high capacity of passenger movement* showed the ca. 1,8 times
243 higher contents of total metals (501 µg/L) in comparison with the monitored *airport with low*
244 *capacity of passenger movement*. These examples show that the level of environmental
245 pollution at an airport is not always directly correlated with either its size or its capacity.

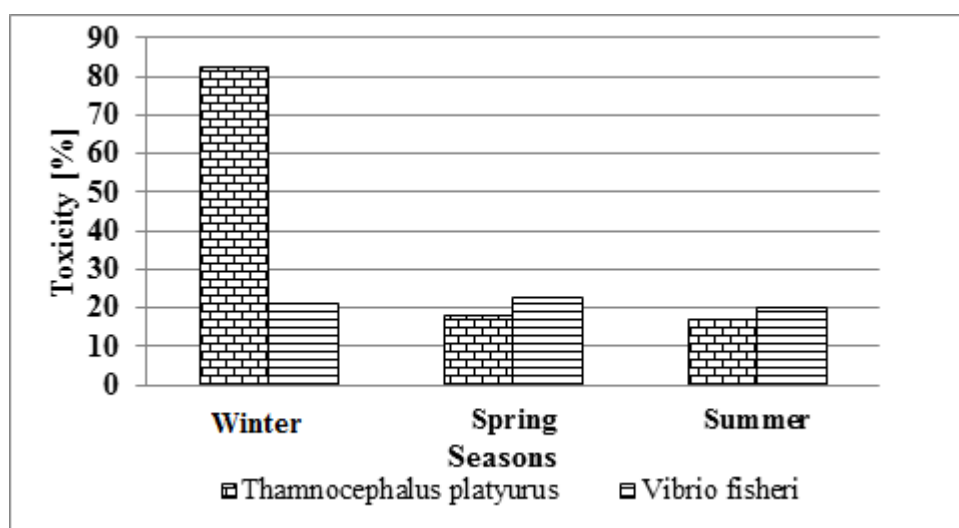
246 Assessing the contamination level of runoff waters from airports requires monitoring of
247 many parameters, which is time-consuming and expensive. Moreover, the results of chemical
248 analyses do not take into account interactions between the compounds present (synergism and
9 antagonism). Therefore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



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



276 passangen movement in 2009) and determined toxicity towards indicator organisms
277 *Thamnocephalus platyurus* and *Vibrio fischeri*. The presented graph confirms the thesis that
278 especially during the winter season the determined toxicity (connected directly with quantity
279 and the specific character of emitted pollutants) of samples is significantly higher in
280 comparison with the toxicity determined for the samples collected in the other seasons of the
281 year when intensity of everyday operations referred to the airport maintenance is much lower
282 than the amount of operations carried out during the winter season.



283 **Figure 1** Toxicity determined in runoff water samples collected in airport area in different
284 season in year 2009.
285

286 Principal components analysis (PCA) was used to explore the data and explain the relationships
287 between the analysed parameters. The results the PCA analysis of are presented in Table 4 and
288 Figure 2. Pesticides were not included in the PCA analysis due to gaps in the database.
289 Principal component 1 (PC1) included 47.2% of the overall variance and was influenced by
290 eight variables: TOC, anions, cations, EC, toxicity towards *Thamnocephalus platyurus*, the sum
291 of detergents, anionic and non-ionic detergents. These parameters are clustered in the plane
2 PC1 and PC2 at the area II (Figure 2). PC1 represents pollutants associated with technological
3 processes carried out during airport operations and related to the maintenance of airport
4 infrastructure, such as cleaning and washing aircraft and airport aprons. The results show that
5 toxicity towards *Thamnocephalus platyurus* is correlated with the other variables forming

296 cluster II, and that this organism can be successfully used as a screening parameter. The
297 number of necessary chemical determinations could be reduced by measurement of toxicity
298 towards *Thamnocephalus platyurus* instead.

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

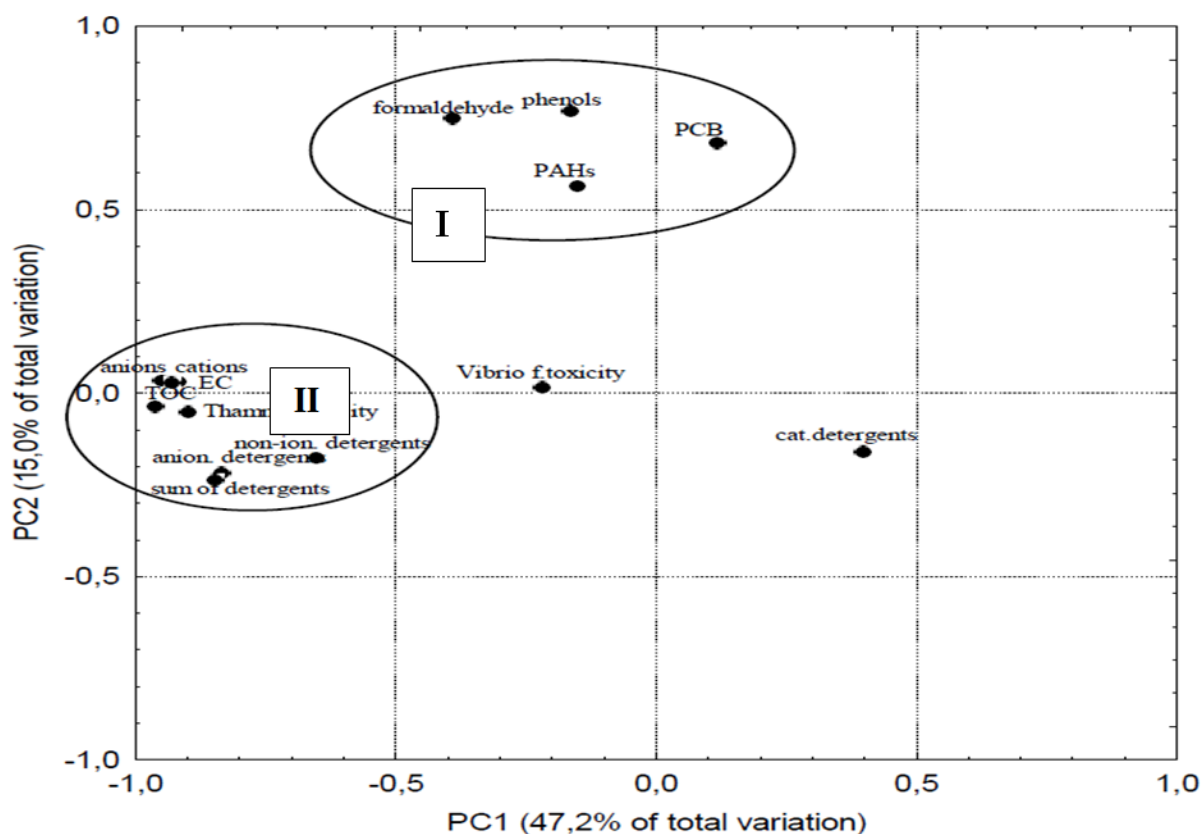
309 The toxicity towards *Vibrio fischeri* appears in third and fourth principal components
310 (PC3 and PC4). The variation of the toxicity towards the *Vibrio fischeri* parameter is positively
311 correlated with the variation of non-ionic (PC3) and cationic detergents (PC4) and negatively
312 correlated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

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

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

8 The results of the PCA of the measurement data revealed that the crustacean
9 *Thamnocephalus platyurus* and bacteria *Vibrio fischeri*, two organisms from different trophic
0 levels, respond differently to the target analytes. This study revealed that *Thamnocephalus*

321 *platyurus* is more sensitive to some of the pollutants (cluster II) determined in the samples than
 322 *Vibrio fischeri* bacteria. However, toxicity to *Vibrio fischeri* bacteria may be important to
 323 indicate other parameters which were either not determined at all or not included in the
 324 monitoring study. For example Pillard et al. in studies on toxicity of benzotriazole and
 325 benzotriazole derivatives mentioned that Microtox® test is more sensitive than tests on
 326 invertebrates (*Ceriodaphnia dubia*) and vertebrates (*P. Promelas*)⁶⁴.



327 **Figure 2** Loadings of the parameters in the plane defined by PC1 and PC2.
 328

329 Figure 3 features the research results (covering the research period from 2009 to 2011)
 330 referring to determined concentrations of particular organic analytes from detergent and phenol
 331 groups, formaldehyde and TOC in the samples of runoff waters collected from the area of the
 2 monitored airport with low capacity of passenger movement. On the graph the clear increasing
 3 tendency of the content level of analytes in airport effluents was observed, beginning with the
 4 year 2009. The successive increase of the pollutant concentration levels in the airport runoff
 5 waters from 2008 to 2011 can be associated with the increased aviation activity at this airport

336 during the research period, which was also presented in Figure 4. Figure 4 shows the
 337 concentration level of the total amount of emitted pollutants while taking into account the
 338 number of passengers handled at the monitored airport with low capacity of passenger
 339 movement from 2009 to 2011. The amount of pollutants present in runoff waters is influenced
 340 mainly by two parameters: aircraft traffic intensity (connected with the increased number of
 341 passengers) and the effort, undertaken by managers of this airport, to reduce the sources of
 342 pollutants emission related to the airport exploitation started in 2010. The documented
 343 fundamental increase of aviation activity at the monitored airports seems to confirm the
 344 prediction of the global growth in the air transport, which is likely to be doubled within the next
 345 15-20 years, and expected therefore considerable growth of the environment pollution being the
 346 result of the airport operations ¹. The results from this study show that it is important to carry
 347 out both chemical analyses and toxicity tests to be able to correctly evaluate the potential
 348 impact of airport stormwater on the environment.

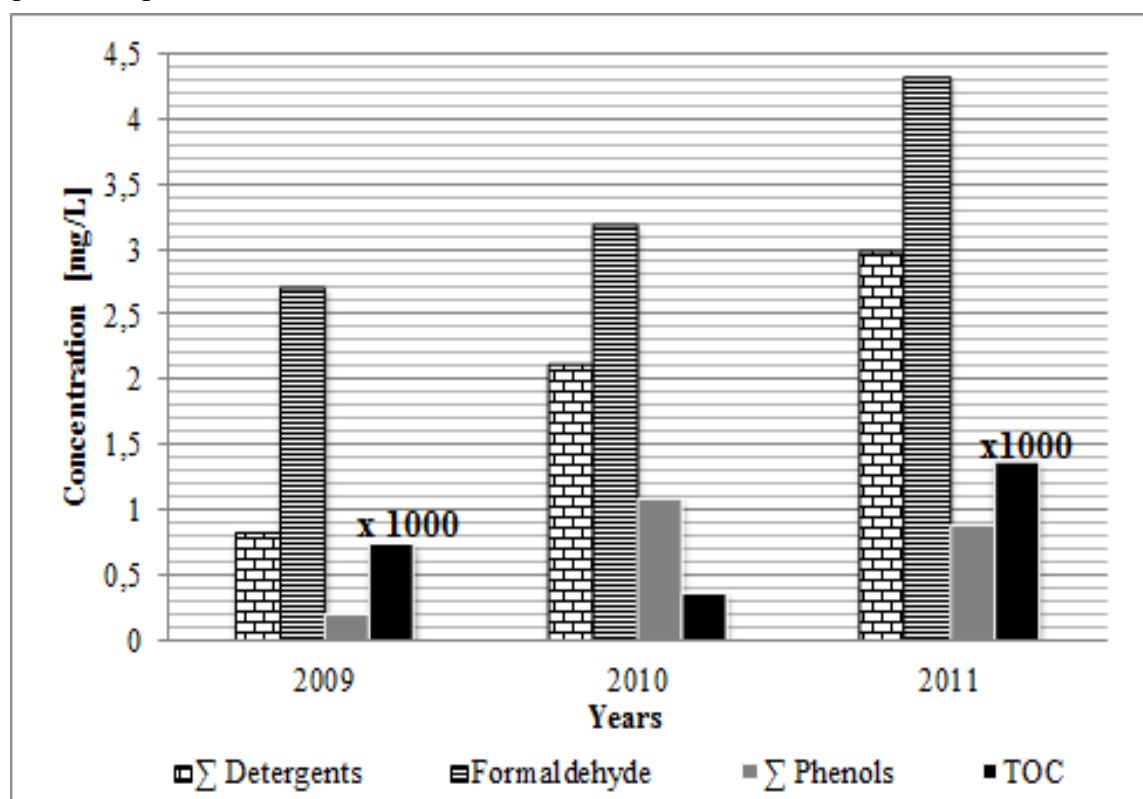


Figure 3 Concentration levels of some selected organic pollutants and TOC parameter in airport runoff water samples.

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 % | |
|--|--|--|--|---|----|
| <i>Vibrio fischeri</i> | | | | | |
| Airport with high capacity of passenger movement | Municipal water catchment area 14.01.11* | Naphthalene= 0.125 [µg/L]; $G_{\text{Naph}}^{**} = 0.015$ $F = 0.278$ [mg/L]; $G_F = 33.1$ Σ metals= 1817 [µg/L]; $G_{\Sigma\text{metals}} = 216$ $Zn = 162$ [µg/L]; $Al = 209$ [µg/L]; $G_{Zn} = 19.3$; $G_{Al} = 24.9$ $TOC = 21999$ [mg/L]; $G_{TOC} = 2.61 \cdot 10^6$ $Formaldehyde = 1.63$ [mg/L]; $G_{Formaldehyde} = 194$ Σ Phenols= 3.33 [mg/L]; $G_{\Sigma\text{Phenols}} = 396$ $Non\text{-}ionic\ detergents = 7.50$ [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 Σ 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] Σ Phenols= 0.302 [mg/L] $Non\text{-}ionic\ detergents = 2.01$ [mg/L] $TOC = 289$ [mg/L] Σ PCB= 0.13 [µg/L] $\gamma\text{-HCH} = 0.149$ [µg/L] $Aldrin = 0.131$ [µg/L] $Endrin = 0.123$ [µg/L] $DDT = 0.00076$ [µg/L] | TOC- permissible norm exceeded 9.6 times Σ Phenols- permissible norm exceeded 3 times PCB exceeded by 0.13 µg/L $\gamma\text{-HCH}$, 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 | Σ Phenols= 0.45 [mg/L] Σ PCB= 0.14 [µg/l] Σ PAH= 5.70 [µg/l] | Σ 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] Σ Phenols= 0.29 [mg/L] Σ PCB= 1.02 [µg/L] $\gamma\text{-HCH} = 0.039$ [µg/L] $Aldrin = 0.0018$ [µg/L] $Endrin = 0.0017$ [µg/L] $DDT = 0.0028$ [µg/L] | TOC- permissible norm exceeded 7.7 times Σ Phenols - permissible norm exceeded 2.9 times PCB - permissible norm exceeded by 1.02 [µg/L] $\gamma\text{-HCH}$, 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 | |
| <i>Thamnocephalus platyurus</i> | | | | | |
| 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] $Non\text{-}ionic\ detergents = 1.85$ [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 | Σ 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]



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375

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 |
| Σ PHENOLS | -0.17 | 0.77 | 0.26 | 0.04 | 0.39 |
| TOC | -0.96 | -0.04 | -0.12 | -0.03 | -0.15 |
| <i>VIBRIO FISCHERI</i> TOXICITY | -0.22 | 0.02 | 0.67 | 0.51 | -0.45 |
| <i>THAMNOCEPHALUS PLATYURUS</i> 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 |

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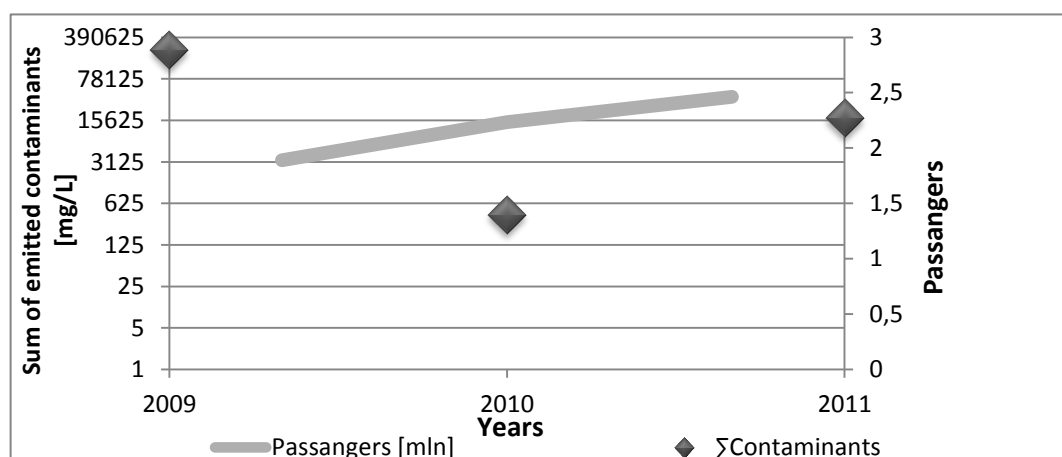


Figure 4 Concentration levels of summary amount of emitted contaminants determined in airport stormwater in correlation with passengers movement during period 2009-2011.

395 5. Conclusions

396 Contaminants generated from different sources of airport infrastructure; including
 397 leakage of fuel, paint materials, tire debris, use the brakes at high speeds especially during of
 398 sharp turns, small fragments of road surfaces and metals, peeled off rust and varnish, vehicle
 399 components, dissolved agents against glazed frost and detergent remains; are washed off the
 400 airport platform into drainage system by rain water, sometimes retained in the drainage
 401 system for a while, and finally transported mainly to the receiving water. Airport runoff

402 water is considered to be an important source of environmental contamination, because
403 runoff not only gets into surface waters, but also to soil, and even to ground water sources of
404 drinking water, and organisms living in this soil and waters as final receptors.

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

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

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



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