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ANALYSIS OF AIRPORT RUNOFF WATERS

Abstract

A particularly important facet of airport operation is the impact of the pollution caused by runoff waters. Runoff waters at an airport may contain relatively high concentrations of different contaminants resulting from the various aspects of its operation: de/antiicing operations; washing and cleaning operations; spills of fuel and lubricants; exhaust fumes; weed removal.

The pollution caused by airport operations affects soil, surface waters and ground waters. This issue is important to various stakeholders, particularly those residing in communities near airports, whose health, property values, and quality of life can be affected by such environmental impacts. The authors' intention is to present a critical review of literature data concerning (1) the types of pollution generated at airports; (2) methods for sampling runoff waters; (3) the analytical methods available for sample preparation; (4) the analytical methods available for determining contaminants produced during airport operations. In addition, the paper supplies literature information on the analytes contained in samples of runoff water from airports in different parts of the world.

Key words: airport runoff waters, pollutants, sources of emission, sample collection, analytical procedures

1. Introduction

Despite the many positives ensuing from the rapid expansion of the air transport sector, airport operations as a whole are a substantial source of environmental pollution (Wensveen, 1999). These operations are connected with aircraft movement of aircraft and airport infrastructure. They include the deicing and anti-icing of aircraft and airfields, the movement of passenger vehicles and airport ground service equipment, the cleaning and maintenance of aircraft, ground service equipment and motor vehicles, airport facility operations and maintenance, removal of weeds and other vegetation from the airport apron (Luther, 2007). Very large amounts of harmful chemicals are utilized during these operations: for example, the quantities of de/anticing sprays range from as few as 11 gallons/plane to as many as 3, 900 gallons/plane for large aircraft during bad weather (Zitomer, 2001).

All airport operations have adverse effects on the water, air, soil and animals, and further environmental problems are associated with climate change and aicraft noise (Douglas and Lawson, 2003; Kijewski, 2001).

A particularly important aspect is the contamination caused by airport runoff waters, which are produced when rain or other precipitation washes the chemicals used during aircraft and airfield deicing and anti-icing, refueling aircrafts, vehicle cleaning and maintenance, etc., off the airport apron. This runoff gets into the soil, surface waters, and even ground waters. Figure 1 shows a diagram of the effects of an airport on the environment.

This issue is important to various stakeholders, particularly those residing in communities near airports, whose health, property values, and quality of life can be affected by such environmental impacts (Luther, 2007).

Continuous monitoring of the airport waste stream is key in controlling runoff. The airport operator should understand the potential for and establish measures and procedures to address situations where there would be adverse consequences following the discharge of airport industrial wastes waters. This may include reviewing spill prevention and countermeasure plans and notifying facility authorities of potential problems (O'Donnell, 2008).

The authors' intention is to present a critical review of literature data concerning:

- the types of pollution generated at airports;
- methods for sampling runoff waters;
- the analytical methods available for sample preparation;
- the analytical methods available for determining contaminants produced during airport operations.

In addition, the paper supplies literature information on the analysis of samples of runoff water from airports in different parts of the world.

2. Types of airport industrial waste

The various activities of an airport may affect the abiotic and biotic environments. We will now discuss the pollution produced by different airport operations. Airport industrial wastewaters are generated during the de/anti-icing of aircraft, aircraft maintenance and repair work, aircraft and ground vehicle washing, aircraft and ground vehicle movements and weed removal. A proper classification of airport-generated industrial wastes includes industrial wastewaters, hazardous wastes and non-hazardous wastes. Industrial wastewaters are generally characterized in terms of conventional pollutants (oil and grease, total suspended solids, pH change of water and 5-day biochemical oxygen demand) and priority pollutants (hydrocarbons, polycyclic aromatic hydrocarbon (PAHs), pesticides, polychlorinated biphenyls (PCBs), heavy metals, cyanides). Hazardous wastes may be inflammable, corrosive, reactive and toxic. Non-hazardous wastes include oily rags or sludge that may be packaged for disposal in plastic bags or shipped to be recycled. Table 1 lists the main types of airport pollutants and their effects on the environment (Luther, 2007; McConnell et al., 1999; O'Donnell, 2008).

3. Analytical procedures used in studies of samples of airport runoff waters

In order to evaluate the threat to surface waters and soils, and by extension, to ground and abyssal waters, the identification of the chemical compounds contaminating airport runoff is essential. Moreover, to assess the rate at which and the means by which runoff contaminants migrate through the environment, we need to know their physical and chemical properties, since it is these that govern the extent to which chemical, biochemical and photochemical processes paprticipate in their environmental fate (Leśko and Pasek, 1997). Waste composition varies greatly from airport to airport. This variability reflects the numerous aspects of aircraft deicing, cleaning, solvents used and stormwater management, including variable meteorological events, different deicing/anti-icing, cleaning practices and collection systems (Switzenbaum et al., 1999).

The analysis of airport runoff samples presents a big challenge to analysts. The main problems in this respect are:

- the low, and even very low, levels of a wide range of contaminants;
- the very considerable variability in the concentrations of particular contaminants in runoff samples from different airports;
- the difficulties in standardizing measurement results because of:
    - ✓ the varying intensity of air traffic;
    - ✓ changes in weather conditions;

    - ✓ the geographical locations of airports;
- the possibility that samples contain analytes with very similar physical and chemical properties but which are of widely differing toxicities with respect to both biota and abiota;
- the lack of standard techniques for sampling runoff waters, which can significantly affect the reliability of measurements;
- the limited availability of suitable standard solutions and the lack of reference materials (with different metrological values), which are essential for:
    - ✓ calibrating monitoring instruments;
    - ✓ validating the various steps in the analytical procedure as well as whole analytical methodologies, which are the tools for obtaining reliable information on the content of and processes occurring in samples of runoff waters during their transport, storage and preparation for analysis.

Figure 2 shows a general scheme of the analytical procedures used for investigating samples of airport runoff.

Sampling and preparing samples for analysis are key stages in every procedure designed to analyze a particular group of constituents. It is most important that the sample is representative. However, the accurate sampling necessary for the correct analysis of airport industrial wastes can be difficult because such wastes are seldom homogenous, e.g., their composition may vary widely within a period of minutes.

For continuously flowing wastewater streams, the flow rates of both individual and combined streams should be measured at representative points and expressed in standard units such as gallons per minute (gpm), gallons per hour (gph), or gallons per day (gpd). The method used by the airport operator to determine the flow rate will depend upon the magnitude of flow. Common metering devices include weirs, nozzles, flumes and flow meters. For wastes that are generated on an intermittent basis, such as spent process baths, certain hazardous wastes, and deicing runoff, generation rates can be determined from the disposal volumes and dates. Flow proportional samples are recommended where applicable (O’Donnell, 2008).

The intensification of air traffic at airports and the expanding number of airports means that this particular human activity is putting significant pressure on the environment. Clearly, then, the monitoring of airport runoff content should cover the broadest possible range of substances. Only monitoring carried out on such a scale is capable of supplying data that will form a reliable basis for assessing the effects of airports on the abiotic and biotic compartments of the environment.

There should be two types of periods during which runoff samples collected from various parts of an airport are analyzed:

- an initial monitoring period, when samples are collected as often as possible, e.g. several samples should be collected each time contaminants are produced;
- a long-term monitoring period, when samples are collected, say, every month or every year, in order to confirm that the properties of airport runoff waters have not changed

3.1 Collection of airport runoff samples

An ideal sampling event may be one which takes advantage of special weather conditions, such as following a major snowstorm, which requires blowing and deicing. The post-storm temperature rise will produce runoff from which it is possible to determine the seasonal and annual fluctuations in constituent concentration (Halm, 1996).

It is important to choose the appropriate location of stormwater monitoring sites (Kent et al., 1999). These should be placed near sites where the largest amounts of pollutants are emitted, e.g. deicing pads, fuel distribution pads, fuel tanks, transshipment points, fuel pipelines, repair shops, or at an upstream reference site, the primary and secondary airport outfalls, and the receiving stream site (Leśko and Pasek, 1997).

Airport runoff waters are usually collected from storm drains, each serving a different land use: the main terminal area, the primary deicing and anti-icing area, taxiways and runways. Moreover, at most airports, aircraft deicing operations are performed on special pads (aircraft parking ramps or at the passenger terminal gates) (U.S. EPA, 2000). To collect the wastewaters generated at these locations, some airports have installed new collection systems or modified existing storm water drainage systems. The typical collection system consists of graded concrete pavement with trench or square drains connected to a wastewater storage facility via a diversion box (O'Donnell, 2008). The storage facility may consist of detention ponds (covered or uncovered), tanks, or underground concrete basins. The diversion box allows uncontaminated storm water to be diverted to storm water outfalls. The construction or modification of drainage collection systems with their associated underground piping, diversion boxes and storage facilities can be extremely expensive, especially for larger airports that have several passenger terminals and a large number of gates. Sometimes ADAF formulations can be collected directly from storage tanks and deicing/anti-icing vehicles (glycol recovery vehicles), which remove the de-icing and anti-icing agents directly from the airport apron (Corsi et al., 2006a).

Sample bottles for different analytes should be of the appropriate type (e.g. tubing model 3700R, Isco Industries, Lincoln, NE; refrigerated glass amber containers for analyzing deicing and anti-icing agents) (Budavari, 1996; Corsi et al., 2006b) and size (e.g. 500 ml) (Corsi et al., 2003) and contain the appropriate preservative. To minimize the possibility of sample contamination, containers must be thoroughly rinsed with deionized water prior to use (Knott et al., 1996).

For airport industrial wastewaters, grab or composite samples should be taken and properly preserved before analysis. The sampling operation should be as frequent as situation-specific requirements dictate (O'Donnell, 2008).

Airport runoff samples may be collected manually or by use automated sampler (for example, ISCO®, Lincoln, NE), from the drain outfall (Corsi et al., 2003; Saito et al., 2004).

3.2 Techniques of sample preparation

The preparation of samples for analysis is often an essential step in analytical procedure, espiecally when constituents present at trace or ultra-trace levels are to be determined. Runoff waters have a complex matrix composition, and the metrological parameters of most analytical techniques preclude the determination of the majority of compounds present in such waters. In order to analyze samples of such waters quantitatively, the analytes they contain must first be isolated and/or preconcentrated before the relevant extracts can be analyzed using the appropriate instrumentation.

The following analyte extraction techniques are routinely used:

- Solid Phase Extraction (SPE) (Knott et al., 1996; U.S. EPA 1999; U.S. EPA, 2000; Vlaming et al., 2000);
- Liquid-Liquid Extraction (LLE) (U.S. EPA 1999; U.S. EPA, 2000; Vlaming et al., 2000; Wan et al., 1996);
- Headspace Solid-Phase Microextraction (HS-SPME) (U.S. EPA Method 1625C).

The use of ultrasound as an assisting agent will accelerate the extraction of hydrocarbons (PAHs, PCBs).

Table 3 lists information on techniques for preparing samples of runoff waters for analysis.

3.3 Analytical procedures for determining the physicochemical parameters and contents of analytes in airport runoff samples

To date, not many results of analyses of runoff waters have been published. This situation is changing, however: interest in this type of data is growing, as it provides a source of information on the potentially negative effects of airports on the environment. The physicochemical parameters of airport runoff and the analytes it contains can be determined using the appropriate analytical procedures.

Usually, airport runoff water samples are analyzed in order to determine the level of pH, chemical oxygen demand (COD), five-day biochemical oxygen demand (BOD_5), total organic carbon (TOC), glycol content, total suspended solids (TSS), total phosphorus and total Kjeldahl nitrogen (TKN). Apart from summary parameters, other groups of compounds are also analyzed (petroleum compounds, surfactants, glycols, benzotriazoles, metals and other inorganic compounds). The following analytical techniques are used to determine target analytes in suitably prepared samples of airport runoff: GC-MS, GC-FID, HPLC, GPC, HPLC-MS, HPLC-UV, HPLC-MS/MS, LC/MS, TLC, AAS, ICP/MS (Fries and Klasmeier, 2009; U.S. EPA 1999; U.S. EPA, 2000; U.S. EPA Method 624; Wan et al., 1996). Table 3 also lists literature information on the analytical procedures used and the concentration ranges of various types of xenobiotics in samples of airport runoff.

In tandem with the chemical analysis of airport runoff waters, their toxicity is also evaluated. Tests using biological material are crucial, since they constitute the basis for assessing the overall degree of contamination of particular compartments of the environment (U.S. EPA Methods 8015b, Namieśnik et al., 2003). Table 2 summarizes the most commonly used tests for assessing the acute and chronic toxicity of airport runoff waters (Kent et al., 1999).

4. Literature data on the level of pollution due to different xenobiotics in airport runoff waters from different geographical regions

Most of cases of pollution by airport runoff waters are defined using total parameters such as Chemical Oxygen Demand, five- day Biological Oxygen Demand, Total Organic Carbon, Total Suspended Solids and certain specific compounds like hydrocarbons, propylene and ethylene glycol. Table 4 lists literature information on the analyses of samples of runoff water from airports in different parts of the world. The waste content of airport runoff waters varies greatly from airport to airport, because the types of chemical agents used in airport operations vary widely. Consequently, the characteristics of airport runoff waters generated by different airports do so, too (Switzenbaum et al., 1999).

6. Conclusions

Airport daily activities, such as fueling operations and ground vehicle maintenance, aircraft de/anti-icing, ground vehicle washing and cleaning, aircraft maintenance and repair work, engine test cell operations and weeding the airport apron, are all sources of environmental wastes.

Airports sometimes have their own sewage treatment plants, but many much smaller airports do not even have facilities for the pre-treatment of wastewater from airports. In these cases most of the substances from airport operations left on the apron eventually enter the airport stormwater and are subsequently transported to the receiving waters. The large discharge of airport wastes to runoff waters may have numerous adverse consequences, especially potential drinking water contamination.

The levels of contaminants determined in airport runoff waters varies greatly from airport to airport. The waste content of airport runoff waters varies greatly from airport to airport, because the types of chemical agents used in airport operations vary widely.

This issue is important to various stakeholders, particularly those living in communities near airports, whose health, property values, and quality of life can be affected by such environmental impacts. The runoff waters generated by airport activities thus require special management procedures, e.g. source reduction, the use of alternative de/anti-icing agents, recycling of materials and remediation technologies.

A very important aspect is the changes that should be made to the standards applicable to airport operations (e.g. deicing operations and oil spills), pollution prevention procedures, as well as state and local agency directives for monitoring and controlling runoff water pollution, particularly toxic water pollutants.

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Figures:

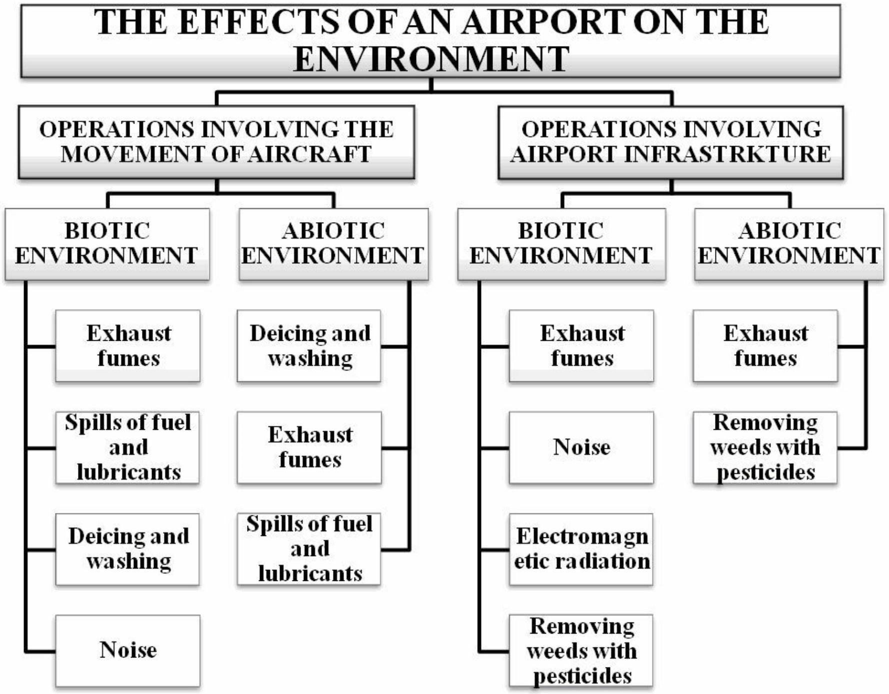

Figure 1. **The effects of an airport on the environment.**

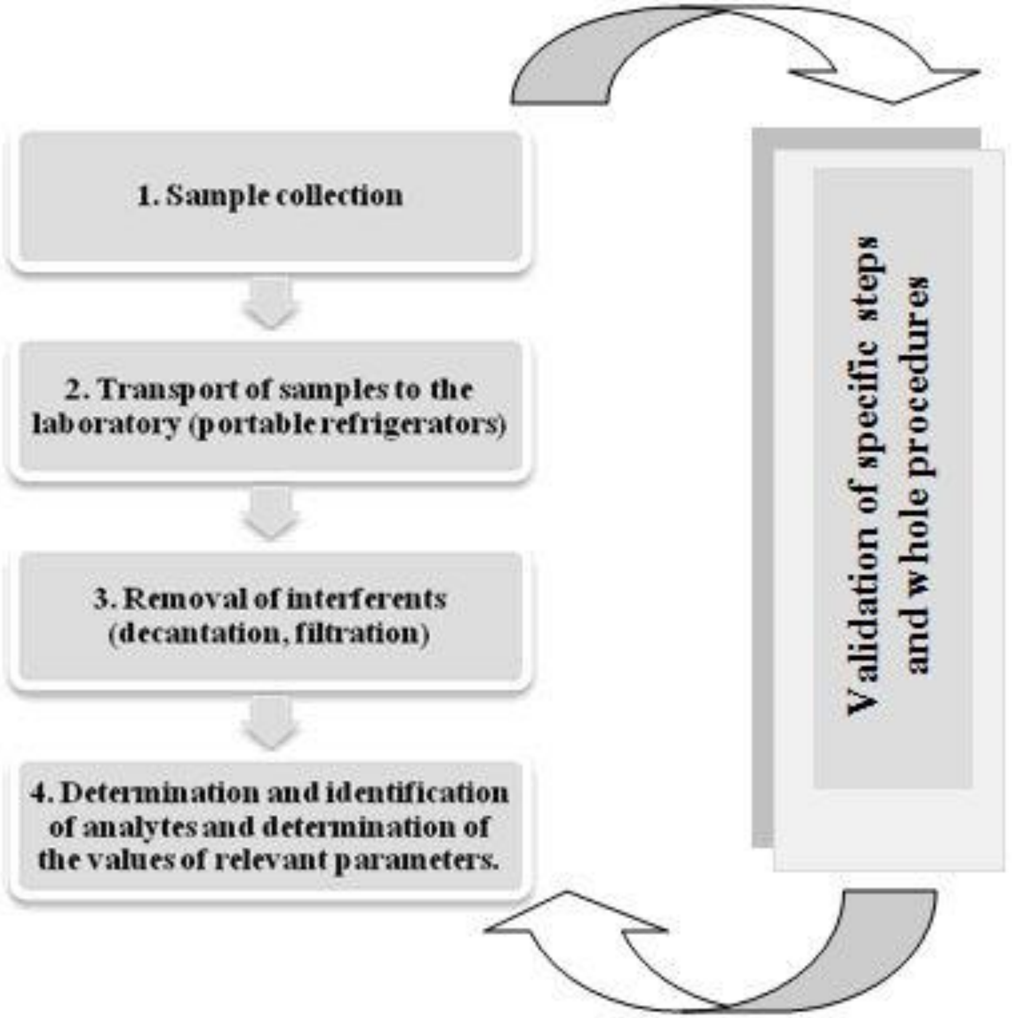

Figure 2. General scheme of the analytical procedures used in studies of samples of airport runoff samples.

Table 1. Types of airport industrial wastes and a short description of their impact on the environment

Type of pollutant	Origin of pollution	Compounds emitted	Environmental impact	References
Combustion gases	• combustion of aviation fuels; • combustion of engine fuels;	$CO_{2;}$ NO_x; H_2O; sulfate ions; particulate matter components (PM10, $PM_{2.5\text{-}10}$, $PM_{2.5}$, $PM_{1.0}$); Polycyclic aromatic hydrocarbons (PAH_s);CO; SO_2, aldehydes, aliphatic hydrocarbons, volatile organic compounds (VOCs);	• present a direct threat to employees' health and safety; • the resistance of trees to pests and disease; • impair growth of biomass and lower its quality; • adverse effect on fungi, algae, lichens; • damage to buildings; • PAHs are mutagenic	(Amato et al., 2010; Fang et al., 2007; Hoffman et al., 1984; Kesgin, 2006; Pison, 2004; Polidori et al., 2010; Ray et al., 2008; Takada et al., 1990; Unal et al., 2005; Westerdahlet al., 2008; Winter et al., 2006)
Fuel, oil, grease	• vehicle maintenance shop operations; • fuelling operations; • engine test cell operations;	• hydrocarbons – aliphatic (n-heptane, pentane, hexane, pentene), olefins, aromatic (benzene, ethylbenzene, toluene, phenol, o-xylene) • PAHs (benzo(a)pyrene, benzo(a)anthracene, naphthalene, phenanthrene) • Polychlorinated biphenyls (PCBs)	• contamination of surface waters and soils; • the consumption of dissolved oxygen; • hinder re-oxygenation of streams; • may form sludge deposits that could interfere with stream self-purification processes; • aromatic hydrocarbons are carcinogenic; • volatile aliphatic hydrocarbons can give rise to an explosion or fire;	(Leśko and Pasek, 1997)
Detergents	• cleaning of aircraft and ground vehicles; • repairs to aircraft engines and ground vehicles; • cleaning airport aprons	• Aqueous-neutral detergent; • Aqueous-nonionic detergent; • Aqueous-alkaline/hydroxide; • Aqueous-alkaline with detergent;	• may cause foaming in aeration basins; • may cause partial sludge flotation through release of carbon dioxide	(O'Donnell, 2008; Sierra et al. 1981)

		• Semi-aqueous; • Semi-aqueous/terpene; • Semi-aqueous/glycol ether; • Semi-aqueous/abrasive; • Semi-aqueous/hydroxide; • Aliphatic/terpene; • Aliphatic/glycol ether; • Glycol ether blends;		
De/anti-icing chemical wastes	• de/anti-icing operations;	• propylene glycol; • ethylene glycol; • diethylene glycol; • urea; • salts, i.e. sodium and potassium acetates; sodium formate; calcium and sodium chlorides	• may interfere with biological activity; • consumption of dissolved oxygen; • may form sludge deposits that could interfere with stream self-purification processes • toxic and endocrine disrupting effects;	(Breedveld et al., 2003; Corsi et al. 2006a, Espey and Legarreta, 1993 U.S. EPA, 2000; Switzenbaum et al., 1999)
Toxic metals and chromium compounds	• bright dipping; • chromium plating; • copper stripping; • anodizing operations; • corrosion of aircraft parts and ground vehicles; • use of road salt; • removal of exterior paint	• Cd, Cr, Cu, Pb, Ni, Zn; • chromium compounds	• may interfere with biological activity and may complicate sludge disposal; • are toxic to human beings, livestock, and aquatic life	(O'Donnell, 2008; Walker et al. 1999)
Alkalis and acids	• pickling and cleaning operations;	• generally acids and alkalis	• may corrode pipes, pumps, and treatment units and may interfere with settling and biological activity	(O'Donnell, 2008)
Specific organic compounds	• cleaning of aircraft and ground vehicles; • paint application and removal;	• Benzotriazole, Totyltriazole; • Phenols,	• the consumption of dissolved oxygen • may form sludge deposits that could interfere with stream self-purification processes	(O'Donnell, 2008; Gigger et al., 2006)

			• may interfere with biological activity	
Batteries	• spent lead-acid, lithium, and nickel-cadmium batteries are generated from routine ground vehicle maintenance;	• cadmium, nickel and lead compounds;	• contaminate surface waters, groundwater; • dissolve metals and other materials • burn human skin ;	(O'Donnell, 2008)
Cyanides	• steel hardening; • metal plating; • rust prevention; • stain removal operations;	HCN, KCN	• are toxic to human beings, livestock, and aquatic life.	(O'Donnell, 2008)
Pesticides	• removing weeds and other vegetation from the airport apron	organophosphate insecticides	• chronic health effects: reduced cholinesterase (adults at work can have reduced attention)	(McConnellet al., 1990)
Electromagnetic radiation	• Formation of electromagnetic radiation by the transmitting, telecommunication, radiolocation and radionavigation equipment used in aviation	-	• Can lead to dysfunction of: • the central nervous system; • the reproductive, • cardiovascular, • hormonal systems, • the organs of sight and hearing	(Amato et al., 2010)
Noise	• the large-scale operation of jet-powered aircraft, both military and civil	-	Differing effect on people; • impaired sight and/or hearing, • apathy, • headache, • difficulties with concentration, • problems with social intercourse, • may adversely affect the nervous system.	(Kil and Podciborski, 2008)

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Table 2. The tests most commonly ued to assess acute and chronic toxicity of runoff waters

CHRONIC										**ACUTE**									
Vertebrates			**Invertebrates**			**Others**				**Vertebrates**					**Invertebrates**				
Fathead minnow	*Rainbow trout*		*Ciliated protozoan*	*Rotifer*	*Ceriodaphnia dubia*	*S. costanum*	*P.phosphoreum*	*C.paramecium*	*S.capricornutum*	*Fathead minnow*	*Rainbow trout*	*Bluegill sunfish*	*Sheepshead*	*Clawed toad*	*Daphnia magna*	*Ceriodaphnia dubia*	*Crayfish*	*Mysidopsis*	Species
7-d LOEC	12-14 d LOEC	12-14 d LC50	24-h EC50	7-d LOEC, 7-d LOEC	7-d LOEC	96-h EC50	5/30 min LC50	7-d LOEC	24-336 h-EC50	96-h LC50	96-h LC50	96-h LC50	96-h LC50	48-h LC50	24/48/96-h LC50	48-h LC50	96-h LC50	96-h LC50	Toxicity End-Point

Table 3. Literature information on the analytical procedures used and the concentration ranges of various types of xenobiotics in samples of airport runoff

Analyte	**Sample collection, preservation, and handling**	**Final determination technique**	**Validation parameters**	**References**
Liquid samples – water				
Physicochemical parameters				
pH	• Calibration in a buffered solution of pH 4.01; • Before each measurement the electrode should be rinsed in demineralized water and dried with absorbent paper;	Electrochemical technique	No data available	(U.S. EPA, 2000)
Conductivity		Electrochemical technique		
Summary parameters				
BOD$_5$	• Keep samples at or below 4°C during composting; Limit composting period to 24 h; • pH 6.5 to 7.5; • Incubation at the standard test temperature (20°C) for 5 days;	Standard Methods for the Examination of Water and Wastewater 5210 B. 5-Day BOD Test	No data available	(U.S. EPA Method 5210)
COD	• Samples should be preserved with sulfuric acid at pH < 2 and maintained at 4°C until analysis; • Interferences: chlorides, mercuric sulfate is added to the digestion tubes to complex the chlorides;	EPA Method 410.4 • Titrimetric;	• measurement range : 3-900 mg/L; • Precision and Accuracy: 86 analysts in 58 laboratories analysed a distilled water solution containing oxidizable organic material equivalent to 270 mg/L COD; • The standard deviation (SD) was 17.76 mg/L COD with an accuracy, expressed as percentage relative error (bias), of -4.7%. (EPA Method Research Study);	(EPA Method 410.4)

TOC	• Collection and preparation of samples in glass bottles (the best way); • Samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen; • In instances where analysis cannot be performed within two hours (2 hours) of sampling, the sample should be acidified to pH 2 with HCl or H_2SO_4; • Carbonates and bicarbonates should be removed;	EPA Method 415.1 Combustion Or Oxidation	• measurement range: the method is best applicable to the measurement of organic carbon above 1 mg/L; • Precision and Accuracy: ✓ Increment as TOC (mg/L)= 4.9; Precision as Standard Deviation TOC, mg/L = 3.93; Accuracy as Bias(%)=+15.27; Bias(mg/L)= +0.75 ✓ Increment as TOC (mg/L)= 107; Precision as Standard Deviation TOC, mg/l = 8.32; Accuracy as Bias(%)= +1.01; Bias(mg/L)= +1.08	(U.S. EPA Method 415.1]
TSS	• Preservation of the sample is not practicable – analysis should begin as soon as possible; • Refrigeration or icing to 4°C; • A well-mixed sample is passed through a glass fibre filter, and the residue retained on the filter is dried to constant weight at 103 -105°C;	EPA Method 160.2 Gravimetric	• measurement range: 4 – 20 000 mg/L; • Precision data are not available at this time;	(U. S. EPA Method 160.2)
Groups of compounds				
TKN (Total Kjehldahl Nitrogen)	• Chloride anion-exchange resins should be used to remove nitrates prior to analysis; • Maximum holding time**:** 28 days; • Sample handling and preservation: may be preserved by the addition of conc. H_2SO_4, stored at 4°C;	EPA Method 351.3 • Colorimetric; • Titrimetric; • Potentiometric;	measurement range: 0.05 – 1400 mg/L;	(U.S. EPA Method 351.3)
Ammonia as nitrogen (NH_3)	• Samples may be preserved with H_2SO_4 and stored at 4°C, pH 9; • Distillation is used prior to analysis to reduce/eliminate interferences (e.g. formaldehyde); • Remove residual chlorine using sodium • thiosulfate;	EPA Method 350.1 • Colorimetric; • Titrimetric; • The electrode method; • FIA;	measurement range: • FIA method: 1.0 – 1000 mg/l NH_4^+; 1.2 - 1 200 mg/L NH_3; • 0.05 to 1.0 mg NH3-N/L (colorimetric procedure); 1.0 to 25 mg/L (titrimetric procedure); • 0.05 to 1400 mg/L (the electrode method);	(U.S. EPA, 2000, U.S. EPA Method 350.2)
Phosphorus, all Forms (P) - total orthophosphate, hydrolyzable	• If the analysis cannot be performed on the day of collection, the sample should be preserved by the addition of conc. H_2SO_4 and refrigeration at 4°C;	EPA Method 365.3 Colorimetric	• measurement range: 0.01 to 0.5 mg P/L range; • Precision and Accuracy: ✓water samples at concentrations of 0.04, 0.19,	(U.S. EPA Method

phosphate, and phosphorus			0.35 and 0.84 mg P/l, standard deviations were +/-0.005, +/-0.000, +/-0.003 and +/-0.000 respectively; ✓In a single laboratory (EMSL), using surface water samples at concentrations of 0.07 and 0.76 mg p/l, recoveries were 99% and 100% respectively;	365.3)
TPH (Total Petroleum Hydrocarbons)	• A representative sample of 1 litre volume should be collected in a glass bottle; • A delay between sampling and analysis of greater than 4 hours requires sample preservation by the addition of HCl. A delay of greater than 48 hours also requires refrigeration for sample preservation;	EPA Method 418.1 Spectrophotometric	The method is sensitive to levels of 1 mg/L and less, and may be extended to ambient monitoring;	(U.S. EPA Method 418.1)
Semi-volatile organic compounds (including tolyltriazoles)	• Sample storage at 0-4°C; • Any residual chlorine in the sample should be removed by the addition of sodium thiosulfate; • Begin sample extraction within seven days of collection, and analyse all extracts within 40 days of extraction; • <u>Extraction:</u> ✓ Samples containing 1% solids or less – liquid/liquid extraction techniques; ✓ Samples containing 1-30% solids are diluted to 1% with reagent water and extracted using continuous liquid/liquid extraction techniques; ✓ Samples containing more than 30% solids are extracted using ultrasonic techniques; • clean up with GPC;	EPA Method 1625C • Gas Chromatography-Mass Spectroscopy (GC-MS); • Gel permeation chromatography (GPC);	No data available	(Wan et al., 1996)
Hexane	• Glassware should be cleaned with great care (wash with detergents, rinse with solvent); • Acidification to pH <2;.	EPA Method 1664 Gravimetry	• measurement range: 5 - 1000 mg/L; • Method detection Limit (MDL)= 1.4 mg/L; • Minimum level of quantitation (ML)= 5.0 mg/L;	(U.S. EPA, 2000, Vlamin

	• Extraction: ✓ Solid Phase Extraction (SPE); ✓ Liquid-liquid extraction (LLE);			g et al., 2000)
Fats, Oils and Grease	• The sample is acidified to a low pH (< 2); • Serially extracted with fluorocarbon-113 in a separating funnel; • Maximum holding time: 28 days;	EPA Method 413.1 Gravimetry	• measurement range: 5-1000 mg/L of extractable material; • Precision: the method determined the oil and grease level in sewage to be 12.6 mg/L. When 1 litre portions of sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 93% with a standard deviation of +/- 0.9 mg/L;	(U. S. EPA Method 413.1)
De-icing agents				
Glycols (PG, EG)	• All samples must be iced or refrigerated from the time of collection until analysis; • If the sample contains residual chlorine, add sodium thiosulfate preservative to the empty sample bottle just prior to shipping to the sampling site; • Grab samples must be collected in glass containers; • Seal the bottle so that no air bubbles are entrapped in it. • If preservative has been added, shake vigorously for one minute.	• EPA Method 624; • EPA Method 8015b; • GC-MS; • Gas chromatography-flame ionization detector (GC-FID);	GC-FID • measurement range: ✓36 to 640 mg/L for ethylene glycol ✓40 to 1150 mg/L for propylene glycol; • Precision 5 to 600 mg/L; • Average recoveries: ✓93.9% for ethylene glycol 100% for propylene glycol • Standard deviations: ✓ 8.8% for ethylene glycol; ✓ 8.9% for propylene glycol; • Limit of detection (LOD) = 18 mg/L (ethylene glycol and propylene glycol); • Relative percent differences (RPD) = 11 for ethylene glycol; RPD=7.9% for propylene glycol;	(Fries, 2009; U.S. EPA, 1999; 2000; U.S EPA Method *624*)
Surfactants				

Nonylphenol Ethoxylates, Alkylphenol Ethoxylates	• SPE (for GC/MS, HPLC-MS, HPLC-MS/MS, LC/MS); • Soxhlet (for HPLC fluorescence); • Gas-stripping (HPLC-UV); • Liquid/liquid (for HPLC fluorescence); • NP*n*EOs were isolated by passing samples through a mixed-bed ion exchange column and then through a column containing octadecylsilica (C18) to remove NP*n*EOs; • The NP*n*EOs were extracted from the C18 using warm methanol, which was subsequently evaporated to dryness under a stream of nitrogen; • The residue was dissolved in chloromethane/hexane	• High-pressure liquid chromatography (HPLC) • GC/MS; • HPLC fluorescence; • HPLC-UV; • HPLC-MS; • HPLC-MS/MS; Liquid chromatography-mass spectrometry (LC/MS);	Measurement range for HPLC • MDLs = 0.005, Relative standard deviation (RSD) = 0.16% for NP1EO; • MDLs =0.236 µg/L, RSD= 8.4%. for NP15EO; • RSD for the entire method (extraction + analysis) was 24% for total NP*n*EO (*n*=1-15); Measurement range for LC/MS ✓ NPEs = 20 ng/mL (NP1EO) and 0.07 ng/mL ✓ NP17EO in the lowest standard to 3,000 ng/mL (NP1EO) and 11 ng/mL (NP17EO) in the highest concentration standard; • OPE concentrations ranged from 1.3 ng/mL (OP1EO) and 0.017 ng/mL (OP17EO) in the lowest concentration standard to 2,000 ng/mL (OP1EO) and 13 ng/mL (OP17EO) in the highest concentration standard;	(U.S. EPA, 1999)
Benzotriazoles • **1H -benzotriazole** • **Tolyltriazole** **-4-methyl-1H-benzotriazole (4-MeBT);** **-5-methyl-1H-benzotriazole (5-MeBT);**	• Samples stored in glass bottles; • Transported to the lab in ice chests; • Passed through 0.45 µm membrane filters and stored in a refrigerator at 4 °C pending analysis, usually within the next 24 h; • Samples were acidified to pH 7 fortified to a 1.0 mg/L concentration of 5,6-dimethylbenzotriazole as a surrogate (for 4-methyl-1*H* benzotriazole); • SPE;	• GC/MS; usually • GC/FID; • HPLC-UV; • Ultraviolet-visible spectrophotometry (UV-VIS) in soil extracts; • LC/MS/MS;	• measurement range =0.03 µg/L - 2900 µg/L; • GC/MS; LOD= 0.1 µg/L - 0.08 mg/L; • HPLC-UV; LOD= 0.5 - 1.0 ppm; • UV-VIS; LOD= 0.1 mg/L for both BT and TT; • LC/MS/MS : ✓LOD= 8 ng/L BT (water samples); ✓LOD= 3 ng/L TT; ✓LOD=0.1 mg/kg BT (for soil extracts); ✓Limit of quantification (LOQ)=0.15 mg/L benzotriazoles (surface water); ✓LOQ=0.25 mg/L benzotriazoles (waste water); ✓LOQ=0.05 mg/L benzotriazoles after SPE (ground water); • MDL=0.08 mg/L (for both 4- and 5-methyl-1*H* benzotriazole);	(U.S. EPA, 1999)

Potassium formate (K+CHOO−)	• All samples were acidified to shift dissociation equilibrium of potassium formate and sodium formate-d solutions towards the free acids formic acid and [2H] formic acid (formic acid-d); • Derivatization to methyl formate and methyl formate-d; • Headspace solid-phase microextraction (HS-SPME);	GC-MS	•LOD=1.2mg/L; •Calibration was linear in the range of 0.5-208.5mg/L; •The detection limit of the method was 0.176 mg/L;	(U.S. EPA Method *1625C*)
Perfluorooctanoate (PFOA)	• Containers were thoroughly rinsed with methanol and deionized water prior to use; • Samples were stored at room temperature (22°C) prior to analysis; • SPE;	LC-MS	• LOD=0.06 ng/L; • LOQ=0.1 ng/L;	(Knott et al., 1995)
Perfluorooctane (PFOS)	• Containers were thoroughly rinsed with methanol and deionized water prior to use; • Samples were stored at room temperature (22°C) prior to analysis; • SPE;	LC-MS	• LOD=0.04 ng/L; • LOQ=0.1 ng/L;	(Knott et al., 1995)
Solid samples - soil				
Polycyclic aromatic hydrocarbons PAHs, polychlorinated biphenyls PCBs	This description applies to HPLC • Transport of samples in polyethylene bags; • Storage of samples at 4°C pending analysis ; • The samples were dried in the dark, twigs and stones were removed; • Grab samples mixed thoroughly to make a composite sample; • After homogenization, the soil samples were passed through a 2 mm sieve; • Extracted by ultrasonication (toluene, later the solvent was replaced with acetonitrile)	• GC-MS; • GC-FID; • MS; • HPLC; • size-exclusion HPLC; • Infra-red Spectroscopy (IR); • Supercritical fluid chromatography (SFC); • Thin- layer chromatography (TLC); • UV; • Fluorescence	The sum of 12 PAHs ranged from 2.39 ng g^{-1} to 7.53 ng g^{-1} with a mean concentration of 4.43±1.45 ng g^{-1}.	(Tzovolou et al., 2009)

		spectroscopy; • Isotope ratio mass spectrometry; • Gravimetric methods;		
VOCs	• Grab samples are collected in glass containers; • Samples are maintained at 0 to 4°C from the time of collection until analysis; • If an aqueous sample contains residual chlorine, add sodium thiosulfate preservative; • Water samples containing aromatic compounds (e.g. benzene, toluene) to be stored for no longer than 7 days; • The medium can also be water; • For aqueous samples, experimental evidence indicates that some aromatic compounds (benzene, toluene and ethyl benzene) should be acidified with HCl to pH ca 2. • Pure: ✓ Samples containing 1% or more solids and low to moderate levels of pollutants are analysed by purging a known weight of sample added to reagent water; • Samples containing 1% or more solids and high levels of pollutants are extracted with methanol; an aliquot of the methanol extract is then added to reagent water and purged;	GC-MS	The detection limits of the method are usually dependent on the level of interferences rather than instrumental limitations;	(U.S. EPA, 2000; U.S. EPA Method 1624)
Metals				
Heavy metals	• The sample bottle, no matter whether of borosilicate glass, polyethylene, polypropylene or teflon, should be thoroughly washed with detergent and tap water, rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finally deionized distilled water, in that order;	• AAS • Inductively coupled plasma mass spectrometry (ICP/MS)	Cadmium (EPA Method 213.2) • Optimum Concentration Range: 0.5-10μg/L; • Detection Limit: 0.1μg/L; • Precision and Accuracy: • SD±0.10; Recoveries=96%, c=2.5μg Cd/L; • SD±0.16; Recoveries=99%, c=5.0 μg Cd/L	(Knott et al., 1995; *Nabizadeh et al., 2005*;

	- For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of less than 2 at the time of collection; - The sample is not filtered before processing; - Choose a volume of sample appropriate to the expected level of metals; - If much suspended material is present, as little as 50-100 ml of well mixed sample will most probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined.)		• SD±0.33; Recoveries=98%, c=10.0 µg Cd/L Chromium (EPA Method 218.2) • Optimum Concentration Range:5-100µg/L; • Detection Limit: 1 µg/L; • Precision and Accuracy: • SD±0.1; Recoveries=97%; c=19 µg Cr/L; • SD±0.2; Recoveries=101%;c=48 µg Cr/L; • SD±0.8; Recoveries=102%; c=77 µg Cr/L; Copper (EPA Method 220.2) • Optimum Concentration Range: 5-100µg/L • Detection Limit: 1 µg/L; • Precision and Accuracy: data not available; Lead (EPA Method 239.2) • Optimum Concentration Range:5-100µg/L • Detection Limit: 1 µg/L • Precision and Accuracy: • SD±1.3; Recoveries=885%; c=25 µgPb/L; • SD±1.6; Recoveries=92%; c=50 µgPb/L; • SD±3.7; Recoveries=95%; c=100 µgPb/L; Nickel (EPA Method 249.2) • Optimum Concentration Range:5-50µg/L; • Detection Limit: 1 µg/L; Precision and Accuracy: data not available Zinc (EPA Method 289.2) • Optimum Concentration Range: 0.2 -4g/L; • Detection Limit: 0.05 µg/L; Precision and Accuracy: data not available at this time.	U.S. EPA, 2000; U.S. EPA Method 1620; 600/4-79-020; 213.2; 218.2; 220.2; 239.2; 289.2)

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Table 4. Literature information on the analyses of samples of runoff water from airports in different geographical regions

Sampling location		**Parameter**	**Range of concentration (mean value)[mg/l]***	**References**
International Airport, Warsaw, Poland		TOC	(446.5)	(Krzemieniowski et al. 2006)
		TN (Total Nitrogen)	(142.1)	
		Oil	(26.4)	
		TSS (Total Suspended Solids)	(159)	
Airport, Gdańsk, Poland	**runways, internal roads, aprons, car park, passenger terminal**	BOD_5	4.1-130.0	(Siedlecka, and Downar, 2004)
		COD	31-807	
		Petroleum ether extract	5.6-553.7	
		Glycols	5.6-553.7	
		TKN	9.2-356.6	

	commuter terminal	BOD$_5$	6.9-47.9	
		COD	42-227	
		Petroleum ether extract	6.1-208.5	
		Glycols	3.1-50.4	
		TKN	2.21-7.1	
Heathrow International Airport London, England		pH	6.4-8.1(7.2)	(Revitt, 1997)
		COD	0.2-18.4	
		Specific conductivity [µS/cm]	347-890(628)	
Glatt River near Zurich International Airport, Switzerland		Benzotriazole [µg/L]	0.16-5.44	(Gigger et al., 2006)
		Totyltriazole [µg/L]	0.04-0.91	
Fornebu International Airport, Oslo, Norway (sampling done 2 years after airport closure)	**aircraft de-icing point**	Benzotriazole [µg/l]	1.2-1,100	(Breedveld et al., 2003)
		PG (Propylene glycol)	-	
		DOC (Dissolved Organic Carbon)	21-79	
		Fe	0,2-6,5	
		SO$_4^{2-}$	87-1,600	
	drainage ditch	Benzotriazole [µg/l]	1,5-3,5	
		PG	-	
Westchester County Airport, New York, USA	**taxiway, drainage system**	pH	6-8	(U.S. EPA, 2000)
		BOD$_5$	2-8.4(2.53)	
		PG	0.05-1.3(0.213)	
		Oil and grease	5	
	buildings, hangars	pH	6.3-8.8	
		BOD$_5$	2-37(4.9)	
		PG	0.05-0.82(0.13)	
		Oil and grease	5	
	ponds	pH	6.9-8.6	
		BOD$_5$	2-7.2(2.8)	
		PG	0.05-220(32.8)	
		Oil and grease	(5)	
Newark International Airport, New York, USA	**runway**	pH	5.1-7.5	(U.S. EPA, 2000)
		COD	49-338(189)	
		TOC	7-1,120(83.5)	
		TSS	<2-64	
		Hydrocarbons	<0.4-8.8	
	terminal	pH	6.1-7	
		TOC	9-23(16)	
		TSS	3-38(11.3)	
		Hydrocarbons	1-3.9(2.45)	
Salt Lake City International Airport, USA		pH	6.6-9.5	(U.S. EPA, 2000)
		BOD$_5$	11-1, 050(332)	
		COD	104-3 ,880(835)	
		Nitrate/Nitrite	0.9-9(4.73)	
Baltimore – Washington	**main terminal**	Conductivity [µmho/cm]	120-540	(U.S. EPA, 2000)

International Airport, USA	**area[a]**	pH	6.36-8.61	
		Alkalinity	38-520	
		Hardness	28-800	
		BOD	3-64	
		BOD$_5$	23-2 ,510(1,010)	
		COD	11 ,000-270, 000	
		TSS	11-31	
		NH$_3$	ND-23	
		TKN	1,1-400	
		EG (Ethylene glycol)	<10	
		P	0.2-60	
		Oil	ND-29	
		TPH	ND	
		Cadmium [µg/L]	ND-3	
		Chromium [µg/L]	ND-1	
		Copper [µg/L]	ND-45	
		Lead [µg/L]	ND-16	
		Nickel [µg/L]	ND-5	
		Zinc [µg/L]	240-1 ,430	
	commuter terminal[a]	Conductivity [µmho/cm]	120-2 ,000	
		pH	5.91-8.48	
		Alkalinity	30-158	
		Hardness	46-168	
		BOD	1,900-138	
		BOD$_5$	197 – 769(412)	
		EG	<10	
		TPH	1	
		COD	700-2 ,700	
		TSS	14-31	
		NH$_3$	ND-5	
		TKN	ND-26	
		P	ND-6	
		Oil	ND-14	
		TPH	ND-28	
		Cadmium [µg/L]	ND-1	
		Chromium [µg/L]	ND	
		Copper [µg/L]	3-9	
		Lead [µg/L]	1-11	
		Nickel [µg/L]	5	
		Zinc [µg/L]	35-60	
Muddy Bridge Branch (receives runoff directly from Baltimore – Washington International Airport), USA		Conductivity [µmho/cm]	210.5-328.0	(Hartwell et al.,1995)
		DO (Dissolved oxygen)	4.5-6.4	
		pH	7.0-7.4	
		Alkalinity	69.0-84.2	
		NH$_3$	0.003-0.042	
		EG	>25[b]	

		PG	>50[b]	
Dallas/Fort Worth International Airport, Texas, USA	**upstream reference**	BOD_5	2-3.1	(Corsi et al., 2006c)
		COD	14-80	
		PG	<18	
		EG	<18	
	airport drainage	BOD_5	93-9,500	
		COD	10-37,900	
		PG	<18 –3,800	
		EG	<18 – 20,000	
	receiving stream	BOD_5	<2 - >100	
		COD	<9 – 1,600	
		PG	<18 - 39	
		EG	<18 - 230	
Sites near General Mitchell International Airport, Milwaukee, USA	**upstream site**	NPnEO [µg/L]	(0.89)	(Budavari, 1996; Corsi et al. 2009)
		PG	<18	
		EG	<18	
		COD	47-84	
		BOD_5	(16.6)	
		4-MeBT	<0.08	
		5-MeBT	<0.08	
		Acetate	<5.0	
		Formate	<2.5	
		Potassium	(6.25)	
	primary outfall	NPnEO [µg/L]	(776)	
		PG	1,900-4,400	
		EG	32-280	
		COD	5,600-10,200	
		BOD_5	738	
		4-MeBT	<0.08 –0.6	
		5-MeBT	<0.08-0.8	
		Acetate	(120)	
		Formate	(11)	
		Potassium	(59.1)	
	receiving stream	NPnEO [µg/L]	(16.9)	
		PG	130-150	
		EG	<18	
		COD	330-480	
		BOD_5	(201)	
		4-MeBT	<0.08	
		5-MeBT	<0.08	
		Acetate	(8.75)	
		Formate	<2.5	
		Potassium	(15.5)	
Kansas City International Airport, USA		BOD_5	(5,100)	(U.S. EPA, 2000)
		TOC	(3,000)	
		5-methylbenzotriazole [µg/l]	(17,000)	
		NH_3	(3.9)	

	Zinc	(140)	
	Phenol [µg/l]	(93)	
	Diethylene glycol	>20,000	
	EG	(3,200)	
	PG	(16,000)	
	Aluminum	(860)	
	Magnesium [µg/l]	(2,500)	
	Manganese [µg/l]	(170)	
	Copper [mg/l]	(14)	
	n-tetradecane [µg/l]	ND	
	Lead	(15)	
	Potassium [µg/l]	(13, 000)	
	Sodium [µg/l]	(1, 100)	
	Calcium [µg/l]	(3, 400)	
Bradley International Airport, USA	BOD$_5$	(39, 000)	(U.S. EPA, 2000)
	TOC	(3, 500)	
	5-methylbenzotriazole [µg/l]	(90, 000)	
	NH$_3$	(23)	
	Zinc	(340)	
	Phenol [µg/l]	(280)	
	Diethylene glycol	(15 ,000)	
	PE	(3 ,000)	
	PG	(160, 000)	
	Aluminum	(1, 100)	
	Magnesium [µg/l]	(2, 000)	
	Manganese [µg/l]	(140)	
	Copper	(44)	
	n-tetradecane [µg/l]	(140)	
	Lead	(50)	
	Potassium [µg/l]	ND	
	Sodium [µg/l]	(10, 000)	
	Calcium [µg/l]	(33, 000)	
Greater Rockford International Airport, USA	BOD$_5$	>7.3	(U.S. EPA, 2000)
	TOC	(12)	
	5-methylbenzotriazole [µg/l]	(120)	
	NH$_3$	(46)	
	Zinc	(45)	
	Phenol [µg/l]	ND	
	Diethylene glycol	ND	
	PE	ND	
	PG	ND	
	Aluminum [µg/l]	(270)	
	Magnesium [µg/l]	(3, 000)	
	Manganese [µg/l]	(360)	
	Copper [mg/l]	(9.2)	
	n-tetradecane [µg/l]	ND	

	Lead [µg/l]	(4.3)	
	Potassium [µg/l]	(64, 000)	
	Sodium [µg/l]	(7, 900)	
	Calcium [µg/l]	(14, 000)	
Louisville International Airport, USA	pH	7-9,1	(U.S. EPA, 2000)
	BOD$_5$	3-1,250	
	TSS	2-3 530	
	DO	0.270-13.0	
	NH$_3$	<0.03-171	
	Benzene [µg/l]	<5-97	
	Ethylbenzene [µg/l]	5-127	
	Naphthalene [µg/l]	5-361	
	Toluene [µg/l]	<5	
	Xylene [µg/l]	<5	
Nashville International Airport, USA	pH	7.2-8.6	(U.S. EPA, 2000)
	BOD$_5$	3-98	
	COD	<20-130	
	TSS	18-55	
	DO	6.4-11.9	

[*]Unless otherwise noted [a] Data sample type: peak, composite and grab. [b] Below detectable concentrations.

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