Treatment of De-icer Contaminated Storm Runoff from Airport Catchments within Artificially Aerated Wetlands.

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Doctor of Philosophy

by

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Glossary

- AAF – aircraft anti-icing fluid
- AD – anaerobic digestion
- ADF – aircraft de-icing fluid
- ALOD – analytical limit of detection
- AMS – aerospace materials standard
- AQC – analytical quality control
- ATU – allylthiourea
- BOD – biochemical oxygen demand
- BOD_5 - five day biochemical oxygen demand
- cBOD – carbonaceous biochemical oxygen demand
- CGE – centre for global eco-innovation
- COD – chemical oxygen demand
- CSR – corporate and social responsibilities
- DG – diethylene glycol
- DMS – de-icer management systems
- DO – dissolved oxygen
- EA – Environment Agency
- EG – ethylene glycol
- EMC – event mean concentration
- EPR – environmental permitting regulations
- ERDF – European Regional Development Fund
- FAR – Federal Aviation Regulations
- FBA™ – forced bed aeration
- FPD – freeze point depressant
- FWS – free water surface
- HLR – hydraulic loading rate
- HRT – hydraulic retention time
- HSSF – horizontal subsurface flow
- IA – inlet only aeration configuration
- ISO – International Organisation for Standardisation
- K – biodegradation constant
- K_La – volumetric mass transfer coefficient
- MCERTS – monitoring certification scheme of the Environment Agency
- MDPE – medium density polyethylene
- MLR – mass loading rate
- MVR – mechanical vapour recompression
- N – nitrogen
- NA – no aeration
- NGR – national grid reference
- NO3 – nitrate
- O_2 – oxygen
- OLR – organic loading rate

- OTE – oxygen transfer efficiency
- OTR – oxygen transfer rate
- O&M – operation and maintenance
- PA – phased aeration configuration
- P – phosphorus
- PCC – Pearson's correlation coefficient
- PE – population equivalent
- PDF – pavement de-icing fluid
- PPM – parts per million
- Q – discharge
- RO – reverse osmosis
- R&D – research and development
- SOTE – standard oxygen transfer efficiency
- SOTR – standard oxygen transfer rate
- SSSI – site of special scientific interest
- TC – total carbon
- TDS – total dissolved solids
- TOC – total organic carbon
- TOD – theoretical oxygen demand
- TSS – total suspended solids
- UA – uniform aeration configuration
- UK – United Kingdom
- USA – United States of America
- WFD – European water framework directive
- WwTP – wastewater treatment plant

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Chapter 1

Introduction, Aims, Objectives and Thesis Structure

1.1. Background

Diffuse and point sources of pollution are major concerns regarding the contamination and associated detrimental impacts to natural ecosystems and water resources including; rivers, streams, lakes, coastal waters and groundwater (receiving waters) (EEA, 2007, DEFRA, 2012a). Despite efforts over recent years to control pollution sources, there remains a need to improve the quality of receiving waters worldwide. For example, in England only 27% of watercourses currently meet the European Water Framework Directive (WFD) classification of good chemical, ecological and biological status (DEFRA, 2015). The specific control and regulation of point source urban and industrial runoff, therefore remains a key priority area in working towards the conditions of the WFD and improving the overall quality of watercourses for the general benefit of stakeholders.

It is widely regarded that the aviation industry is a large scale polluter of the environment (Sulej et al., 2012b). Surface water discharges from airports are often characteristically similar to that of urban and highway runoff, containing a wide range of pollutants (Sulej et al., 2012b, Wilson, 1996). Surface water is defined as the storm runoff that is discharged from a catchment area, into a surface water system such as a receiving water, drain or sewer (Wilson, 1996). Storm runoff is generated at airports when precipitation or snow melt flows across impermeable surfaces, including aprons, stands, taxiways and runways. This process is responsible for mobilising pollutants from within catchment stores and transporting them into surface water systems. Pollutant sources are generated through everyday airport operations such as; cleaning and maintenance of aircraft and ground handling vehicles, vehicle and aircraft engine testing, aircraft refuelling, combustion of aviation fuel, apron maintenance, construction work and de-icer application (Sulej et al., 2011c, Sulej et al., 2012b). Contaminants derived from these operations include; hydrocarbon based oil and lubricants, heavy metals, suspended solids and organic compounds (Chong et al., 1999, Sulej et al., 2012a, Sulej et al., 2012b). Most of these contaminants are present in low or very low concentrations, therefore having a negligible environmental impact (Sulej et al., 2011b). De-icer compounds however are abundant during winter months and are therefore of much greater environmental and ecological concern (Hartell et al., 1995, Corsi et al., 2006a, ACRP, 2008, Corsi et al., 2009, ACRP, 2010, ACRP, 2012a, Freeman et al., 2015).

Aviation regulations necessitate the use of de-icers at airports worldwide as a safety precaution against winter weather conditions (Transport Canada, 2010). Ice, frost and snow (frozen contamination) on aircraft and runway surfaces, poses a major safety risk for departing and arriving aircraft (Switzenbaum et al., 2001, Vasilyeva, 2009, Chen and Wang, 2012). For instance, frozen contamination on aircraft wings or critical surfaces significantly reduces aerodynamic performance resulting from increased drag and subsequent loss of lift (Switzenbaum et al., 2001, Valarezo et al., 1993, Transport Canada, 2010). Over the past 50 years this issue has been linked to numerous aircraft accidents globally, which have killed crew and passengers and destroyed aircraft (Civil Aviation Authority, 2000). To mitigate the risks, airport tenants contracted by the airlines apply aircraft de-icing fluid (ADF) and aircraft anti-icing fluid (AAF) prior to take off, while the airport maintains safe runway operating conditions by applying pavement de-icing fluid (PDF) (ACRP, 2008, ACRP, 2010, Huttunen-Saarivirta et al., 2011, Freeman et al., 2015).

De-icer formulations primarily consist of propylene glycol and acetate or formate based compounds for ADF and PDF respectively (Switzenbaum et al., 2001, ACRP, 2008). The threat from these compounds to receiving water quality is substantial. Naturally occurring aquatic bacteria can rapidly degrade de-icer compounds, a process that consumes dissolved oxygen (DO) from within the water column through respiration. This creates an oxygen demand known as biochemical oxygen demand (BOD), which is determined analytically over five days and typically expressed as a five day biochemical oxygen demand (BOD_5) (HMSO, 1988). Concentrations of BOD_5 in airport runoff during the de-icing season are typically elevated beyond the receiving waters ability to replenish DO concentrations. If discharged into a receiving water without prior treatment, airport runoff could result in DO depletion thereby having severe consequences for the survival of fish and other aquatic organisms (Wilson, 1996, Corsi et al., 2001a, ACRP, 2008, Corsi et al., 2012). The scale of this issue is significant with just one litre of the most commonly used ADF having a BOD_5 of approximately 354 g, which is equivalent to the typical strength of wastewater generated by 6 people in one day. These values escalate rapidly, given that on average almost 300 litres is required to de-ice a single aircraft (Freeman et al., 2015). During severe freezing conditions, a high capacity airport such as Manchester Airport in the United Kingdom (UK) can use over 88,000 litres per day, with a population equivalent of 520,066 which is greater than the current population of the city of Manchester (UK) (UK Government, 2014a). Strict regulations therefore govern the release of airport runoff into receiving waters.

Currently in the UK, 220 environmental permits to discharge have been issued to airports in an attempt to control and minimise the threat to receiving water quality from airport surface water runoff (Environment Agency, 2015b). A diverse range of pollution prevention technologies, technical approaches and pollution prevention measures are currently used within the aviation industry to help airports to remain compliant with environmental permit to discharge limits. Four broad categories exist including, off-site biological treatment, off-site recycling, on-site biological treatment and on-site recycling (ACRP, 2013b). The preferred approach for an airport is one that most economically achieves discharge compliance, therefore providing the greatest protection against civil and statutory liability (Wilson, 1996). Management approaches vary significantly between airports to address diversities in airport layout, infrastructure, storm water storage capacity, de-icer application, environmental permit limits, climate conditions and site constraints. Many of these factors contribute to variability in water quality and quantity, which is discussed in further detail within Chapter 3. Selecting the most suitable solution is therefore a complex and challenging process, which is bespoke to each individual airport and its unique characteristics. Effective selection can only be made on the basis of scientifically robust and long term monitoring data, which defines the existing site conditions and constraints (ACRP, 2013b). Although the quantification of de-icer contamination forms a crucial element of the selection process, limited guidelines have been published to date. To address this, methods developed and applied at a major UK airport to quantify de-icer contamination, are reported in Chapter 3 of this thesis. These methods are transferable to other airport sites and would be useful for future incorporation into the decision making process for the selection of pollution prevention methods.

Recently, there has been growing international interest in artificially aerated wetlands; a relatively new and emerging technology for on-site treatment of de-icer contaminated runoff. Aerated wetlands are based on the principles of traditional passive systems including constructed wetlands and reed beds, however have been engineered to increase DO concentrations within the media treatment zone. This is achieved through the installation of diffusers beneath a gravel media through which a blower is used to deliver artificial aeration into the treatment zone, therefore increasing the availability of DO for aerobic microbial consumers of organic matter (Wallace, 2001, Kadlec and Wallace, 2009, Murphy et al., 2012b). This helps to meet the O_2 demand of untreated effluents such as de-icer contaminated runoff, resulting in higher pollutant removal efficiency (Wallace and Liner, 2011a, Murphy et al., 2014) within a reduced system footprint in comparison to alternative systems such as constructed wetlands or reed beds (Toit et al., 2013). The aeration technology known as forced bed aeration (FBA™), was invented in the United States of America (USA) in 2001 (Wallace, 2001) and has since been applied to numerous industrial applications. The first airport application of the technology was built in 2008/09 adjacent to the runway at Buffalo Niagara Airport in the USA (Wallace and Liner, 2011a, Wallace and Liner, 2011b). After initial start-up problems linked to nutrient limitations were rectified, the Buffalo Niagara Airport aerated wetland system demonstrated excellent potential, removing on average 98 % of BOD_5, whilst operating under loads in excess of 20,000 kg d^{-1} BOD_5 (Wallace and Liner, 2011a). This success provided the basis for upgrading the passive constructed wetland systems at Heathrow International Airport Limited in the UK (Murphy et al., 2014) and Edmonton International Airport in Canada (Toit et al., 2013). Amongst other adjustments including increasing the media fill depth, artificial aeration was retrofitted to the existing constructed wetland systems at both sites, thereby transforming the systems from a passive constructed wetland to an intensified aerated wetland system. A new aerated wetland system is currently in the design stages at Macarthur Airport in Islip, Long Island (New York, USA) (Toit et al., 2013) and there has been interest in the technology from Dublin International Airport in Ireland, Newcastle Airport in the UK, Manchester Airport in the UK and Ted Stevens Anchorage International Airport (Alaska, USA).

As airports develop to meet the projected demand for air travel (DFT, 2013), it is likely that de-icer usage will increase in line with aircraft movements and increasing airport surface areas. Further, airport expansion plans and global climate change will contribute significantly towards increased runoff volumes which will challenge existing infrastructure, storm water storage capacity and pollution prevention measures. New technologies, solutions and pollution prevention measures will be required globally within the aviation industry, in order to meet these future challenges, within the remit of environmental regulations. At some airports, aerated wetlands may prove to be an economically feasible option. At others the economic feasibility of the aerated wetland technology may only be achieved through optimisation of the technology, thereby reducing energy consumption and operational costs associated with the FBA™ system (Nivala et al., 2013b).

The increased use of aerated wetlands since the development of the technology in 2001, has led to significant advances in understanding the aerobic treatment processes primarily responsible for pollutant reduction. Despite this, there is currently no industry design standard for the aerated wetland technology (Nivala et al., 2013b). In contrast to other wastewater aeration technologies such as the activated sludge process, aerated wetlands have not been extensively researched within the specific area of oxygen transfer efficiency (Nivala et al., 2013a). New data regarding the design and optimisation of aerated wetlands is revealed in Chapters 4 and Chapter 5 of this thesis, highlighting opportunities to reduce energy consumption and operational costs within aerated wetland systems. Overall, this thesis contributes new knowledge to the field of aerated wetland research, with specific advances in the areas of aeration configuration and oxygen transfer efficiency design and optimisation. It is envisaged that the findings reported within this thesis are used to inform the design of more economical and sustainable aerated wetland systems, thereby leading to more widespread use of the technology within the global aviation industry and beyond.

1.2. Aims and Objectives

The overall aim of this thesis is to improve understanding of de-icer pollutant mobilisation, transport and fate within airport catchments and to develop and test novel, sustainable and low cost treatment systems for contaminated discharges. Five specific thesis objectives are defined as follows (Fig. 1.1.);

1. Review catchment processes and aerated wetland literature, to improve understanding of the principles, processes and pathways of pollutant transfer to surface water systems and how this ultimately impacts the treatment of airport runoff and the design and operation of treatment systems operating under these conditions. A literature review is presented in Chapter 2 to address this objective.

2. Evaluate the fate of chemical de-icers following application within airport catchment areas, thereby establishing the risks of water quality degradation due to surface water runoff from airports. A case study describing the results of a monitoring programme designed to quantify these parameters is reported in Chapter 3.

3. Determine the impact of altering aeration configurations on pollutant removal within pilot-scale aerated wetlands and identify optimal aeration configurations for incorporation within aerated wetland design. The results of experiments to address the hypothesis that; organic removal efficiency can be improved within aerated wetlands, through altering the spatial distribution of aeration inputs, to better match the supply and demand of O_2 throughout the system are reported within Chapter 4.

4. Evaluate the removal of widely regulated pollutants within a pilot-scale aerated wetland operating under new aeration configurations and different hydraulic and organic loading rates. Further research objectives were defined to assess the impact of i) hydraulic retention time and ii) pollutant loading, on treatment efficiency within aerated wetlands and the results are reported within Chapter 4.

5. Evaluate the impact of media depth and airflow rates on standard oxygen transfer efficiency (SOTE) within media-filled aerated wetland systems. Bubble frequency and bubble diameters were investigated to improve understanding and interpretation of SOTE within media-filled and open water columns. Column experiments to address the hypothesis that SOTE can be

increased within aerated wetlands by altering media depth and aeration rates are reported in Chapter 5, along with bubble observations to support the findings.

The aim and objectives of this thesis support the wider aim of the Centre for Global Eco-Innovation (CGE) through which this PhD was part funded. This is to underpin small to medium sized enterprise research and development of new products, processes and services for the global market place, which deliver positive environmental benefits and address major environmental challenges of the twenty first century.

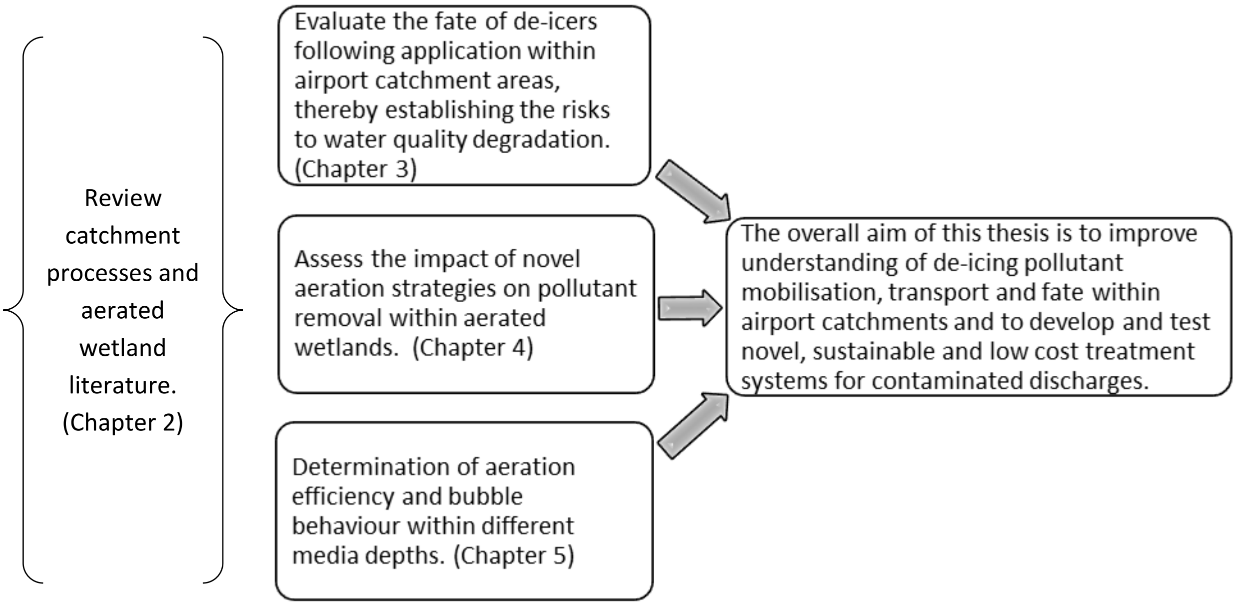


Figure 1.1. Summary of thesis aims and objectives.

1.3. Thesis Structure

This thesis is presented as a series of six chapters (Table 1.1). A broad overview of the subject area is presented within Chapter 1, which incorporates the introduction and the aims objectives and structure of this thesis. In Chapter 2, a literature review is presented to improve understanding of the impacts of airport winter operations on water quality discharges. A summary of the management approaches and treatment technologies currently used to prevent pollution of receiving waters surrounding airports is discussed, leading to a synthesis of key design specifications for full-scale aerated wetland systems currently being used to treat airport runoff. Current knowledge of the principles and processes required for efficient operation of aerated wetlands, for the specific application of airport storm runoff treatment is also discussed within Chapter 2. In conclusion, the literature review describes opportunities, future challenges and further research required to optimise aerated wetlands for the application of airport runoff. The literature review presented within Chapter 2 has been peer reviewed and published as a review article within the journal of Environmental Technology and Innovation [3] 2015 (Freeman et al., 2015). Within Chapter 3, catchment science has been used to improve understanding of pollutant (de-icer) mobilisation, transport and fate across airport landscapes. A combination of storm water monitoring, real time water quality data and mass balance calculations were used to define the water quality characteristics during two consecutive winters (2013/14 and 2014/15) at Manchester Airport. Further, the analytical results from the water quality monitoring programme are presented within Chapter 3, thereby defining the impact of airport de-icer application on surface water runoff which subsequently requires managing to avoid pollution of surrounding soils and receiving waters. Chapter 4 presents experimental results from a six month study carried out at Manchester Airport between February and June 2015, designed to identify de-icer degradation rates and pollutant removal efficiencies, within a field-scale aerated wetland. Further, experimental results supporting the use of phased aeration; which is a new approach to aerating gravel beds are presented, along with tests designed to optimise the operation of aerated wetlands in regards to hydraulic and organic loading rates. These results are highly relevant to the design of future aeration distribution systems within aerated wetland technology. Chapter 4 is currently being prepared for publication submission. Chapter 5 addresses oxygen transfer efficiency in aerated wetlands. Results from experiments conducted within full depth media-filled columns are reported. Assessment of SOTE was conducted under different media depths to establish optimal design depths. Findings are supported with data from bubble observation experiments conducted on the experimental columns. Finally, a broad discussion of the overall impact of the research and development (R&D) is discussed within Chapter 6, along with the strengths and limitations of the research and recommendations for further work.

Table 1.1
Overview of thesis structure, with journal submission plan for each chapter

Chapter No.	Objectives addressed	Title	Journal/ target journal	Progress
1		Introduction, aims, objectives and thesis structure.	-	-
2	1	Understanding and managing de-icer contamination of airport surface waters: a synthesis and future perspectives.	Environmental Technology & Innovation	Published
3	2	Understanding the temporal variability of water-soluble organic pollutants within airport storm runoff.	Science of the total environment	To be prepared in 2017
4	3,4	Aerated wetlands for airport runoff treatment: Optimisation of aeration configurations and operating conditions.	Water Resources	In preparation
5	5	Oxygen transfer in aerated wetlands: the impact of media presence, media depth and air flow rates	-	-
6	-	Discussion	-	-

Chapter 2

Understanding and Managing De-icer Contamination of Airport Surface Waters: A Synthesis and Future Perspectives

A version of this chapter has been published as: FREEMAN, A. I., SURRIDGE, B. W. J., MATTHEWS, M., STEWART, M. & HAYGARTH, P. M. 2015. Understanding and Managing De-icer Contamination of Airport Surface Waters: A Synthesis and Future Perspectives. *Environmental Technology and Innovation*, 3, 46-62.

Statements of author contributions to the paper are as follows:

Andrew I. Freeman undertook the literature review, wrote the paper and edited the paper following comments from the peer review panel A Freeman

Ben W.J. Surridge reviewed and edited the paper prior to submission

Mike Matthews reviewed and edited the paper prior to submission

Mark Stewart reviewed and edited the paper prior to submission MA STEWART

Philip M. Haygarth reviewed and edited the paper prior to submission *P Haygarth*

2.1. Introduction

The application of de-icers is required at airports during the winter to facilitate safe air travel. As a safety precaution, all airlines follow the clean aircraft concept ISO11076 by ensuring that there is no frozen contamination on critical aircraft surfaces during take-off (ACRP, 2009). This is achieved through the application of an ADF, an AAF or a combination of the two as part of a two stage de-icer approach. A typical ADF/AAF formulation contains approximately 88 % freeze point depressant, 10 % to 11 % water and 1 % to 2 % proprietary additives (ACRP, 2008, Johnson, 2012). The most commonly used freeze point depressant is currently propylene glycol ($C_3H_8O_2$) which is a low molecular weight alcohol derived from the petroleum industry (Barbelli et al., 2012). Aircraft anti-icing fluids are used proactively in anticipation of a frozen precipitation event. The main difference between ADF and AAF is the increased addition of polymer based thickening agents to AAF, which improves adherence to aircraft surfaces resulting in increased holdover time. The airport has responsibility for ensuring the safe operation of runways, taxiways and operational areas at all times, regardless of weather conditions (Huttunen-Saarivirta et al., 2011). Potassium acetate ($C_2H_3KO_2$) based PDFs are most commonly applied to runways, taxiways and operational areas to remove frozen contamination and provide increased friction for ground handling vehicles and aircraft (Corsi et al., 2008, Fay and Shi, 2012b). Due to improved environmental performance, the use of $C_2H_3KO_2$ has replaced urea as the PDF of choice at most international airports.

Although critical for airport operations, de-icers are major sources of organic compounds that can contaminate airport surface waters during the de-icing season. The compounds used in de-icer formulations are linked to a range of detrimental environmental and ecological effects, particularly if they are discharged into receiving surface waters prior to treatment. These effects include the development of thick biofilm growths near to the location of discharge, resulting in adverse aesthetic and olfactory effects (Koryak et al., 1998, ACRP, 2008). Ecological effects include macro-invertebrate and fish fatalities (Turnbull and Bevan, 1995) and loss of migratory fish species such as salmon and sea trout (Environmental Protection Agency, 2000). Further, toxicity towards aquatic flora (Pillard and DuFresne, 1999) and fauna (Pillard, 1995) is a concern which is linked primarily to the additive ingredients alkyphenol ethoxylate (a surfactant) and benzotriazole (a corrosion inhibitor), which are found in ADF and AAF (ACRP, 2008). Within a PDF, the freeze point depressant is the primary source of toxicity (ACRP, 2008). Where surface water runoff at an airport is not adequately contained, soil and groundwater contamination may also occur (Bausmith and Neufeld, 1999a, Cancilla et al., 2003b, McNeill and Cancilla, 2009, Nunes et al., 2011). This is a particular concern because proprietary additives, such as benzotriazole, degrade slowly in the natural environment or can produce highly toxic degradation by-products, although research in this field is currently limited (Jia et al., 2006, ACRP, 2008).

However, the primary environmental concern associated with airport de-icer application is the depletion of DO concentrations in receiving waters (ACRP, 2008, Corsi et al., 2012). This occurs during biodegradation whereby heterotrophic bacteria aerobically oxidise organic compounds in a process that consumes DO creating an oxygen (O_2) demand. The potential O_2 demand associated with contaminated runoff from airports can be quantified through determination of BOD_5. Typical BOD_5 concentrations for a 75 % concentrate Type IV ADF and a 50 % concentrate PDF are 354,000 mg L^{-1} and 250,000 mg L^{-1} respectively. When diluted in storm event runoff and snow melt, BOD_5 concentrations >20,000 mg L^{-1} are possible (Environmental Protection Agency, 2000, Corsi et al., 2012). Over the course of a de-icing season c. 1,000,000 litres of ADF/AAF may be applied to aircraft at an international hub airport, alongside similar volumes of PDF (Castro et al., 2005).

Due to the frequency, scale and possible environmental consequences of de-icer applications, surface waters contaminated with de-icers are increasingly subject to stringent regulations. For example, the WFD currently provides a framework for all member states in Europe to achieve good chemical and ecological status for inland waters by 2015 (DEFRA, 2013b). To assist in meeting the objectives of the framework in England and Wales, the environmental permitting regulations (EPR) 2010 were developed and implemented. These regulations state that all industrial discharges into receiving waters, including lakes, rivers and streams must comply with environmental permits to discharge (previously called discharge consents) (DEFRA, 2013a). Environmental permits are designed to constrain the release of pollutants, including BOD_5 into the environment and are set on the basis of site-specific conditions. Typically, BOD_5 EPR limits for airport runoff discharging into a receiving water range between 10 mg L^{-1} to 40 mg L^{-1}. Failure to meet EPR requirements may result in prosecution and payment of appropriate damages.

To comply with EPR limits, airports often convey contaminated runoff to the local water companies public sewer for treatment at a wastewater treatment plant (WwTP), as part of an airport de-icer management plan. This is currently the management strategy adopted by 45 % of airports globally (ACRP, 2013b). As a consequence of increased demand for air transport and the projected growth in the global aviation industry, increased application of de-icers will be required in the future. However, long term constraints on sewer network capacity and increasing conveyance, reception and treatment costs are of growing concern, defining the need for alternative sustainable treatment solutions. In this context, Chapter 2 focuses on the characteristics of airport runoff contaminated with de-icers and the implications for treatment. The research objectives for Chapter

2 were defined as: i) conceptualise pollutant transport pathways within the airport environment; ii) synthesise current treatment alternatives and associated considerations for implementation; and iii) define an innovative technology with the potential to meet future demand for de-icer treatment in a sustainable and economic manner.

2.2. Environmental Impact Assessment of Airport Surface Waters

Understanding the mechanisms by which de-icers are applied, dispersed and transported across the airport landscape is required in order to assess the environmental risks associated with the use of chemical de-icers. In addition, these mechanisms often have important implications for the development of an airports de-icer management plan and the selection and operation of appropriate de-icer treatment technologies (ACRP, 2008).

2.2.1. Application

Aircraft de-icing fluid and AAF is applied by handling agents contracted by the airlines operating from an airport. Handling agents operate to the Association of European Airlines, Civil Aviation Authority and Federal Aviation Administration recommendations for de-icing and anti-icing aircraft on the ground. The SAE international aerospace recommended practice advises that aircraft de-icer application is performed using specifically designed vehicles. These typically have a highly manoeuvrable aerial boom, from which a de-icer spraying system can be deployed by an operator (SAE International, 2013). Aircraft de-icing fluids are typically heated to 65 ^{o}C to 80 ^{o}C and applied to aircraft on de-icing stands, designated de-icing pads, at the gate, or at a combination of locations depending on airport operations, layout and infrastructure (EPA, 2012). All ADF products must conform to the aerospace material specifications (AMS) 1424 and 1428E (Corsi et al., 2012). Additionally PDF must conform to AMS 1435 for liquids and 1431B for solids (Environmental Protection Agency, 2000). Despite this, the environmental characteristics and performance of de-icers vary considerably in relation to the specific product and dilution ratio used (Table 2.1).

Table 2.1.
Summary characteristics of commonly used de-icers at airports

De-icer	Primary function	Main active ingredient	Dilution ratio (FPD [a] /water)	BOD_5 [b] ($mg\ L^{-1}$)	COD [c] ($mg\ L^{-1}$)
Kilfrost DF Plus (TI)	AAF [d]	$C_3H_8O_2$ [g]	60/40	590,000	1,390,000
Kilfrost ABC-K Plus (TII)	ADF [e]	$C_3H_8O_2$ [g]	75/25	270,000	850,000
SafeWing (TII)	ADF [e]	$C_3H_8O_2$ [g]	75/25	350,000	850,000
Kilfrost ABC-S Plus (TIV)	ADF [e]	$C_3H_8O_2$ [g]	75/25	354,000	834,000
Safegrip	PDF [f]	$C_2H_3KO_2$ [h]	50/50	270,000	330,000

[a] freeze point depressant,
[b] five day biochemical oxygen demand stated on manufacture's product safety data sheet,
[c] chemical oxygen demand stated on manufacture's product safety data sheet,
[d] aircraft anti-icing fluid,
[e] aircraft de-icing fluid,
[f] pavement de-icing fluid,
[g] $C_3H_8O_2$ = propylene glycol,
[h] $C_2H_3KO_2$ = potassium acetate.

The volume of de-icer applied typically varies in relation to weather conditions, thickness and extent of frozen contamination, aircraft type, number of aircraft movements and airline or handling agent policy. For example, Manchester Airport is situated on the southern edge of Manchester in the UK and is owned by the UKs largest airport operator Manchester Airport Group Plc. (MAG). In 2013 annual passenger numbers at Manchester Airport were 20,687,423 (Aero, 2014) and these are projected to increase to c. 50,000,000 by 2030 (MAG, 2007). Annual aircraft movements were 159,000 in 2013 and these are projected to increase to c. 353,000 by 2050 (MAG, 2007). Previously unpublished data from the period 2009 to 2014 reveals a mean annual ADF usage of c. 624,000 L and a mean annual PDF usage of c. 545,000 L at Manchester Airport (Table 2.2). The primary ADF/AAF used at Manchester Airport is currently a Type IV $C_3H_8O_2$ based product (Kilfrost ABC-S Plus), which is typically diluted to a 75/25 concentration prior to application. Between 02/09/2012 to 02/05/2013, a total of 4,925 aircraft were de-iced by two on-site handling agents operating at Manchester Airport. During this period, an average of 33 aircraft per day were de-iced with a maximum of 152 aircraft de-iced in a single day on 18/01/2013. Mean application volumes per aircraft were approximately 295 L across a range of weather conditions. The mean increased to approximately 600 L when aircraft were snow laden, with a mean of 927 L applied per aircraft under freezing snow conditions. The largest single aircraft application was 3,458 L which was applied to an Airbus (A380) during freezing snow conditions on 26/01/2013. Over the entire 2012/13 de-icing season, a total of 1,349,719 L of ADF/AAF were applied to aircraft with a mean daily application volume of 9,575 L, equivalent to a daily population equivalent (PE) of 56,492. In order to prevent detrimental environmental impacts from de-icer application at Manchester Airport, surface water runoff can be contained within the de-icer management system (DMS) as part of the airports pollution prevention strategy (Section 2.4).

Table 2.2.
Summary of aircraft and pavement de-icer usage [a] at Manchester Airport (2009 – 2014)

De-icing Season	ADF [b] /AAF [c] (L)	PDF [d] (L)
2013/14	388,276	156,100
2012/13	633,919	615,500
2011/12	519,098	292,640
2010/11	728,127	709,300
2009/10	848,113	951,850
Mean	623,507	545,078
St.dev. (±)	159,835	287,200

[a] ADF/AAF volume from main handling agent only is reported,
[b] aircraft de-icing fluid,
[c] aircraft anti-icing fluid,
[d] pavement de-icing fluid,
± = 1 standard deviation of the mean.

2.2.2. Deposition

Following application, approximately 75 % to 80 % of ADF is deposited on to the ground surface at the de-icing location by overspray, deflection and drip (Switzenbaum et al., 2001, Castro et al., 2005) (Fig. 2.1). Due to the nature of typical spray devices, overspray can be up to 50 m from the de-icing location (Wayson et al., 2000). In addition, some of the applied product forms mist droplets which are transported significant distances by wind or by jet blast (Wayson et al., 2000). After aircraft pushback, any remaining ADF adhering to an aircraft drips onto taxiways or shears from the aircraft onto the runway during take-off (EPA, 2012, Fan et al., 2011). Thickening and gelling agents are included in the ADF additives package to increase holdover time defined as the period of time which the fluid remains effective for. These additives increase product viscosity, which improves adherence to aircraft surfaces. However, this also leads to accumulation of spent fluids following deposition on surfaces across an airport during dry weather conditions.

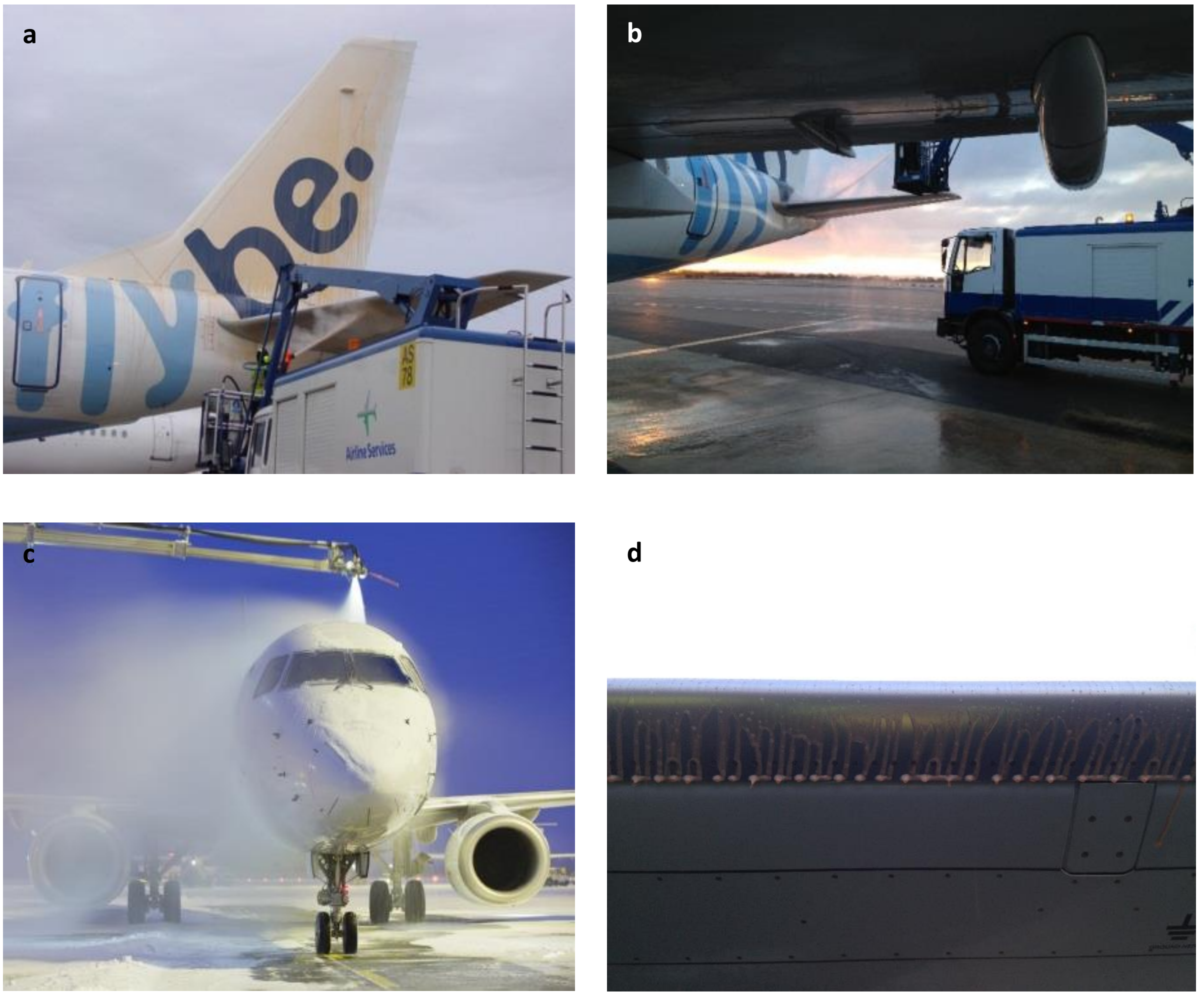


Figure 2.1. (a) Photograph of handling agent de-icing an aircraft, (b) de-icer deflection during application (note spent fluid being deposited on the de-icing stand to the rear of the aircraft), (c) aircraft de-icing fluid droplets forming a mist, (d) aircraft de-icing fluid dripping from an aircraft wing following application. Photographs taken during field work at Manchester Airport and published with permission of Flybe.

2.2.3. De-icer Mobilisation, Transport and Fate

The transport and fate of spent de-icers is site specific and relates to environmental conditions, operational procedures and policies and airport infrastructure. Generally, de-icers are soluble in water and are therefore transported freely through an airport hydrological system, including within surface water runoff across impermeable surfaces, soil through-flow, groundwater flow and within the surface water drainage system (Fig. 2.2) (ACRP, 2009).

2.2.4. Hydrology

Several meteorological variables are used to define a winter design storm at airports. The design storm is defined as a specific meteorological condition which components of a DMS (i.e. conveyance, attenuation and treatment facilities) are designed to accommodate (ACRP, 2012b). These variables include rainfall volume, rainfall intensity, temporal variation, probability, event duration and inter-event period (ACRP, 2012b). Each of these variables has the potential to strongly influence pollutant transport mechanisms. Surface runoff and infiltration through permeable surfaces are the main mechanisms for de-icer transport through the airport landscape. Runoff volumes are often large and depend directly on meteorological events (rain, snow, sleet, hail) and the size of catchment being drained. Airport surface drainage systems are designed to quickly convey surface water away from critical areas, thereby reducing the risk of system surcharge and flooding which could result in operational issues and flight delays (ACRP, 2012b). However, this results in the transport of large volumes of storm event runoff over a short period of time. The associated runoff rates are particularly important when designing and sizing conveyance and treatment systems to ensure that sufficient capacity to attenuate peak flows is available (ACRP, 2009).

Infiltration capacity varies in relation to site layout and soil permeability and can be incorporated into surface water runoff models. However, infiltration rates are often reduced during the winter as a result of frozen soils, thereby increasing storm event runoff rates (ACRP, 2009). Finally, evaporation from the aircraft surface and de-icing stand is negligible during the winter months (Wayson et al., 2000, ACRP, 2009). The hydrological factors, alongside their interactions, that influence de-icer transport are conceptualised in Fig. 2.2.

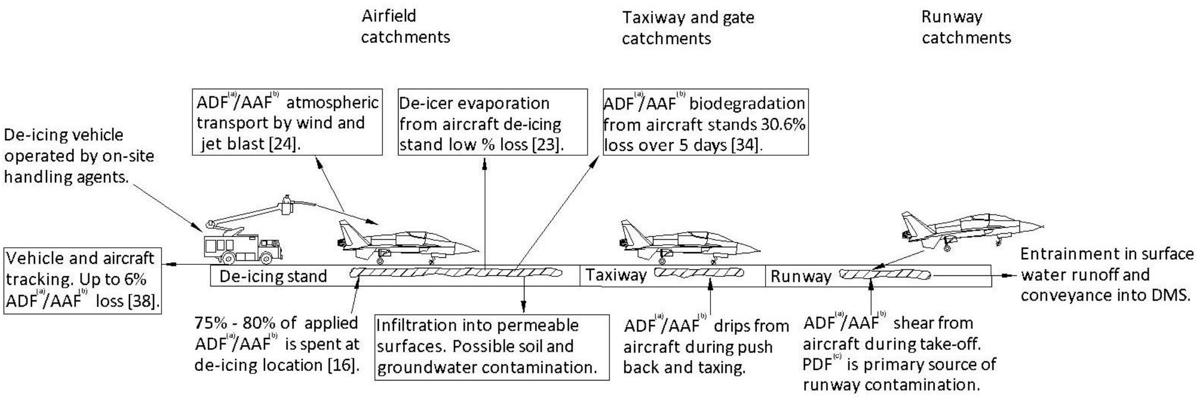


Figure 2.2. Conceptual model describing the transport and fate of de-icers at airports. Loss mechanisms are highlighted within text boxes. (a) Aircraft de-icing fluid, (b) aircraft anti-icing fluid, (c) pavement de-icing fluid.

Figure 2.2 identifies a number of transport pathways which result in de-icer loss from the system. These losses refer to the percentage or mass of applied de-icer load that is lost or undetected by monitoring during transport through the airport landscape. Although some methods for directly measuring de-icer losses have been developed, further research is required in order to accurately quantify the individual components of de-icer transport within airport catchments (ACRP, 2009). The main mechanisms for de-icer losses highlighted in Fig. 2.2 are biodegradation, tracking and jet blast. Both $C_3H_8O_2$ and $C_2H_3KO_2$ are readily biodegradable by naturally occurring bacteria in soil and water (Evans and David, 1974, French et al., 2001), limiting the environmental persistence of these compounds. Biodegradation constants (k) vary depending primarily on temperature (Revitt and Worrall, 2003), nutrient availability (Adeola et al., 2009, Gooden, 1998) and microbial seed used within experimental methodologies (Staples et al., 2001). On airport stands, k of 0.07 d^{-1} and 0.03 d^{-1} for $C_3H_8O_2$ and $C_2H_3KO_2$ respectively have been identified at 4 ^{o}C over five days (Revitt and Worrall, 2003). This is equivalent to BOD_5 load reductions of approximately 31 % and 15 % for $C_3H_8O_2$ and $C_2H_3KO_2$ respectively in samples containing 20 mg L^{-1} of ADF (Revitt et al., 2002). However, temperature has a significant, inverse effect on k of $C_3H_8O_2$ present on an airport surface, for example k decreased from 0.08 d^{-1} to 0.05 d^{-1} with a decrease in temperature from 8 ^{o}C to 1 ^{o}C, although k for $C_2H_3KO_2$ increased slightly from 0.04 d^{-1} to 0.05 d^{-1} with the same change in temperature (Revitt and Worrall, 2003).

During storm runoff events, some of the spent de-icers are washed onto permeable areas of land at the edge of aircraft stands, taxiways and runways where infiltration into soil and percolation to groundwater can occur (Bausmith and Neufeld, 1999a, Cancilla et al., 2003b, McNeill and Cancilla, 2009, Nunes et al., 2011, Fay and Shi, 2012a). Therefore, biodegradation experiments in different soil and substrate types have been conducted. For example, in sandy loam soils with no previous exposure to chemical de-icers, k for $C_3H_8O_2$ ranged from 0.07 d^{-1} to 0.30 d^{-1} at 22 ^{o}C (Bausmith and Neufeld, 1999b). In contrast, soil samples taken adjacent to a runway that were hypothesised to contain microbial communities accustomed to de-icers, revealed $C_3H_8O_2$ biodegradation rates of 19 mg kg d^{-1} to 27 mg kg d^{-1} at 8 ^{o}C and 2.3 mg kg d^{-1} to 4.5 mg kg d^{-1} at -2^{o}C in soil microcosm experiments (Klecka et al., 1993). Degradation of >90 % of $C_3H_8O_2$ was achieved in sand microcosms between 22 ^{o}C to 25 ^{o}C when dosed with 810 mg L^{-1} $C_3H_8O_2$ at flow rates of 0.72 ml min^{-1} to 0.92 ml min^{-1} (Bausmith and Neufeld, 1999b). Within stream water, the complete biodegradation of ethylene glycol ($C_2H_6O_2$) has been observed at 4 ^{o}C and 8 ^{o}C under laboratory conditions (Evans and David, 1974). Complete degradation in these experiments occurred between 5 days to 14 days at 8 ^{o}C, increasing to >14 days at 4 ^{o}C, in samples containing 0.2 mg L^{-1} to 10 mg L^{-1} of $C_2H_6O_2$ (Evans and David, 1974). Furthermore, k for $C_3H_8O_2$ was 0.80 d^{-1} in stream water in which a controlled release of

1,514 L of Type I ADF containing 50 % propylene glycol was added. However, *k* within stream water was found to be significantly higher than that in parallel laboratory trials (in which *k* between 0.05 d^{-1} to 0.07 d^{-1} were reported), likely due to the absence of *Sphaerotilus* and *Beggiatoa* benthic microorganisms which were abundant in stream samples but not within the controlled laboratory trials (Corsi et al., 2001a).

Ground handling vehicles and aircraft are also responsible for the transport of spent de-icers, termed tracking. Subsequent to application, an average of 8 L of ADF/AAF is tracked off a de-icing stand by ground handling vehicles (Dawson, 2005a). In addition, an aircraft is also responsible for tracking ADF/AAF off the de-icing stand during push back and taxiing, with a large commercial aircraft capable of tracking up to 11 L of spent fluid from the de-icing stand (Dawson, 2005b). Tracking is therefore a major contributor to ADF dispersal, often transporting de-icers across multiple airport sub-catchments. Finally, jet blast, defined as the rapid movement of air produced by an aircraft engine can transport ADF/AAF significant distances of up to 91 m from the de-icing location (Dawson, 2005a).

2.3. Quantifying De-icer Transport

2.3.1. Mass Balance Approach

A mass balance or material balance, based on the law of mass conservation can be used to quantify the de-icer load entering and leaving an airport system (Himmelblau and Riggs, 2012). A mass balance approach is potentially useful for identifying key pollutant transport pathways that maybe difficult to detect through direct measurement. To calculate a mass balance in the airport environment, knowledge of the mass loading rate (MLR) attributed to de-icer application within an individual catchment and the MLR measured from the catchment discharge location is required. Further, it may be appropriate to determine the MLR of discharges from different catchments to account for spatial dispersions of de-icers across multiple airport sub-catchments. The MLR defines the mass of a pollutant transported through a system, typically expressed as kilograms per day (kg d^{-1}) and is calculated using Eq. 2.1:

$$\mathrm{MLR}\ (\mathrm{kg\ d^{-1}}) = \mathrm{volume}\ (\mathrm{m^3\ d^{-1}}) * \mathrm{concentration}\ (\mathrm{mg\ L^{-1}}) * 0.001 \tag{2.1}$$

The sum of the MLR from multiple discharge locations is compared to the application MLR which can be calculated from handling agent ADF/AAF and airport PDF application volume records and de-icer product data safety sheets which report the O_2 demand of the individual de-icer products. De-icer loss from the system can be determined by subtracting the de-icer application MLR from the MLR measured from catchment discharge locations (Fig. 2.3).

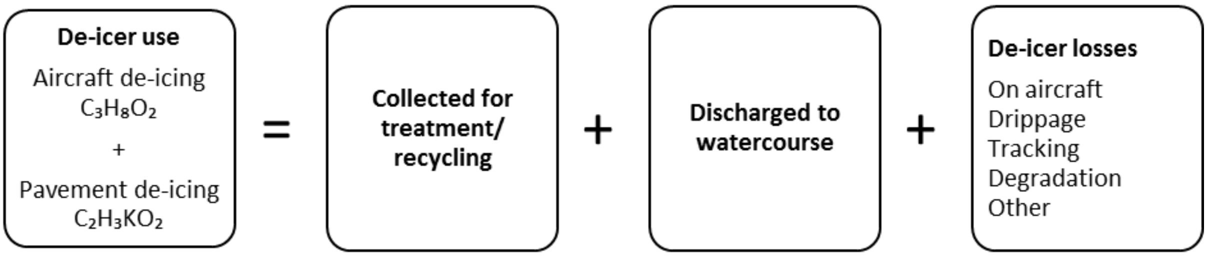


Figure 2.3. Simplified de-icer mass balance approach for use at airports (ACRP, 2009).

In airport settings, mass balance analyses have revealed de-icer losses ranging between 2 % to 62 % of the total de-icer load applied (Table 2.3). However, in many cases the mass balance model is too simplistic to adequately describe the complex and dynamic nature of de-icer contaminated runoff and therefore is used to support more sophisticated modelling and monitoring tools (ACRP, 2009).

Table 2.3.
Summary of de-icer losses at international airports identified by mass balance

Reference	Airport	De-icer loss (%)
[1]	Baltimore Washington International Airport, USA	2 – 36
[1]	Detroit Metropolitan Wayne County Airport, USA	37 – 48
[2]	General Mitchell International Airport, USA	47 – 62

Sources: [1] (ACRP, 2008), [2] (Corsi et al., 2001a).

2.3.2. Storm Event Monitoring

Surface water runoff generated by storm events represents the main transport mechanism through which pollutant loads are delivered to airport surface water drainage systems. For example, in unmanaged systems up to 99 % of applied de-icer load can be transported from the de-icing location to the final discharge location during storm runoff events (Corsi et al., 2001a). For this reason, event-based water quality monitoring maybe used alongside a mass balance approach to provide robust quantification of peak flow, concentration and load. These parameters are critical for evaluating and designing treatment technologies and other components of a DMS. One method for quantifying pollutant transport associated with storm events is to develop a rating curve based on a discharge (Q) – concentration relationship. This relies on the collection of multiple, discrete samples throughout the duration of a storm event, followed by sample analysis for pollutants of concern. This approach has been used widely to examine *Q* – concentration dynamics in storm water runoff events, for example focussing on mercury mobilisation in urban runoff (Eckley and Branfireun, 2008), phosphorus transport through agricultural landscapes (Haygarth et al., 1999) and turbidity, pH, DO and ammonium (NH4+) dynamics in runoff from densely populated urban areas (Lawler et al., 2006). An alternative sampling strategy is to collect a flow-weighted average or event mean concentration, based on a composite sample collected throughout a storm event. This approach has been used previously to monitor a wide range of pollutants, including polycyclic aromatic hydrocarbons (PAH) (Zheng et al., 2014), Escherichia coli and total suspended solids (TSS) (McCarthy et al., 2012) in urban storm water runoff and nitrogen composition in highway storm water runoff (Taylor et al., 2005). Despite wide application, EMC sampling is of limited use in the context of de-icer management at airports because peak pollutant concentrations associated with event driven systems are diluted (EPA, 2002). A combination of Q – concentration and EMC has previously been used to assess the fluxes of organic compounds (BOD_5) in storm event runoff at General Mitchell International Airport, USA. In ten storm events assessed using the Q – concentration relationship a high variation of the percentage of applied de-icers transported to monitoring locations (2 % to 99 %) was observed (Corsi et al., 2001a). Regardless of the sampling strategy used, sufficient field data is required to ensure that results are representative of actual event-driven water quality characteristics, thereby enabling suitable selection of treatment options as part of an airports DMS.

2.3.3. Quantification of Water Quality Parameters

Three clearly defined drivers for monitoring airport surface waters exist (ACRP, 2012a):

1. to comply with EPR limits to discharge,
2. for process control based on the requirement to divert and convey storm water to different areas of the drainage system,
3. to assess treatment system performance.

Each of these drivers requires extensive monitoring and quantification of water volume (m^3), pollutant concentration (mg L^{-1}) and organic load (kg d^{-1}). A range of methods to quantify organic carbon concentrations currently exist. Almost all of these methods involve the measurement of a de-icer surrogate parameter, whereby de-icers containing $C_3H_8O_2$ and $C_2H_3KO_2$ are the main source of organic load, but are typically measured indirectly using more readily available and widely accepted analytical techniques (ACRP, 2012a). The three most commonly used de-icer surrogate parameters are BOD_5, chemical oxygen demand (COD) and total organic carbon (TOC).

Five day biochemical oxygen demand is a measure of O_2 depletion during microbial respiration of organic carbon over five days (HMSO, 1988). In contrast to BOD_5, COD and TOC measure the oxidation of organic compounds in the presence of chemical oxidising agents. Each of these methods has its own inherent limitations. For instance, in the BOD_5 method substances such as metals, free chlorine, pesticides and phenols are toxic to micro-organisms and can result in under estimation of BOD_5. On the other hand, nitrifying bacteria enhance the O_2 demand during the nitrification process by oxidising NH4+ to nitrite and subsequently nitrate. For this reason, allylthiourea (ATU) can be added to suppress the activity of nitrifying bacteria in which case carbonaceous BOD_5 ($CBOD_5$) is reported (HMSO, 1988). Further, the five day sample incubation period presents a significant analytical delay, meaning that BOD_5 is not a suitable process control parameter.

To avoid the complexities arising from the use of micro-organisms in the BOD_5 test, COD is often used as an alternative. Chemical Oxygen Demand results can typically be obtained with three hours (Boyles, 1997), allowing for more rapid process control decisions to be made. However, the O_2 demand associated with inorganic compounds and with organic compounds that are not biodegradable is included within a COD test, potentially over-estimating the actual O_2 demand which would be expected following discharge of a contaminated water source to the natural environment. The TOC test uses heat, ultraviolet light and a chemical oxidant to oxidise organic C, which produces CO_2 as a by-product. Total organic carbon is then measured indirectly by detection of CO_2 using infrared, spectroscopy, conductivity or colourimetry based detection methods (Boyles, 1997).

2.3.4. Relationships between De-icer Surrogate Parameters

It is often necessary to identify the relationship between analytical results and other parameters for regulatory compliance purposes. For example, relationships can be sought between the results from online TOC analysers and surrogate parameters COD or BOD_5 which are more commonly stipulated on EPR discharge limits. The ratio of TOC to COD is well defined because both methods involve the chemical digestion of organic compounds. When individual compounds are present in significant concentrations within a solution, a linear relationship between TOC and COD exists based on chemical oxidation rates and the associated theoretical oxygen demand (TOD) for that compound. For example, Fig. 2.4a reports results from synthetic solutions comprising 50 % $C_2H_3KO_2$ PDF and 50 % $C_8H_8O_2$ Kilfrost ABC – S plus Type IV ADF that were prepared in concentrations between 80 ppm to 1,464 ppm COD. These were dosed under steady-state conditions into a continuous TOC analyser that is used to monitor TOC concentrations within trade effluent discharges at Manchester Airport. Comparison of COD and TOC data reveal a strong positive correlation between the parameters under these experimental conditions (Fig. 2.4a). However, it is preferable to perform correlations at low organic carbon concentrations because the O_2 demand at high concentrations will be almost entirely from $C_8H_8O_2$ and $C_2H_3KO_2$, which yields an ideal correlation between COD and TOC (ACRP, 2012a). At lower organic carbon concentrations, several compounds influence the correlation, potentially increasing the variability in any COD to TOC relationship (ACRP, 2012a). To test this assumption, spot samples were collected at TOC concentrations <55 ppm using environment agency (EA) monitoring certification scheme (MCERTS) accredited automatic samplers from catchment discharge locations at Manchester Airport. The samples were sent for analysis of COD and BOD_5 at the EA accredited National Laboratory Service. Linear regression statistical analysis was applied to the COD analytical results and TOC concentrations as read from the online analyser (Fig. 2.4b). In addition, linear regression statistical analysis was used to compare BOD_5 analytical results and TOC concentrations reported by the online TOC analyser (Fig. 2.4c).

A significant relationship was observed for both COD to TOC (p=.0001) and for BOD_5 to TOC (p=.0001). However, for regulatory compliance purposes it is important to identify the variation between parameters which can be achieved by applying 99 % confidence intervals to the linear regression model. This may pose an issue for airports constrained by very low BOD_5 or COD discharge limits, especially if a TOC value is sought to initiate an automated diversion away from a receiving watercourse and into a containment system for subsequent treatment. This is because to be 99 % confident that the TOC concentrations are below consented discharge limits, very low TOC concentrations determined by the analyser would require diverting. For example, in this data if the BOD_5 consent limit was 20 ppm, to be 99 % confident that concentrations are below this, the TOC result must be <6 ppm which would include background concentrations (Fig. 2.4c). Based on these findings it is apparent that TOC can be used to determine COD and BOD_5 concentrations and to inform the airport of when concentrations are increasing or decreasing towards the regulatory consent limit. However it is important that sufficient samples are collected in order for the 99 % confidence intervals to be accurately determined and that the correlation between the parameters is regularly reviewed, especially if the formulation of de-icers used on site changes. Further, correlations should be identified individually for each monitoring location and where the composition of the water has been changed via a treatment process for example, as the relationship between the parameters may vary in relation to the presence or absence and ratio of different organic compounds.

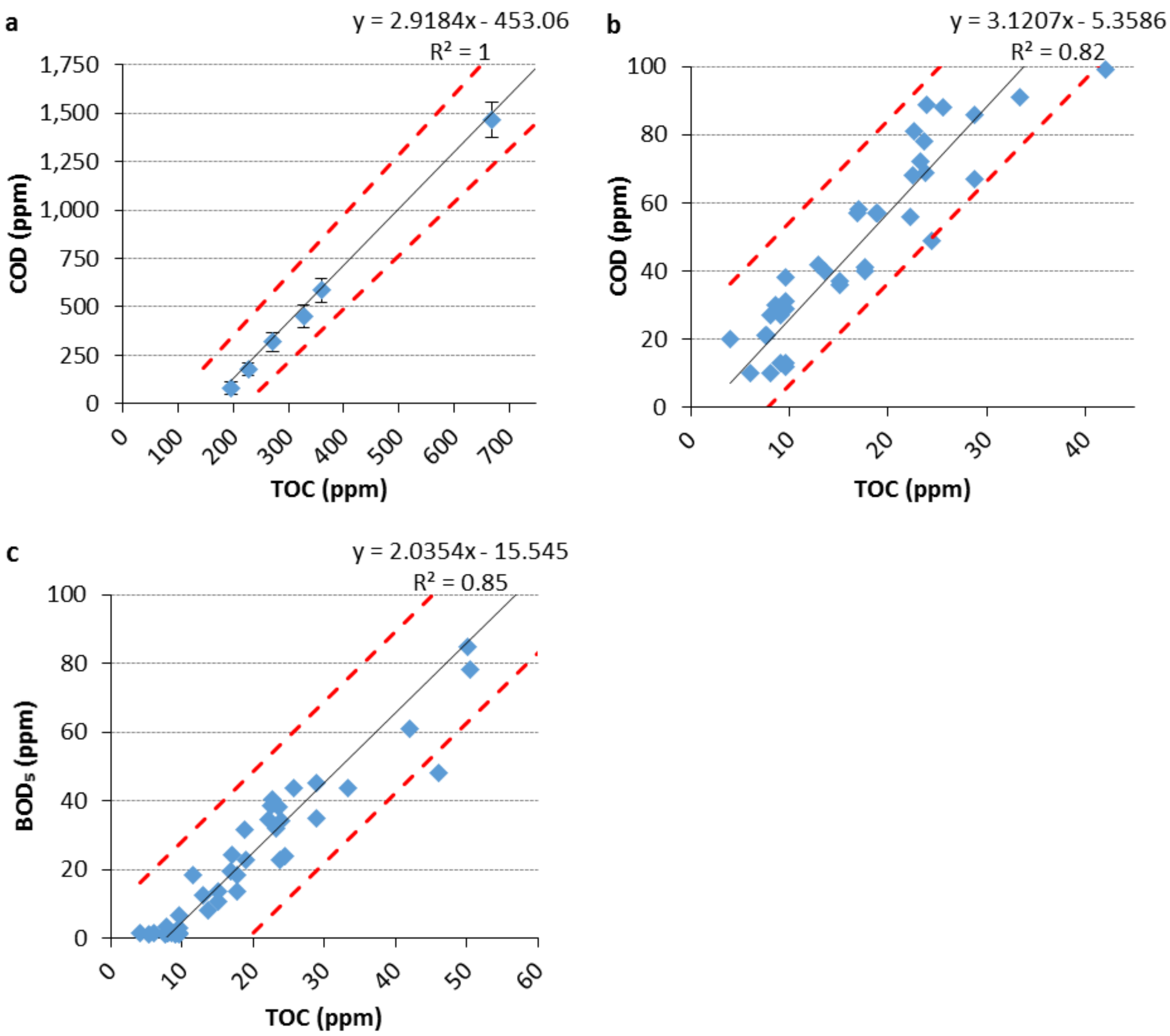


Figure 2.4. (a) Linear regression plot with 99 % confidence intervals (dotted red lines) comparing mean TOC and COD concentrations (PPM) recorded during three replicate dosing experiments (Pearson's r = 1, *p*=<.0001, n = 8), (b) linear regression plot with 99 % confidence intervals comparing TOC and COD concentrations (PPM) recorded from spot samples collected between 17/02/2014 – 27/03/2014 (Pearson's r = 0.90, *p*=<.0001, n = 45), (c) linear regression plot with 99 % confidence intervals comparing TOC and BOD_5 concentrations (PPM) recorded from spot samples collected between 17/02/2014 to 27/03/2014 (Pearson's r = 0.93, *p*=<.0001, n = 45).

2.3.5. Challenges for Treatment of De-icer Contaminated Runoff from Airports

In uncontrolled (event driven) systems, de-icers are mobilised from impermeable surfaces during precipitation and surface water runoff, meaning that both flow volume and pollutant concentration can fluctuate significantly. In such systems, a detailed understanding of event characteristics is required for appropriate design and sizing of treatment options and to ensure sufficient attenuation and treatment capacity is available. The implication of fluctuating flow volume and pollutant concentration is high variation in MLR, which is not desirable for most available treatment technologies. In biological treatment technologies for example, the mass of bacteria responsible for the majority of pollutant removal is governed by the MLR (food source) entering the system. Variation in MLR results in an unstable bacterial population and reduced treatment efficiency particularly where pollutant concentrations increase or decrease significantly over a short period of time (Crites and Tchobanoglous, 1998, ACRP, 2013b), primarily due to lagged microbial response. Secondly, the first flush phenomenon can occur in which the majority of the load is transported during the initial stages of a storm event and over a short period of time (Cristina and Sansalone). This can result in a shock load to the treatment system whereby only partial treatment of the influent occurs or toxicity and shearing of microbial communities occurs as a result of the increased pollutant load (Jank et al., 1974, Nitschke et al., 1996). A further consequence of increasing water volume is reduced pollutant removal efficiency, resulting from a decrease in hydraulic retention time (HRT) within a treatment system. Beyond the issue of shock loads, the first flush phenomenon means that only a small fraction of storm water maybe sufficiently highly polluted to require treatment, with the remaining volume being dilute and suitable for direct discharge to receiving waters. Finally, de-icer contaminated runoff is highly seasonal, with the highest level of treatment typically required during the lowest temperature conditions. Low temperatures may affect biological removal processes, primarily as a consequence of reduced microbial activity (Kadlec and Wallace, 2009).

2.4. Pollution Prevention, De-icer Management Systems and Treatment Technologies

A recent survey of airports in the USA, Canada and Europe revealed that 45 % of airports discharge de-icer contaminated surface water to private off-site treatment or recycling facilities as a key component of their DMS (ACRP, 2013b). This primarily includes storage and discharge of contaminated surface water runoff to the WwTP of a local water company. As a case study example the de-icer management and pollution prevention system at Manchester Airport is described below. At Manchester Airport, aircraft are currently de-iced on stand. Spent de-icers are transported into the surface water drainage system during rainfall events. As a component of the DMS, the surface water drainage network can be operated in a ‘containment mode’ (Section 3.2.4). In this mode, a series of automated penstock valves divert suspected contaminated water into a 73,000 m^3 below ground storage reservoir, therefore preventing discharge into receiving waters. Contaminated surface water is discharged as trade effluent to United Utilities public sewer and conveyed to the Davy Hulme WwTP for off-site treatment. When water quality within the storage reservoir falls below the EPR discharge limit of 23 mg L^{-1} BOD_5, water is once again discharged into the River Bollin.

The surface water drainage system is segregated into several sub-catchments as conceptualised in Fig. 2.5. Online TOC analysers compliant with MCERTS are used to inform the management and diversion process. For instance, when water quality deteriorates and approaches the EPR limit, as evidenced by data from the TOC analysers, diversion into the containment system is initiated.

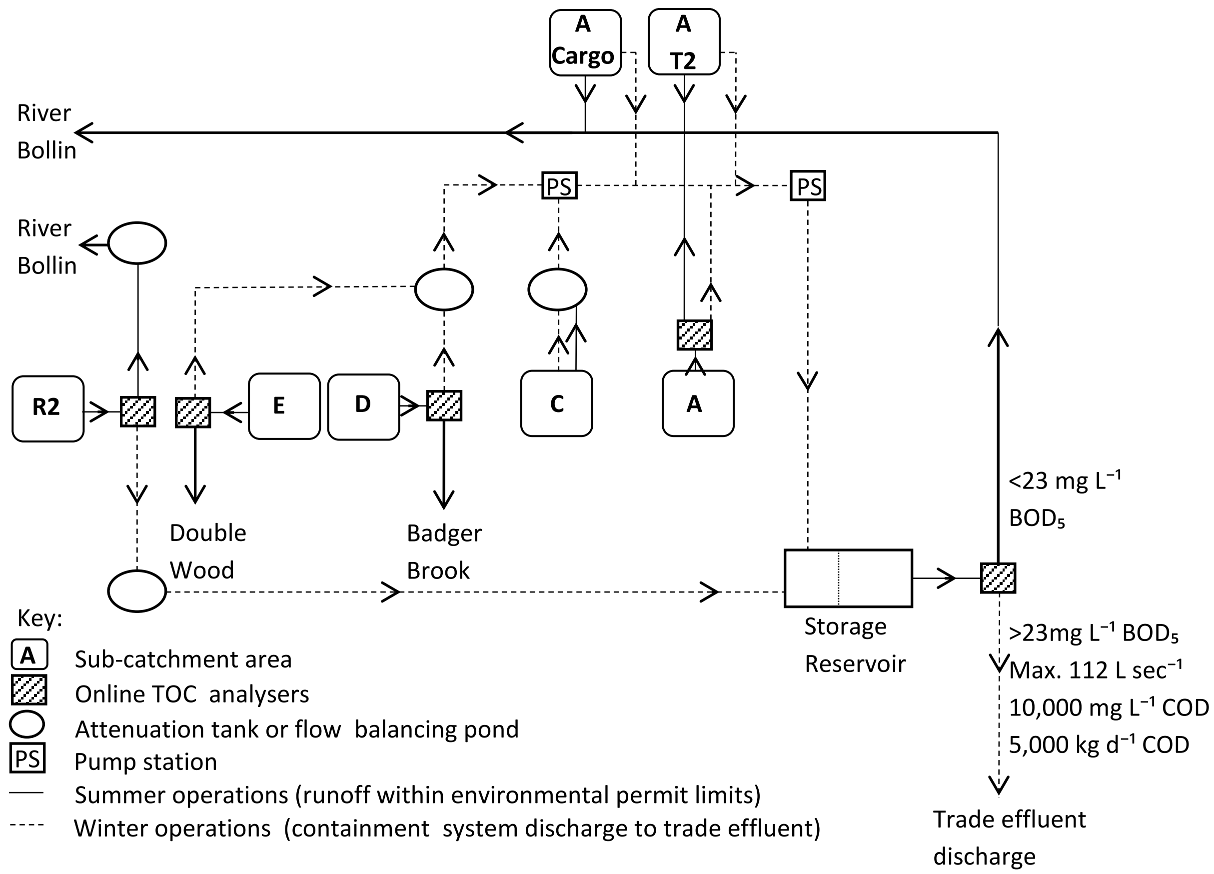


Figure 2.5. Conceptual model of Manchester Airport's existing surface water drainage and pollution prevention strategy (07/2016).

2.4.1. Alternative Treatment Technologies

Despite the popularity of airports discharging de-icer contaminated storm runoff to private WwTP's, there are concerns regarding future capacity and escalating reception, conveyance and treatment costs. A range of alternative de-icer treatment technologies exist. Furthermore, 50 % of airports discharging to WwTP also use some form of on-site pre-treatment (ACRP, 2013b). A synthesis of the most popular technologies identified through this review is reported in Table 2.4 including design MLR, performance and considerations for implementation. Generally, as the level of mechanical complexity involved in the treatment technology increases, the energy, operation and maintenance costs required to ensure a high level of performance also increase, whilst the footprint and land requirement decreases in comparison to the more natural passive technologies (Wallace, 2012).

The range of reported removal efficiencies (Table 2.4) suggests that not all currently available treatment technologies are suitable for inclusion within airport DMS. The reported removal efficiencies are likely to be a function of operating conditions, process settings, maintenance and consistency of influent and should therefore be interpreted with caution (ACRP, 2013b). For instance, it is unknown whether each of the systems reported in Table 2.4 was operating within their design MLR during the period that monitoring was conducted. Regardless, the summary reveals >98 % removal efficiency for five of the nine technologies. These were reverse osmosis, mechanical vapour recompression and anaerobic digestion, activated sludge, artificially aerated wetlands and land application through irrigation. Out of these technologies, the activated sludge process and aerated wetland maintained high removal efficiencies despite operating under high organic loading rates (OLR). Although the activated sludge process has been widely applied in municipal sewage applications, when $C_3H_8O_2$ concentrations exceeded the design treatment capacity (16,329 kg d^{-1}) at the Cincinnati airport in the USA loss of treatment biomass was experienced from within the activated sludge plant (ACRP, 2013b). In addition, treatment efficiency of the activated sludge process can be adversely affected by fluctuating temperatures (Appels et al., 2008), with reduced BOD_5 removal efficiency identified at temperatures below 7 ^{0}C (Martin, Martin, 2005). In contrast, computer modelling of aerated wetland insulation suggests that well insulated systems can operate effectively at temperatures as low as -20 ^{0}C (Jenssen et al., 2005). In addition, an aerated wetland installed at Buffalo Niagara airport in the USA retained a high level of removal efficiency despite MLR (20,000 kg d^{-1} BOD_5) of almost five times the treatment design (4,500 kg d^{-1} BOD_5) (Wallace and Liner, 2011a). Furthermore, aerated wetlands are operationally simple and require low operation and maintenance costs (Kadlec and Wallace, 2009). There appears to be significant potential for future application of aerated wetlands at airports, designed specifically to treat de-icer contaminated surface water runoff. Therefore, the remainder of this chapter focuses on the aerated wetland technology, current applications and possible future developments.

Table 2.4.

Summary of throughput, performance and considerations for implementation of a range of treatment technologies currently operating at international airports

Airport	Technology	Ave. MLR [(a)] COD (kg/d)	COD removal efficiency (%) [(b)]	Considerations
Bradley International USA	RO [(c)] and MVR [(d)]	1,224 (RO) [(c)] 1,360 (MVR) [(d)]	99 %	High glycol concentration required. Operationally complex. Process can produce glycol to offset O&M [(e)] costs.
Akron-Canton USA	Anaerobic digestion	1,685	100 %	Requires nutrient dosing and consistent temp. and pH. Requires sludge disposal. Small footprint. Labour intensive.
Cincinnati USA	Activated sludge	9,071	99 %	Treatment is limited by temperature. Requires nutrient dosing and steady-state loading. Requires sludge disposal.
Oslo Gardermoen Norway	Moving bed biofilm reactors	-	96 %	Also treats municipal wastewater providing nutrients and increased temperature and dilution of de-icer peak loads.
Buffalo Niagara USA	Artificially aerated wetland [(f)]	8,618	98 % (Wallace and Liner, 2011a)	Requires nutrient dosing and steady-state loading. Excellent for cold weather operation due to below ground insulation.
Nashville International USA	Aerated lagoon	272	<50 %	Challenge to maintain suspended biomass. Open water issues with low temperature and bird strike hazard.
Zurich Switzerland	Irrigation	580	99 %	Soil, water and air temperature affects performance. Groundwater depth and soil saturation dependent.
Wilmington Air Park USA	Reciprocating gravel bed	2,160	86 % – 88 %	Biological treatment limited by temperature and DO [(g)]. MLR requires adjustment in relation to temperature.
Westover Air Force Reserve Base USA	Constructed Wetland (passive)	703	10 % – 80 %	Inconsistent effluent concentrations (mean 2,094mg/L BOD_5). Large footprint. Cannot treat high de-icer loadings.

High O&M cost/complexity

Low O&M cost/complexity

Large footprint

Source: adapted from Airport Co-operative Research Programme (ACRP, 2013b)

[(a)] mass loading rate, [(b)] mean percentage of influent concentration removed within the treatment system, [(c)] reverse osmosis, [(d)] mechanical vapour recompression, [(e)] operation and maintenance, [(f)] subsurface flow treatment wetland, [(g)] dissolved oxygen, (-) data not available.

2.5. Subsurface Flow Constructed Wetlands

Subsurface flow constructed wetlands are engineered systems that are designed to use natural processes to remove a wide range of pollutants from within wastewater in a controlled environment prior to discharging into receiving waters or to reduce the pollutant load required for trade effluent disposal (Vymazal et al., 2006, Kadlec and Wallace, 2009). When compared with alternative treatment technologies, the advantages of constructed wetlands include low capital cost, operational simplicity, low operation and maintenance costs, construction from locally sourced materials and that no sludge is produced requiring disposal (Kadlec and Wallace, 2009). A further benefit of subsurface flow designs is that no water surface is exposed during treatment. This serves to minimise energy loss through evaporation and convection, provide insulation for microbial communities, reduce wildlife attraction (where this is undesirable, such as at airports) and reduce hydraulic failures caused by ice formation (Wittgren and Mæhlum, 1997, Wallace, 2000, Jenssen et al., 2005). These characteristics make subsurface flow constructed wetlands ideal for operation at airport settings in cold climates where wastewater treatment under low temperatures is required. The advantages of these systems have led to their widespread implementation within a range of industrial applications that require advanced treatment or where disposal to WwTP is not feasible (Nivala et al., 2013a). Current full-scale applications include municipal wastewater (Nivala et al., 2013a), landfill leachate (Nivala et al., 2007), fish farm effluent (Ouellet-Plamondon et al., 2006), heavily polluted river water (Dong et al., 2012), diffuse agricultural runoff (Gottschall et al., 2007) pharmaceutical wastes (Ong et al., 2010a) and airport surface water (Higgins et al., 2010, Wallace and Liner, 2011a).

2.5.1. Organic Pollutant Removal Mechanisms within Wetland Systems

A variety of mechanisms contribute to pollutant removal within constructed and aerated wetland systems. These include uptake by vegetation in planted systems, filtration, sedimentation, settling, volatilisation, precipitation, adsorption, microbial metabolism and biosynthesis. (Faulwetter et al., 2009, Kadlec and Wallace, 2009, Vymazal, 2009). Microbial metabolism, associated with the microbial communities present as a biofilm on the surfaces of fixed media, is the primary removal mechanism for organic compounds in both constructed and aerated wetland systems (Chong et al., 1999, Faulwetter et al., 2009, Zhou et al., 2009). All wetland systems are dominated by a range of microbial communities that can be classified by their metabolic requirements (Kadlec and Wallace, 2009). Heterotrophic bacteria including the genera *Pseudomonas*, *Aerobacter and Flavobacterium* derive their energy requirements from the oxidation of carbonaceous organic matter, simplified as glucose ($C_6H_{12}O_6$). This forms the basis for biosynthesis and reproduction in a biochemical oxidation process whereby O_2 is consumed and CO_2, H_2O and energy are produced (Vymazal and Kröpfelová, 2009) (Eq. 2.2):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 12e- + \text{energy} \quad (2.2)$$

Biochemical oxidation and biosynthesis are therefore key factors in the removal of organic compounds within aerated wetlands. However the rate at which these processes operate depends on the size of the microbial population and the bioavailability of organic compounds within a system. Because microbial populations increase or decline in response to fluctuating MLR, maintaining a steady MLR is important in order to achieve consistent removal through biochemical oxidation and biosynthesis. Further, macro and micro nutrient availability is a major rate limiting factor for many biochemical processes because microbial communities require nutrient elements for effective reproduction and growth (Ammary, 2004). Nutrient addition may therefore be required to optimise treatment efficiency in some aerated wetland applications (Wallace and Liner, 2011a). Finally, biochemical oxidation of organic compounds proceeds more rapidly under aerobic conditions compared to anaerobic conditions (Wallace and Liner, 2011a). Therefore O_2 availability is perhaps the most critical biochemical rate limiting factor and must be carefully maintained for optimal removal of organic compounds in constructed wetland systems.

2.5.2. Supplementary Artificial Aeration

Low DO availability in constructed wetlands is a major rate-limiting factor for the removal of BOD_5, COD and TOC because most effluents have an O_2 demand many times greater than can be supplied to a system by passive processes, including diffusion from the atmosphere and root transfer from vegetation (Nivala et al., 2013b). Further, in subsurface flow designs, O_2 must flow by convection through layers of insulating material before coming into contact with water. This limits the oxygen transfer rate (OTR) to as low as 0.3 g O_2 d^{-1} m^2 (Kadlec and Wallace, 2009). Plant-meditated transfer rates are assumed to be 5 g O_2 d^{-1} m^2 to 25 g O_2 d^{-1} m^2 (Brix and Schierup, 1990), although rates between 0.01 g O_2 d^{-1} m^2 to 12 g O_2 d^{-1} m^2 have been measured (Ye et al., 2012, Bezbaruah and Zhang, 2005, Wu et al., 2001, Armstrong et al., 1990, Brix and Schierup, 1990). Supplementary artificial aeration in the form of FBA™ can be used to overcome low OTR in constructed wetlands (Murphy et al., 2012b). This is achieved by diffusing O_2 through subsurface diffusers, which increases the contact time between a gas bubble and the water-biofilm interface (Nivala et al., 2013b). The main objective of artificial aeration is to supply sufficient O_2 to bacteria to maintain aerobic biochemical oxidation processes. The addition of artificial aeration to constructed wetlands has been shown to result in an order of magnitude improvement in BOD_5 removal efficiency (Wallace and Liner, 2011a) and reduce system footprint by two thirds in full-scale systems treating de-icer contaminated airport runoff (Toit et al., 2013). The major drawback of artificial aeration is increased operating costs when compared with passive treatment. Maximising the aeration efficiency within a system is therefore crucial to ensure cost-effective operation.

2.5.3. Factors Affecting Oxygen Transfer Efficiency

Oxygen input accounts for 45 % to 80 % of operating costs in wastewater treatment systems, resulting in the need to maximise oxygen transfer efficiency (OTE) (Gillot et al., 2005, Rosso et al., 2011). Oxygen transfer is defined as the process by which O_2 is transferred from a gaseous to a liquid phase. Several factors affect the OTE including O_2 distribution (Nivala et al., 2013b), bubble diameter (Burris, 1999), bubble coalescence (Nivala et al., 2013b), subsurface diffuser depth (Zhen et al., 2003) and process conditions (Stenstrom et al., 2008).

2.5.3.1. Distribution

Artificial aeration in tanks and open water treatment technologies, such as activated sludge plants, has been widely used and therefore the processes and mechanisms affecting OTE are well understood. In an open water body, O_2 bubbles released from the diffuser membrane spiral in a hydrodynamic motion towards the surface, resulting in a uniform and efficient distribution (Nivala et al., 2013a). This motion increases the bubble influence zone either side of a diffusion location, increasing distribution and residence time within the water column. However, the mechanisms affecting OTE in aerated wetland systems are more poorly defined. When a media is present within a system, the ascent pathway of bubbles is restricted and preferential pathways occur in relation to pore space and the random positioning of the media. The maximum influence zone in a gravel matrix is thought to be 300 mm either side of a diffusion location (Nivala et al., 2013a). This suggests that diffusers should be positioned in close proximity across the length of a wetland bed to ensure a uniform O_2 distribution. In fixed film systems such as aerated wetlands, it is understood that biomass growth and microbial oxidation of BOD_5 decreases exponentially towards the system outlet (Fig. 2.6), associated with progressive increases in filtration of particulate organic matter and declining concentrations of biodegradable organic carbon towards the outlet (Kadlec and Wallace, 2009). This theory is supported by observations of two-thirds of BOD_5 removal occurring in the first third of a full-scale biological filter system operating under moderate BOD_5 loading rates (Stenstrom and

Rosso, 2006). Therefore, it is hypothesised that a phased aeration configuration could be used in order to optimise current practices for removal of organic carbon by better matching the supply and demand of O_2 throughout the system from the inlet to the outlet.

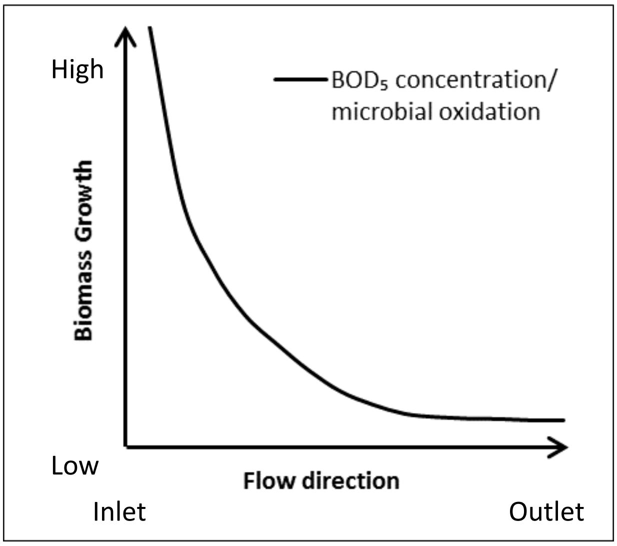


Figure 2.6. Visual representation of five day biochemical oxygen demand (BOD_5) concentration and microbial oxidation as a function of biomass growth and flow throughout a subsurface flow aerated wetland system. Adapted from (Kadlec and Wallace, 2009).

2.5.3.2. Bubble Diameter and Coalescence

The volume of O_2 (L min^{-1}) in relation to the treatment volume (m^3) is an important factor in OTE (Burris, 1999). However, bubble diameter is also an important control on OTE. Fine bubble aeration devices improve OTE through increasing the bubble surface area in relation to the treatment volume and have therefore been the industry standard for many years (Environmental Protection Agency, 1999). Oxygen transfer efficiency is reduced through bubble coalescence, whereby smaller individual bubbles merge to form a larger bubble which acts to decrease the bubble surface area to treatment volume ratio. In open water systems, O_2 bubbles are unimpeded during their ascent to the surface and are therefore less likely to coalesce than within media-filled aerated wetlands. In addition, aeration increases agitation, resulting in the division of larger bubbles (Al-Ahmady, 2006). However, in media-filled systems such as aerated wetlands, the pathways available to O_2 bubbles during ascent to the surface are greatly restricted, resulting in preferential pathways through the media pore space which encourages bubble coalescence (Nivala et al., 2013a). Despite this, the ascent of O_2 bubbles through media is retarded in comparison to open water systems, which serves as a mechanism to increase OTE through increased holdover and residence time (Nivala et al., 2013a).

2.5.3.3. Depth

The depth of a treatment system is one of the most important controls on OTE. A range of full-scale treatment technologies have been constructed at various depths in an attempt to maximise OTE. In the activated sludge process, system depth is typically between 3 m and 5 m with depths of up to 8.5 m reported (Moore, 1972). In comparison, constructed wetland systems have traditionally been designed based on the vegetation root zone method with shallower depths typically between 0.3 m to 1.2 m to increase the influence of the vegetation root zone (Conley et al., 1991). In contrast the design depths of aerated wetlands range from 900 mm to 1,500 mm, which acts to improve OTE efficiency in artificially aerated systems and reduce the system footprint compared with constructed wetlands. The importance of depth for OTE has been reported in a range of laboratory and field-scale treatment systems. For instance, OTE increased linearly when the depth of water increased from 0.24 m to 0.32 m within a laboratory-scale batch tank (Zhen et al., 2003). At the field-scale, OTE was measured in a number of activated sludge systems operating at different depths, revealing increased OTE from 18 g O_2 m^3 at 0.5 m to 160 g O_2 m^3 at 4.6 m (Al-Ahmady, 2006). It was hypothesised that the increase in OTE could be attributed to reduced bubble coalescence due to the increased retention time and therefore dissolution from gaseous to solution phases (Al-Ahmady, 2006). Increasing the depth resulted in elongated retention time of O_2 bubbles, thereby increasing the potential for dissolution. However despite its importance, few studies have assessed OTE in aerated wetlands as a function of media depth and the lack of an industry design standard for this technology has resulted in a wide range of depth variation within constructed systems.

2.6. Review of Modifications to Artificially Aerated Wetlands

The major drawback to artificial aeration is the additional costs derived from the energy consumption (<0.2 kWh m^{-3} of wastewater treated) associated with operating blowers which deliver O_2 to the diffusers (Nivala et al., Murphy et al., 2012a). This is a particularly significant issue in systems which operate in continuous mode, 24 hours a day. In order to address this, a range of modifications to artificial aeration inputs have been tested in laboratory-scale, pilot-scale and field-scale systems (Table 2.5).

2.6.1. Intermittent Aeration

Intermittent aeration is one method for reducing the number of operational hours associated with blowers. In a domestic wastewater treatment application, operating blowers for 4 hours per day maintained high removal efficiencies of 96 % COD and 97 % COD in laboratory and pilot-scale studies respectively (Fan et al., 2013a, Fan et al., 2013b). In contrast, 63 % COD removal efficiency was reported when blowers were operated intermittently on an hourly basis in laboratory-scale microcosms, dosed with poor quality river water (Dong et al., 2012). Furthermore, a removal efficiency of 94 % BOD_5 was achieved within pilot-scale studies treating domestic wastewater by only operating blowers at DO concentrations <0.60 mg L^{-1} (Zhang et al., 2010).

2.6.2. Inlet-only Aeration

As wastewater passes through a treatment system, the concentration of organic compounds decreases due to the removal mechanisms described previously (Fig. 2.6). This results in the food source becoming a limiting factor for microbial communities in final treatment zones, which in turn results in a thinning of the microbial biofilm. This suggests that microbial respiration and therefore O_2 requirement, maybe reduced during the passage of wastewater through a system. In attempt to address this characteristic, inlet limited aeration has been previously tested in mesocosm experiments dosed with fish farm effluent, revealing >90 % COD removal efficiency when dosed with effluent containing 540 mg L^{-1} COD and a HLR of 30 L d^{-1} m^2 (Ouellet-Plamondon et al., 2006). In addition to these findings, two thirds of the BOD_5 has been shown to be removed within the first third of an aerated wetland when dosed with MLRs of 2.6 g d^{-1} m^2 to 8.8 g d^{-1} m^2 BOD_5 (Zhang et al., 2010, Akratos and Tsihrintzis, 2007).

Table 2.5.
Summary of aeration modifications, loading rates and treatment efficiency within artificially aerated wetlands

Ref.	Scale	Application	Aeration volume (L min^{-1} d^{-1})	Aeration configuration	Organic load [(a)]	Hydraulic load	Treatment efficiency
Horizontal Subsurface Flow							
[1]	Pilot	Domestic sewage	120	Intermittent 4 hours/day	301 mg L^{-1} COD	10 cm d^{-1}	97 % COD
[2]	Pilot	Domestic sewage		Uniform grid 0.07 m² spacing	236 mg L^{-1} $CBOD_5$	130 L d^{-1} m^{-2}	99 % $CBOD_5$
[3]	Pilot	Domestic sewage	1,000	When DO = 0.20 – 0.60 mg L^{-1}	17.7 g d^{-1} m² BOD_5	130 L d^{-1} m^{-3}	94 % BOD_5
[4]	Lab	Airport runoff	4	Uniform/ continuous	1,070 mg L^{-1} BOD_5	-	98 % BOD_5
[5]	Pilot	Landfill Leachate	1,800	Uniform (length)/ continuous	41 – 177 mg L^{-1} BOD_5	400 L d^{-1} m^{-2}	88 – 97 % BOD_5
[5]	Pilot	Landfill Leachate	1,800	Uniform (width)/ continuous	41 – 177 mg L^{-1} BOD_5	400 L d^{-1} m^{-2}	88 – 97 % BOD_5
[6]	Lab	Fish Farm Effluent	2	Inlet-only	540 mg L^{-1} COD	30 L d^{-1} m^{-2}	>90 % COD
Vertical Subsurface Flow							
[7]	Lab	Domestic sewage	2	Uniform/ continuous	352 mg L^{-1} COD	207 L d^{-1} m-²	97 % COD
[7]	Lab	Domestic sewage	2	Intermittent 4 hours/day	352 mg L^{-1} COD	207 L d^{-1} m^{-2}	96 % COD
[2]	Pilot	Domestic sewage		Uniform grid (0.078 m² spacing)	233 mg L^{-1} $CBOD_5$	95 L d^{-1} m^{-2}	98 % $CBOD_5$
[8]	Lab	Polluted river water		Uniform/ continuous	158 mg L^{-1} COD	76 cm d^{-1}	72 % COD
[8]	Lab	Polluted river water		Intermit every hour	158 mg L^{-1} COD	76 cm d^{-1}	63 % COD
[9]	Lab	Pharmaceuti cal		Uniform/ continuous	326 mg L^{-1} COD	-	94 % COD
[10]	Lab	azo dye Acid Orange 7		Uniform/ continuous	326 mg L^{-1} COD	1.04 ml min^{-1}	>86 % COD
[11]	Lab	Airport runoff	14.16 – 33.3	Uniform/ continuous	Various	Various	96 – 99 % BOD_5
[12]	Lab	Airport runoff	-	Uniform/ continuous	1,250 mg L^{-1} COD	-	>99 % COD

[(a)] COD = chemical oxygen demand, $CBOD_5$ = five day carbonaceous oxygen demand, BOD_5 = five day biochemical oxygen demand.

Sources: [1] (Fan et al., 2013b), [2] (Nivala et al., 2013a), [3] (Zhang et al., 2010), [4] (Higgins et al., 2007), [5] (Nivala et al., 2007), [6] (Ouellet-Plamondon et al., 2006), [7] (Fan et al., 2013a), [8] (Dong et al., 2012), [9] (Ong et al., 2010a), [10] (Ong et al., 2010b), [11] (Wallace and Liner, 2011a), [12] (Higgins and Maclean, 2002).

2.7. Use of Wetlands within the Aviation Industry

In the aviation industry, full-scale wetland systems are currently limited to a small number of airports globally (Table 2.6), dating back to approximately 1996 when the first recorded system was constructed at Kalama Airport in Sweden. A synthesis of the key design and operation criteria for existing airport wetland applications is presented below including, Kalama Airport in Sweden, Toronto Pearson Airport in Canada, Wilmington Airport in the USA, Westover Air Reserve Base in the USA, Edmonton Airport in Canada, Heathrow Airport in the UK and Buffalo Niagara Airport, USA.

2.7.1. Kalama Airport (Sweden)

In approximately 1996, a constructed wetland was commissioned at Kalama airport in Sweden consisting of four separate 1.5 m deep ponds totalling 18 ha. The system was planted with *phragmites australius* around the edges and colonised by the submerged macrophyte *elodea canadensis.* Organic removal efficiency was not reported, however an average of 40 % urea removal was achieved (Kadlec and Wallace, 2009). This system is the single largest airport constructed wetland system identified from within the literature and has large areas of open water, requiring additional management considerations, such as waterfowl control.

2.7.2. Toronto Pearson International Airport (Canada)

Toronto Pearson International Airport in Canada has an operational hybrid wetland system comprising of a vertical flow and open water treatment zones. Surface water runoff from a catchment area of 382 ha is conveyed into a 0.42 hectare vertical flow wetland followed by a 1.38 ha open water system for final treatment. Both wetlands are planted with *phragmites australius* and have been in operation since 2000 (Kadlec and Wallace, 2009).

2.7.3. Wilmington Airport (USA)

Two reciprocating wetland systems have been implemented at Wilmington Air Park (USA) to treat runoff from two separate catchments (Fig. 2.7). Each system comprises of two alternatively saturated wetland cells. The mean COD removal efficiency for the two separate systems ranged between 86 % to 88 % COD, however it was hypothesised that during periods of high loading the systems were operating under anaerobic conditions (ACRP, 2013b).

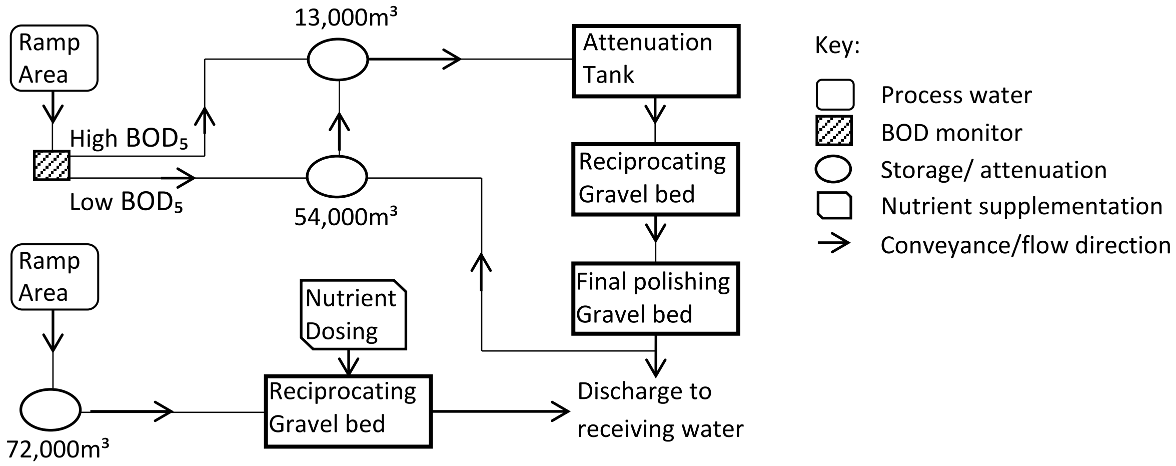


Figure 2.7. Simplified conceptual model of Wilmington Air Park de-icer management system. Source: adapted from ACRP (ACRP, 2013b).

2.7.4. Westover Air Reserve Base (USA)

At the Westover Air Reserve (USA), a passive a 0.24 hectare subsurface flow constructed wetland has been in operation since 2001. The system is storm event driven and receives direct runoff from aircraft de-icing stands, resulting in high MLR variation. This is reflected in variable COD removal efficiencies between 10 % to 80 % (ACRP, 2013b). Research conducted in 2002 revealed significant exceedance of the design organic loading rate (54.5 kg d^{-1} BOD_5) during storm runoff events, resulting in low mean BOD_5 removal efficiencies of 21 % (Naval Facilities Engineering Comand, 2004, Kadlec and Wallace, 2009).

2.7.5. Edmonton International Airport (Canada)

At Edmonton International Airport in Canada, a horizontal subsurface flow constructed wetland was implemented following successful pilot-scale trials using worst case scenario glycol concentrations observed within airport runoff (Higgins and Maclean, 2002). The trials comprised of horizontal subsurface flow wetlands which were dosed with 1,250 mg L^{-1} of $C_2H_6O_2$ based ADF. The effect of aeration was tested and it was identified that >99 % $C_2H_6O_2$ removal was achieved regardless of aeration in aerated and non-aerated tests (Higgins and Maclean, 2002). Following the initial pilot-scale trial, a system comprising 12 non-aerated individual treatment cells planted with *cattails,* with a combined footprint of 2.7 ha was commissioned (Higgins and Maclean, 2002). The system was designed not to operate during the winter months and instead stores contaminated runoff in a large 440,000 m^3 storage lagoon until temperatures began to rise in the spring (Higgins and Maclean, 2002). In 2011, the system was upgraded to include nutrient dosing and artificial aeration to increase throughput and provide treatment during the winter months (Toit et al., 2013).

2.7.6. Heathrow Airport (UK)

As part of the Heathrow Airport DMS, surface water runoff from the southern catchment of the airport is conveyed to the Mayfield Farm treatment system for on-site treatment (Fig. 2.8). The system comprises of an aerated storage reservoir (45,000 m³), a storage pond (19,000 m³), a one hectare phytoremediation channel and 12 constructed wetland cells (Adeola et al., 2009). The original system was designed to treat 590 kg d^{-1} BOD_5 and to achieve a 40 mg L^{-1} BOD_5 final effluent concentration. However, airport growth and increased de-icer application volumes led to MLRs in surface water runoff which exceeded the system design capacity (Murphy et al., 2014). This resulted in final effluent concentrations unsuitable for discharge into the receiving water, within the 40 mg L^{-1} BOD_5 discharge consent limit (Adeola et al., 2009). To address this, the system was upgraded in 2010/11 to include artificial aeration, based on the results of field trials which revealed 14 times more BOD_5 removal in aerated wetland cells compared to non-aerated wetland cells (Murphy et al., 2014). To complement the artificial aeration, a nutrient dosing system was incorporated in order to meet the nutrient requirements of the treatment biomass within the upgraded aerated wetland system (Murphy et al., 2014).

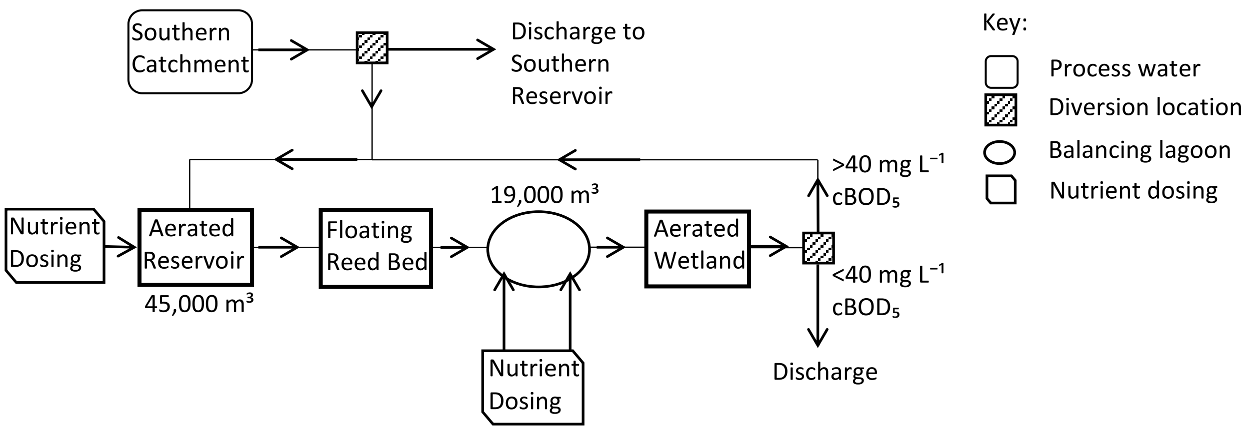


Figure 2.8. Simplified conceptual model of the Heathrow Airport Mayfield Farm de-icer treatment facility. Source: adapted from (ACRP, 2013b, Murphy et al., 2014).

2.7.7. Buffalo Niagara International Airport (USA)

Buffalo Niagara International airport (USA) also operates an aerated wetland system to treat de-icer contaminated runoff. The system comprises four completely submerged 1.5 m deep vertical flow treatment cells, each with a surface area of 4,640 m^2. During the 2010/11 winter de-icing season, BOD_5 removal efficiency between 90 % to 100 % was achieved despite concentrations of BOD >20,000 kg d^{-1} (Wallace and Liner, 2011a). Pre-construction experiments within one m^3 vegetated, aerated and non-aerated vertical flow subsurface flow constructed wetland cells established that artificial aeration significantly enhanced the removal efficiency of BOD_5 when aerated at 0.85 m^3 per m^3 of media. The study concluded that the aerated wetland technology has the potential to provide sufficient treatment without the requirement for pre-aeration of the wastewater (Wallace and Liner, 2011a, Higgins et al., 2010, Higgins et al., 2007).

Table 2.6.
Details of full-scale operational treatment wetland systems used within the aviation industry for treatment of de-icer contaminated storm runoff

Parameter	**Buffalo Niagara International Airport (USA)**	**Heathrow Airport (UK)**	**Edmonton International Airport (Canada)**	**Toronto Pearson Airport (Canada)**	**Wilmington Air Park (USA)**	**Kalmar Airport (Sweden)**
Wetland Type	Vertical Subsurface Flow	Horizontal Subsurface Flow	Hybrid – Vertical and Horizontal	Hybrid – Vertical and open water	Reciprocating Subsurface Flow	Free water surface
Aeration (kW)	4 x 186 kw blowers	6 x 240	2 x 56 kw blowers	No	No	No
Wetland Area (Ha)	0.46	2.08	2.7	1.8	2.4	18
No. of Treatment Cells	4	12	12	0.42 VSSF followed by 1.38 FWS [(a)]	2	4
Media Depth (mm)	1,500	1,100	900	-	2,100	1,500
Drainage Area (Ha)	-	290	293	382	890	4,800
Substrate	Gravel (10-15 mm washed)	Gravel	Gravel	Sand/gravel (graded)	Gravel	-
Design HLR [(b)] (m^3/d)	4,600	6,912	747	-	6,546	-
Design OLR [(c)] (BOD_5 kg/d)	4,500	3,500	711	-	6,667	-
Treatment Efficiency (%)	98 % BOD_5 (2010/11)	<93 %	-	-	86 % – 88 % COD (2000 – 2009)	-
Discharge Consent Limit	30 mg L^{-1} BOD_5	40 mg L^{-1} BOD_5	100 mg L^{-1} COD	-	-	-
Construction Costs	$10 million	$5 million 2010 upgrade undisclosed	$2 million and $3 million upgrade 2011	$2 million	$6.2 million 2000 and-$0.6 million upgrade 2006	-
References	[1], [2]	[3], [4]	[5], [6]	[7]	[8], [9]	[7]

[(a)] Free water surface wetland, [(b)] hydraulic loading rate, [(c)] organic loading rate, (-) data unavailable.
Source: [1] (Wallace and Liner, 2011a), [2] (Higgins et al., 2010), [3] (Adeola et al., 2009), [4] (Murphy et al., 2014), [5] (Higgins and Maclean, 2002), [6] (Toit et al., 2013), [7] (Kadlec and Wallace, 2009) [8] (Naval Facilities Engineering Comand, 2004) [9] (ACRP, 2013b).

2.8. Concluding Remarks and Research Priorities

The conveyance, attenuation and treatment systems incorporated into airport DMS are likely to be placed under increasing pressure within the foreseeable future, as new airports and expansion of existing airports will be required to meet the projected increase in demand for air travel (DFT, 2003, DFT, 2013). In addition, increasingly stringent environmental legislation may require airport operators to review their existing DMS. Further, there is uncertainty regarding how potential climate change scenarios will influence future de-icer application requirements. Currently, there is no forecasted technological advancement that will alleviate the requirement for aircraft and pavement de-icer application at airports and although the environmental performance of de-icer chemicals has improved over recent years, it is unlikely that products associated with very low environmental impact will be produced within the current remit of the aerospace materials specifications.

A range of de-icer treatment technologies have been implemented at airports to address the challenges of treating de-icer contaminated storm event runoff. However, it is clear that the design and operation of these technologies must be optimised in relation to the operational characteristics and variability in water quality at each airport, in order to deliver effective treatment of storm event runoff, whilst minimising capital and operating costs from economic, energy and carbon perspectives. In this context, aerated wetlands appear to offer significant potential for application at airports, as part of future DMS. To realise the full potential of aerated wetlands for the treatment of de-icer contaminated runoff at airports, future research is required in order to:

- Develop robust assessment criteria and protocols for monitoring the transport of pollutant loads across the airport landscape during storm runoff events. Each airport has unique characteristics in relation to environmental, meteorological, layout, drainage infrastructure and de-icer application. Therefore a wide range of water quality characteristics and associated environmental risks exist. Sound decision making can only proceed when monitoring has properly quantified existing site conditions, constraints and water quality characteristics. The aim of such monitoring should be to assist airport operators, engineers, designers and consultants in obtaining the necessary and correct quality of data to enable bespoke DMS and treatment solutions to be designed. In this context a background assessment of existing operating conditions and water quantity and quality characteristics has been undertaken and the results presented within Chapter 3. Following on from background assessments it is recognised that key challenges exist in relation to 'future proofing' airport investments. For instance, projected air travel demand, future airport expansion projects and global climate change are major uncertainties. Each of these has an implication towards future de-icer application and surface water loading and therefore water volumes and pollutant loads required for treatment must therefore be incorporated within any assessment of airport treatment requirements.

- Optimise aeration techniques in artificially aerated wetlands. The use of the aerated wetland technology to treat surface water runoff containing de-icers has developed significantly during the past decade. It has been established that supplementary O_2 is required to support the microbial communities that are responsible for the biodegradation of commercial de-icers within aerated wetlands. However, the cost of aeration devices drives the need for further research to deliver optimal aerated wetland design and operation criteria. The aim is to improve oxygen transfer efficiency within the wetland media, contributing to reduced operational costs. Artificially aerated wetlands have been in use from approximately 2001 for this purpose. However, there is currently no design standard for this technology (Kadlec and Wallace, 2009, Nivala et al., 2013b). This has led to significant variation in full-scale operational systems and, in consequence, variable system performance. Therefore, further research into optimal aeration techniques would assist not only by increasing the cost-effectiveness of individual systems, but also through incorporation into a much needed industry standard.

The literature review presented within this Chapter was structured to address the objective defined within Section 1.1 which was to 'review catchment processes and aerated wetland literature, to improve understanding of the principles, processes and pathways of pollutant transfer to surface water systems and how this ultimately impacts the treatment of airport runoff and the design and operation of treatment systems operating under these conditions'. The review identifies key processes and transport pathways of de-icers from the de-icing location and into surface water systems and establishes a simplified mass balance approach to help understand and define these processes. Further, treatment challenges resulting from the processes and transport pathways unique to airport runoff have been identified and a review of existing treatment technologies used by airports undertaken, to understand how these systems are designed and operated in order to efficiently address these challenges.

Chapter 3

Understanding the Temporal Variability of Water-soluble Organic Pollutants within Airport Storm Runoff

3.1. Introduction

Aviation regulations including the International Organisation of Standardisation (ISO) 11076: 2012 and the Federal Aviation Regulations (FAR) part 121, 125 and 135, require all aircraft to be free of frozen contamination on take-off (ISO, 2012, ACRP, 2011, Transport Canada, 2010). To meet these requirements and ensure flight safety, airlines apply Type I AAF and Type II, III and IV ADF (Types I-IV are termed ADF from this point forward) to critical areas of the aircraft such as wings, propellers and stabilisers to remove any frozen contamination that maybe present (Transport Canada, 2010). Following application ADF becomes 'spent' as it runs off the aircraft onto the de-icing stand, drips onto taxiways during taxiing and shears from the aircraft and onto the runway during take-off (ACRP, 2012a). Further, PDF is applied to aircraft stands, taxiways and runway surfaces to maintain safe conditions for aircraft operations, also becoming spent following application. Spent de-icers are water-soluble organic pollutants which can be mobilised during storm runoff events and transported into surface water systems (Corsi et al., 2001a, ACRP, 2012b). Large volumes of storm runoff from airports typically become contaminated due to the large surface areas over which spent de-icers are deposited and accumulate. Typical de-icer formulations primarily consist of propylene glycol and acetate or formate based compounds for ADF and PDF respectively (Switzenbaum et al., 2001, ACRP, 2008). Biodegradation of these compounds takes place naturally within aquatic environments in a process where microbial respiration is responsible for the consumption of DO concentrations (Evans and David, 1974, D'Itri, 1992, Corsi et al., 2001a, French et al., 2001, ACRP, 2008, Corsi et al., 2012). If these pollutants are exported from airports due to poor management practices, they may lead to point source pollution of surrounding watercourses, degradation of surface water quality, depletion of DO, detrimental impacts towards aquatic organisms and noncompliance with water legislation (Fisher et al., 1995, Hartell et al., 1995, Novak et al., 2000, Corsi et al., 2001a, Corsi et al., 2001b, Cancilla et al., 2003a, Corsi et al., 2006a, United States Geological Survey, 2007, ACRP, 2008, Corsi et al., 2009, Corsi et al., 2012, Sulej et al., 2012b).

Managing de-icer contaminated storm runoff to prevent environmental pollution, comply with regulatory requirements and meet an airport's corporate and social responsibilities is a costly and complex global issue. In Europe, the WFD was implemented in 2000 to improve the ecological and chemical quality of surface water systems, for the general benefit of stakeholders (DEFRA, 2012b, Dworak et al., 2005, Liefferink et al., 2011). Airports are therefore responsible for ensuring that no negative impacts are caused to receiving waters through the activity of discharging storm water runoff. In England and Wales, the Environment Agency (EA) are currently tasked with implementing the WFD and ensuring airports comply with the legislative requirements. At present this is primarily achieved through River Basin Management Plans (UK Government, 2014b), EPR (Environment Agency, 2012b) and routine monitoring of approximately 4,500 waterbodies (Outram et al., 2013). Outside of the European Union, airports are subject to different national legislation and regulations, although aquatic organisms and surface water systems are generally protected by similar standards irrespective of national borders.

A wide range of methods and technologies have been implemented at airports, to manage the risks associated with de-icer contaminated storm event runoff (ACRP, 2013b, ACRP, 2013a, Freeman et al., 2015). Currently, almost 50 % of airports globally collect storm runoff and discharge this as trade effluent to the local water company sewer, where it is ultimately conveyed to WwTP and treated off-site (ACRP, 2013b). Using this method, liability for meeting discharge permit limits for the treated effluent is passed onto the water company, however trade effluent discharge is costly and subject to its own volumetric and pollutant load limits due to capacity restrictions at WwTP's (Nitschke et al., 1996, Wilson, 1996). To comply with these limits, large storage capacity is typically required at an airport to attenuate peak discharge volumes and pollutant loads, although conditions that exceed the limits and available storage capacity result in storm runoff discharging into surrounding watercourses via storm water overflows.

As airports develop to meet the projected 1 % to 3 % annual increase in demand for air travel within the UK up to 2050 (DFT, 2013, DFT, 2003), de-icer usage will increase in line with aircraft movements and expanding airport surface areas that will require additional de-icer applications. Further, airport expansion and global climate change may contribute significantly towards increased storm event runoff volumes, thereby placing pressure on existing infrastructure, storm water storage capacity, pollution prevention measures and compliance with regulatory limits. New technologies, solutions and pollution prevention measures will be required globally in the aviation industry, in order to meet these future challenges, within the context of environmental regulations. However, our current knowledge of the catchment processes which impact the temporal dynamics of pollutant mobilisation and transport into surface water systems at airports is limited and therefore needs to be improved to fully understand the risks posed to receiving waters and to design effective and robust treatment solutions. Understanding catchment processes, such as runoff flow pathways, catchment residence time and remobilisation of pollutant stores however remain significant research challenges, which have proven difficult to quantify and conceptualise to date. For example, complex biogeochemical processes occur on airport surfaces (Revitt et al., 2002), within soils and groundwater (Evans and David, 1974, French et al., 2001, Nunes et al., 2011) and within catchment drainage channels, which significantly modify de-icer transport and fate. Further, there are often uncertainties to be addressed when making quantitative measures of precipitation, discharge volume and concentration such as sample location and frequency which can influence the representativeness of the measurements.

Traditionally, the common practice of monitoring water quality at airports has been to collect routine samples, sending these to a commercial laboratory on a weekly, fortnightly or monthly basis (ACRP, 2012a). This practice typically takes seven to ten working days for results to be issued by the laboratory, which is of limited use in the context of near real-time management and decision making and provides poor insight into pollutant concentrations, which can fluctuate over very short periods of time. High temporal resolution water quality monitoring is therefore crucial for providing scientific data and evidence to improve our understanding of pollutant transport processes and to inform reliable and transparent decision making, for both practitioners and policy makers (Collins et al., 2012). High resolution analysers help airports to respond quickly to pollution incidents, without the need to wait up to ten days for commercial laboratory results, therefore reducing the risk to receiving waters and allowing more sustainable management of storm event runoff from airport catchments. However, results from such high resolution analysers must typically be correlated with regulated parameters such as BOD_5 and COD for compliance purposes and to allow meaningful interpretation of the data, which leads to improved understanding of pollutant transport processes and the risks posed to receiving waters (Chandler et al., 1976).

The aim of this chapter is to improve understanding of the temporal dynamics of de-icer mobilisation, transport and ultimate fate following application within airport catchments, in order to inform future management options for de-icer contaminated catchment storm runoff and improve our ability to effectively manage this large scale environmental challenge. Research objectives have been defined to help achieve the aim as follows; (i) to determine the extent to which storm runoff events are responsible for the mobilisation and transport of de-icer pollutants, (ii) to determine whether relationships exist between discharge volume and pollutant concentration and (iii) determine the impact of de-icer application and storm event runoff on water quality and trade effluent discharge costs.

3.2. Case Study Site

3.2.1. Background

Manchester Airport is located in the North West of England (53.36˚N, 2.27˚W), approximately eight miles south of Manchester city centre (Fig. 3.1). The airport first opened in 1938, serving 7,600 passengers in its first 14 months of operation (MAG, 2007). Today Manchester Airport has developed into one of the UKs busiest airports, serving over 20 million passengers a year (MAG, 2014). The airport site covers approximately 900 ha (Fig. 3.2), including approximately 565 ha of operational area, with the remaining area owned for the management of landscape and habitat (MAG, 2011). Manchester Airport is one of only two airports in the UK to have a second runway, with approximately 70 airlines transporting passengers to over 200 destinations worldwide (MAG, 2014). Annually, aircraft movements are c. 150,000 and are projected to increase by approximately 1 % to 3 % annually up to 2050, to meet the projected increased demand for air transportation (DFT, 2003, DFT, 2013). Manchester Airport is owned and operated by the Manchester Airport Group (MAG), who also own Bournemouth, Stansted and East Midlands Airport.

3.2.2. Climate

To the North East of Manchester Airport lies the Pennines, a chain of rolling gritstone moors rising some 893 m above sea level at their highest location. This undulating topography contributes to a highly variable climate (Met Office, 2015). Mean annual temperatures for the region from 1981 to 2010 were 9 ˚C, compared with a mean of 2.5 ˚C during the winter months defined as October to March (Met Office, 2015). Mean annual rainfall for the region from 1981 to 2010 ranged between 800 mm to 830 mm, with mean monthly rainfall of approximately 70 mm over the same period (Met Office, 2015). Further, the number of days where rainfall was >1 mm per day from 1981 to 2010 ranged from 35 days to 40 days during the winter months (Met Office, 2015). On average between 1981 to 2010, 20 days of snowfall were observed within the region, resulting in approximately 3 days to 7 days of ground lying snow per year (Met Office, 2015).

Figure 3.1. Site location plan. Manchester Airport site location is indicated by the red marker. Based on LCM2007 © NERC CEH 2011. Contains OS data. © Crown copyright and data base right 2015.

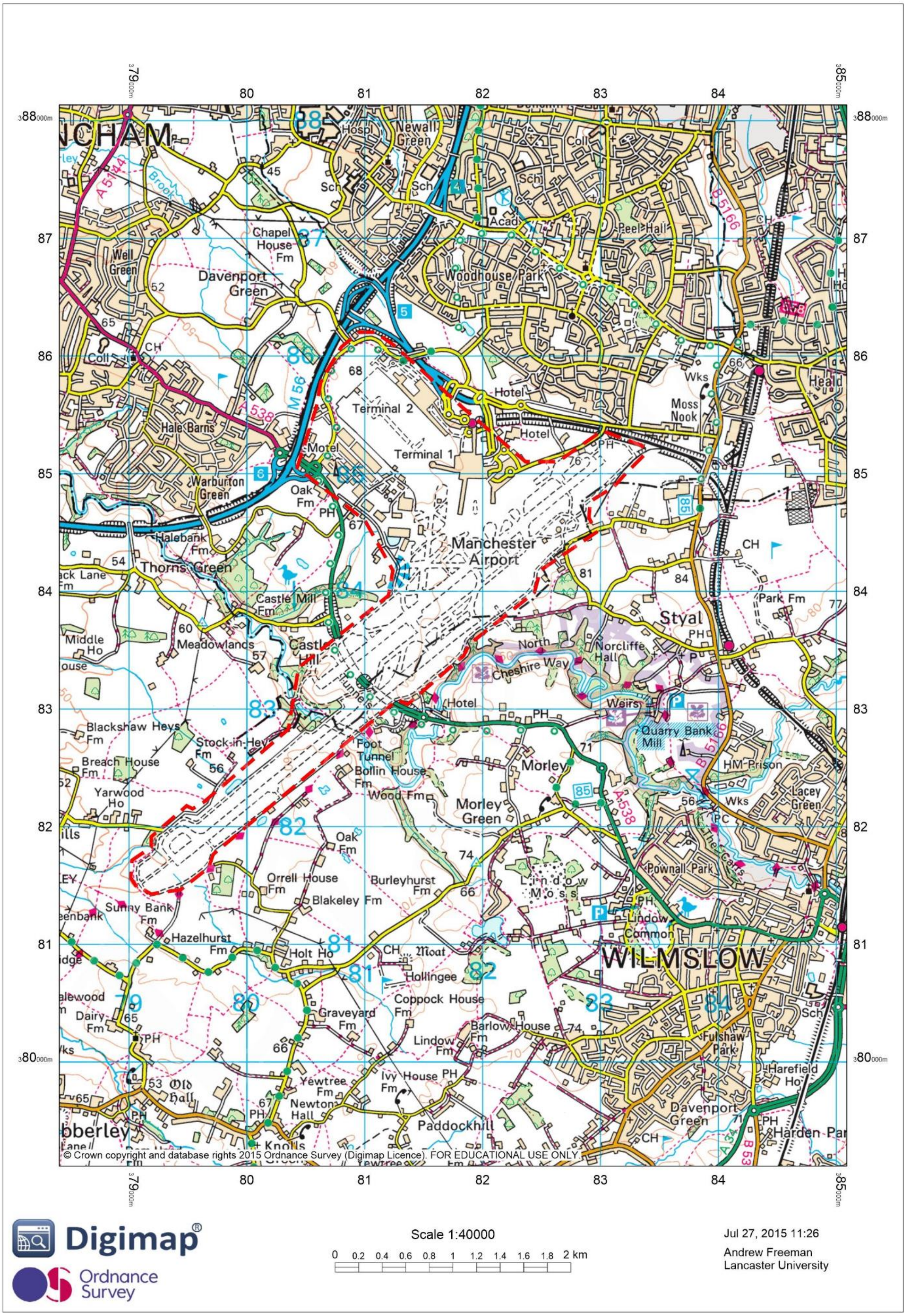


Figure 3.2. Approximate site boundary of Manchester Airport is indicated by dashed red line. Based on LCM2007 © NERC CEH 2011. Contains OS data. © Crown copyright and data base right 2015.

3.2.3. Overview of Surface Water Catchment Areas

The Manchester Airport site is divided into separate surface water sub-catchments (Fig. 3.3). The volume and quality of storm runoff varies considerably between the catchments, reflecting the size and nature of operations undertaken within the catchment area (Table 3.1). Catchment A is approximately 30 ha, consisting of nine aircraft stands and 8.5 ha of runway and grass land. The cargo and terminal 2 catchments have footprints of approximately 25 ha each and comprise of 17 and 23 aircraft stands respectively along with areas of taxiway. Storm runoff from these catchments along with the landside areas which comprise of terminal building and road networks, discharge into United Utilities (UU) surface water tunnel sewer, through an oil interceptor and into the R. Bollin at Mill Lane (NGR SJ 801000 383688). Catchment C is mainly operational airfield and aircraft stands and receives significant inputs of both ADF and PDF during the de-icing season. A detailed description of catchment C characteristics is presented in Section 3.3.1. Catchment D consists of approximately 11 ha of grassland, seven ha of runway and three ha of taxiway. Storm runoff from catchment D is typically discharged into Badger Brook at NGR SJ 81086 83941. Catchment E consists of approximately 21 ha of grassland, nine ha of runway and four ha of taxiways and discharges into Double Wood Brook during typical conditions. The runway two catchment consists of approximately 102 ha grassland, 20 ha runway and 14 ha of taxiway and discharges into the R. Bollin at NGR SJ 80622 82906 during typical conditions.

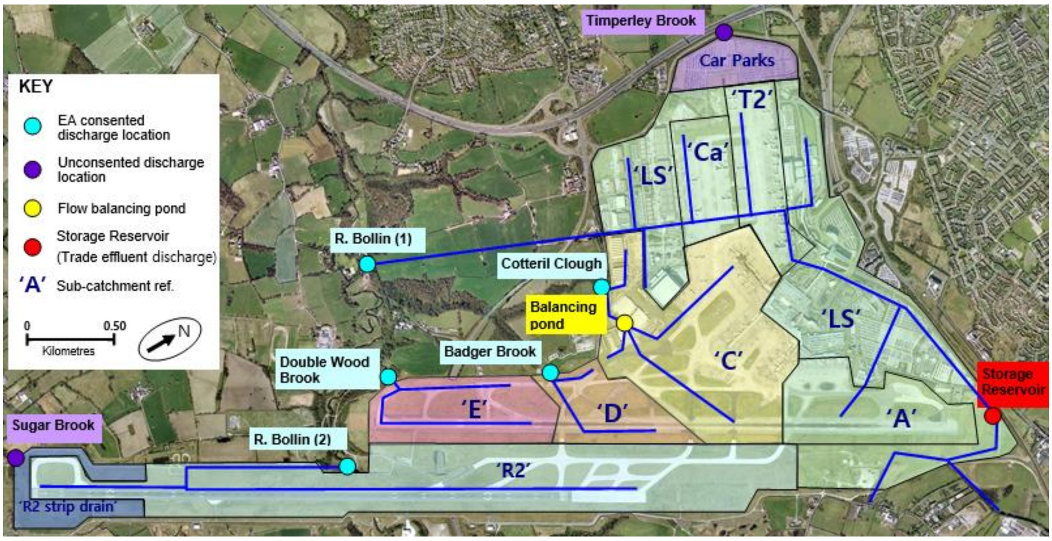


Figure 3.3. Approximate surface water sub-catchment boundaries at Manchester Airport. Boundaries are defined based on the surface area draining to a specific discharge location. Sub-catchment areas are represented by coloured shaded areas. Blue lines indicate key subsurface drainage sewers. Coloured circles highlight discharge locations with blue and purple circles indicating discharge to receiving waters, yellow circles discharge to a flow balancing pond and red circles discharge to the public sewer. Terminal 2 (T2), Cargo (Ca), Landside areas (LS).

Table 3.1.
Summary of Manchester Airports surface water catchment operations and characteristics [a]

Sub – Catchment	Catchment Function	Key contaminant sources and contaminants	Impermeable areas (Ha)	Permeable areas (Ha)	Total area (Ha)
A, Ca, T2 and AS	Terminals, freight and cargo	Vehicle, aircraft movements, washing, refuelling, maintenance, de-icers. Solids, metals, hydrocarbons, glycol, acetate.	111	123	235
C	Airfield ops, taxiway and runway	Vehicle, aircraft movements, refuelling, washing, maintenance, de-icers. Solids, metals, hydrocarbons, glycol, acetate.	99	39	138
D	Taxiway and runway	Aircraft movements, fuel combustion, pavement de-icer and spent aircraft de-icers. Acetate and glycol.	3	18	21
E	Taxiway and runway	Aircraft movements, fuel combustion, pavement de-icer and spent aircraft de-icers. Acetate and glycol.	17	17	34
R2	Taxiway and runway	Aircraft movements, fuel combustion, pavement de-icers and spent aircraft de-icers. Acetate and glycols.	35	102	137
Site Total		**-**	**255**	**301**	**565**

[a] Catchment areas provided by Manchester Airport personnel and are based on the sub-catchment overview plan (Fig 3.3).

Discharges from the site must comply with environmental permit limits implemented by the EA for discharge to a receiving water and UU for discharge to the public sewer (Table 3.2). For example discharges into the R. Bollin must remain within the 23 mg L^{-1} BOD_5 limit. To comply with these limits the water quality discharging from individual catchments at Manchester Airport is monitored using high resolution TOC analysers (Fig. 2.5.). If pollutant concentrations approach the discharge limit storm runoff is diverted into the containment system to prevent regulatory noncompliance.

Table 3.2.
Key regulatory discharge limits at Manchester Airport [a]

Discharge location	Parameter	Discharge permit limit	Consent number
R. Bollin (receiving water) [b]	BOD_5	23 mg L^{-1}	EPR/CB3299EN
United Utilities Sewer (trade effluent)	COD	10,000 mg L^{-1} (5,000 kg d^{-1})	EPR/CB3299EN

[a] Based on 2015 (EPR/CB3299EN) consolidated permit limits (Environment Agency, 2015a), [b] Permits exempt storm water overflows due to system capacity being exceeded during exceptional rainfall events (Environment Agency, 2015a).

3.2.4. Overview of the Pollution Prevention 'Containment' System

The containment system ultimately drains into a 73,000 m^3 below ground storage reservoir near to the eastern site boundary at NGR SJ 835556 831444 (Fig. 3.4). Effluent contained within the reservoir is continuously monitored using TOC analysers and discharged through a flume into Baguley Brook when BOD_5 concentrations are within the 23 mg L^{-1} discharge permit limit. Storm event runoff is discharged as trade effluent when concentrations are above the 23 mg L^{-1} BOD_5 discharge limit. Trade effluent is discharged into the UU public foul sewer and conveyed approximately 14 km to the Davey Hulme WwTP, for off-site biological treatment, prior to discharging into the Manchester ship canal. Trade effluent discharges from the storage reservoir are subject to limits of 10,000 mg L^{-1} COD and 5,000 kg d^{-1} COD (Table 3.2).

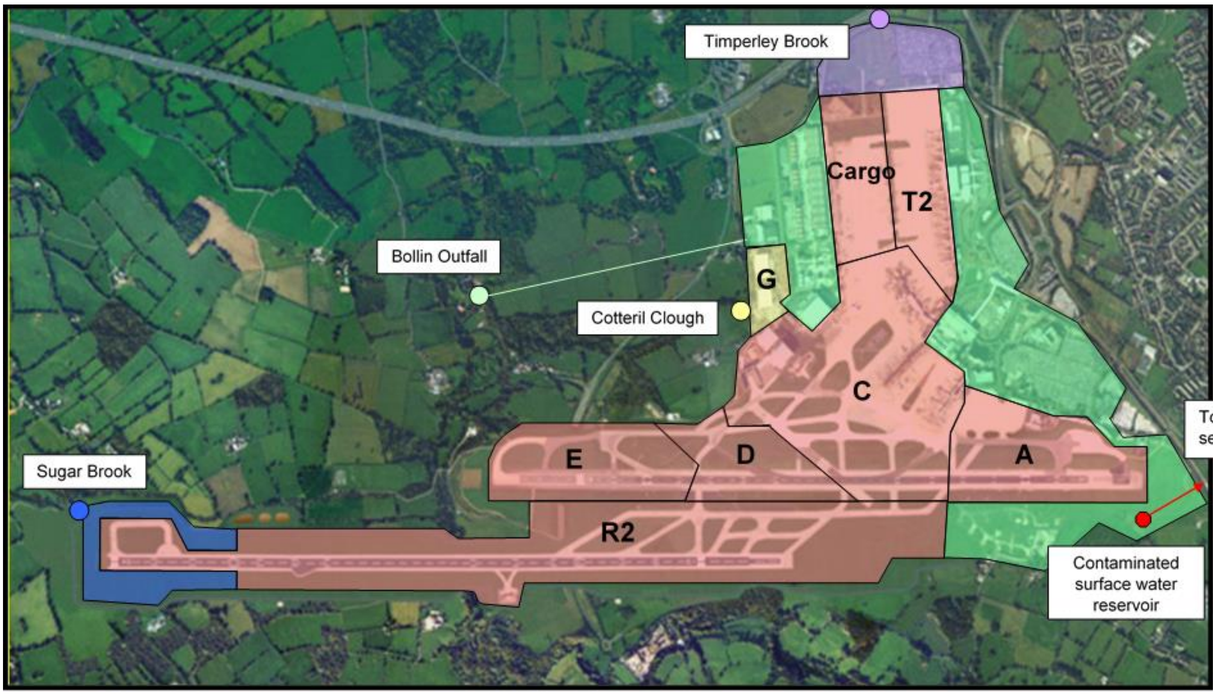


Figure 3.4. An overview of the Manchester Airport surface water containment catchments, where areas shaded in red (Cargo, T2, C, E, D, A and R2) drain into the containment system, areas shaded blue and yellow drain to Sugar Brook and Cotteril Clough, areas shaded green drain to the R. Bollin and the purple shaded area drains to Timperly Brook.

3.3. Methodology

3.3.1. Study Catchment Details

Surface water drainage catchment C is at the centre of aircraft operations at Manchester Airport. It is the largest individual catchment on site, covering some 138 ha (Fig. 3.5a). Approximately 72 % of the catchment area is impermeable surface, totalling 99 ha, with the remaining 39 ha being grassland. The catchment comprises of 39 aircraft stands, approximately 42 ha of apron, 10 ha of taxiway and 5 ha of runway one (Table 3.3).

Table 3.3.
Details of Manchester Airports surface water drainage catchment C

Parameter	Value
Total catchment area (ha)	138
Grass/soil (ha)	39
Impermeable surfaces (ha)	99
No. of aircraft stands [a]	39
Apron area (ha)	42.3
Taxiway area (ha)	10.2
Runway area (ha)	5.3
Size of flow balancing pond (ha)	3.8
Volumetric storage capacity in flow balancing pond (m^3)	1,905

[a] 42 % of the total number of aircraft de-icing stands at Manchester Airport are within catchment C boundary.

Storm runoff from the catchment C is conveyed through four main sewers (Fig. 3.5b) and into a drainage channel (Fig. 3.5c) near to the South West catchment boundary. During dry weather conditions, base-flow discharging from catchment C is discharged into a floating arm arrangement (Fig. 3.5d), diverted into the containment system and pumped approximately 2.2 km to the storage reservoir. During storm events, water overflows into an attenuation pond of approximately 3.8 ha with a storage capacity of 1,905 m^3. The pond receives the first flush of storm runoff from catchment C and therefore often contains highly contaminated water, especially following de-icer application within the catchment. Water within the pond is delivered into the containment system, via a pump station sited in the North West corner of the pond. The pond is typically pumped dry to provide storage capacity for future storm event runoff volumes. Storm event runoff discharging through the catchment C drainage channel (Fig. 3.5c) has been monitored extensively during consecutive winter de-icing seasons (defined as October to April) 2013/14 and 2014/15, with the monitoring results presented throughout the remainder of this chapter.

Figure 3.5. (a) Approximate catchment C boundary indicated by dashed red lines and monitoring location, (b) catchment C surface water sewers, (c) catchment C drainage channel and monitoring location, (d) floating arm for base-flow discharge conditions (e) catchment C attenuation pond.

3.3.2. Data and Sample Collection

A Shlumberger mini diver was installed within a standpipe at the monitoring location (Fig. 3.5c), to record water level (± 0.01 m) at 15 minute intervals, following barometric correction for atmospheric pressure. Velocity was calculated by the manning formula (Eq. 3.1), using a manning roughness coefficient (*n)* of 0.011 for a uniform channel of cement and mortar (Arcement and Schneider, 1989). The channel width was measured to be 1.85 m whilst a level survey confirmed a slope of 0.043 m/m. Discharge values were therefore calculated using the slope – area – velocity method (Gershon and Phillip, 1975).

$$V = \frac{1.486}{n} AR^{2/3} Se^{1/2} \tag{3.1}$$

where:

V = mean velocity of flow (m sec^{-1})
A = sectional area of flow
R = hydraulic radius (m)
Se = slope (m/m)
n = manning's roughness coefficient

Samples of storm event runoff discharging through catchment C drainage channel (Fig. 3.5c) were collected during the 2013/14 and 2014/15 de-icing season, to determine the pollutant concentrations and loads associated with de-icer application and transported from the de-icing location to the catchment discharge location. The method of sample collection varied slightly between the two de-icing seasons (Table 3.4). In winter 2013/14 an Isco-STIP BIOX-1010 analyser retrieving a sample from catchment C drainage channel was used to measure storm runoff quality on an hourly basis between 12/12/2013 to 31/03/2014 (Fig. 3.6a). The operational principal for the BIOX analyser is to measure the O_2 consumed by an acclimated bacteria attached to plastic support media within a bioreactor, every 3 minutes (BODm_3) (Endress + Hauser, 2007). The Isco-STIP BIOX-1010 analyser was withdrawn from service prior to the 2014/15 winter season and therefore the method for water quality measurements was adapted as follows. Discrete samples were taken every 12 hours during dry weather and base-flow conditions between 12/11/2014 to 23/03/2015, with sample frequency increasing to 15 min to 90 min intervals during storm runoff events. Water quality samples were collected using ISCO 3700 automatic wastewater samplers (Fig. 3.6b), equipped with 10 mm PVC braided hose sample tubing which led from the effluent stream to the sampler's internal peristaltic pump. During collection, samples were pumped through a 300 mm length of silicon tubing and deposited into disposable LDPE plastic sample bags within a foam insulated (R-11) base. A water level trigger was installed 100 mm from the channel bed (Fig. 3.6c). This was connected to the ISCO 3700 automatic sampler and used to initiate the increased frequency of sample collection during storm water discharge.

Figure 3.6. Methods of monitoring airport storm runoff, (a) Isco-STIP BIOX-1010 BOD analyser (b) ISCO 3700 automatic wastewater samplers, (c) ISCO 3700 level trigger used to initiate automatic sample collection.

Two sources of weather data were used throughout the study (Table 3.4). During winter 2013/14, temperature and rainfall data at 30 minute intervals were obtained from a weather station located at Manchester Airport, approximately 0.3 km from the catchment C monitoring location. Hourly temperature and rainfall data from the Met Office Rostherne weather station located approximately 7 km from the monitoring location, was obtained for the winter period of 2014/15.

Table. 3.4.
Summary of sample and data collection methods in winters 2013/14 and 2014/15 during the study of catchment C discharges at Manchester Airport

Parameter	**Winter 2013/14**	**Winter 2014/15**
Flow	Shlumberger mini diver installed in well, with barometric compensation. Manning N used to compute volume	Shlumberger mini diver installed in well, with barometric compensation. Manning N used to compute volume
Sample collection	Isco-STIP BIOX-1010 (continuous [a])	12 hour discrete samples during base-flow. 15 - 90 min discrete samples during storm runoff events (when discharge > 2 L sec^{-1})
Chemical analysis [b]	Oxygen demand determined by BIOX 1010 instrument [a] calibrated by correlation for COD, BOD_5	COD, BOD_5, TOC, TSS, pH
Weather	Weather station located near to monitoring site	Met office (Rostherne station)
De-icer application	PDF data available. Total daily ADF volumes extrapolated from Airline Service application volumes	PDF data available. Total daily ADF volumes extrapolated from Airline Service application volumes

[a] BIOX-1010 measures oxygen demand within a bioreactor every 3 three minutes (BOD m^3),
[b] chemical analysis parameters include chemical oxygen demand, five day biochemical oxygen demand, total organic carbon, total suspended solids and pH.

Close monitoring of weather forecasts and regular communication with personnel at Manchester Airport was used to determine when significant de-icer application had been undertaken. A breakdown of daily ADF and PDF application volumes were provided by the main handling agents and Manchester Airport personnel respectively at the end of each de-icing season. These were used to determine the BOD_5 and COD annual and daily loads applied within the monitoring catchment C which were calculated based on the volume of ADF and PDF applied, the concentration of BOD_5 and COD (mg g^{-1}) of each de-icer product, de-icer dilution and fluid density (g cm^{-2}) as detailed on the individual de-icer product data safety sheets.

3.3.3. Chemical Analysis

During winter 2014/15 base-flow samples comprising 12-hourly discrete samples were transported the short distance to an on-site laboratory and analysed for pH, TSS, COD and TOC on a weekly basis. During winter 2014/15 storm water samples were also collected and analysed on-site for pH, TSS, COD, TOC and BOD_5 within 48 hours of collection. Standard laboratory procedures were followed to ensure high sample result integrity for each determinant.

Measurements of pH were conducted using a HQ11d digital pH meter which was subject to a 3 point daily calibration using Hach DIN 19266 accredited quality standards of pH 4.01 ± 0.02, pH 7.01 ± 0.02 and pH 10.01 ± 0.02 at 25˚C. The Hach photometric method 8006 for determination of TSS was used which involved vigorously blending 200 ml of sample for two minutes, transferring 10 ml to a sample cell and measuring the 810 nm wavelength absorbance through the sample using a DR2800 photospectometer. Blank samples of de-ionised water were used as a zero prior to the determination of TSS and the analytical limit of detection (ALOD) was 0.2 mg L^{-1}. Digestion of samples for both COD and TOC were performed using a LT200 instrument followed by colorimetric determination using a DR2800 photospectrometer. Hach methods were used to standards ISO 6060-1989, DIN 38409-H41-H44 for COD and EN 1484, DIN 38409-H3 purging method for TOC. Hach Addista LCA standards of 50 mg L^{-1} ± 4 COD and 16.5 ± 2.5 TOC were used to verify COD and TOC results respectively for each batch of samples processed. The ALOD was 15 mg L^{-1} and 3 mg L^{-1} for COD and TOC respectively and all samples outside of the method range were discarded and repeated following dilution with deionised water. Analysis for BOD_5 was performed at 20°C using a BODTrak ™ II instrument and following a Hach standard manometric sample dilution, five day test procedure (Hach, 2013). Samples for BOD_5 analysis were inoculated with 35 ml of poly seed solution prior to incubation. The BOD_5 of the seed solution was tested and deducted from final sample results. Sample dilutions were performed to ensure that the sample oxygen demand remained within the range of the BODTrak ™ II instrument during incubation. Dilutions were carried out on the basis of an estimated BOD_5, which was determined using a COD: BOD_5 correlation factor of 0.68. Dilution water comprised 1 ml of nutrient solution and de-ionised water. Blanks comprised of de-ionised water, 1 ml of nutrient solution and 35 ml of seed solution which was frequently tested and discarded if the BOD_5 was > 0.2 mg L^{-1}, in which case sample results were adjusted to offset any cross contamination of the dilution water. Results for BOD_5 were verified using glucose and glutamic acid (GGA) standards of 300 mg L^{-1}, inoculated with 35ml of prepared poly seed solution and incubated at 20˚C for five days following the appropriate dilution. Several duplicate BOD_5 samples across the two winter monitoring periods were also couriered to Envirolab to verify the results from the BODTrak ™ II instrument against UKAS accredited ISO/IEC 17025 standard methods.

3.3.4. Data Analysis and Interpretation

From the 2013/14 winter data, surface water pollutant loads were calculated using 15-minute flow data and hourly sample concentration data retrieved from the Isco-STIP BIOX-1010. Concentration data from the Isco-STIP BIOX-1010 instrument was multiplied by the mean correlation ratios (Table 3.5) and presented as de-icer surrogate parameters COD, BOD_5 or TOC. During the 2014/15 de-icing season, loads were calculated using 15 minute flow data and concentration data obtained through analysis of samples collected at 12 hour intervals and at frequencies of 15 min to 90 min intervals during storm runoff events. Concentrations were assumed to remain constant between samples and therefore concentration was multiplied by the 15 minute flow data to determine 15 minute loads which were summed to give daily or total storm event load in kg of BOD_5 or COD.

The correlation of the Isco-STIP BIOX-1010 analyser results to de-icer surrogate parameters BOD_5, COD and TOC was evaluated over a 10 month period, between 03/10/2013 to 28/08/14, during which samples were collected from the instrument at approximately weekly intervals and analysed within 24 hours in the airport laboratory for COD, TOC and $BOD_{5,}$ following the protocols described above in Section 3.1.1. At the time of sample collection, data was recorded from the analyser display to compare against laboratory results. Pearson's correlation coefficient (PCC) and significance (*p*) of the relationship for each parameter was determined using IBM SPSS statistics 20 software and simple linear regression analysis was used to model the relationship between the analyser results and the surrogate parameters (Fig. 3.7). Prior to sample collection the BIOX-1010 analyser was checked for correct operation, specifically that the analyser was receiving sample and dilution water and that the O_2 concentration within the bioreactor was recording a pre-determined concentration of 3 mg L^{-1} as recommended by the operating manual (Endress + Hauser, 2007). The Isco-STIP BIOX-1010 results ($BODm_3$) generally correlated well with BOD_5 (R^2 = 0.88, PCC = 0.94, p=<0.01, n = 39), COD (R^2 = 0.76, PCC = 0.88, p=<0.01, n = 64) and TOC (R^2 = 0.78, PCC = 0.93, p=<0.01, n = 29) (Fig. 3.7). Mean ratios of 1: 1.61, 1: 3.50 and 1: 1.02 were established for BOD_5, COD and TOC respectively which reflects the high proportion of samples that were taken during baseline conditions when pollutant concentrations were at or near to background concentrations (Table 3.5).

Table 3.5.
Mean parameter ratios determined for airport storm runoff at Manchester Airport using an Isco-STIP BIOX-1010 analyser [(a)]

Location of analyser	Ratio BOD m^3 [(c)] : BOD_5 [(d)]	Ratio BOD m^3 : COD [(e)]	Ratio BOD m^3 [(f)] : TOC [(e)]
Manchester Airport catchment C discharge including baseline samples [(b)]	1 : 1.61	1 : 3.50	1 : 1.12

[(a)] Correlation is likely to vary significantly from site to site depending on the ratios of pavement and aircraft de-icers present, the proportion of baseline samples and the general characteristics of the effluent being tested. Mean ratio results rounded to 2 decimal places are reported including baseline samples (n = 32). [(b)] Baseline samples defined as <8 mg L^{-1} BOD_5.
[(c)] BOD m^3 = three minute BOD measurements from the BIOX-1010 analyser, [(d)] five day biochemical oxygen demand, [(e)] chemical oxygen demand, [(f)] total organic carbon.

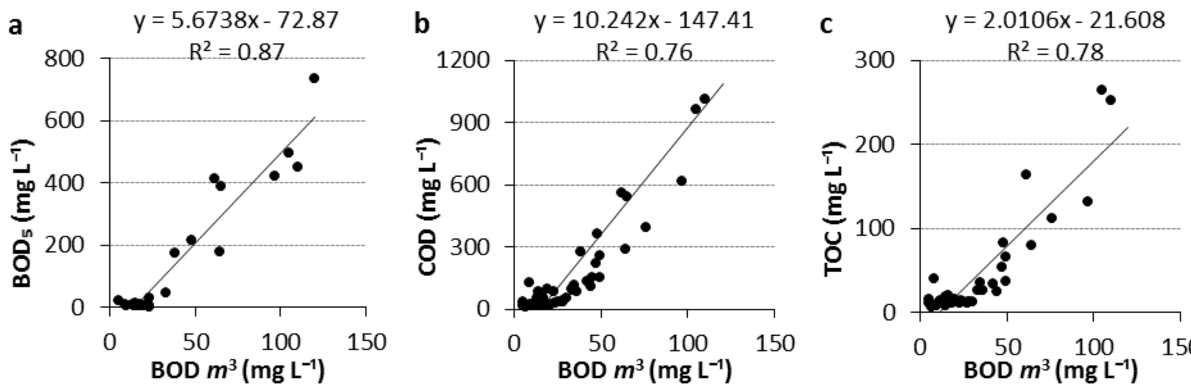


Figure 3.7. Correlation between BIOX-1010 (BOD m^3) and (a) BOD_5 where: R^2 = 0.88, PCC = 0.94, p=<0.01, n = 39, (b) COD where: R^2 = 0.76, PCC = 0.88, p=<0.01, n = 64, (c) TOC where: R^2 = 0.78, PCC = 0.93, p=<0.01, n = 29 as measured within catchment C discharges.

A mass balance approach comparing de-icer loads applied with loads measured at the catchment C discharge location was used to determine the impact of storm runoff events on the transport of de-icers from the de-icing location to surface water system. Whilst descriptive PDF application locations were provided, ADF locations were not supplied by the handling agents and therefore the total ADF load applied over the entire airport was adjusted to estimate the load applied within catchment C only, based on the percentage of the total number of de-icing stands present within catchment C. The total load calculated for each event therefore included the estimated ADF and actual PDF applied within catchment C. Further, to account for de-icer accumulation at the de-icing location the load applied within the immediate 24 hour period prior to the beginning of the storm runoff event was also included within the calculation of the total event load. As de-icers degrade quickly following application (Revitt et al., 2002), ADF and PDF applied > 24 hours prior to the beginning of each event were excluded from the calculation of total event load based on the assumption that they would have been degraded in-situ before being mobilised.

Hysteresis plots were used to further interrogate storm runoff event data. To aid interpretation of these plots, the hysteresis index (HI_{mid}) (Lawler et al., 2006, Outram et al., 2013) was calculated using Eq. 3.3 and Eq. 3.4. The HI_{mid} was then used to identify the direction (i.e. positive HI_{mid} = clockwise or negative HI_{mid} = anti clockwise) and magnitude of the hysteretic effect. The method is based on the width measurement of a 'hysteresis loop', at the midpoint (median) of the discharge event (Q_{mid}) and is calculated in two stages. First, the Q_{mid} is calculated using Eq. 3.2:

$$Q_{mid} = (Q_{max} - Q_{min}) + Q_{min} \tag{3.2}$$

where:

Q_{mid} = midpoint of the discharge event
Q_{max} = peak event discharge
Q_{min} = event starting discharge

Following calculation of the Q_{mid}, interpolation of pollutant concentrations such as BOD_5 at the rising limb i.e. (BOD_{5RL}) and falling limb i.e. (BOD_{5FL}) can be measured from the vertical Q_{mid} line through the hysteresis loop. A clockwise direction hysteresis represents storm events whereby the pollutant source in this example BOD_5 is depleted or diluted prior to the hydrograph returning to base-flow discharge (i.e. $BOD_{5RL} > BOD_{5FL}$). In this instance the HI_{mid} is calculated using Eq. (3.3):

$$HI_{mid} = (BOD_{5RL} / BOD_{5FL}) - 1 \tag{3.3}$$

Alternatively, anticlockwise loops maybe observed (i.e. $BOD_{5RL} < BOD_{5FL}$) and are often associated with processes acting to delay the delivery of sediment and other pollutants to the catchment drainage channel. In this instance Eq. 3.4 is selected to calculate the Hi_{mid}:

$$HI_{mid} = (-1 / (BOD_{5RL} / BOD_{5FL})) + 1 \quad (3.4)$$

To establish the impact of de-icer application on storm water management and business operating costs, the cost of trade effluent discharges for storm runoff and individual storm runoff events from catchment C were calculated using mean daily COD (mg L^{-1}) and TSS (mg L^{-1}) concentrations and the fixed parameter charges determined by OFWAT. Costs were calculated using the Mogden formula (Eq. 3.5) which is used by UK water companies to calculate trade effluent disposal costs (OFWAT, 2010).

$$TE\ Charge = R + V + B1 + (Ot / Os) * B2 + (St / Ss) * S \quad (3.5)$$

where:

R = reception and conveyance charge (p m^3)
V = volumetric treatment charge (p m^3)
$B1$ = biological treatment charge (p m^3)
Ot = settled effluent COD (mg L^{-1})
Os = crude sewage COD (mg L^{-1})
$B2$ = biological oxidation of settled sewage charge (p kg)
St = total suspended solids (mg L^{-1})
Ss = total suspended solids of crude sewage (mg L^{-1})
S = treatment and disposal of sewage sludge charge (p kg)

3.4. Results

3.4.1. Weather Conditions and De-icer Application during Monitoring Periods

Winter 2013/14 was characterised by predominantly wet and mild conditions, with mean daily temperatures of 6.2 °C, mean daily rainfall of 2.7 mm and below average snowfall (only 6 days of snowfall observed). In contrast, winter 2014/15 was much cooler and drier, with mean daily temperatures of 4 °C, mean daily rainfall of 2 mm and 13 days of snowfall (Table 3.6). Aircraft de-icing is typically conducted when temperatures fall below 4 °C, which was recorded during 93 days and 122 days for winter 2013/14 and 2014/15 respectively. Consequently 1,768 de-icing operations were conducted during the 2013/14 winter season, increasing by 80 % to 3,175 aircraft de-icing operations within winter 2014/15 (Table 3.7). In contrast, pavement de-icing is typically conducted in anticipation of ice or snow and was required on 4 and 24 days during winter 2013/14 and 2014/15 respectively (Table 3.7).

Table 3.6.
Summary of winter characteristics during the 2013/14 and 2014/15 winter monitoring of catchment C discharges at Manchester Airport

Parameter	Winter 2013/14	Winter 2014/15
Mean daily temperature (°C)	6	4
No. day's minimum temp. < 4°C	93	122
No. day's minimum temp. < 0°C	15	47
No. days snow recorded	6	13
Mean daily rainfall (mm)	2.7	2.2
No. of days daily rainfall >1 mm	81	75

Significantly more de-icer was used at Manchester Airport during the 2014/15 winter, compared to the 2013/14 winter (Table 3.7). The mean number of aircraft de-iced per day were 21 and 30 within de-icing seasons 2013/14 and 2014/15, with mean daily ADF application volumes of 3,306 L and 4,002 L respectively. This amounted to total annual ADF application volumes of 274,261 L and 856,428 L for the 2013/14 and 2014/15 de-icing seasons. During 2013/14 the most frequently applied ADF formulation was Type II (Kilfrost ABC Plus and EcoWing) with 173,699 L used in total compared to 90,303 L of Type IV (Kilfrost ABC-S Plus) and 10,259 L of Type I (Kilfrost DF plus). In 2014/15 airline services switched from Type II to Type IV ADF formulation (Kilfrost ABC-S Plus), which subsequently became the most frequently applied ADF, with 568,226 L used in total compared to 234,070 L and 54,132 L of Type II and Type I ADF formulations (Table 3.7).

Annual application volumes were calculated to be equivalent to total pollutant loads of 134 tonnes of BOD_5 and 247 tonnes of COD during winter 2013/14, compared to 305 tonnes BOD_5 and 613 tonnes COD during the 2014/15 winter. Mean daily pollutant loads during the monitoring periods were calculated as 906 kg d^{-1} BOD_5 and 1,671 kg d^{-1} COD in winter 2013/14 in contrast to 1,511 kg d^{-1} BOD_5 and 3,035 kg d^{-1} COD in winter 2014/15.

Table 3.7.
Summary of de-icer applications and surface water pollutant loading at Manchester Airport during de-icing seasons 2013/14 and 2014/15

Parameter	**Winter 2013/14**	**Winter 2014/15**	**Mean**
<u>De-icing Days</u>			
No. ADF [(a)] de-icing days	83	107	95
No. PDF [(b)] de-icing days	14	24	19
<u>Application Volume</u>			
Total ADF [(a)] volume (L)	274,261	856,428	565,345
Mean ADF [(a)] volume/day (L)	3,306	4,002	3,654
Max. ADF [(a)] volume/day (L)	13,359	113,572	63,466
Type I [(c)] volume (L)	10,259	54,132	32,196
Type II [(d)] volume (L)	173,699	234,070	203,885
Type IV [(e)] volume. (L)	90,303	568,226	329,265
Total PDF [(b)] volume (L)	168,300	144,500	156,400
<u>No. of Aircraft de-iced</u>			
Total No. of aircraft de-iced during season	1,768	3,175	2,472
Mean No. of aircraft de-iced/month	354	454	404
Max. No of aircraft de-iced/month	518	1,030	774
Mean No. of aircraft de-iced/day	21	30	26
Max. No. of aircraft de-iced/day	78	109	94
<u>Pollution loads (from ADF/ PDF)</u>			
Annual load (tonnes BOD_5)	134	305	220
Mean daily load (kg d^{-1} BOD_5)	905	1,511	1,208
Max daily load (kg d^{-1} BOD_5)	9,593	31,555	20,574
Annual load (tonnes COD)	247	613	430
Mean daily load (kg d^{-1} COD)	1,671	3,035	2,353
Max daily load (kg d^{-1} COD)	13,172	67,760	40,466

[(a)] Aircraft de-icing fluid, [(b)] pavement de-icing fluid, [(c)] Type I aircraft anti icing fluid, [(d)] Type II aircraft de-icing fluid, [(e)] Type IV aircraft de-icing fluid.

3.4.2. Temporal Variability of Catchment C Storm Runoff Event Quantity and Quality

Discharge and pollutant concentration responses to precipitation events showed high variation throughout the two winter monitoring periods (Fig. 3.8), as summarised in Table 3.8. Mean discharge volumes were 707 ± 779 $m^3\ d^{-1}$ and 789 ± 1,024 $m^3\ d^{-1}$ for the 2013/14 and 2014/15 winter monitoring seasons. Whilst minimum discharge volumes were low (i.e. <3 $m^3\ d^{-1}$), peak 24 hour discharge values were 4,076 $m^3\ d^{-1}$ and 5,192 $m^3\ d^{-1}$ during winter 2013/14 and winter 2014/15.

During the 2013/14 de-icing season, mean pollutant concentrations were 160 ± 391 mg L^{-1}, 81 ± 185 mg L^{-1} and 55 ± 133 mg L^{-1} for COD, BOD_5 and TOC respectively. Peak concentrations (as observed during winter storm runoff events) were 4,356 mg L^{-1}, 1,964 mg L^{-1} and 1,523 mg L^{-1} for COD, BOD_5 and TOC respectively. Mean daily pollutant loads within the 2013/14 season, amounted to 146 ± 308 kg d^{-1} COD and 74 ± 779 kg d^{-1} BOD_5, with peak loads of 1,727 kg d^{-1} COD and 786 kg d^{-1} BOD_5. As expected and in line with de-icer application volumes, mean and peak concentrations increased significantly during the 2014/15 monitoring season in comparison to the 2013/14 season. For example, during the 2014/15 season mean concentrations of 1,312 ± 2,495 mg L^{-1}, 363 ± 823 mg L^{-1} and 265 ± 583 mg L^{-1} were observed for COD, BOD_5 and TOC respectively, with peak concentrations of 21,768 mg L^{-1}, 7,105 mg L^{-1} and 4,467 mg L^{-1} observed for COD, BOD_5 and TOC respectively during winter storm runoff events. Mean daily pollutant loads during 2014/15 were 811 ± 2,940 kg d^{-1} COD and 133 ± 433 kg d^{-1} BOD_5 with peak loads of 20,980 kg d^{-1} COD and 3,730 kg d^{-1} BOD_5 observed. Base-flow discharges of <2 L s^{-1} (173 $m^3\ d^{-1}$) revealed significantly lower BOD_5 loads than observed during storm event conditions (i.e. >2 L s^{-1} discharge) with base-flow means of 2.7 kg d^{-1} and 2.5 kg d^{-1} for the 2013/14 and 2014/15 winter de-icing seasons.

Table 3.8.
Summary of water quality characteristics from drainage catchment C at Manchester Airport during 2013/14 and 2014/15 de-icing seasons

Parameter	De-icing season	Min.	Max.	Median	Mean	St.dev.	N
BOD_5 [(a)] (mg L^{-1})	2013/14	<1	1,964	24	81	185	3,287
COD [(a)] (mg L^{-1})		<10	4,356	44	160	391	2,754
TOC [(a)] (mg L^{-1})		<1	1,523	18	55	133	3,007
pH		6.6	8.4	7.8	7.8	0.4	148
TSS (mg L^{-1})		-	-	-	-	-	-
Flow [(b)] (m^3 d^{-1})		-0.05	4,076	328	707	779	138
Load (kg d^{-1} BOD_5)		<1.00	786	72	74	779	145
Load (kg d^{-1} COD)		<1.00	1,727	13	146	308	145
BOD_5 (mg L^{-1})	2014/15	4.58	7,105	46	363	823	334
COD (mg L^{-1})		<10	21,768	109	1,312	2,495	339
TOC (mg L^{-1})		3.55	4,467	37	265	583	334
pH		6.3	8.6	7.6	7.6	0.4	229
TSS (mg L^{-1})		3	670	24	40	71	229
Flow (m^3 d^{-1})		2.8	5,192	268	789	1024	171
Load (kg d^{-1} BOD_5)		<1	3,730	3	133	433	118
Load (kg d^{-1} COD)		<1	20,980	9	811	2,940	118

[(a)] Parameters correlated from Isco-STIP BIOX-1010.

[(b)] Negative flow indicates balancing pond capacity has been exceeded and surcharging of the catchment drainage channel.

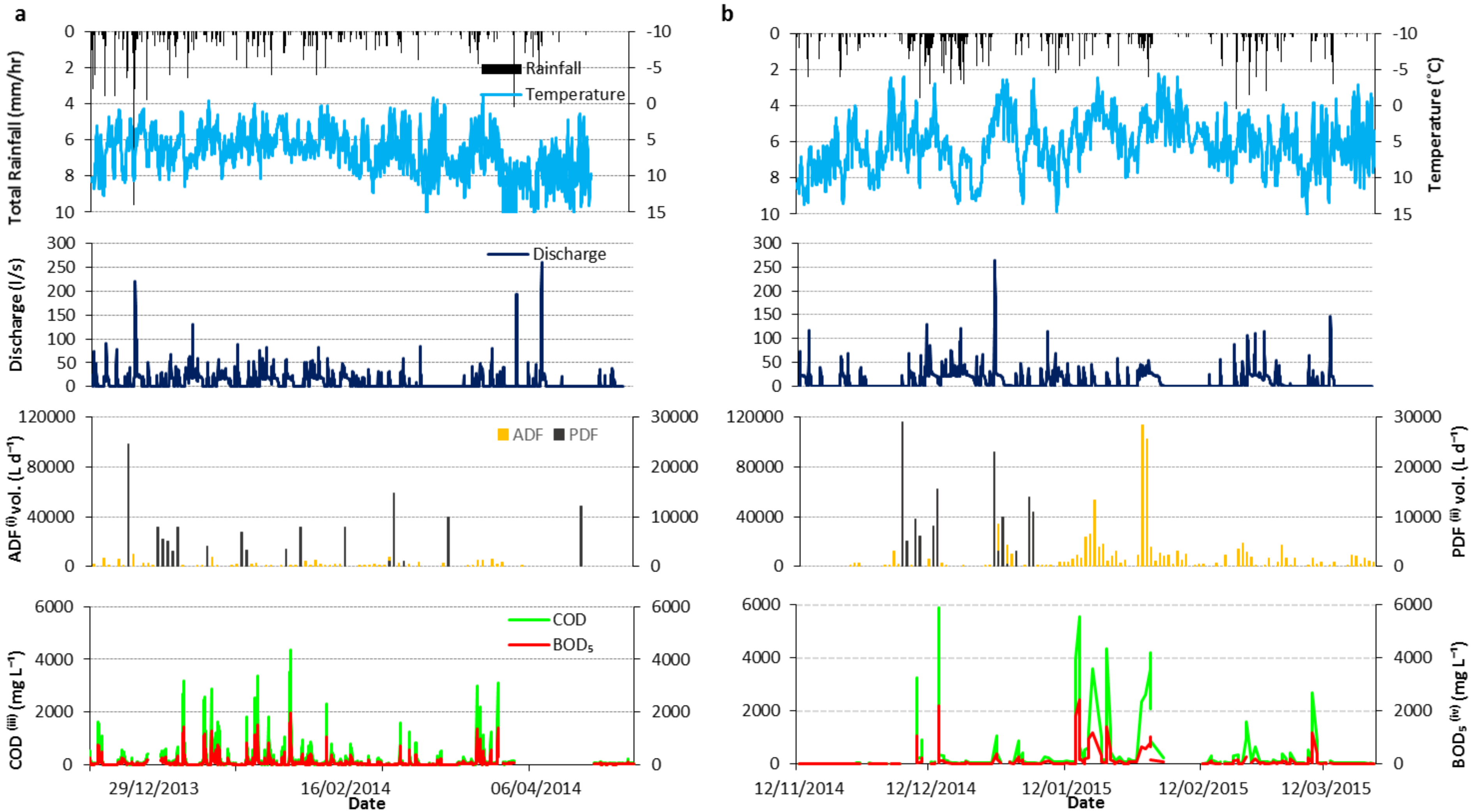


Figure 3.8. Data for Manchester Airport surface water catchment C, showing discharge and pollutant responses to meteorological and daily de-icer application inputs during (a) 2013/14 de-icing season and (b) 2014/15 de-icing season. (i) Aircraft de-icing fluid, (ii) pavement de-icing fluid, (iii) chemical oxygen demand, (iv) five day biochemical oxygen demand.

3.4.3. Winter Storm Runoff Events

Pollutant dynamics were investigated further during ten individual storm runoff events from catchment C, four of which were measured within winter 2013/14 and six during winter 2014/15 (Table 3.9, Fig. 3.9 and Fig. 3.10). Individual runoff events lasted between 17 and 96 hours from the beginning of the precipitation event to the discharge volume returning back to base-flow conditions which depended on the length of the precipitation event. Total precipitation across the ten events ranged from 2.1 mm to 28.6 mm, with intensities between 0.6 mm h^{-1} and 2.4 mm h^{-1} (Table 3.9). Snowfall was recorded during four of the winter events (events five, seven, eight, ten), which generally resulted in higher ADF and PDF de-icer application volumes and applied loads and higher pollutant loads measured at the catchment discharge location.

Application of ADF ranged from low to high intensity, with volumes between 1,619 L (event four) and 96,748 L (event ten) applied during and 24 hours prior to the beginning of a precipitation event. Almost half of the winter storm events had no PDF applied (events four, six, seven, nine), whilst events one, two, three, five, eight and ten had a range of PDF volumes from 350 L to 1,650 L applied during or within 24 hours of the precipitation beginning. Total pollutant loads applied through de-icer application within catchment C ranged from 451 kg BOD_5 (event four) to 25,835 kg BOD_5 (event 10) during the ten storm runoff events monitored.

During the ten winter storm events, total storm runoff volumes ranged from 143 m^3 (event nine) to 11,825 m^3 (event 10) which is equivalent to 149 m^3 d^{-1} and 2,956 m^3 d^{-1} respectively (Table 3.9). Base-flow discharge volumes were typically <0.3 L sec^{-1} with mean storm runoff volumes of 2.3 L sec^{-1} (Q_{min}) recorded. The peak discharge volume across the ten storm runoff events was 41 L sec^{-1} (Q_{max}), whilst median discharge volumes during storm runoff events were determined to be 22 L sec^{-1} (Q_{mid}), ranging from 13 L sec^{-1} in event five to 32 L sec^{-1} in event ten (Table 3.10).

Measured loads within catchment C storm event runoff ranged between 375 kg BOD_5 (event six) and 12,342 kg BOD_5 (event 10). The mass balance calculation revealed that a mean of 55 % of the total de-icer loading applied was transported into the surface water system and measured within catchment C discharges across the ten events monitored. The percentage of the applied BOD_5 load transported by an individual runoff event ranged between 97 % in event one and 28 % in event eight (Table 3.9). All events were characterised by a rapid and flashy runoff and pollutant concentration response to precipitation of varying volume and intensity (Fig. 3.9 and Fig. 3.10). This is illustrated on the hydrographs by the typically short lag time between the peak precipitation and peak discharge, which ranged from one to four hours with a mean of 1.6 hours across the 10 storm runoff events.

Table 3.9.
Summary of storm runoff event characteristics monitored at Manchester Airport catchment C during winter 2013/14 and 2014/15

Event No.	Date	Event duration (hours) [(a)]	Total event precipitation (mm)	Precipitation intensity (mm h^{-1})	Total discharge vol. (m^3)	De-icer (kg BOD_5) [(b)]	Monitored load (kg BOD_5)	Mass balance (% of applied load) [(c)]
1	05/01/2014	26	5.0	2.0	1,774	875**	853	97
2	12/01/2014	27	3.2	1.2	996	1,438**	639	45
3	20/01/2014	19	4.2	0.6	901	611**	375	62
4	01/03/2014	17	5.8	1.2	1,621	451	232	51
5*	31/12/2014	13	2.1	1.2	356	1,695**	1,384	82
6	01/01/2015	20	2.9	1.2	1,240	741	375	51
7*	14/01/2015	17	3.9	1.8	856	1,370	733	54
8*	17/01/2015	27	4.7	1.2	1,670	10,645**	3,013	28
9	23/01/2015	23	4.0	1.8	143	2,200	723	33
10*	28/01/2015	96	28.6	2.4	11,825	25,835**	12,342	48
Mean		29	6.4	1.5	2,138	4,586	2,067	55

[(a)] Event duration is defined as the beginning of precipitation event to discharge returning back to base-flow conditions. [(b)] Total de-icer loading from aircraft and pavement de-icers applied within catchment C during and 24 hours prior to the precipitation event. [(c)] Mass balance between total de-icer load applied and load measured in catchment C storm runoff.
* Snowfall recorded during or within 24 hours prior the beginning of monitoring.
** Pavement de-icer applied prior to and during event.

In all ten winter storm runoff events, the concentrations of COD, BOD_5 and TSS respond positively to the rising limb of the hydrograph (Fig. 3.9 and Fig. 3.10). Some of the events, most notably events six, eight and ten resulted in two or more concentration peaks in response to discharge variation on the hydrograph. Typically, peak concentrations for the measured parameters coincided with peak discharge volumes, a relationship which was most notable in events one, two, three, five and eight. Event ten differs from events one to nine in length and displays multiple discharge peaks on the hydrograph. Throughout this event, heavy snowfall and intermittent precipitation events followed one another resulting in a prolonged winter storm event. Above average daily de-icer applications occurred throughout event 10, resulting in multiple pollutant concentration peaks and troughs which coincided with peaks and troughs in discharge volume.

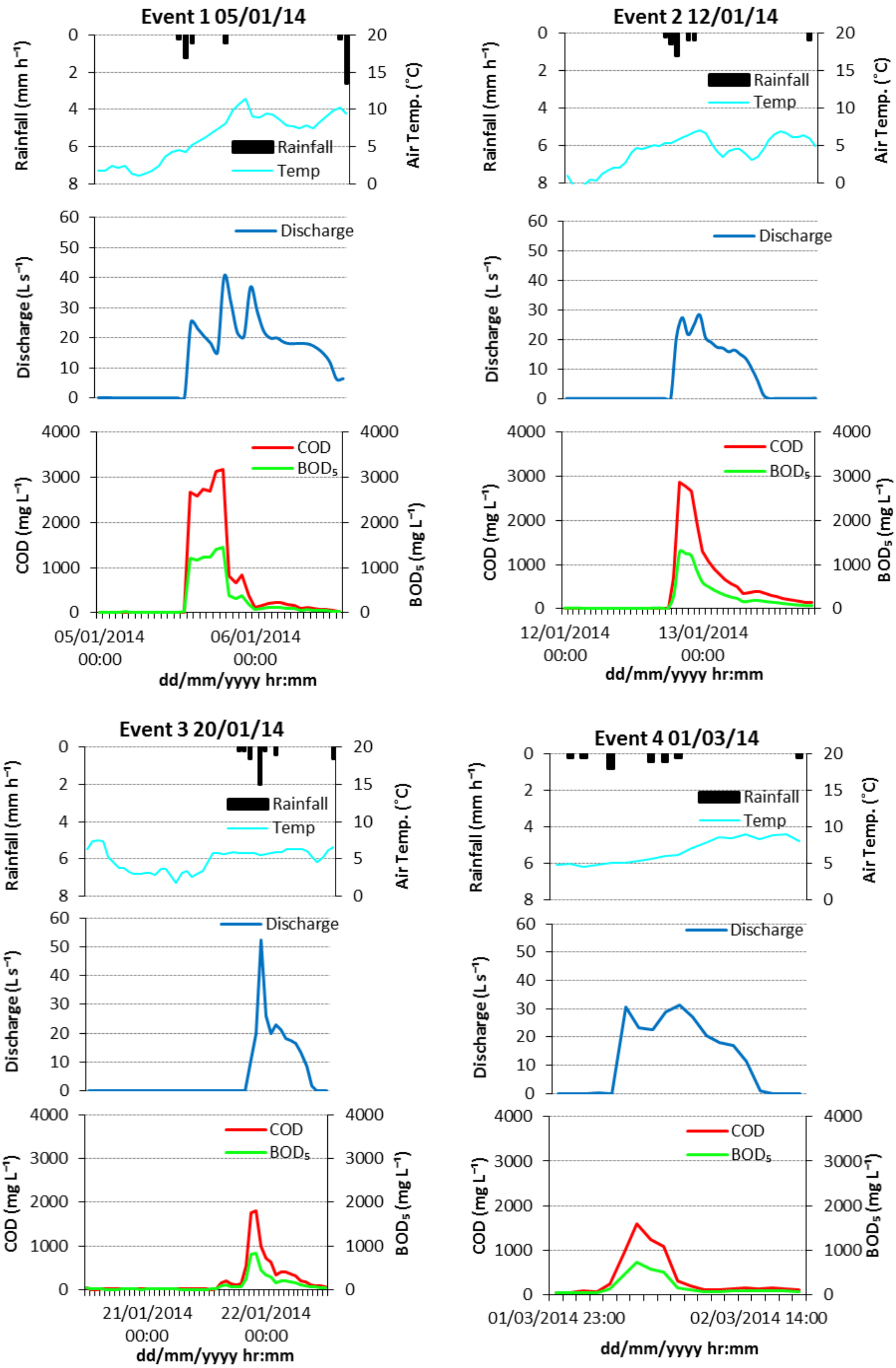
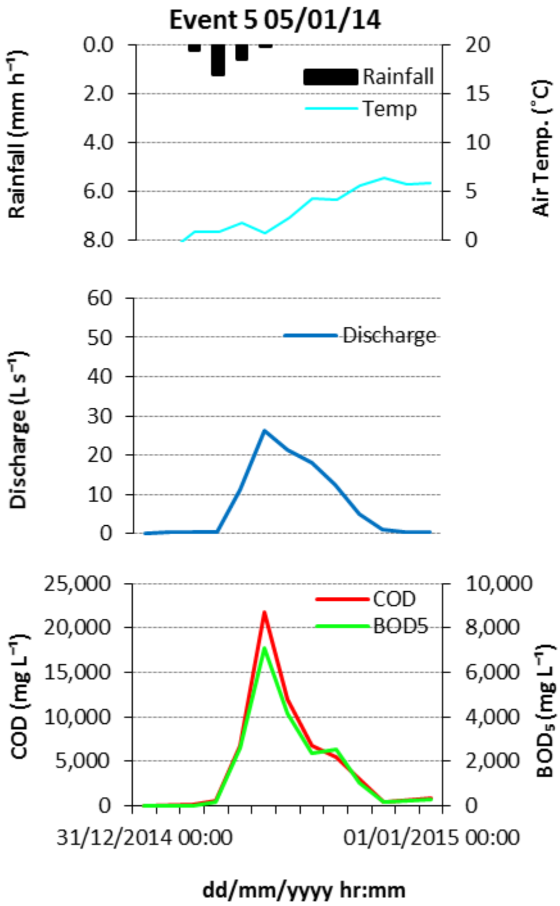
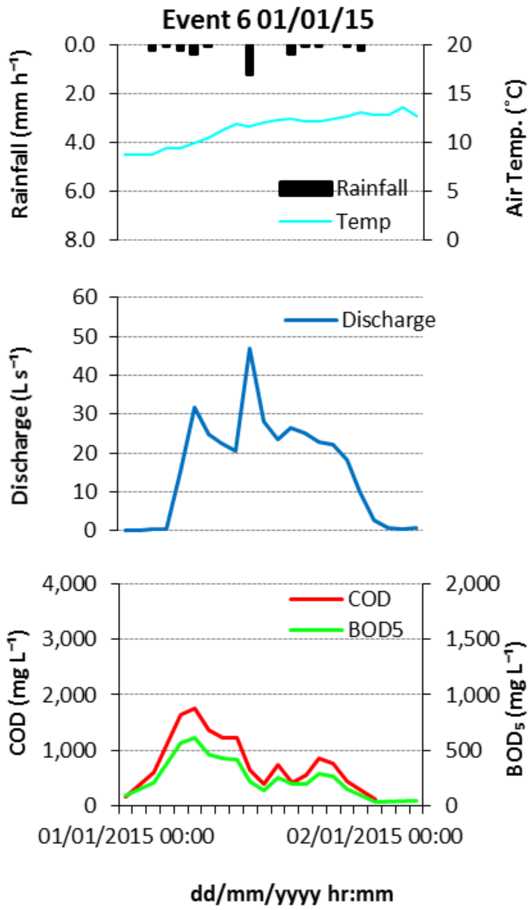
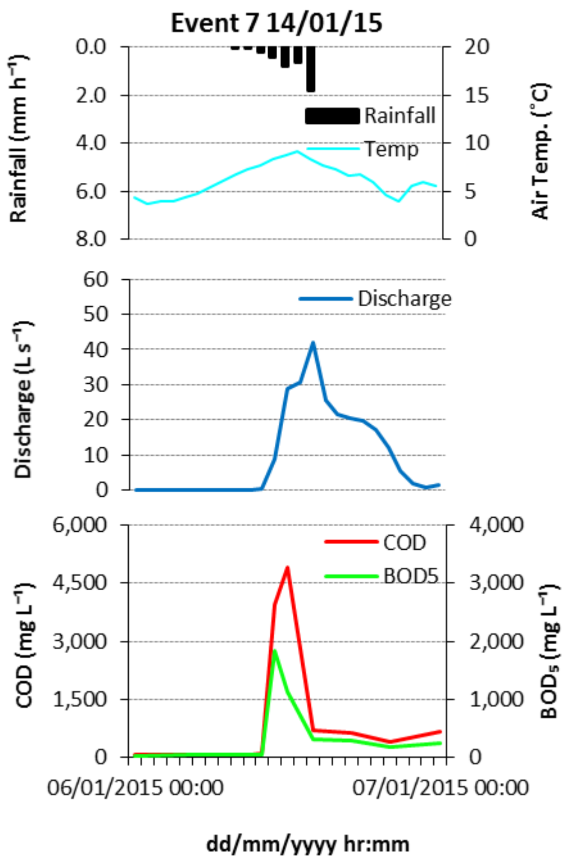
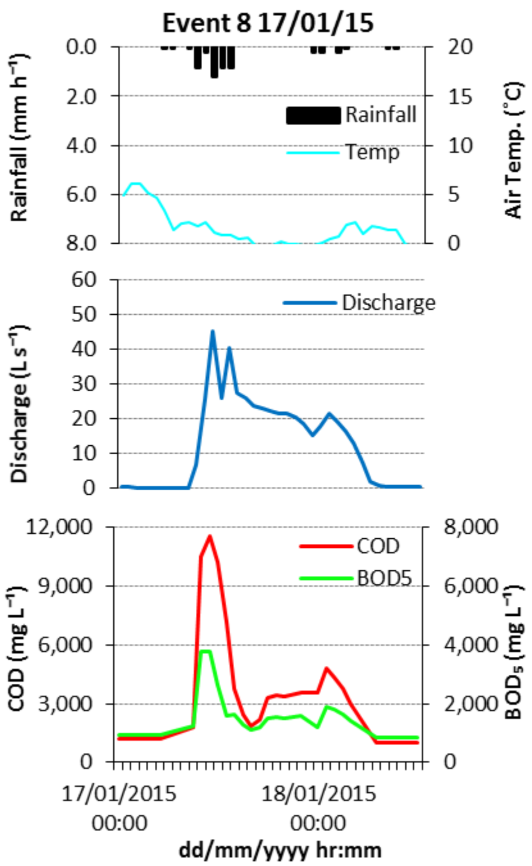


Figure 3.9. Individual winter storm event hydrographs and responses of chemical oxygen demand (COD) and five day biochemical oxygen demand (BOD_5) during the 2013/14 de-icing season.


Event 5 05/01/14
Rainfall (mm h⁻¹)
Air Temp. (°C)
Rainfall
Temp
Discharge (L s⁻¹)
Discharge
COD (mg L⁻¹)
BOD₅ (mg L⁻¹)
COD
BOD5
31/12/2014 00:00
01/01/2015 00:00
dd/mm/yyyy hr:mm


Event 6 01/01/15
Rainfall (mm h⁻¹)
Air Temp. (°C)
Rainfall
Temp
Discharge (L s⁻¹)
Discharge
COD (mg L⁻¹)
BOD₅ (mg L⁻¹)
COD
BOD5
01/01/2015 00:00
02/01/2015 00:00
dd/mm/yyyy hr:mm


Event 7 14/01/15
Rainfall (mm h⁻¹)
Air Temp. (°C)
Rainfall
Temp
Discharge (L s⁻¹)
Discharge
COD (mg L⁻¹)
BOD₅ (mg L⁻¹)
COD
BOD5
06/01/2015 00:00
07/01/2015 00:00
dd/mm/yyyy hr:mm


Event 8 17/01/15
Rainfall (mm h⁻¹)
Air Temp. (°C)
Rainfall
Temp
Discharge (L s⁻¹)
Discharge
COD (mg L⁻¹)
BOD₅ (mg L⁻¹)
COD
BOD5
17/01/2015 00:00
18/01/2015 00:00
dd/mm/yyyy hr:mm

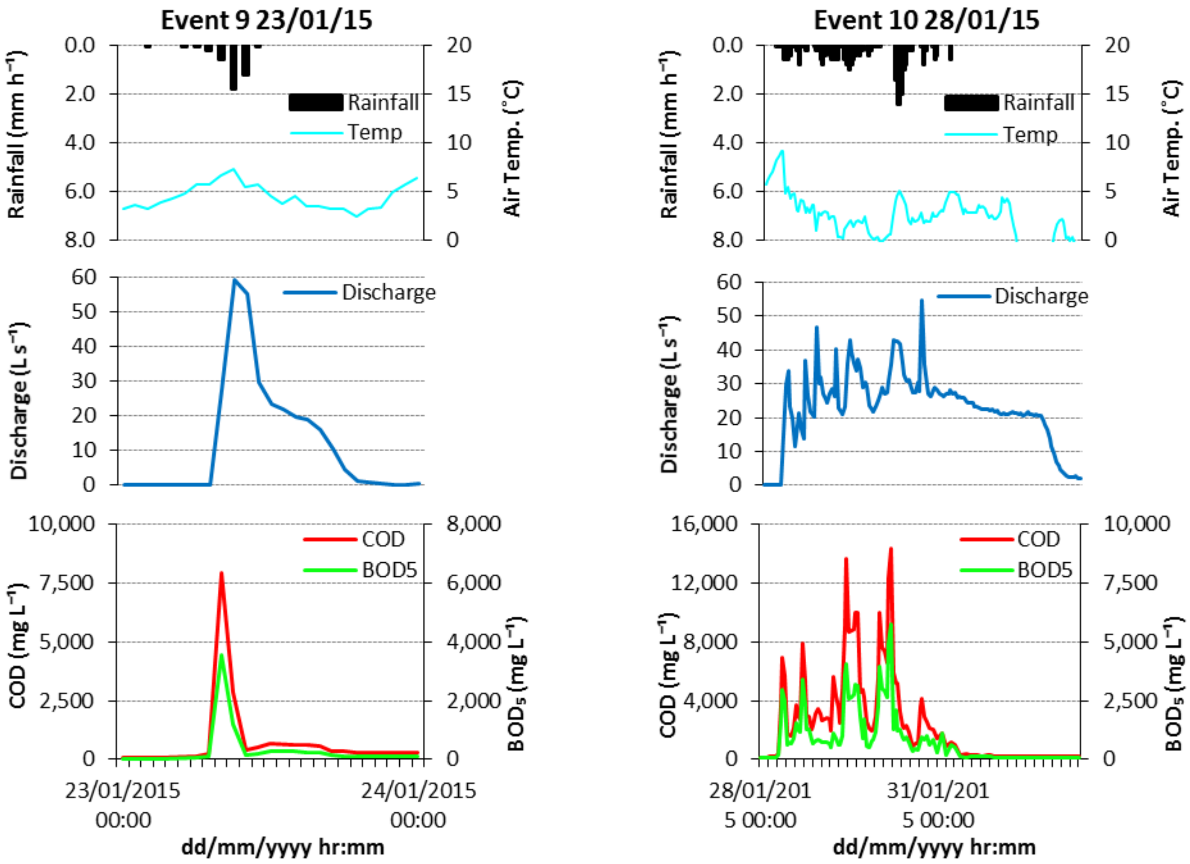


Figure 3.10. Individual winter storm event hydrographs and responses of chemical oxygen demand (COD) and five day biochemical oxygen demand (BOD_5) concentrations during the 2014/15 de-icing season.

3.4.4. Hysteretic Behaviour

Hysteresis plots for the ten storm runoff events monitored during the 2013/14 and 2014/15 de-icing seasons at Manchester Airport (Fig. 3.11 and Fig. 3.12), revealed a consistent clockwise hysteresis direction (Table 3.10). The magnitude of hysteretic behaviour of BOD_5 varied between storm runoff events, with mean HI_{mid} values of 3.9, ranging from 0.1 (event two) to 10.1 (event nine), with higher HI_{mid} values indicating a stronger hysteretic effect (Lawler et al., 2006). The hysteresis loops for events one, four, seven and nine were well-defined, with HI_{mid} values of 7.1, 6.7, 8.0 and 10.1, in contrast to events six, eight and ten where hysteresis loops were less well defined and resulted in a smaller hysteresis effect as indicated by the lower HI_{mid} values of 1.4, 1.7 and 3.0 respectively. Hysteresis loops were poorly defined in events two, three and five resulting in low magnitude hysteresis effects indicated by the smaller HI_{mid} values of 0.1, 0.7 and 0.3 respectively. Event two displays a figure of eight hysteresis pattern, with the hysteresis loop switching from an anticlockwise to a clockwise direction through the Q_{mid} (hence the clockwise classification) before returning to an anticlockwise direction (Fig. 3.11, Table 3.10).

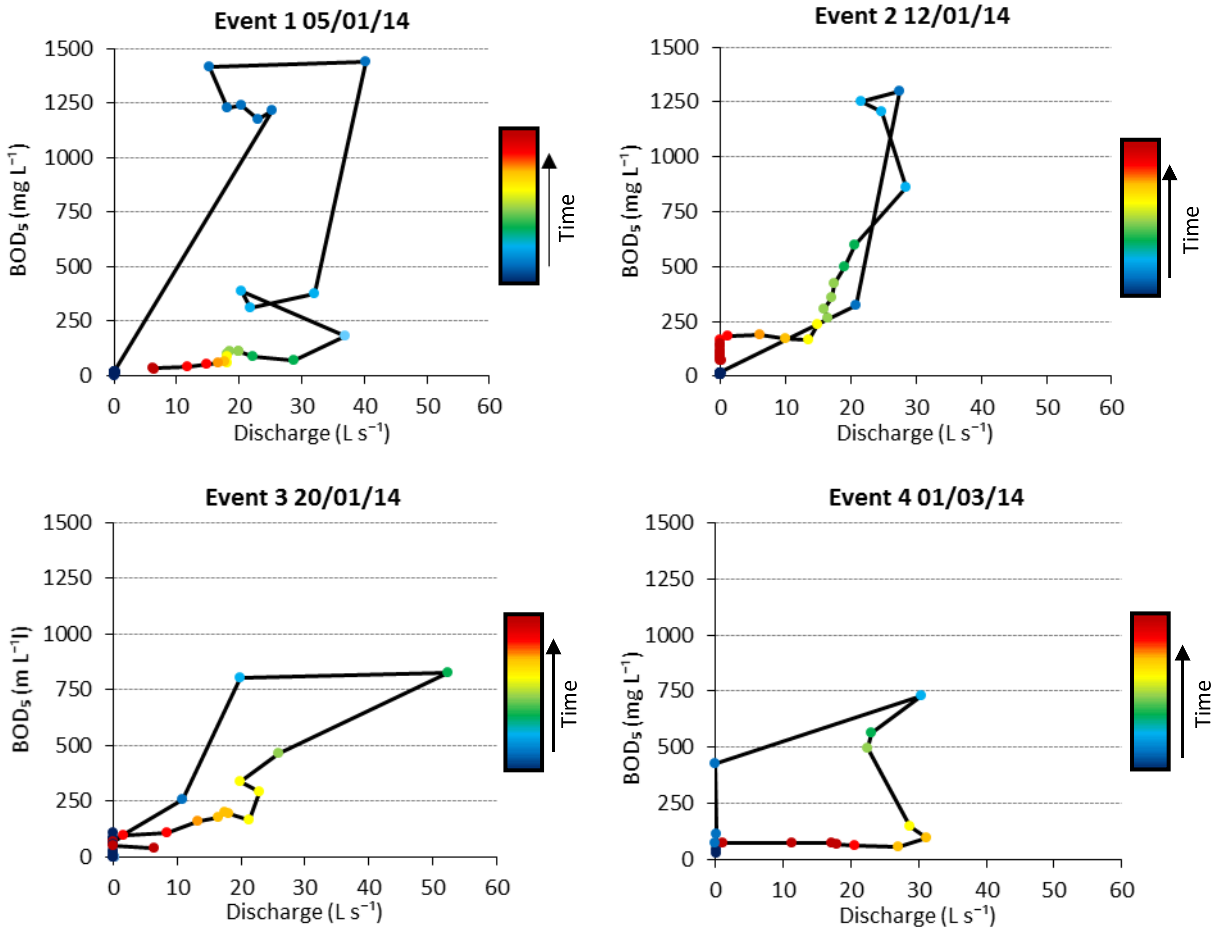


Figure 3.11. Hysteresis plots of five day biochemical oxygen demand (BOD_5) concentrations (mg L^{-1}) and discharge volume (L sec^{-1}) during storm runoff events one to four measured during the 2013/14 de-icing season at catchment C Manchester Airport. Hysteresis direction is indicated by the colour scale which changes from blue to red as the event progresses.

Table 3.10.
Summary of hysteresis effect and HI_{mid} values for discharge and five day biochemical oxygen demand (BOD_5) during storm runoff events at Manchester Airport catchment C, during 2013/14 and 2014/15 de-icing seasons

Event number	Date	Discharge variable (L s^{-1})			BOD_5 at Q_{mid}		Hysteresis index (HI_{mid})	Hysteresis direction [(a)]
		Q_{min}	Q_{max}	Q_{mid}	BOD_{5RL}	BOD_{5FL}		
1	05/01/2104	0.05	40.34	20.19	960	118	7.1	C
2	12/01/2014	0.01	28.43	14.22	215	195	0.1	C
3	20/01/2014	0.02	52.51	26.26	810	470	0.7	C
4	01/03/2014	0.03	31.22	15.63	580	75	6.7	C
5	31/12/2014	0.24	26.19	13.22	3,120	2,500	0.3	C
6	01/01/2015	0.22	46.98	23.6	595	245	1.4	C
7	14/01/2015	0.13	41.87	21	2,260	250	8.0	C
8	17/01/2015	0.15	44.97	22.56	3,490	1,315	1.7	C
9	23/01/2015	0.06	59	29.53	3,450	310	10.1	C
10	28/01/2015	21.75	42.86	32.31	3,950	985	3.0	C
Mean		**2.27**	**41.44**	**21.85**	**1,943**	**646.3**	**3.9**	

[(a)] AC = anticlockwise and C = clockwise hysteresis.

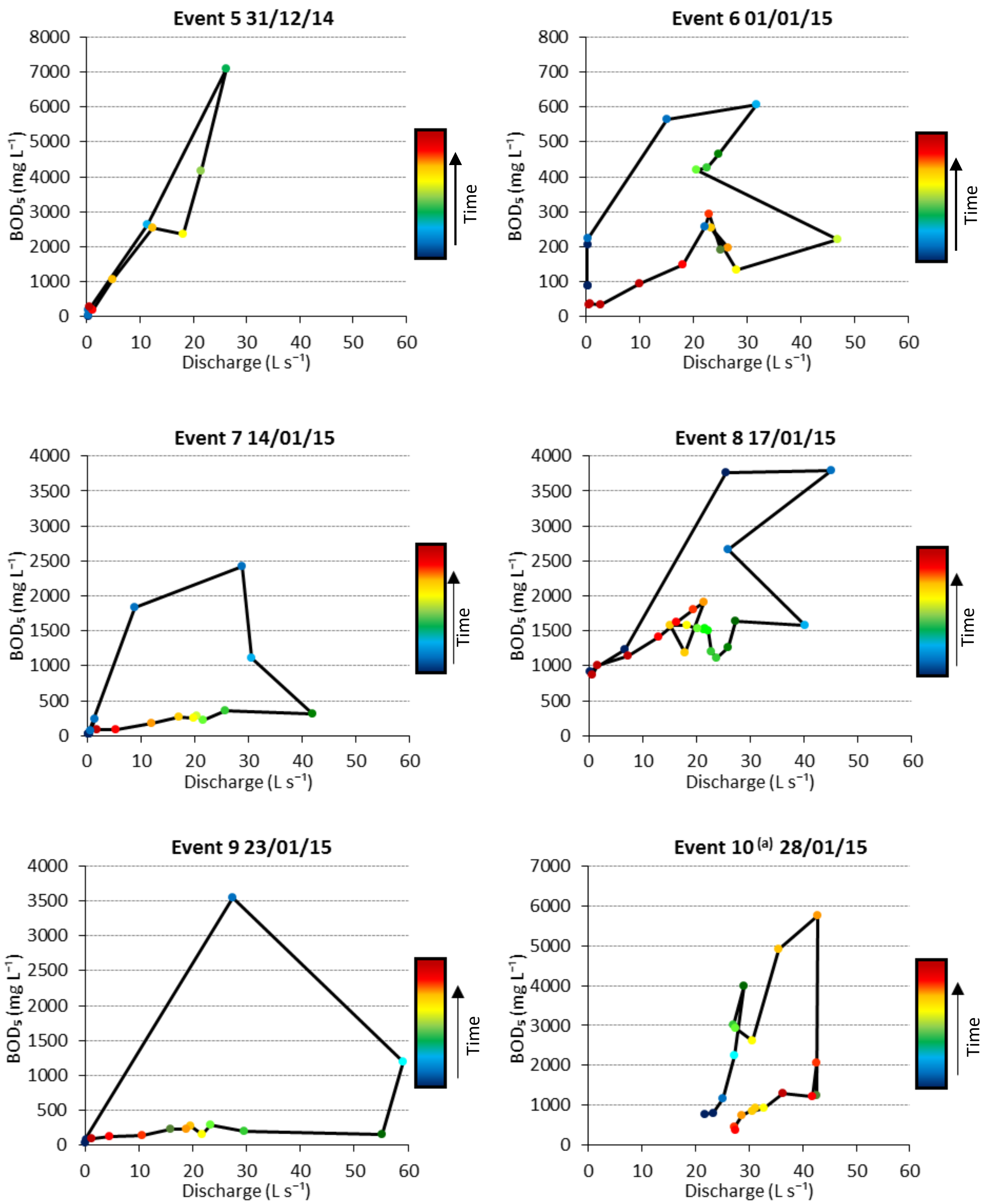


Figure 3.12. Hysteresis plots of five day biochemical oxygen demand (BOD_5) concentrations (mg L^{-1}) and discharge volume (L sec^{-1}) during storm runoff events five to ten measured during the 2014/15 de-icing season at catchment C Manchester Airport. Concentration scales vary to illustrate the hysteresis effect between BOD_5 and discharge. Event ten was split into 4 separate events for the purpose of hysteresis plot production and the peak discharge event displayed as event ten [(a)].

3.4.5. Cost of Discharging Storm Runoff Events as Trade Effluent

In total, catchment C trade effluent discharge costs more than doubled from £52,522 during winter 2013/14 to £116,589 during winter 2014/15, with a mean cost of £84,556 over the two de-icing seasons. Further, mean daily costs also increased from £448 ± 135 to £1,024 ± 2,248 between the 2013/14 and 2014/15 de-icing seasons, averaging £736 per day (Table 3.11). Mean minimum daily costs over the two seasons, representing base-flow discharges during dry weather conditions, were £1.63 ranging from £0.28 to £2.98 between the 2013/14 and 2014/15 winter de-icing seasons. Trade effluent costs for the ten individual storm runoff events ranged from £681 in event four to £28,109 in event 10, with a mean cost of £4,611 across the ten events (Table 3.12).

Table 3.11.
Catchment C trade effluent discharge costs [(a)] during the 2013/14 and 2014/15 de-icing seasons at Manchester Airport

Winter	Total costs (£)	Min. daily cost (£)	Max. daily cost (£)	Mean daily cost (£)	St.dev.	N
2013/14	52,522	0.28	1,770	448	135	110
2014/15	116,589	2.98	14,824	1,024	2,248	115
Mean	**84,556**	**1.63**	**8,297**	**736**	**1,192**	**113**

[(a)] Determined using the 2013/14 and 2014/15 Mogden formula charging parameters, discharge volume ($m^3\ d^{-1}$), chemical oxygen demand (COD) and total suspended solids (TSS) concentrations ($mg\ L^{-1}$) measured at the catchment C discharge location during the winter de-icing seasons 2013/14 and 2014/15 (defined as October – April).

Table 3.12.
Summary of catchment C winter storm runoff event trade effluent discharge costs determined by the Mogden formula

Storm event	Cost (£)
1	1,972
2	1,320
3	934
4	681
5	2,629
6	1,364
7	1,405
8	6,081
9	1,617
10	28,109
Mean	**4,611**

3.5. Discussion

A number of noteworthy results have been established by addressing the research objectives presented within Section 3.1. The first research objective was to determine the extent that storm runoff events are responsible for the mobilisation and transport of de-icer pollutants. Findings from this study demonstrate that a large but highly variable proportion of pollutant load applied through the application of de-icers was transported during storm runoff events in contrast to base-flow conditions. This indicates that storm runoff generated by precipitation events plays a major role in the transport of spent de-icers from the de-icing location and into surface water systems and emphasises the importance of managing storm runoff to minimise the risk to the environment associated with de-icer application at airports. The second research objective was to determine whether relationships exist between discharge volume and pollutant concentration. Findings revealed that a consistent clockwise hysteresis effect is evident for BOD_5 concentrations within airport storm event runoff from catchment C at Manchester Airport, whereby BOD_5 concentrations are typically higher on the rising limb and lower on the recessional limb of the hydrograph. The magnitude of the hysteresis effect varied considerably with high magnitude events demonstrating first flush characteristics whereby source depletion and dilution of BOD_5 concentrations occurs following an initial discharge peak. In contrast, events which were impacted by PDF applications demonstrated a reduced hysteresis effect, potentially caused by a protracted mobilisation and transport of de-icers to the catchment discharge location. The third objective was to determine the impact of de-icer application and winter storm runoff events on water quality and trade effluent discharge costs. Calculations of trade effluent disposal costs reveal that the mean cost of discharging individual storm runoff events from catchment C was £4,611 ranging from £681 to £28,109, whilst annual discharge costs from catchment C alone were £52,522 and £116,589 for winters 2013/14 and 2014/15. These findings and their relevance to managing de-icer contaminated storm runoff are discussed further in the following sections.

3.5.1. Mobilisation and Transport of De-icers to Surface Water Systems

The results presented within this chapter demonstrate that storm runoff generated during precipitation events at airports results in the mobilisation of substantial quantities of spent de-icers from de-icing locations and catchment stores, transporting these to catchment discharge locations. For example, in the research reported throughout Chapter 3 from Manchester Airport, between 28 % and 97 % of the applied ADF and PDF within catchment C was transported to the catchment C discharge location during storm runoff events. This is generally consistent with findings reported from General Mitchell International Airport in the USA, where de-icer transport during eight individual storm runoff events ranged from 2 % to 99 % (Corsi et al., 2001a). Further, mass balance calculations presented within Chapter 3 (Table 3.9) indicates that the mean export of de-icer to the catchment C discharge location was 55 % of the applied load, across the ten storm runoff events monitored, suggesting that a large proportion of the ADF and PDF applied during and within 24 hours prior to the event is not mobilised and/or transported to the catchment discharge location. This generally concurs with mass balance results from studies conducted at airports within the USA including; Baltimore Washington International Airport, Detroit Metropolitan Wayne County Airport and General Mitchell International Airport, where mean storm event de-icer exports from the de-icing location to the catchment discharge locations of 81 %, 57 % and 45 % have been previously reported (ACRP, 2008, Corsi et al., 2001a). These losses can be attributed to several environmental processes including atmospheric transport of de-icer chemicals during application, whereby fine droplets of ADF form into a mist at the nozzle of the de-icer spray system which can subsequently be transported by wind drift and deposited outside of the monitoring catchment (Fan et al., 2011). Further, biodegradation on aircraft stands, within pipes and storage tanks and infiltration of storm event runoff into soils and groundwater also act as a major organic carbon sink within de-icing catchments (Revitt et al., 2002, Staples et al., 2001, Cancilla et al., 2003b, Freeman et al., 2015). However, there are also a number of potential limitations to the mass balance approach applied in this research, including complexities relating to aircraft operations and airport layout, which increase uncertainty surrounding the ultimate fate of de-icers within the airport environment. For instance, it is difficult to accurately quantify the de-icier load applied within individual catchment areas because the nature of airport operations and airport layout typically results in an unknown quantity of de-icer being transferred into and out of catchments following ADF and PDF application through mechanisms such as vehicle and aircraft tracking. At Manchester Airport for example, aircraft de-iced on the Cargo or Terminal 2 apron must taxi through catchment C to access the runway which results in an unquantified and difficult to measure amount of de-icier deposition within catchment C. Further, aircraft de-iced within catchment C also deposit an unquantified amount of de-icer onto taxiways and onto the runway during take-off, both of which fall outside of the catchment C boundary, yet this unquantified de-icer load will be incorporated as part of the applied load to catchment C in any mass balance calculation. Further storm event monitoring would be required at Manchester Airport to specifically target catchments D, E and Runway 2 discharge locations, in order to establish the extent of deposition within these catchments and therefore reduce the level of existing uncertainty resulting from aircraft movements between sub-catchments.

The pollutant loads measured at the catchment C discharge location during the ten storm events reported in Section 3.2.3 were significantly higher than base-flow loads, regardless of the percentage of the applied de-icer load that was transported from the de-icing location to the catchment discharge location. For example, the mean event BOD_5 load transported to catchment C discharge location was 2,067 kg d^{-1} across the ten storm runoff events, in contrast to base-flow BOD_5 loads of 3 kg d^{-1} determined during dry weather conditions and base-flow conditions of < 2 L sec^{-1} (173 m^3 d^{-1}). This indicates that storm runoff generated by precipitation events plays a major role in the transport of spent de-icers from the de-icing location into airport surface water systems, which generally concurs with the results of storm runoff assessments undertaken at General Mitchell International Airport, (Corsi et al., 2001a), Dallas Fort Worth Airport (Fan et al., 2011), Baltimore Washington International Airport (ACRP, 2008) and Detroit Metropolitan Wayne County Airport in the USA and Newcastle International Airport in the UK (Turnbull and Bevan, 1995), where large proportions of BOD_5 have been exported to catchment outfalls during storm runoff events. In addition to BOD_5 export from airport catchments, storm runoff is important for the mobilisation and transport of other pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) from airport catchments (Sulej et al., 2011d), heavy metals, COD, BOD_5 and particulate matter within urban catchments in the UK and China (Cristina and Sansalone, 2002, Li et al., 2007, Eckley and Branfireun, 2008) along with nutrients and TSS from agricultural catchments (Ockenden et al., 2014). During base-flow conditions the low pollutant load observed in airport systems indicates limited transport of spent de-icers into surface water systems during dry weather conditions, which is primarily linked to the high viscosity of de-icer formulations used. At Manchester Airport, the most frequently used ADF is currently a Type IV formulation which contains thickening and gelling agents to improve adherence to applied surfaces. This characteristic also improves the adherence of spent de-icers to stands, taxiways and runway surfaces, resulting in accumulation within catchment stores during dry weather conditions (ACRP, 2008). The findings of previous research and the results presented within this chapter emphasise the importance of managing storm runoff event discharges in contrast to base-flow conditions in order to minimise the environmental risks associated with de-icer application at airports.

3.5.2. Hysteresis Effect in Storm Runoff

Analysis of ‘hysteretic behaviour' is frequently used to support enhanced understanding of pollutant mobilisation and transport processes within drainage catchments (Aich et al., 2014, Bieroza and Heathwaite, 2015). The analysis of hysteresis effect in ten storm runoff events measured at the catchment C discharge location at Manchester Airport reveals a consistent clockwise hysteresis effect, whereby BOD_5 concentrations are higher on the rising limb and lower on the recessional limb of the hydrograph for a given discharge value (Fig. 3.11 and Fig. 3.12). The predominance of a clockwise hysteresis direction suggests that de-icers are mobilised and transported to the catchment discharge location during the early stages of a precipitation event, thereby following the 'first flush' storm runoff characteristic. Following the typical first flush, subsequent depletion of pollutant sources within the catchment during an event occurs. This characteristic is evident during events two, three, five, seven, eight and nine in which BOD_5 concentrations can be seen to peak preceding the peak discharge and subsequently decrease throughout the duration of the event as de-icer stores within the catchment become progressively depleted. This results in lower BOD_5 concentrations on the falling limb compared to the rising limb of the hydrograph, for a given discharge value (Fig. 3.9 and Fig. 3.10). This type of clockwise hysteresis effect is common within environmental systems, having been previously observed for storm runoff events related to TSS export from forest, cropland, upland and urban catchments (Smith and Dragovich, 2009, Gellis, 2013), ammonium (NH_4^+) export from agricultural catchments (Outram et al., 2013) and BOD_5 and COD export from commercial and industrial catchments (Nazahiyah, 2005). In contrast, anticlockwise hysteresis effects whereby pollutant concentrations are lower on the rising compared to the falling limb of the hydrograph for a given discharge value indicate that a de-icer store remains active throughout the storm event. The active pollutant stores are potentially associated with PDF applications over a wider area resulting in protracted export to the discharge location, in contrast to ADF applications whereby spent product is more localised on de-icing stands. Anti-clockwise hysteresis directions have been observed for turbidity in urban catchments (Lawler et al., 2006) and nutrients in managed agricultural catchments (Outram et al., 2013), although all of the events presented within this chapter displayed clockwise hysteresis directions. Further, a figure of eight hysteresis effect occurs as a result of a shift between the hysteresis direction midway through an event, indicating a delayed pollutant peak or new catchment source being activated during an event (Seeger et al., 2013, Gellis, 2013), such as de-icer application as a response to snowfall for example. The clockwise figure of eight pattern observed in event two was characterised by an initial anti-clockwise direction whereby the BOD_5 concentration was lower on the rising than the falling limb of the hydrograph, indicating protraction of BOD_5 export to the catchment discharge location. However, the hysteresis direction becomes clockwise at the Q_{mid} whereby the BOD_5 concentration is higher on the rising than the falling limb of the hydrograph, indicating that the catchment BOD_5 store is becoming depleted or that concentrations are diluted by the prolonged rainfall which results in an overall clockwise classification. Following the Q_{mid} in event two, the hysteresis direction returns back to an anticlockwise direction whereby BOD_5 concentrations are lower on the rising than the falling hydrograph limb. This suggests that a source of BOD_5 remained active within the catchment for prolonged periods during event two and/or that de-icers were mobilised and transported immediately following application that occurred midway through the event, thereby supplying a new source of BOD_5 following the initial dilution and resulting in an equivalent low hysteresis effect.

A consistent clockwise hysteresis direction was observed for all ten storm runoff events presented within this chapter. Despite this, the magnitude of the hysteresis effect (HI_{mid}) observed in storm runoff events at catchment C discharge location was not constant and varied considerably between individual events. For example, events one, four, seven and nine were associated with HI_{mid} values >6, suggesting a high magnitude hysteresis effect with an initial first flush of BOD_5 followed by source depletion and dilution of BOD_5 concentrations, likely caused by the large surface runoff volume generated within the catchment. From a treatment perspective, it would be beneficial to segregate this first flush from the subsequently diluted storm runoff, thereby minimising the volume of runoff requiring treatment and directing any diluted runoff to a receiving watercourse providing that pollutant concentrations are within environmental permit to discharge limits. In contrast, a moderate or low magnitude clockwise hysteresis effect was observed in events six, eight and ten and two, three and five respectively. Apart from event six, these events were associated with PDF applications and the presence of an elevated BOD_5 concentration in excess of the base-flow concentrations throughout the duration of the runoff event. Although the hysteresis direction remains clockwise in these events, the low magnitude or collapsed hysteresis loop maybe a result of the wider surface area over which PDF is applied and therefore mobilisation and transport to the catchment discharge location is protracted. These events represent a very different management and treatment challenge whereby the segregation of the first flush would not be possible resulting in lower concentrations but higher volumes requiring treatment, compared to the higher concentration but low volume treatment requirements expected within first flush segregated runoff.

3.6. Conclusion

The requirement for high resolution, robust scientific evidence to establish sustainable pollution prevention methods for managing de-icer contaminated storm event runoff at airports is unquestionable and key to improving understanding of the fundamental processes which underpin pollutant mobilisation and transport within airport catchments. The aviation industry faces future environmental and sustainability challenges, specifically relating to impacts on surface water discharge volume and quality, as a result of airport expansion plans, increased demand for organic resources (de-icers) and global climate change. New innovative solutions to mitigate these impacts and allow airport operators to remain compliant with stringent discharge limits are likely to be required within the foreseeable future, with effective design of these systems reliant on our understanding of pollutant transfer processes and associated treatment requirements. The methodologies and results reported in this chapter provide important insights into the governing processes and extent of de-icer pollutant mobilisation, transport and export from airport catchments, highlighting the importance of manging storm runoff events to minimise the environmental risks associated with de-icer application at airports.

Many airports, including Manchester Airport, discharge de-icer contaminated storm runoff as trade effluent. Charges for this service results in significant business operating costs, with annual costs of £52,522 and £116,589 calculated for the 2013/14 and 2014/15 de-icing seasons for catchment C discharges alone at Manchester Airport. Charges for the parameters within the Mogden formula are fixed (excluding Ot and St) and determined annually by OFWAT (OFWAT, 2010), therefore airports have limited control over future business operating costs within this area. However, discharge volume and parameters Ot and St are variable relating to the volume and concentrations of COD and TSS respectively discharged from the site as trade effluent. Therefore trade effluent discharge savings can be achieved by reducing disposal volumes and/or pollutant concentrations for COD and TSS. For this purpose, a number of treatment technologies currently exist and have been implemented at airports globally to facilitate more economical and sustainable management of de-icer contaminated storm event runoff (Table 2.4). Results presented within this chapter indicate that where possible it would be beneficial to segregate the first flush of storm event runoff from base-flow conditions and the subsequently diluted concentrations following the first flush, in order to minimise treatment volumes and the required treatment system and storm runoff attenuation capacities. The challenge is therefore to size a treatment solution which minimises design and construction costs but provides sufficient capacity to meet the requirements of winter storm runoff events. To address these challenges research presented within Chapter 4 has been undertaken to establish the effectiveness of aerated wetlands for the sustainable, on-site treatment of de-icer contaminated storm runoff from airports. Further, chapter 4 and chapter 5 are concerned with the optimisation of artificially aerated wetlands to improve the cost-effectiveness and sustainability of this technology compared to alternative management strategies.

Chapter 4

Aerated Wetlands for Airport Runoff Treatment: Optimisation of Aeration Configuration and Operating Conditions

4.1. Introduction

Aviation regulations necessitate the use of large volumes of AAF and ADF, alongside PDF, to facilitate safe winter operating conditions at airports globally (Freeman et al., 2015, Environmental Protection Agency, 2000, Vasilyeva, 2009, Transport Canada, 2010). However, the primary ingredients of ADFs and PDFs ($C_3H_8O_2$ and $C_2H_3KO_2$) are major sources of organic pollutant loads within airport storm event runoff during winter months (Chapter 3). De-icer contaminated runoff poses a significant risk to the status of receiving waters if discharged untreated, due to possible DO depletion and other detrimental environmental and ecological impacts, such as toxicity to aquatic organisms resulting from chemical additives including akylphenol and ethoxylate surfactants and benzotriozole corrosion inhibitors contained within de-icer formulations (Fisher et al., 1995, Hartell et al., 1995, Corsi et al., 2001a, Corsi et al., 2001b, Staples et al., 2001, Cancilla et al., 2003b, Nunes et al., 2011, Fay and Shi, 2012a). In order to protect receiving water quality, environmental policy implemented at the European and national levels (Liefferink et al., 2011, DEFRA, 2012b, DEFRA, 2013a, DEFRA, 2013b, Environment Agency, 2012a, Environment Agency, 2013) has imposed strict pollutant limits on point source airport discharges. Further, the corporate and social responsibility of individual airports requires that the environmental impact of airport operations is minimised and in full compliance with regulatory requirements (Wilson, 1996). Therefore, the need for effective pollution prevention systems for surface water runoff has never been more important within the aviation industry.

Management of storm event runoff contaminated with de-icers is a costly and complex challenge, given the scale and variation of airport operations, de-icer application procedures and application volumes that results in variable pollutant concentration and load within airport discharges (Chapter 3). In response to this challenge, airports adopt a range of management and pollution prevention techniques within the broad categories of: recovery and recycling; off-site treatment; and on-site treatment (ACRP, 2013b). Recovery and recycling is most effective from designated de-icing pads. However, this approach does not directly address the issue of contamination outside of the de-icing pad footprint, resulting from PDF application and ADF deposition from aircraft onto a taxiway and runway. Conveyance of effluent to an off-site treatment facility is costly and subject to volumetric and contaminant load limits, due to capacity restrictions at the off-site WwTP (Nitschke et al., 1996). To comply with these limits, large storage capacities for runoff attenuation are required, especially during peak discharge volumes and loads during storm runoff events which may exceed permit limits. Alternatively, on-site treatment can be used to remove pollutants and to improve runoff quality, potentially offering a more sustainable and cost-effective means of managing storm event runoff from airports (Higgins et al., 2007, Higgins and Maclean, 2002, Freeman et al., 2015). However, the efficiency and optimal operating conditions for on-site treatment technologies, given the characteristics of de-icer contaminated surface runoff from airports, remain to be established, providing the context for the research presented within Chapter 4.

The primary treatment objective for de-icer contaminated runoff is to reduce BOD_5 and COD concentrations, which would otherwise contribute to the depletion of DO concentrations within receiving waters and detrimental impacts towards aquatic organisms (ACRP, 2008, Adeola et al., 2009, Freeman et al., 2015, ACRP, 2013b). Although a number of potential treatment technologies exist for this purpose, the characteristics of airport runoff are relatively distinct from other sources of wastewater and can challenge conventional treatment processes such as activated sludge, anaerobic digestion and rotating biological contactors. For example, the typical BOD_5 concentration within de-icer contaminated runoff is over one order of magnitude greater than the BOD_5 of raw domestic sewage and over two orders of magnitude greater than the BOD_5 of storm runoff from catchments dominated by urban land use (Wilson, 1996) (Table 4.1). Further, storm runoff BOD_5 concentrations are dependent on de-icer application volumes and the characteristics of precipitation events, meaning that they fluctuate widely on monthly, weekly, daily and even hourly timescales, presenting particular challenges to maintaining treatment efficiency within conventional biological systems. Treatment requirements are also seasonal, with peak pollutant loads delivered during winter storm runoff events (Chapter 3). During these events, air and water temperatures are typically low, which may constrain the effectiveness of pollutant removal through metabolic processes (Klecka et al., 1993, Wittgren and Mæhlum, 1997, Werker et al., 2002, Revitt and Worrall, 2003, Akratos and Tsihrintzis, 2007). Winter storm events generate large volumes of contaminated runoff due to the deposition and dispersal of de-icers across a large surface area, resulting in the need to process effluent quickly through treatment systems with low HRTs or provide pre-treatment storage capacity. Further, the chemical composition of de-icer contaminated runoff is stoichiometrically imbalanced, typically containing a large excess of organic carbon (C) relative to nitrogen (N) and phosphorus (P), due to the lack of N or P within commercial de-icer formulations (Wallace and Liner, 2010, Wallace and Liner, 2011a). Therefore, nutrient supplementation is required for effective treatment of de-icer contaminated storm event runoff in order to stimulate microbial growth and avoid microbial stress responses, such as foam formation and production of polysaccharide slime which can lead to clogging of media pore space and subsequent operational issues such as effluent short circuiting (Wallace and Liner, 2010, Wallace and Liner, 2011a). Each of these factors potentially affects treatment system performance and must therefore be understood and considered within the design and implementation of on-site treatment technologies.

Table 4.1.
Typical five day biochemical oxygen demand (BOD_5) values in different wastewater types [(a)]

Sample type	BOD_5 (mg L^{-1})
River water (good WFD [(b)] status)	<4
Raw domestic sewage	300 – 400
Storm event runoff (urban)	5 – 50
Storm event runoff (containing de-icers)	300 - 10,000
Neat PDF (Safegrip acetate base)	270,000
Neat ADF (TIV Kilfrost ABC-S Plus)	354,000

[(a)] edited from Wilson 1996 (Wilson, 1996).
[(b)] European Water Framework Directive.

In comparison with conventional treatment technologies such as activated sludge, anaerobic digestion and rotating biological contactors, the natural pollutant remediation processes within aerated wetland systems offer particular advantages, given the treatment challenges surrounding de-icer contaminated storm runoff described above. Passive constructed wetlands have been commercialised and applied worldwide, following pioneering research and development conducted throughout the 1960's and 1970's in Germany (Seidel, 1964, Seidel, 1965, Vymazal and Kröpfelová, 2009, Vymazal, 2009, Vymazal et al., 2006), whilst the aerated wetland technology is a more recent development. Kinetically, biodegradation of organic compounds proceeds at a quicker rate under aerobic conditions, due to the higher metabolic rates of aerobic compared to anaerobic bacteria (Wang et al., 2015). For example, complete anaerobic degradation of de-icers may take up to several weeks (Dwyer and Tiedje, 1983, Kameya et al., 1995, Staples et al., 2001), due to the multiple steps within the fermentation process (Switzenbaum et al., 2001), alongside inhibition of microbial communities caused by de-icer additives (Johnson et al., 2001). In contrast, aerobic degradation is a much quicker process taking a few hours to <3 days (Evans and David, 1974, McGahey and Bouwer, 1992, Kent et al., 1999) and is up to 63 % more efficient than anaerobic degradation pathways (Huang et al., 2005). Oxygen transfer into constructed wetlands therefore poses a major barrier to the implementation of these treatment systems for effluents characterised by high BOD_5 concentrations, including de-icer contaminated surface runoff from airports.

The early development of artificially aerated wetlands in the USA in 2001 (Wallace, 2001) represented a major breakthrough in overcoming poor OTR and subsequent barriers to implementing wetlands for high BOD_5 effluents and as such there are now 40 full-scale systems operating within the UK and over 200 globally, across a broad range of applications (Murphy et al., 2016). Aerated wetlands have aeration diffusers installed at the base of a system beneath the media, enabling the controlled delivery of air directly into the treatment zone (Fig. 4.1), therefore vastly improving OTRs (Wallace, 2001, Murphy et al., 2012b, Nivala et al., 2013b). For example, OTRs increased from 0.01 kg d^{-1} m^2 to 0.08 kg d^{-1} m^2 when aeration diffusers were retrofitted into the full-scale passive constructed wetland system operating at Heathrow Airport in the UK, contributing to an increase in design treatment load from 0.02 kg d^{-1} m^2 to 0.10 kg d^{-1} m^2 BOD_5 (Murphy et al., 2014). The increased design loadings realised through artificial aeration act to reduce a treatment system footprint (Murphy et al., 2012b, Dechanie, 2013, Toit et al., 2013), thereby minimising land requirements and capital costs of aerated wetland designs. For instance, re-engineering and addition of aeration devices to the full-scale constructed wetland at Edmonton International airport in Canada increased BOD_5 removal by an order of magnitude (Wallace and Liner, 2011b) within one third of the original system footprint (Toit et al., 2013).

Despite the apparent advantages, a major drawback of aerated wetlands is the energy consumption of the aeration devices, which is approximately 1.5 kWh kg^{-1} O_2 delivered (Murphy et al., 2012b) which translates to £0.15 kg O_2 based on typical UK energy costs of £0.10 kWh (Energy Saving Trust, 2014). However, the ability of aerated wetlands to process large volumes of wastewater, serves to minimise overall treatment costs which are approximately 17 p m^3 for aerated wetlands (Wallace et al., 2006, Murphy et al., 2012b), in contrast to approximately 26 p m^3 and 63 p m^3 for activated sludge systems (Brix, 1999) and trade effluent discharges (United Utilities, 2016). Typical treatment costs for other technologies used to treat de-icer contaminated runoff are reported within Table 4.2. Whilst the running costs of aerated wetlands are less than trade effluent discharge and technologies including activated sludge, reverse osmosis and distillation (Table 4.2), maximising the efficiency of aeration devices within aerated wetlands is essential for sustainable cost-effective operation and could deliver further reductions in treatment costs.

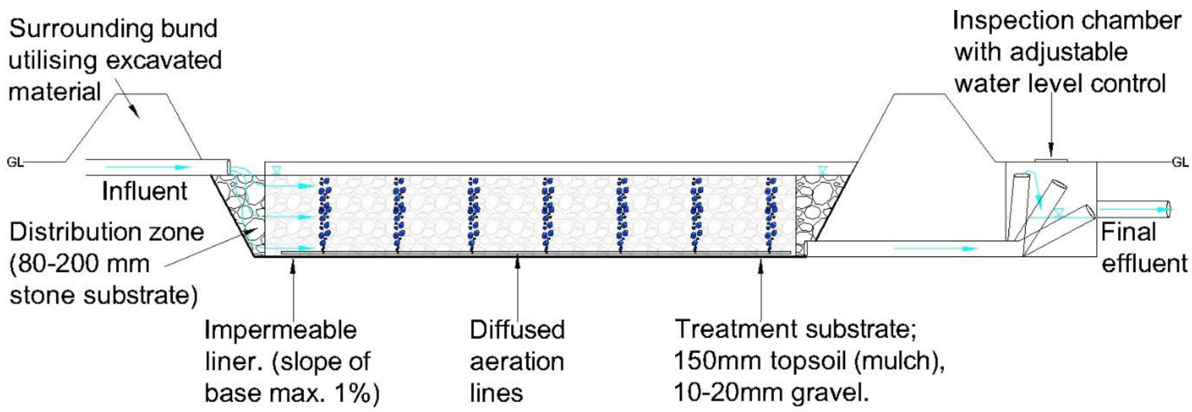


Figure 4.1. Cross section of a typical horizontal subsurface flow aerated wetland key features (not to scale).

Table 4.2.
Typical energy consumption and treatment costs for de-icer treatment technologies

Reference	Technology/ Method	Approximate energy consumption (kWh m³)	Approximate cost of treatment (p m³) [(a)]
[1]	Evaporation and distillation (thermal)	40 – 120	426 – 1,272
[2]	Reverse osmosis (ultrafiltration)	10	106
[3]	Trade effluent disposal	-	45 – 82
[1]	Evaporation and MVR [(b)] (electrical)	3 – 5	27 – 53
[4]	Activated sludge	1 – 2	8 – 26
[5], [6]	Aerated wetlands	2	17
[5]	Trickling filters	0.6	6
[7]	Aerated pond/ lagoon	0.6	6
[4], [5]	Passive wetland, reedbed, pond, lagoon	0.1	1
[8]	Anaerobic digestion [(c)]	0.1	1

Sources: [1] (Campos, Undated), [2] (Rautenbach et al., 1997), [3] (United Utilities, 2016), [4] (Brix, 1999), [5] (Murphy et al., 2012b), [6] (Wallace et al., 2006), [7] (Mara, 2004), [8] (Reith et al., 2003).
[(a)] p m^3 = kWh * 10.64p (typical 2015 UK price for electricity consumption (Energy Saving Trust, 2014)).
[(b)] MVR = mechanical vapour recompression.
[(c)] Energy consumption is off set against energy generated.

Various aeration strategies and modifications to aerated wetlands have been proposed to maximise aeration efficiency and reduce operational costs (Table 2.5). For instance, intermittent aeration modes (Fan et al., 2013a, Fan et al., 2013b) and low DO concentration limited aeration (Zhang et al., 2010), serve to reduce air blower operating time. Whilst these studies have considered aeration mode and aeration frequency, there is very limited reference to the spatial distribution and configuration of aeration diffusers throughout a wetland system, especially with respect to the challenges of treating de-icer contaminated airport runoff. Most aerated wetland designs are based on a uniform distribution of aeration throughout the system, whereby aeration volumes are delivered equally from the inlet zone through to the outlet in attempt to minimise anaerobic pockets and improve mixing within the media (Nivala et al., 2007, Wallace, 2001). The relationship between organic pollutant concentration and distance from the system inlet is often exponential, decreasing towards the system outlet. For instance, up to two thirds of BOD_5 removal is expected to occur within the first third of a horizontal subsurface flow aerated wetland (Zhang et al., 2010, Akratos and Tsihrintzis, 2007). In this scenario, two thirds of the O_2 demand is within the first third of the system, which is not addressed efficiently through a uniform aeration configuration design. As a consequence, suboptimal operating conditions may occur through under-aeration at the inlet zone generating anaerobic conditions and over-aeration towards the outlet of the system resulting in unnecessary aeration, energy consumption and running costs. This leads to the hypothesis that organic pollutant removal efficiency can be enhanced within aerated wetlands through altering the spatial distribution of aeration inputs to better match the supply and demand of O_2 throughout the system. Further, the aerated wetland is a relatively new technology, in comparison to alternative technologies and therefore some of the operational conditions which affect treatment efficiency such as HRT and pollutant MLRs are still poorly defined.

In this context, the aim of Chapter 4 is to understand the impact of alternative aeration configurations and operating conditions within aerated wetlands on de-icer pollutant removal and effluent quality characteristics, in order to establish optimal operating conditions for aerated wetlands treating airport runoff. To achieve this three research objectives were defined as follows: (i) to determine the impact of altering the spatial distribution of aeration inputs in aerated wetlands on treatment efficiency, (ii) to determine the impact of changing influent concentration in aerated wetlands on treatment efficiency and (iii) to determine how treatment efficiency in aerated wetlands is influenced by hydraulic retention time.

4.2. Materials and Methods

4.2.1. Experimental System Configuration

An experimental system at the field-scale (Fig. 4.2), was designed to replicate a horizontal subsurface flow aerated wetland and was constructed on site at Manchester Airport (NGR SJ 81295 84400). The system was positioned on a causeway sloping down into a flow attenuation pond, which receives run-off from the same airfield drainage catchment from which monitoring data were reported in Chapter 3. A 1,000 L tank was positioned at the front of the system and used to mix synthetic solutions to dose into the system via a Marlow Watson 520R peristaltic process pump (Fig. 4.2b). Three cylindrical tanks (1,600 mm deep x 1,400 mm diameter) each of 2,500 L capacity were positioned in series and connected with 50 mm internal diameter flexi-hose to replicate treatment cells (Fig. 4.2). The elevation of the three cells decreased in -250 mm intervals, to allow gravity flow throughout the system. Within each cell, a narrow inlet distribution zone comprising of 40 mm to 100 mm diameter crushed brick (Fig. 4.2c) and a main treatment zone containing 10 mm to 20 mm diameter angular limestone gravel media, were separated by a 5 mm x 25 mm slotted mesh screen (Fig. 4.2d). Total media depth was 1,400 mm, resulting in a total media volume of 6.45 m^3 within the three treatment cells (Table 4.3). The main treatment zone media was capped with a porous membrane and a 200 mm deep layer of bark chippings to provide insulation from fluctuating air temperatures. The inlet zone of each cell was left clear of insulation to allow both visual observation and sample collection. Three 30 mm internal diameter piezometers, with 50 mm long screens at the base, were installed in each cell to depths of -250mm, -750mm and -1,250mm below the top of the gravel media to enable measurement of physicochemical conditions within each cell (Fig. 4.2d). A 210 w Charles Austen ET200 linear diaphragm blower was used to deliver up to 200 L min^{-1} (45 L min^{-1} m^{-3} of media) of air into the system at 0.15 bar of pressure (Table 4.3). Braided airlines of 10 mm diameter connected the blower to uniformly distributed tubular fine bubble membrane diffusers, which were positioned below the main treatment zone media at the base of each cell. A manifold system was fitted to the aeration line, to control the delivery and spatial distribution of aeration volumes into each cell.

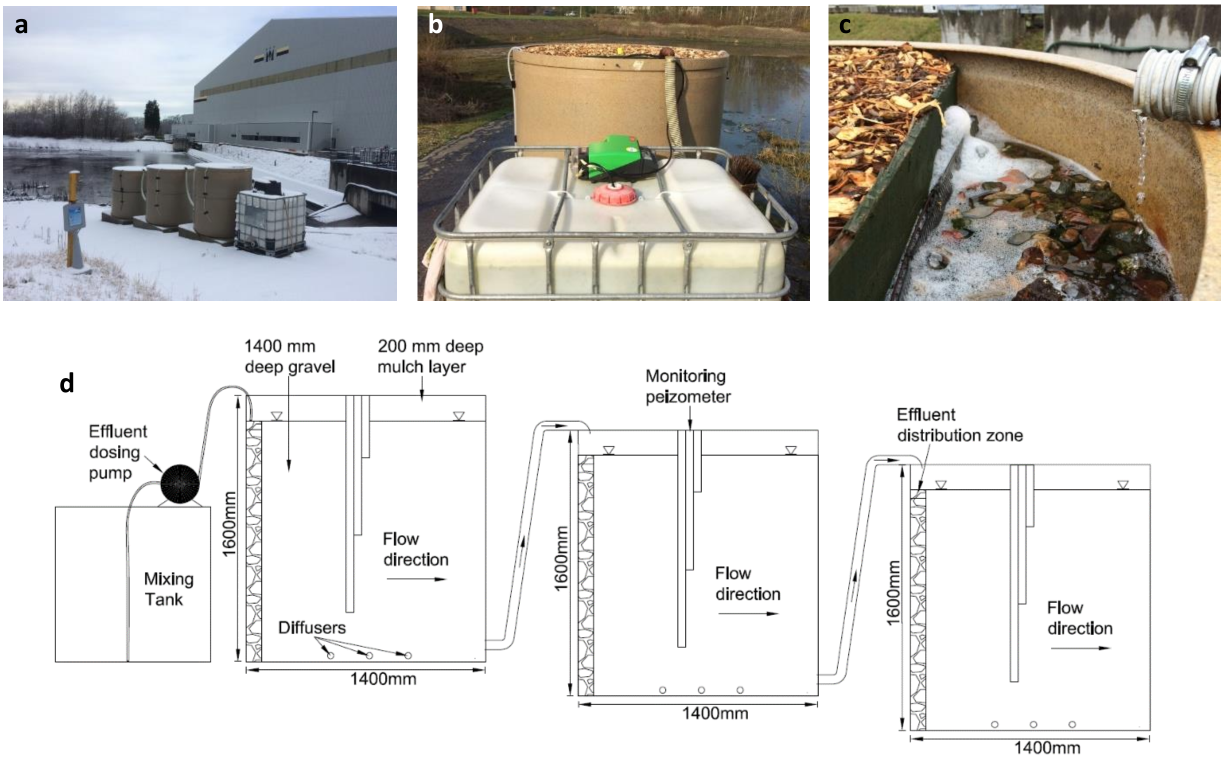


Figure 4.2. Photographs of (a) overview of the experimental system, (b) effluent mixing tank and process dosing pump, (c) inlet distribution zone for one of the three treatment cells and (d) a cross section diagram of the experimental system.

Table 4.3.
Details of the field-scale experimental aerated wetland located at Manchester Airport

Parameter	Details
Design Specification:	
No. of cells	3
Cell dimensions (mm)	1,600 deep * 1,400 diameter
Inlet zone media (mm)	40 – 100 of crushed brick
Media diameter (mm) and type	10 – 20 angular limestone gravel
Media porosity (%)	34.75
Media depth (mm)	1,400
Media volume (m^3)	6.45 (2.15 /cell)
Surface area (m^2)	4.62 (1.54 /cell)
Surface insulation depth (mm)	200
Sampling locations	Inlet and outlet of each cell, plus piezometers
Hydraulics:	
Flow details	Horizontal subsurface
Hydraulic load (m^3 d^{-1})	1 – 2
Hydraulic retention time (days)	1.14 – 2.24
Artificial aeration:	
Air blower model	Charles Austen ET 200 linear diaphragm blower
Aeration rate (m^3 d^{-1} m^3 of media)	44.64
Diffusers	Tubular fine bubble membrane diffusers (3 per cell)

4.2.2. Influent Production

Synthetic influent was created within the 1,000 L mixing tank to replicate BOD_5, COD and TOC concentrations typically observed within airport runoff at Manchester Airport from 2013 to 2015, as reported within Chapter 3. The synthetic influent primarily comprised of dry weather runoff (base-flow conditions) discharging from the airfield drainage catchment (catchment C) at Manchester Airport which contained only background concentrations of BOD_5. This was spiked with widely used aviation de-icer chemicals, Kilfrost ABC-S plus Type IV ADF and Safegrip PDF, to achieve the target influent concentrations. Throughout the experiment, three different influent strengths were created within the mixing tank, replicating low (L), medium (M) and high (H) runoff concentrations which comprised of 0.2 %, 0.3 % and 0.4 % volume of de-icer to volume of runoff and were equivalent to mean BOD_5 concentrations of 831 ± 35 mg L^{-1}, 1,355 ± 81 mg L^{-1} and 1,853 ± 99 mg L^{-1} respectively. Nutrient solutions containing urea and ammonium phosphate (Nutromex 123) were added to the synthetic influent solution to ensure that microbial nutrient availability was not a limiting factor during testing. Nutrients were added on the assumption that 0.3 kg of biomass is produced per every 1 kg of influent BOD_5 (Wallace and Liner, 2010) and following the basic understanding that the optimal nutrient requirements per kilogram of biomass is 85 g of nitrogen and 17 g of phosphorous in addition to small proportions of micronutrients such as potassium calcium and magnesium (Grady et al., 1999, Wallace and Liner, 2010, Wallace and Liner, 2011a). This resulted in the ratio of supplementary nutrients increasing relative to the influent organic strength. An example of the chemical characteristics of the synthetic influent is presented in Table 4.4.

Table 4.4.
Example of the medium strength (M) synthetic influent characteristics used during tests four, five and six as reported in Section 4.3.6

Parameter [(a)]	Details
COD (mg L^{-1})	2,502 ± 261
TOC (mg L^{-1})	1,184 ± 14
BOD_5 (mg L^{-1})	1,444 ± 179
PO_4-P (mg L^{-1})	79 ± 4
NO_3- (mg L^{-1})	3.0 ± 0.4
NH_4-N (mg L^{-1})	110 ± 11
TSS (mg L^{-1})	119 ± 18
pH	6.8 ± 0.5
Temperature. °C	15.7 ± 1.1

[(a)] COD = chemical oxygen demand, TOC = total organic carbon, BOD_5 = five day biochemical oxygen demand, PO_4-P = orthophosphate, NO_3-N = nitrate, NH_4-N = total ammonium, TSS = total suspended solids. ± 1 standard deviation of the mean.

4.2.3. Configuration of Artificial Aeration

Four aeration configurations: phased aeration (PA), uniform aeration (UA), inlet-only aeration (IA) and no aeration (NA) were tested to assess the impact of aeration configuration on pollutant removal efficiencies. This was achieved by adjusting the manifold system to alter the spatial distribution and volume of aeration delivered into each cell during testing (Table 4.5).

Table 4.5.
Spatial distribution of aeration volumes (L min^{-1}) within cells one to three during aeration configuration tests [(a)]

Aeration Configuration	Position within system		
	Cell 1	**Cell 2**	**Cell 3**
Phased (PA)	100	66.6	33.3
Uniform (UA)	66.6	66.6	66.6
Inlet-only (IA)	200	0	0
None (NA)	0	0	0

[(a)] Tests conducted with a hydraulic retention time of 1.49 days within the three cells.

Within the artificial aeration configuration experiments described in Table 4.5 and Table 4.6, operating conditions of 1.49 d HRT for the three cells were maintained with mean BOD_5 concentrations of 810 ± 60 mg L^{-1} and mean MLRs of 0.09 ± 0.01 kg d^{-1} m^2 BOD_5. Prior to undertaking each individual aeration configuration test, the system was conditioned for twice the HRT using the test influent concentration to promote steady-state conditions and microbial acclimatisation. Each test was repeated in triplicate.

Table 4.6.
Summary of hydraulic loading rates (HLR) hydraulic retention time (HRT) and five day biochemical oxygen demand (BOD_5) influent concentration and mass loading rates used during testing of different wetland aeration configurations

Aeration configuration	HLR (m^3 d^{-1})	HRT [(a)] (days)	BOD_5 concentration (mg L^{-1})	BOD_5 load (kg d^{-1} m^{-2})
Phased (PA)	1.5	1.49	834	0.10
Uniform (UA)	1.5	1.49	727	0.08
Inlet-only (IA)	1.5	1.49	812	0.09
None (NA)	1.5	1.49	868	0.10
Mean			**810 ± 60**	**0.09 ± 0.01**

[(a)] Hydraulic retention time within the three cells, see Equation 4.3.
± 1 standard deviation of the mean.

4.2.4. Optimisation of Operating Conditions

In separate tests designed to establish optimal operating conditions, three different influent HRTs of 2.24 d, 1.49 d and 1.14 d within the three cells were implemented to assess the impact of HRT on final effluent concentrations and pollutant removal efficiency. Each of the three HRTs, were dosed with three influent concentrations (L, M and H) to establish the impact of influent concentration on pollutant removal efficiency. Mean BOD_5 concentrations within the influent were 831 ± 35 mg L^{-1}, 1,355 ± 81 mg L^{-1} and 1,853 ± 99 mg L^{-1} during these tests (Table 4.7). Across these tests, the operating conditions were equivalent to mean MLRs of 0.07 kg d^{-1} m^2 BOD_5 to 0.28 kg d^{-1} m^2 BOD_5 (Table 4.7). The BOD_5 loads tested in this study were within the range of typical aerated wetland MLR of 0.05 kg d^{-1} m^2 BOD_5 to 0.28 kg d^{-1} m^2 BOD_5 which were identified within the literature for uniformly aerated wetlands (Envirodynamics Consulting, 2012, Moshiri, 1993). Phased aeration (PA) was maintained as opposed to UA, IA or NA during optimisation tests one to nine, in attempt to match the supply of O_2 to the O_2 demand within each cell. Prior to undertaking each test the system was conditioned for twice the HRT using the test influent concentration to promote steady-state conditions and microbial acclimatisation. Each of these tests was also repeated in triplicate.

Table 4.7.
Summary of operating conditions including hydraulic loading rate (HLR), hydraulic retention time (HRT) five day biochemical oxygen demand (BOD_5) concentrations and mass loading rates (MLR) used during phased aeration optimisation tests

Test No.	HLR (m^3 d^{-1})	HRT (days) [(a)]	BOD_5 concentration (mg L^{-1}) [(b)]	BOD_5 areal MLR (kg d^{-1} m^{-2})
1	1	2.24	864 (L)	0.07
2	1.5	1.49	834 (L)	0.10
3	2	1.12	795 (L)	0.12
Mean (tests one to three)			**831 ± 35**	**0.10 ± 0.03**
4	1	2.24	1,286 (M)	0.10
5	1.5	1.49	1,444 (M)	0.17
6	2	1.12	1,335 (M)	0.21
Mean (tests four to six)			**1,355 ± 81**	**0.16 ± 0.05**
7	1	2.24	1,812 (H)	0.14
8	1.5	1.49	1,967 (H)	0.23
9	2	1.12	1,782 (H)	0.28
Mean (tests seven to nine)			**1,853 ± 99**	**0.22 0.69**

[(a)] hydraulic retention time within the three cells,
[(b)] five day biochemical oxygen demand (BOD_5) influent concentrations interpreted as L = low, M = medium and H = high strength,
± 1 standard deviation of the mean.

4.2.5. Data and Sample Collection

Ambient air temperature at the field site was measured at 15 minute intervals using a Shlumberger mini diver, located <10 m from the experimental system. Physiochemical conditions including pH, air temperature, water temperature, redox potential (ORP) and DO were measured from within the piezometers three times during each test, with measurements staggered to account for the HRT within each trial cell. This was achieved using a Hannah 9828 multi-parameter probe within a sealed flow cell through which a low sample flow rate of approximately 16 ml min^{-1} was pumped (Fig. 4.3a). Results were recorded when probe readings had stabilised, following purging of stagnant water from each piezometer.

Water samples were also collected at staggered intervals throughout the duration of each test to account for the HRT within the trial system, assuming steady-state conditions. A total of four water spot samples were collected for each individual test, including a sample of the influent plus one sample from each of the three cell outlets. This sample methodology was limited in that the variability of effluent quality is not fully captured; however real time continuous monitoring to capture this variability would have been impractical. Samples were collected either manually into one litre clean plastic bottles or via MCERTS compliant Aquacell P2 portable water samplers which were connected to the treatment cell outlets (Fig. 4.3b).

Figure 4.3. Photographs showing (a) arrangement of Hannah 9828 multi-parameter probe, flow cell and low flow peristaltic pump during measurement of water quality conditions within each cell during testing, (b) automatic wastewater sampler used for sample collection.

4.2.6. Chemical Analysis

Following collection, samples were transported the short distance to the Manchester Airport environment laboratory and analysed for pH, temperature, TSS, COD, BOD_5 and TOC. The analytical methods of determination for each of these parameters are described within Section 3.1.1. In addition, samples selected for nutrient analyses were filtered through 25mm diameter Nalgene™ nonsterile 0.45 µm syringe filters on site and transferred to Lancaster University within a cool box for analysis within 24 hours. Total ammonium (NH_4-N) and phosphate (PO_4-P) were analysed using a Seal Analytical AQ_2 automated discrete analyser following HMSO methods for the examination of waters and associated materials 1981 (ISBN 0117515930 oxidized nitrogen in waters and ISBN: 0117515825 phosphorus in waters, effluents and sewages) (HMSO, 1981, HMSO, 1992). Nitrate (NO_3 - N) was determined by ion chromatography using a Thermo Scientific Dionex AS-AP instrument.

4.2.7. Analytical Quality Control

Standard analytical quality controls (AQCs) were practiced and recorded to ensure integrity of the data for each determinant as described for pH, COD, TOC and BOD_5 within Section 3.1.1. Additionally duplicates of 12 individual samples were collected and sent to a commercial (UKAS accredited) laboratory in order to validate BOD_5 test results. Internal laboratory standards were used to calibrate the Seal Analytical AQ_2 automated discrete analyser and external reference standards were tested with each batch of samples to verify the calibration curve. A minimum of two blank samples of de-ionised water and two sample duplicates were also analysed with each batch of six samples for the parameters NH_4 + N, PO_4-P and NO_3 - N respectively. The limit of detection (LOD) was 0.02 mg L^{-1} 0.001 mg L^{-1} and 0.15 mg L^{-1} for NH_4 + N, PO_4-P and NO_3 - N respectively. The Hannah 9828 multi-parameter probe used for determining conditions within each individual cell was calibrated prior to each test using Hannah HI 9828-0 calibration solution as described in Section 3.1.1.

4.2.8. Data Interpretation and Statistical Analysis

Pollutant removal efficiency for each test was calculated as an overall (cumulative) percent removal (R) from the influent to the final effluent, assuming that the system was in equilibrium at the time of sample collection, following Eq. 4.1.:

$$R = \frac{C_i - C_e}{C_i} * 100 \tag{4.1}$$

where:

R = pollutant removal (%)

C_i = mean influent concentration of triplicate tests (mg L^{-1})

C_o = mean final effluent concentration (mg L^{-1})

Mass pollutant loading rates (kg d^{-1} m^2) were calculated in accordance with Eq. 4.2.:

$$MLR = \frac{Q*C_i}{A} \tag{4.2.}$$

where:

MLR = mass pollutant loading rate

Q = volumetric flow rate (m^3 d^{-1})

C_i = influent pollutant concentration, i.e. BOD_5 (mg L^{-1})

A = wetland area (m^2)

Hydraulic retention time (HRT) was calculated in accordance with Eq. 4.3. (Çakir et al., 2015, Metcalf and Eddy Inc, 1991):

$$HRT = \frac{\pi\, r^2 * \phi * d}{Q} \tag{4.3.}$$

where:

HRT = hydraulic retention time (days)

$\boldsymbol{\pi}$ = pi (3.142)

r = cell radius (m)

ϕ = media porosity (%)

d = media depth (m)

Q = influent flow rate (m^3 d^{-1})

Analysis of variance (ANOVA) and Tukey's-b tests were complete using IBM SPSS statistics 20 software, to identify significant effects of aeration configuration on COD, BOD_5, TOC and TSS removal efficiency. Two-way ANOVA and Tukey's-b tests were used to identify significant effects of the HRT within the three cells and influent concentration on the removal efficiencies of COD, BOD_5, TOC and TSS. Significance was accepted at p=≤0.05 for each test.

4.3. Results

4.3.1. Water Quality Characteristics during Testing

A summary of the mean water quality characteristics determined from three piezometer samples from within cells one to three during the four aeration configuration tests previously described within Table 4.6, is reported within Table 4.8 including the results for pH, temperature, ORP and DO. Across the four aeration configuration tests, mean ambient air temperature was 16.5 ± 5.7 ˚C, ranging from 8.6 ± 3.4 ˚C to 21.6 ± 0.1 ˚C in PA and IA tests. Overall, mean water temperatures were more consistent and sometimes slightly higher than mean air temperatures, ranging from 13.0 ± 0.5 ˚C to 19.5 ± 0.6 ˚C for PA and IA test respectively, with an overall mean of 17.4 ± 3.0 ˚C across the four tests. The mean pH across the four aeration configuration tests was 7.4 ± 0.5, whilst mean results of -131 ± 53 mV and 1 ± 1 mg L^{-1} were determined for ORP and DO respectively (Table 4.8).

Table 4.8.
Summary of the mean water quality conditions including pH, temperature, redox (ORP) and dissolved oxygen (DO) determined from three piezometer samples from within cells one to three during aerated wetland aeration configuration tests. n = 9 for each aeration configuration.

Aeration configuration	pH	Air temperature (˚C)	Water temperature (˚C)	ORP (mV)	DO (mg L^{-1})
Phased (PA)	8.0 ± 0.2	8.6 ± 3.4	13.0 ± 0.5	-131 ± 13	3.5 ± 4.3
Uniform (UA)	7.2 ± 0.7	19.3 ± 0.8	17.9 ± 0.9	-193 ± 8	0.5 ± 0.4
Inlet-only (IA)	6.8 ± 0.2	21.6 ± 0.1	19.5 ± 0.6	-249 ± 35	0
None (NA)	7.6 ± 0.1	16.7 ± 0.3	19.1 ± 0.6	-237 ± 42	0
Mean	**7.4 ± 0.5**	**16.5 ± 5.7**	**17.4 ± 3.0**	**-131 ± 53**	**1.0 ± 1.7**

± 1 standard deviation of the mean.

The mean water quality characteristics determined from three piezometer samples taken within cells one to three during the individual aerated wetland optimisation tests, one to nine previously described within Table 4.7 are presented in Table 4.9. Optimisation tests were conducted over a four month period between 17/02/2015 to 14/06/2015, where mean ambient air temperatures were 10.1 ± 2.2 ^{o}C. During this period temperatures ranged from -0.1 ˚C to 20.1 ˚C, representing the wide range of temperatures typically observed during the winter and spring within the UK. Overall, water temperatures within cells one to three determined from piezometer samples in tests one to nine, indicate that the system was well insulated with a mean water temperature of 14.0 ± 0.5 ˚C, which was 40 % higher than mean air temperature of 10 ± 2.2 ˚C determined during the testing period.

Water temperatures ranged between 9.2 ± 0.5 ˚C to 19.4 ± 0.3˚C during optimisation tests one to nine.

Table 4.9.
Summary of mean water quality conditions including pH, temperature, redox (ORP) and dissolved oxygen (DO) determined from three piezometer samples from within cells one to three during aerated wetland operational optimisation tests one to nine. n = 9 for each individual test.

Test no.	pH	Air temperature (˚C)	Water temperature (˚C)	ORP (mV)	DO (mg L^{-1})
1	8.0 ± 0.1	5.1 ± 2.6	9.2 ± 0.5	-149 ± 10	4.0 ± 3.1
2	8.0 ± 0.2	8.6 ± 3.4	11.6 ± 0.1	-131 ± 13	3.5 ± 4.3
3	8.1 ± 0.3	10.7 ± 4.5	14.5 ± 0.8	-167 ± 25	0.7 ± 1.2
4	8.1 ± 0.1	12.5 ± 3.0	16.0 ± 0.6	-149 ± 37	1.6 ± 1.5
5	8.2 ± 0.2	11.1 ± 3.8	14.8 ± 0.4	-265 ± 148	1.9 ± 3.3
6	7.8 ± 0.6	11.4 ± 2.4	15.2 ± 1.1	-182 ± 12	0.5 ± 0.8
7	8.4 ± 0.2	11.6 ± 4.8	19.4 ± 0.3	-173 ± 25	1.3 ± 1.5
8	8.3 ± 0.4	9.4 ± 3.7	11.8 ± 0.4	-135 ± 16	1.1 ± 2.0
9	8.1 ± 0.4	10.4 ± 2.2	13.3 ± 0.1	-166 ± 14	0.4 ± 0.6
Mean	**8.1 ± 0.3**	**10.1 ± 2.2**	**14.0 ± 0.5**	**-168 ± 33**	**1.7 ± 2.0**

± 1 standard deviation of the mean.

Overall, pH measurements taken from samples of the influent solution used within optimisation tests one to nine, established that the synthetic influent used throughout the study was near neutral, ranging from pH 6.5 to pH 7.4 with a mean pH of 7.0 ± 0.2. In contrast, overall conditions within the treatment cells measured from three piezometers samples within cell one to three during optimisation tests one to nine, revealed that pH was slightly alkaline, ranging from 7.8 ± 0.6 to 8.4 ± 0.2, with a mean pH of 8.1 ± 0.3 (Table 4.9). Final effluent pH conditions were also slightly alkaline, ranging from pH 7.2 to pH 8.5, with a mean pH of 7.8 ± 0.4. Further, ORP determined from the piezometer samples was consistently low and negative, ranging from -131 ± 13 mV to 265 ± 148 mV with an overall mean of -168 ± 33 mV (Table 4.9). Dissolved oxygen concentrations fluctuated from 0.4 ± 0.6 mg L^{-1} to 4.0 ± 3.1 mg L^{-1} with mean concentrations of 1.7 ± 2.0 mg L^{-1} observed across the three cells during testing (Table 4.9).

4.3.2. Impact of Aeration Configuration and Position within the System on Redox Potential and Dissolved Oxygen Concentrations

The effect of aeration configuration on ORP was significant ($F(3,24) = 150.12$, $MSE = 36,645$, $p=\leq.0001$), however there was no significant effect of cell position on ORP. There was also no significant interaction between aeration configuration and cell position on ORP, although ORP did decrease slightly from -118 ± 5 mV to -143 ± 4 mV and -194 ± 4 mV to -197 ± 6 mV during PA and UA tests. In contrast ORP increased slightly from cell one to cell three from -266 ± 12 mV to -209 ± 16 mV and -289 ± 16 mV to -255 ± 6 mV during IA and NA tests (Fig. 4.4). Further, post-hoc Tukey's HSD tests revealed that PA configuration resulted in significantly lower ORP ($p=\leq.0001$) in comparison to UA, IA and NA configurations and that UA resulted in significantly lower ORP ($p=\leq.0001$) in comparison to IA and NA configurations. There was no significant difference between the ORP observed between IA and NA configurations.

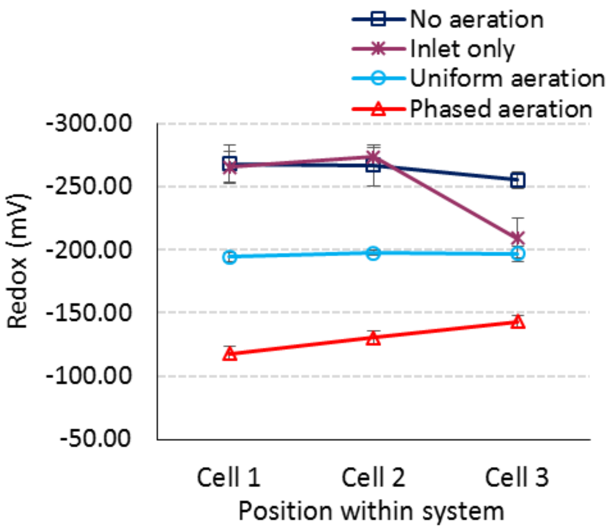


Figure 4.4. Mean redox potential (ORP) determined from three piezometer samples from test cells one, two and three during aeration configuration tests. Error bars represent ± 1 standard deviation of the mean, n = 9 for each aeration configuration.

The effect of aeration configuration on DO concentrations was significant ($F(3,24) = 84.19$, $MSE = 2,158$, $p=\leq.0001$) as was the cell position within the system ($F(2,24) = 57.19$, $MSE = 1,466$, $p=\leq.0001$). The combined interaction between aeration configuration and cell position had a significant effect on DO concentrations within PA and UA tests ($F(6,24) = 45.61$, $MSE = 1,169$, $p=\leq.0001$), with DO concentration increasing from 0 mg L^{-1} to 8.3 ± 0.2 mg L^{-1} in PA tests and 0 mg L^{-1} to 0.8 ± 0.4 mg L^{-1} in UA tests (Table 4.10). Further, post-hoc Tukey's HSD tests revealed that PA configuration resulted in significantly higher mean DO concentrations ($p=\leq.0001$) in comparison to UA, IA and NA configurations, whilst there was no statistical significant difference between UA, IA and NA configurations towards DO concentrations. Dissolved oxygen concentrations were zero within cell one regardless of the aeration configuration and remained at zero throughout cells two and three in IA and UA aeration configurations.

Table 4.10.
Summary of mean dissolved oxygen (DO) concentrations (mg L^{-1}) determined from three piezometer samples within cells one to three during aeration configuration tests. n = 9 for each aeration configuration

Aeration configuration	Position within system		
	Cell 1	Cell 2	Cell 3
Phased (PA)	0	2.1 ± 1.2	8.3 ± 0.2
Uniform (UA)	0	0.7 ± 0.4	0.8 ± 0.4
Inlet-only (IA)	0	0	0
None (NA)	0	0	0

± 1 standard deviation of the mean.

4.3.3. Impact of Artificial Aeration Configuration and Position within the System on Organic Pollutant Removal

Aeration configuration had a significant effect on the removal of COD ($F(3,24) = 327.57$, MSE = 3,403, p=≤.0001), BOD_5 ($F(3,24) = 361.21$, MSE = 3,665, p=≤.0001) and TOC ($F(3,24) = 98.81$, MSE = 2,412, p=≤.0001) within the test system from influent to final effluent. The position within the system also had a significant effect on pollutant removal as a proportion of the influent concentration for COD ($F(2,24) = 364.47$, MSE = 3,787, p=≤.0001), BOD_5 ($F(2,24) = 512.26$, MSE = 5,197, p=≤.0001) and TOC ($F(2,24) = 197.77$, MSE = 4,828, p=≤.0001). Further, a significant interaction effect between aeration configuration and position throughout the system was observed on the pollutant removal as a proportion of the influent concentration for COD ($F(6,24) = 62.18$, MSE = 645.98, p=≤.0001), BOD_5 ($F(6,24) = 82.00$, MSE = 831.95, p=≤.0001) and TOC ($F(6,24) = 35.55$, MSE = 819.09, p=≤.0001).

Post-hock Tukey's HSD tests revealed that pollutant removal as a proportion of the influent concentration was significantly higher within cells one and two compared to cell three for COD (p=≤.0001), BOD_5 (p=≤.0001) and TOC (p=≤.0001), although no significant difference between pollutant removal was identified between cells two and three for COD, BOD_5 and TOC during IA configurations. Further, post-hoc Tukey's HSD tests revealed that pollutant removal efficiencies as a proportion of influent concentrations were significantly lower (p=≤.0001) during NA tests in comparison to the other aeration configurations tested, with mean removal of 38.13 ± 3.47 %, 45.06

± 6.08 % and 46.10 ± 5.68 % for COD, BOD_5 and TOC observed from the influent to the final effluent, resulting in high final effluent concentrations from cell 3 outlet of 730 ± 44 mg L^{-1} COD, 477 ± 55 mg L^{-1} BOD_5 and 428 ± 35 mg L^{-1} TOC (Table 4.11, Fig. 4.5). A significant (p=≤.0001) increase in pollutant removal efficiency was observed in IA tests compared to NA tests, with mean removal in the IA tests of 43 ± 2 %, 48 ± 7 % and 51 ± 6 % for COD, BOD_5 and TOC observed from the influent to the final effluent, although final effluent concentrations from cell 3 outlet remained high under IA configurations with mean results of 676 ± 21 mg L^{-1} COD, 421 ± 61 mg L^{-1} BOD_5 and 266 ± 9.71 mg L^{-1} TOC recorded. In contrast to NA and IA configurations, post-hoc Tukey's HSD tests revealed that UA configurations had significantly higher pollutant removal efficiencies (p=≤.0001) from the influent to the final effluent of 78 ± 1 %, 95 ± 1 % and 88 ± 4 % for COD, BOD_5 and TOC, representing a 53 %, 53 % and 47 % overall increase in removal efficiencies from the influent to the final effluent for COD, BOD_5 and TOC in UA tests compared to NA tests. Final effluent concentrations observed during UA tests were 246 ± 25 mg L^{-1}, 36.2 ± 6 mg L^{-1} and 68.2 ± 13 mg L^{-1}, for COD, BOD_5 and TOC (Table 4.11, Fig. 4.5). Pollutant removal efficiencies were significantly higher (p=≤.0001) during PA configurations in comparison to the other configurations tested, with 92 ± 1 %, 98 ± 1 % and 92 ± 2 % reductions in concentration observed from the influent to the final effluent for COD, BOD_5 and TOC. This represents increased pollutant removal efficiencies of 60 %, 54 % and 50 % for COD, BOD_5 and TOC in PA tests compared to NA tests and a 15 %, 3 % and 5 %, for COD, BOD_5 and TOC reduction compared to the performance of the more conventional UA configuration. The higher removal efficiencies observed during PA tests resulted in low final effluent concentrations of 98.1 ± 12.9 mg L^{-1} COD, 20.7 ± 5.2 mg L^{-1} BOD_5 and 34.8 ± 6.1 mg L^{-1} TOC (Table 4.11, Fig. 4.5).

Table 4.11.
Summary of influent concentration, final effluent concentration and mean pollutant removal efficiency (%) for chemical oxygen demand (COD), five day biochemical oxygen demand (BOD_5) and total organic carbon (TOC) during operation of four different aeration configurations. n = 3 for each aeration configuration.

Aeration configuration	COD Influent (mg L^{-1})	COD Final effluent (mg L^{-1})	COD Removal efficiency (%) [a]	BOD_5 Influent (mg L^{-1})	BOD_5 Final effluent (mg L^{-1})	BOD_5 Removal efficiency (%) [a]	TOC Influent (mg L^{-1})	TOC Final effluent (mg L^{-1})	TOC Removal efficiency (%) [a]
Phased (PA)	1,217 ± 28	98 ± 13	92 ± 1	834 ± 63	21 ± 5	98 ± 1	430 ± 11	35 ± 6	92 ± 2
Uniform (UA)	1,130 ± 48	246 ± 25	78 ± 1	727 ± 19	36 ± 6	95 ± 1	575 ± 106	68 ± 13	88 ± 4
Inlet-only (IA)	1,193 ± 6	676 ± 21	43 ± 2	812 ± 29	421 ± 61	48 ± 7	544 ± 57	266 ± 10	51 ± 6
None (NA)	1,161 ± 23	730 ± 44	37 ± 4	868 ± 21	477 ± 55	45 ± 6	796 ± 18	428 ± 35	46 ± 6

[a] Cumulative pollutant removal efficiency (%) determined from influent to final effluent concentration, see Equation 4.1.
± 1 standard deviation of the mean.

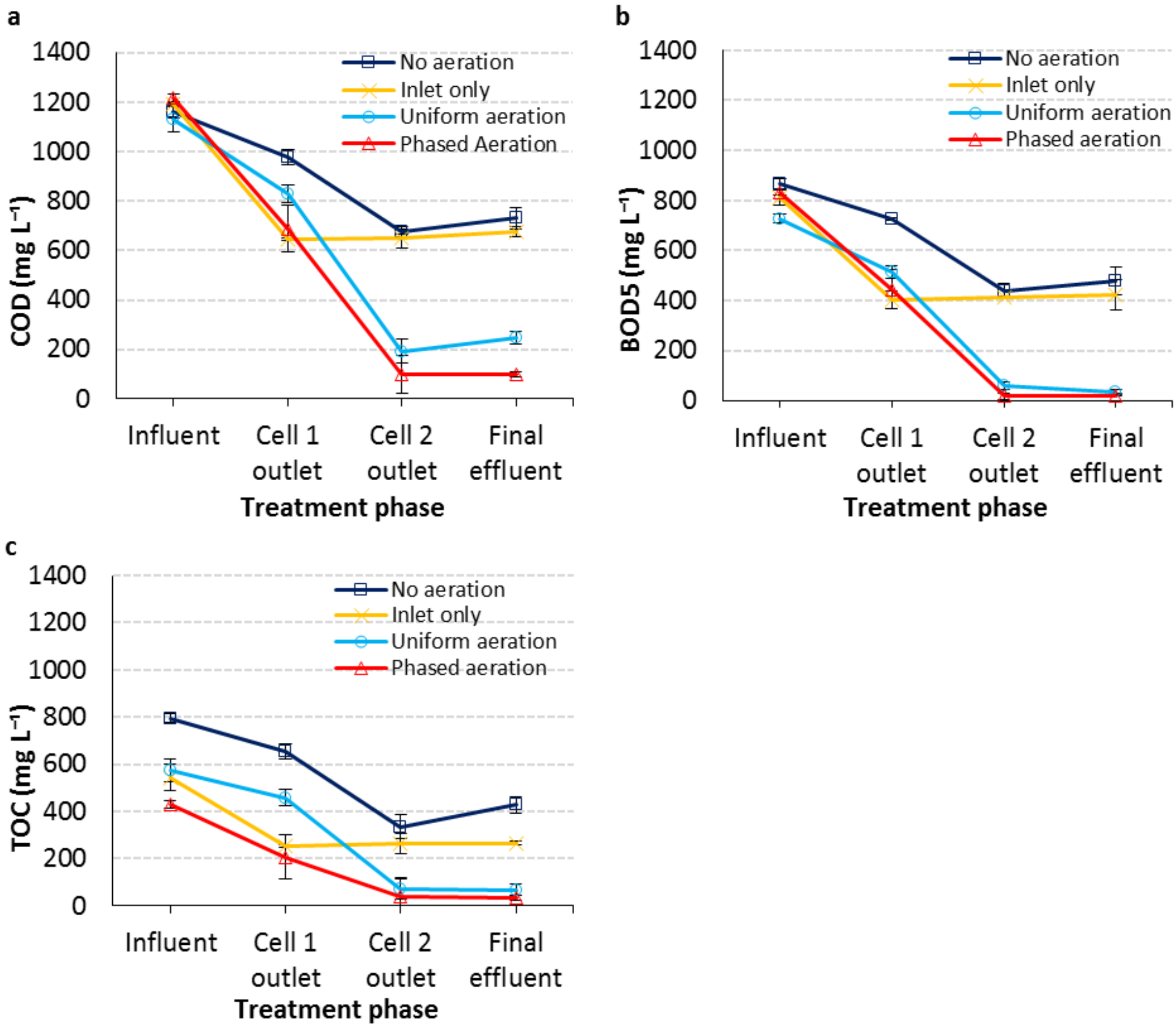


Figure 4.5. Results of (a) chemical oxygen demand (COD), (b) five day biochemical oxygen demand (BOD_5) and (c) total organic carbon (TOC), concentrations (mg L^{-1}) throughout the trial system from influent to final effluent, when tested under different aeration configurations.

4.3.4. Impact of Aeration Configuration on Total Suspended Solids Removal

Aeration configuration had a significant effect on TSS removal as a proportion of the influent concentration ($F(3,11) = 4.77$, $MSE = 5{,}966$, $p=.034$). There was no significant difference between PA and UA configurations, however PA had significantly higher removal efficiencies in comparison to IA ($p=.030$) and NA ($p=0.23$) configurations, whilst UA also had significantly higher TSS removal efficiencies in comparison to IA ($p=.036$) and NA ($p=.027$) configurations. Further, positive removal efficiencies for TSS were 57 ± 13 % during PA tests and 54 ± 33 % during UA tests, in contrast to negative removal efficiencies of -56 ± 34 % and -72 ± 51 %, meaning that an overall net increase of TSS from the influent to the final effluent was observed during IA and NA tests. Aeration configuration also had a significant effect on mean TSS final effluent concentrations ($F(3,11) = 4.75$, *MSE* = 5,105, *p*=.035). For example, TSS final effluent concentrations of 24 ± 8 mg L^{-1}, 31 ± 27 mg L^{-1}, 76 ± 27 mg L^{-1} and 112 ± 53 mg L^{-1} were observed during PA, UA, IA and NA tests respectively, with PA having a significantly lower (*p*=.044) TSS final effluent concentration in comparison to NA (Table 4.12) .

Table 4.12.
Summary of total suspended solids (TSS) influent and final effluent concentrations (mg L^{-1}) and removal efficiency (%) for different wetland aeration configurations. n = 3 for each aeration configuration.

Aeration configuration	Influent (mg L^{-1})	Final effluent (mg L^{-1})	Removal efficiency [(a)] (%)
Phased (PA)	55 ± 7	24 ± 8	57 ± 13
Uniform (UA)	63 ± 14	31 ± 27	54 ± 33
Inlet-only (IA)	66 ± 11	76 ± 27	-56 ± 34
None (NA)	88 ± 6	112 ± 53	-72.39 ± 51

[(a)] Cumulative pollutant removal efficiency (%) from influent to final effluent, see Equation 4.1.
± 1 standard deviation of the mean.

4.3.5. Impact of Hydraulic Loading Rate and Influent Strength on Pollutant Removal

A summary of the results from the nine different operating condition tests (three hydraulic retention times * three influent strengths, see Table 4.7) is reported in Table 4.13 and Fig. 4.6 for COD, BOD_5 and TOC. A significant effect of the HRT within the three cells on pollutant removal as a proportion of the influent concentration was observed for COD (F(2,18) = 105.40, *MSE* = 1,467, *p*=≤.0001), BOD_5 (F(2,18) = 98.40, *MSE* = 1,892, *p*=≤.0001) and TOC (F(2,18) = 28.00, *MSE* = 989.39 *p*=≤.0001). No significant effect of influent concentration on pollutant removal throughout the system was observed for COD, BOD_5 and TOC and there was no significant interaction effect between HRT and influent concentration on the removal efficiency of COD, BOD_5 and TOC observed during optimisation tests one to nine. Further, post-hoc Tukey's HSD tests revealed significantly higher pollutant removal rates as a proportion of the influent concentration within tests conducted with HRTs of 2.24 d (*p*=≤.0001) and 1.49 d (*p*=≤.0001) within the three cells for COD, BOD_5 and TOC compared to tests with a HRT of 1.14 d. For example in tests with HRTs of 2.24 d or 1.49 d within the three cells, removal efficiencies ranged between 89 % to 96 %, 91 % to 99 % and 90 % to 96 % for COD, BOD_5 and TOC respectively compared to ranges of 60 % to 76 %, 70 % to 73 % and 69 % to 82 %, for COD, BOD_5 and TOC respectively when HRT was 1.14 d.

Table 4.13.
Summary of operating conditions, organic pollutant removal efficiency and final effluent concentrations for parameters chemical oxygen demand (COD), five day biochemical oxygen demand (BOD_5) and total organic carbon (TOC) during operational optimisation experiments tests one to nine. n = 3 for each test

			COD			BOD_5			TOC		
Test No.	Influent strength [(a)]	HRT (d) [(b)]	Influent (mg L^{-1})	Final effluent (mg L^{-1})	Removal efficiency [(c)] (%)	Influent (mg L^{-1})	Final effluent (mg L^{-1})	Removal efficiency [(c)] (%)	Influent (mg L^{-1})	Final effluent (mg L^{-1})	Removal efficiency [(c)] (%)
1	L	2.24	1,206 ± 14	53 ± 9	96 ± 1	864 ± 14	3 ± 2	99 ± 1	424 ± 13	18 ± 2	96 ± 1
2	L	1.49	1,217 ± 28	98 ± 13	92 ± 1	834 ± 62	21 ± 5	98 ± 1	430 ± 11	35 ± 6	92 ± 2
3	L	1.14	1,247 ± 44	494 ± 69	60 ± 6	795 ± 41	234 ± 57	71 ± 6	462 ± 1	141 ± 38	69 ± 9
4	M	2.24	2,405 ± 179	199 ± 65	92 ± 3	1,286 ± 19	46 ± 7	96 ± 1	1,104 ± 129	82 ± 15	92 ± 2
5	M	1.49	2,502 ± 261	211 ± 9	92 ± 1	1,444 ± 179	47 ± 17	97 ± 1	1,184 ± 14	91 ± 8	92 ± 1
6	M	1.14	2,671 ± 36	647 ± 14	76 ± 1	1,335 ± 151	359 ± 25	73 ± 2	1,186 ± 20	210 ± 70	82 ± 6
7	H	2.24	3,404 ± 438	308 ± 86	91 ± 2	1,812 ± 67	79 ± 59	96 ± 3	1,534 ± 298	77 ± 23	95 ± 1
8	H	1.49	3,392 ± 374	392 ± 150	89 ± 4	1,966 ± 100	177 ± 102	91 ± 5	1,283 ± 38	127 ± 31	90 ± 3
9	H	1.14	2,978 ± 237	786 ± 185	73 ± 9	1,782 ± 31	541 ± 182	70 ± 9	1,318 ± 66	348 ± 173	73 ± 14

[(a)] L = low, M = medium, H = high strength influent previously described within Table 4.7.
[(b)] Hydraulic retention time within the three treatment cells (days), see Equation 4.3.
[(c)] Cumulative pollutant removal efficiency (%), see Equation 4.1.
± 1 standard deviation of the mean.

Hydraulic retention time also had a significant effect on the final effluent concentrations discharging from treatment cell 3 for COD ($F(2,18) = 69.11$, $MSE = 565,484$, $p=\leq.0001$), BOD_5 ($F(2,18) = 53.50$, $MSE = 302,871$, $p=\leq.0001$) and TOC ($F(2,18) = 18.86$, $MSE = 79,994$, $p=\leq.0001$). Further, influent concentration had a significant effect on final effluent concentrations of COD ($F(2,18) = 21.59$, $MSE = 176,618$, $p=\leq.0001$), BOD_5 ($F(2,18) = 13.23$, $MSE = 74,891$, $p=\leq.0001$) and TOC ($F(2,18) = 7.59$, $MSE = 32,183$, $p=.004$). Despite the significant effect of factors HRT and influent concentration on final effluent concentrations, no significant interaction effect between the HRT within the three cells and influent concentration was observed in terms of the final effluent concentration of COD, BOD_5 and TOC. Further, post-hoc Tukey's HSD tests reveal that final effluent concentrations were significantly lower for COD, BOD_5 and TOC during tests with HRTs of 2.24 d ($p=\leq.0001$) and 1.49 d ($p=\leq.0001$)

compared to 1.14 d (p=≤.0001). Regarding influent concentrations, post-hoc Tukey's HSD tests reveal that final effluent concentrations were significantly lower during tests conducted with a low influent strength in comparison to medium (p=.005) and high strength (p=≤.0001) influent concentrations for COD. Final BOD_5 effluent concentrations were also significantly lower in tests conducted with low (p=≤.0001) and medium (p=.012) strength influent concentrations in comparison to a high influent strengths whilst TOC final effluent concentrations were significantly lower in tests with a low influent strength (p=.003) in contrast to medium and high strength influent TOC concentrations.

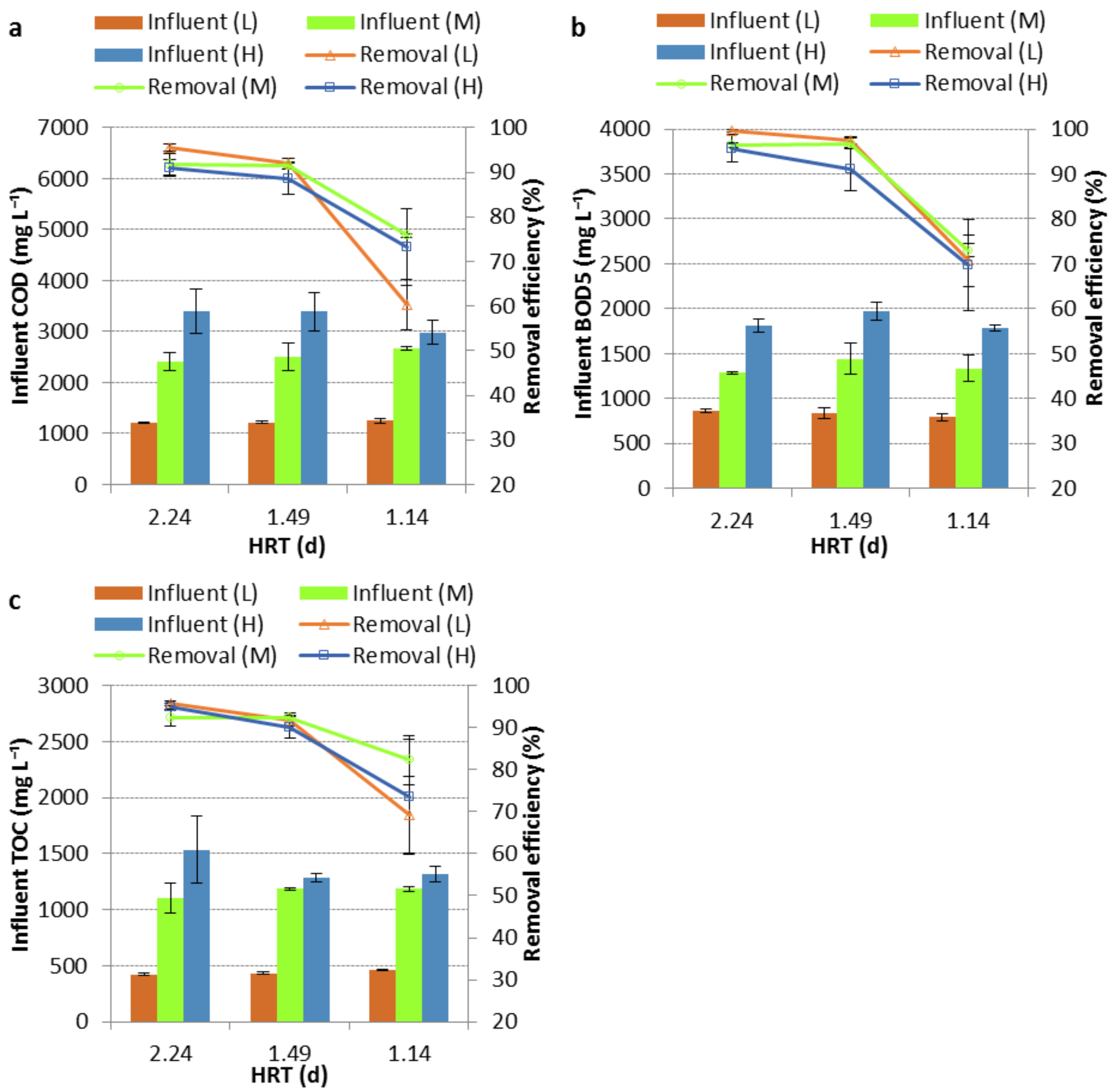


Figure 4.6. Results of (a) chemical oxygen demand (COD), (b) five day biochemical oxygen demand (BOD_5) and (c) total organic carbon (TOC), cumulative removal efficiency (%), when tested with three test influent concentrations (mg L^{-1}) and 3 different hydraulic retention times (2.24 d, 1.49 d and 1.14 d) as previously described within Table 4.7.

A significant effect of HRT on pollutant removal efficiency as a proportion of influent concentration was identified for TSS $F(2,18) = 14.42$, $MSE = 144{,}294$, $p=\leq.0001$ during operation optimisation tests one to nine, however no significant effect of influent concentration on overall removal efficiency from the influent to the final effluent was observed for TSS. Further, no significant interaction effect between HRT and TSS influent concentration was identified on the removal efficiency of TSS. Post-hoc Tukey's HSD tests reveal that TSS removal efficiency as a proportion of the influent concentration was significantly higher when HRT of 2.24 d ($p=\leq.0001$) or 1.49 d ($p=.001$) were maintained throughout the three cells, compared to 1.14 d (Table 4.14).

Hydraulic retention time also had a significant effect on the final effluent concentration of TSS ($F(2,18) = 19.68$, $MSE = 137{,}109$, $p=\leq.0001$) as did influent TSS concentration ($F(2,18) =18.21$, $MSE = 126{,}874$, $p=\leq.0001$). A significant interaction effect of HRT and influent TSS concentration was observed on the final effluent concentration of TSS ($F(4,18) = 4.21$, $MSE = 29{,}311$, $p=.014$). Post-hoc Tukey's HSD tests revealed that final effluent concentrations were significantly lower when HRT of 2.24 d ($p=\leq.0001$) or 1.49 d ($p=.001$) were maintained throughout the three cells, compared to 1.14 d (Table 4.14) and that significantly lower TSS final effluent concentrations were observed in tests with low ($p=\leq.0001$) and moderate ($p=.001$) influent concentrations.

Table 4.14.
Summary of mean total suspended solids (TSS) influent and final effluent concentrations and removal efficiency (%) during operational optimisation tests one to nine [(a)]. n = 3 for each individual test

Test no.	HRT (d)	Influent TSS concentration (mg L^{-1})	Final effluent TSS concentration (mg L^{-1})	Removal efficiency [(b)] (%)
1	2.24	50 ± 0.1	8 ± 4	84 ± 5
2	1.49	55 ± 6.5	24 ± 8	57 ± 13
3	1.14	80 ± 18	146 ± 62	-91 ± 106
4	2.24	151 ± 26	23 ± 3	84 ± 4
5	1.49	119 ± 18.	52 ± 35	56 ± 28
6	1.14	100 ± 50	136 ± 73	-110 ± 227
7	2.24	147 ± 8.5	70 ± 59	53 ± 36
8	1.49	194 ± 11	209 ± 84	-9 ± 47
9	1.14	146 ± 48	532 ± 204	-285 ± 152

[(a)] Nine tests in total (3 different HRT * 3 different influent strengths).
[(b)] Cumulative removal efficiency (%) from influent to final effluent, see Equation 4.1.
± 1 standard deviation of the mean.

4.4. Discussion

Several noteworthy findings have been ascertained through the research presented within Chapter 4. Firstly, aeration is key to efficient organic pollutant removal within wetland systems as demonstrated by the significantly higher removal efficiencies observed for COD, BOD_5, TOC and TSS during tests where artificial aeration was supplied in contrast to tests where no artificial aeration was supplied. Secondly, the results presented within Section 4.3.3 indicate that the hypothesis that organic pollutant removal efficiency can be enhanced in aerated wetlands through altering the spatial distribution of aeration inputs to better match the supply and demand of O_2 throughout the system can be accepted. For example, addressing the research objective to determine the impact of altering the spatial distribution of aeration inputs into aerated wetlands on treatment efficiency established that simple adjustments to the aeration configuration can enhance the removal of key pollutants of concern, within airport storm runoff. In this context, PA configurations performed better than the current industry standard UA approach and alternative aeration strategies tested. Two further research objectives to determine the impact of (i) influent concentration and (ii) hydraulic retention time, on pollutant removal efficiency revealed that influent strength did not significantly impact overall pollutant removal, although a significant impact was noted for final effluent concentrations of COD, BOD_5 and TOC. Hydraulic retention time had a significant effect on pollutant removal and final effluent concentrations for all pollutants investigated, with 2.24 d and 1.49 d HRT performing significantly better than 1.14 d HRT. The results presented within this chapter are discussed within further detail in the remaining sections within this chapter.

4.4.1. Water Quality Conditions and Effect of Aeration Configuration within the Experimental Aerated Wetland

Dissolved oxygen represents a critical parameter for pollutant removal within wetland systems as microbial degradation of de-icers occurs more rapidly under aerobic conditions compared to anaerobic conditions (Johnson et al., 2001). Aeration configuration tests reported within this chapter revealed that aeration configuration had a substantial impact on DO concentrations within the pilot-scale aerated wetland system. For example, whilst mean DO concentrations remained at 0 mg L^{-1} in cells one to three during NA and IA tests, significantly higher mean concentrations were observed within cell two during UA (0.69 ± 0.35 mg L^{-1}) and PA (2.13 ± 1.16 mg L^{-1}) tests, despite equal volumes of air being injected into cell two during UA and PA tests. The higher mean DO concentration in PA tests compared to UA tests was even more pronounced in cell three of the experimental wetland system, with mean DO concentrations of 0.80 ± 0.43 mg L^{-1} versus 8.32 ± 0.18

mg L^{-1} for UA and PA tests respectively, despite 50% more air being input into cell three during UA tests compared to PA tests. These findings can be explained by higher BOD_5 removal rates within cell one during PA tests (Fig. 4.5), due to the increased availability of O_2 to micro-organisms, which subsequently resulted in less BOD_5 and O_2 demand being carried over to cells two and three, in contrast to the UA configuration. In fixed-film biological treatment systems such as the aerated wetland evaluated here, sustained DO concentrations <0.60 mg L^{-1} may result in colonisation and dominance of anaerobic filamentous bacteria over aerobic heterotrophic bacteria, whilst DO concentrations >2.00 mg L^{-1} are no longer limiting for microbial respiration of organic matter (Davis, 2005) and nitrification (Goreau et al., 1980). Whilst the PA configuration reported in this chapter appears more likely to maintain DO concentrations that support optimum aerobic degradation pathways in cells two and three of the experimental system than the other aeration configurations, the data suggests that the spatial distribution of aeration inputs could have been further optimised in order to maintain a 0.6 mg L^{-1} to 2 mg L^{-1} DO concentration range within each cell, by additional reductions in DO inputs within cell three and increasing DO inputs within cell one under the PA configuration.

The ORP increased significantly in PA and UA tests compared to IA and NA tests. However, even in the PA and UA tests, ORP never exceeded -115 mV. In subsurface soils and media, ORP can range from -400 mV within strongly reducing systems to +700 mV in strong oxidising systems (Kadlec and Wallace, 2009). The low ORP results observed even under PA and UA configurations where DO concentrations increased within cells two and three, indicate very intense periods of microbial pollutant reduction (Dušek et al., 2008), typically associated with anaerobic processes such as sulphate reduction and methanogenesis (Faulwetter et al., 2009). This would suggest that both anaerobic and aerobic zones exist locally within each treatment cell as a result of the media preventing complete mixing taking place within each treatment cell.

Temperature is widely known as being a rate limiting factor for microbial metabolism and therefore pollutant removal efficiency (Akratos and Tsihrintzis, 2007, Faulwetter et al., 2009, Kadlec and Reddy, 2001). Mean water temperatures within the test system ranged between 9.2 ± 0.5 ˚C to 19.4 ± 0.3˚C, which is less than the optimal microbial temperature range of 20 ˚C to 35 ˚C in mesophilic systems (Kadlec and Reddy, 2001), but well in excess of 5 ˚C which would be expected to inhibit the functioning of microbial communities with respect to efficient COD, BOD_5 and TOC removal (Faulwetter et al., 2009). Further, the mean water temperature was 14.0 ± 0.5 ˚C which was 40 % higher than mean air temperatures determined during the testing period, indicating good levels of insulation which is consistent with cold climate wetland designs (Kadlec and Wallace, 2009).

Without sufficient insulation, operational issues such as increased hydraulic failures as a result of freezing, alongside thermal inhibition of microbial activity, may occur during winter de-icing seasons, adversely impacting pollutant removal rates during critical loading events (Klecka et al., 1993, Wittgren and Mæhlum, 1997, Mæhlum and Stålnacke, 1999, Wallace, 2000). Final effluent temperatures ranged from 12.6 ˚C to 16.2 ˚C, with overall mean final effluent temperatures of 14.1 ± 1.4 ˚C which falls below the 98th annual percentile (20 ˚C) required to achieve a high WFD classification for cold-water (salmonid fisheries), as outlined within UK national environmental quality standard (EQS) for thermal discharges (UK TAG, 2013). This suggests that discharges from aerated wetlands to receiving waters would not typically be constrained by the existing statutory UK environmental regulations.

4.4.2. Impact of Aeration Configuration on Pollutant Removal within the Experimental Aerated Wetland

Microbial communities present as a biofilm attached to media surfaces within aerated wetlands are primarily responsible for the degradation of organic pollutants within de-icer contaminated runoff through respiration. The results reported in Section 4.3.3 demonstrate that artificial aeration is essential in order to supply sufficient O_2 to support efficient microbial respiration and removal of pollutants such as COD, BOD_5 and TOC from de-icer contaminated storm runoff at airports. In the absence of artificial aeration, microbial metabolism is inhibited by limited DO availability within the system and anaerobic respiration prevails as indicated by DO concentrations of 0 mg L^{-1} within cells one, two and three during NA tests reported within Section 4.3.3. The maintenance of insufficient DO concentrations given the DO demand associated with pollutants in the NA tests resulted in poor removal efficiencies of 38 ± 4 %, 45 ± 6 % and 46 ± 7 % for COD, BOD_5 and TOC respectively. Consequently, final effluent concentrations in the NA tests remained high and well in excess of the typical UK environmental permit to discharge limits for receiving waters, resulting in the requirement for tertiary treatment or provision for trade effluent discharge following treatment in non-aerated passive constructed wetland designs. Despite adding air into cell one during IA tests, anaerobic conditions prevailed throughout the system as indicated by O_2 concentrations of 0 mg L^{-1} in cells one, two and three. Again, this resulted in low pollutant removal efficiencies and high final effluent concentrations during IA tests. Whilst final effluent concentrations of COD, BOD_5 and TOC were significantly lower in IA tests compared to NA tests, they remained well above typical UK regulatory limits for discharge into a receiving watercourse. The low removal rates observed during NA and IA tests, generally concur with the results of pilot-scale subsurface flow aerated wetlands dosed with base-flow runoff and de-icers from Edmonton Airport in Canada and Buffalo Airport in the USA, where mean BOD_5 removal efficiencies of 55 % and 68 % were achieved in the absence of artificial aeration (Higgins et al., 2007).

The primary rationale for applying artificial aeration is to improve OTRs, thereby providing microbial communities with increased availability of DO to support aerobic respiration and the more efficient removal of organic pollutants than would otherwise be possible under anaerobic conditions (Faulwetter et al., 2009, Chong et al., 1999). Within existing aerated wetlands operating at Buffalo Airport in the USA and Heathrow Airport in the UK, BOD_5 removal rates of 98 % and 74 % respectively have been achieved by supplying artificial aeration into the system through diffusers positioned in a uniform configuration from the system inlet to the outlet (Wallace and Liner, 2011a, Murphy et al., 2014). This is generally consistent with the results presented in Chapter 4, which reveal significantly higher BOD_5 removal rates during UA tests in contrast to NA tests, equivalent to a 53 % increase in BOD_5 removal comparing influent to effluent. Whilst high removal rates can be achieved using UA configurations, Fig. 4.5 demonstrates that organic pollutants are mainly removed within the first two-thirds of a system, consistent with findings from previous aerated wetland studies where up to two thirds of organic matter was removed within first quarter of an aerated wetland system (Akratos and Tsihrintzis, 2007, Zhang et al., 2010). Further, DO concentrations within cell one were 0 mg L^{-1} in all aeration configurations tested, indicating high rates of aerobic respiration and insufficient input of air to meet the O_2 demand exerted by the influent within cell one. This is a characteristic which has been addressed using tapered aeration designs in biological reactors such as the activated sludge treatment process, whereby 55 % to 70 % of the total air is typically applied to the first half of the system to address the high O_2 demand near to the inlet (Orhon and Artan, 1994). In the current chapter, this aeration principal has been applied to an aerated wetland for the first time in the form of PA tests, in which 50 % of the total aeration was applied to the first-third of the pilot-scale system. This PA configuration enhanced removal rates by 15 %, 3 % and 5 % for COD, BOD_5 and TOC, when compared to the results obtained under the more conventional UA configuration, although pollutant removal was only significantly higher for the parameter COD. Further, the mean final effluent concentration of 21 ± 5 mg L^{-1} BOD_5 determined during PA tests was within typical UK environmental permit to discharge limits for receiving waters, suggesting that discharge of treated effluent to a nearby watercourse would be permitted by the Environment Agency.

Filtration and sedimentation of particulate organic matter forms an important process for the reduction of TSS concentrations within aerated wetland systems (Faulwetter et al., 2009, Vymazal and Kröpfelová, 2009). The PA and UA aeration configurations demonstrated a significantly higher

TSS removal compared to IA and NA configurations. This is consistent with other studies that have shown artificial aeration to significantly increase TSS removal, possibly due to a reduction in the accumulation of material, reduced media pore space clogging and a subsequent reduction in the release of TSS from the system resulting from the increased rate at which organic matter is respired under aerobic conditions compared with anaerobic conditions (Ouellet-Plamondon et al., 2006, Tao et al., 2010, Butterworth et al., 2013). Further, a net increase in TSS concentration was observed in both IA and NA test configurations. Net increases in TSS concentration during water movement through aerated wetlands has previously been linked to biomass shearing resulting from high flow events (Birch et al., 2004), or shifts in microbial community composition where decomposition of biomass to make way for new species can contributes to increases in TSS concentration within a final effluent (Kadlec and Wallace, 2009). As the flow rates were constant within the aeration configuration tests it is assumed that the increase in TSS was a result of a shift in microbial community composition from aerobic heterotrophic bacteria previously established during the PA and UA tests to anaerobic dominating species within IA and NA tests, therefore resulting in increased shearing of aerobic heterotrophs.

4.4.3. Hydraulic Retention Time and Organic Loading Rates

The research reported within this chapter demonstrates that pollutant removal efficiencies for COD, BOD_5, TOC and TSS were significantly higher when HRTs of 2.24 d and 1.49 d were maintained in comparison to an HRT of 1.14 d within the three cells. The optimal HRT in the three cells during testing appeared to be 1.49 d. This is slightly higher than the HRT of 1.2 d which was determined as the optimal HRT for effective ammonium removal as a proportion of the influent concentration within a pilot-scale downward vertical flow aerated wetland, with a surface area of 1.08 m^2 and treating domestic wastewater from the Canadian town of North Glengarry (Wallace et al., 2006). Further, HRT of 2 d was reported to provide efficient nitrification and reduction of ammonium concentrations within a pilot-scale vertical flow aerated wetland with a 10 m^2 surface area, treating domestic wastewater (Murphy et al., 2016). In contrast, a HRT of 5.5 d was reported to achieve efficient ammonium and organic removal within a pilot-scale system with a surface area of 7.9 m^2 treating septic tank effluent (Uggetti et al., 2016). Further, HRT was reported as approximately 6.1 d within a vertical flow subsurface aerated wetland with four individual cells each with a footprint of 4,640 m^2, treating de-icer contaminated airport storm runoff at the Buffalo Niagara International airport in the USA (Wallace and Liner, 2011a, Envirodynamics Consulting, 2012).

Although pollutant removal was not significantly affected by the range of influent concentrations tested, the final effluent concentrations of each parameter tested were significantly lower when the experimental system was dosed with low (831 ± 35 mg L^{-1}) and medium (1,355 ± 81 mg L^{-1}) BOD_5 influent concentrations in contrast to high (1,853 ± 99 mg L^{-1}) influent BOD_5 concentrations. This would suggest that influent concentration and therefore the pollutant MLRs determined from the influent concentration and HLR (Equation 2.1) is a key factor within the optimal operation of aerated wetland systems. Within the individual experiments, MLRs were maintained at steady-state ranging from 0.05 kg d^{-1} m^2 to 0.28 kg d^{-1} m^2 BOD_5 which in practice would require the influent flow rate to be increased when influent strength is low and decreased when influent strength is high, in order to maintain steady-state conditions and optimal pollutant removal efficiency. The research reported within this chapter suggests that areal MLRs of 0.10 kg d^{-1} m^2 BOD_5 should be maintained to achieve final effluent concentrations within a 23 mg L^{-1} BOD_5 environmental permit limit, although the system performed well under areal MLRs of up to 0.23 kg d^{-1} m^2 BOD_5 where >90 % BOD_5 removal was observed. Mass loading rates of 0.10 kg d^{-1} m^2 BOD_5 are comparatively low to existing aerated wetlands treating airport runoff. For instance, MLRs of 0.24 kg d^{-1} m^2 BOD_5, 0.18 kg d^{-1} m^2 BOD_5 and 0.25 kg d^{-1} m^2 BOD_5 have been reported to achieve environmental permit to discharge limits of 30 mg L^{-1}, 40 mg L^{-1} and 100 mg L^{-1} respectively for Buffalo Airport in the USA, Heathrow Airport in the UK and Edmonton Airport in Canada (Wallace and Liner, 2011a, Murphy et al., 2014, Dechanie, 2013). Whilst it is desirable to process de-icer contaminated storm runoff quickly to ensure maximum available storage capacity within treatment systems, storm attenuation ponds and storm water infrastructure, the long term operation of aerated wetlands exceeding 0.20 kg d^{-1} m^2 BOD_5 is not recommended (Envirodynamics Consulting, 2012) suggesting that existing aerated wetlands used to treat airport storm runoff are already operating at the upper range of their capabilities in regards to mass pollutant loadings. Significant long term exceedance of the design MLR however would likely result in microbial clogging of the media pore space, which potentially leads to operational issues including hydraulic malfunctioning, surface flooding and reductions in pollutant removal efficiency (Nivala et al., 2012, Pedescoll et al., 2013).

4.5. Conclusion

The results reported within Chapter 4 demonstrate that artificially aerated wetlands can be an effective on-site treatment option for reducing regulated pollutant concentrations derived from the application of aircraft and pavement de-icers, which is a fundamental requirement for safe winter operating conditions at airports worldwide. The research presented throughout this chapter demonstrates that aeration configuration significantly effects DO concentrations and oxygen reduction potential (ORP) within aerated wetlands, which in turn regulates microbial pollutant removal processes and therefore impacts pollutant removal efficiency. Results show that organic pollutant removal efficiency can be enhanced significantly in aerated wetlands through altering the spatial distribution of aeration inputs, in order to better match the supply and demand of DO throughout a system. Aeration configuration is therefore an important factor for consideration in future aerated wetland designs. The research reported in this chapter also demonstrates that an areal MLR of 0.10 kg d^{-1} m^2 BOD_5 should be maintained to achieve final effluent concentrations within typical discharge consent limits of <23 mg L^{-1} BOD_5. Whilst good performance was maintained under areal MLR of up to 0.23 kg d^{-1} m^2 BOD_5 within this study, long term MLR >0.20 kg d^{-1} m^2 BOD_5 is not recommended (Envirodynamics Consulting, 2012). At the loading rates tested, the optimal HRT within the system was 1.49 d, although in practice this would be reduced during periods of low influent BOD_5 concentrations in order to maintain a sufficiently high MLR to meet microbial requirements. Overall these findings offer important insights into the design and operation of aerated wetlands to help improve economic feasibility through reduction in operating costs and reduced energy consumption and carbon emissions associated with blower operation. This would help to ensure that aerated wetlands provide a more sustainable alternative to alternative wastewater management strategies used within the aviation industry and within other industries producing effluents characterised by a high organic strength and BOD_5 concentrations.

Finally, the research presented within this chapter indicates that artificial aeration is a crucial component within wetland systems for the efficient removal of wastewaters characterised by a high organic load and BOD_5 concentrations, such as airport storm event runoff during the de-icing season. However, the energy consumption required to operate aeration devices results in increased operation and running costs when compared to the more traditional passive constructed wetland designs. Optimisation of aeration devices and aerated wetland designs is therefore essential to maximise OTE from the gaseous to the dissolved phase and ensure cost-effective and sustainable operation of aerated wetlands. Research on standard oxygen transfer efficiency (SOTE) within experimental columns representing aerated wetlands is presented within Chapter 5.

Chapter 5

Oxygen Transfer in Aerated Wetlands: The Impact of Media Presence, Media Depth and Air Flow Rates

5.1. Introduction

The threat to aquatic systems from the by-products of industrial processes has increased significantly in recent decades, as a consequence of increasing global demand for nutrient and organic resources and the potential for these resources to be transported into receiving watercourses (Tilman et al., 2002, Tregear et al., 1994). For example, in the aviation industry the increasing demand for air travel is forecast to result in increased aircraft de-icer requirements and contamination of surface water runoff at airports globally (Freeman et al., 2015). Like many industrial wastewaters, de-icer contaminated storm event runoff poses a significant threat to aquatic organisms through depletion of DO concentrations within receiving waters, if discharged without prior treatment (Corsi et al., 2001a, ACRP, 2008, Freeman et al., 2015). Fortunately, increasing understanding of the biochemical processes responsible for O_2 depletion of receiving waters has led to the design and implementation of a wide range of treatment technologies over the past century to reduce pollutant loads from industrial wastewater, mitigate detrimental water quality impacts and improve water quality for stakeholders.

Most industrial wastewaters have significantly greater O_2 demands than can be transferred into a treatment system through passive processes, primarily diffusion from the atmosphere. To overcome this, artificial aeration can be applied to treatment systems to maintain DO concentrations at levels required to facilitate efficient biological removal processes, such as aerobic microbial metabolism of organic carbon. Aeration systems are typically comprised of mechanical surface aerators which are designed to improve mixing and O_2 transfer at the water-atmosphere interface, but are limited to open water systems only. Alternatively, coarse or fine bubble subsurface diffusers can be installed at the base of treatment systems to produce rising air bubbles within the water column creating additional gas to water interfaces (Al-Ahmady, 2006). Typically, subsurface diffusers have higher OTRs compared to surface diffusers (Stenstrom and Gilbert, 1981, Krampe and Krauth, 2003) and can be used in media-filled systems. The mass of O_2 per unit of power input is typically described as the oxygen transfer efficiency (OTE), expressed in kg O_2 kWh. This is important as it defines the amount of energy required to treat the wastewater which subsequently contributes to the overall operation, maintenance and running costs of a treatment system, therefore defining the economic feasibility and long term sustainability of aerated systems. In open water systems, the oxygen transfer efficiency of fine bubble diffusers typically ranges from 4.3 kg O_2 kWh to 6.1 kg O_2 kWh (Stenstrom, 2006), which is higher than alternative devices including coarse bubble diffusers and mechanical surface aerators which typically range from 1.8 kg O_2 kWh to 2.4 kg O_2 kWh and 1.2 kg O_2 kWh to 2.1 kg O_2 kWh respectively (Stenstrom, 2006) (Table 5.1.). The higher OTE has resulted in widespread use of fine bubble diffusers within conventional wastewater treatment applications such as activated sludge systems and submerged aerated filter systems (Mulinix, 2012, Stenstrom, 2006, Hebert, 2010).

Table 5.1.
Summary of typical oxygen transfer efficiencies for common aeration devices in open water systems

Aeration device	Oxygen transfer efficiency (kg O_2 kWh)	SOTE [(a)] (%)
Mechanical surface aerator	1.2 – 2.1	-
Coarse bubble diffuser	1.8 – 2.4	2 – 12
Fine bubble diffuser	4.3 – 6.1	5 – 32

[(a)] Standard oxygen transfer efficiency (SOTE) expressed as a percentage of the total oxygen absorbed at depths ranging from 3 m to 6 m with airflow rates ranging from 7 m^3 h to 68 m^3 h (Mueller et al., 2002, Stenstrom, 2006).
- Not applicable.

The standard oxygen transfer efficiency (SOTE) for subsurface diffusers is primarily controlled by bubble diameter, gas hold-up (bubble retention time) and airflow rate because these factors control the gas to liquid interfacial surface area, where O_2 transfer from a gas to a dissolved phase occurs (Fujie et al., 1992, Butterworth et al., 2013). Bubble diameter is primarily controlled by the diffuser orifice size, with fine bubble diffusers typically producing bubble diameters of 2 mm to 3 mm in comparison to 6 mm to 10 mm which are typical of coarse bubble diffusers (Ashley et al., 1992). Compared to larger bubbles, smaller bubble diameters provide a greater surface area to O_2 volume ratio, which increases the gas and water interface, therefore improving the OTE (Burris, 1999). Gas hold-up is primarily improved by placing the diffusers near to the treatment system bed, thereby extending the bubble ascent time through the water column which increases bubble retention time and contact between the gas bubble and the liquid (Zhen et al., 2003, Al-Ahmady, 2006). For example, SOTE in potable water increased from 4.0 % to 4.6 % when the total depth of a diffuser within a bench scale treatment bed increased from 0.24 m to 0.32 m, when operating under airflow rates of 15.50 $m^3 h^{-1}$ (Zhen et al., 2003). Typically, subsurface diffusers operate at depths between 3 m and 6 m below the surface level of a treatment system, resulting in SOTEs of 5 % to 32 % for fine bubble diffusers and 2 % to 12 % for coarse bubble diffusers at airflow rates ranging from 7 $m^3 h^{-1}$ to 68 $m^3 h^{-1}$ (Table 5.1) (Mueller et al., 2002, Stenstrom, 2006). Further, when the depth of a diffuser within a treatment bed remains constant, air flow rates have been shown to impact bubble formation, with SOTE decreasing from 16 % to 8 % for fine bubble diffusers and 7 % to 6 % for coarse bubble diffusers when airflow rates were increased from 5 $m^3 h^{-1}$ to 35 $m^3 h^{-1}$ respectively (Collingnon, 2006, Ashley et al., 1991). Efforts to enhance SOTE therefore includes the use of fine bubble diffusers (Krampe and Krauth, 2003), increasing the diffuser depth within a treatment system (Zhen et al., 2003, Al-Ahmady, 2006), optimisation of air flow rates and increasing diffuser coverage to provide a uniform distribution within the treatment bed (Fujie et al., 1992). The optimal OTE can therefore be achieved by establishing the most effective airflow rate which minimises the bubble diameter whilst maximising the diffuser depth within the treatment bed to improve bubble retention time within the treatment system water column (Butterworth et al., 2013).

However, much of the research within this field has previously addressed OTR and SOTE within open water aeration tanks in attempts to optimise the conventional and widely applied activated sludge process. This type of system operates under different physical conditions to media based systems such as biological aerated filters, submerged aerated filters and artificially aerated wetlands, in which the optimisation of diffused aeration systems is complicated due to the presence of media (Butterworth et al., 2013). In media-filled systems, the pathway which O_2 bubbles must take during ascent to the surface is greatly restricted, promoting bubble coalescence and resulting in larger bubble diameters and subsequently lower SOTE. For instance, one study found that fine bubble diffusers produced SOTEs of 6.6 % and 4.7 % within one meter deep bench scale tanks containing no media and gravel media respectively (Kadlec and Wallace, 2009). In contrast, a further study tested coarse bubble diffusers within a 1.5 m deep integrated fixed film activated sludge system and found that the mean SOTE increased from 5 % without media to 6.5 % with media, in which it was hypothesised that the effect of bubble coalescence was negated by bubble hold-up and increased residence time within the media pore space (Collingnon, 2006). The net effect of media on the efficiency of aeration devices and SOTE is therefore unclear, due to the competing effects of bubble coalescence verses bubble hold-up time. To address this, further research is required in media based systems such as aerated wetlands to understand the net effect of media on SOTE, providing the context for this chapter.

One of the major drawbacks of artificial aeration is the power consumption required to operate aeration devices, which typically accounts for 45 % to 80 % of the total operational costs of wastewater treatment systems (Gillot et al., 2005, Stenstrom and Rosso, 2006, Zhou et al., 2013). Further, aerated wetlands are a relatively new form of media-filled system having developed from passive constructed wetlands and reed bed systems. Therefore, limited data exists regarding many of the key factors affecting OTR and SOTE within this technology. Further research to improve our understanding of the mechanisms which affect the efficiency of O_2 transfer within media-filled systems, such as airflow rates, bubble coalescence and the effect of total media depth, is therefore essential to ensure cost-effective future design and operation of diffused aeration systems within aerated wetland systems.

Therefore, the aim of this chapter was to evaluate the effects of specific design criteria on O_2 transfer within aerated wetland systems, in order to inform optimal future designs of aerated wetlands. This chapter reports research designed to test the hypothesis that SOTE can be increased within aerated wetlands by optimising the total media depth and airflow rates. The objectives of the chapter were to: i) determine SOTE for different media depths and airflow rates; ii) evaluate the effect of media depth on bubble frequency; and iii) assess the effect of media depth on bubble diameter and bubble coalescence to support interpretation of the SOTE data related to objective i).

5.2. Methodology

5.2.1. Experimental Column Design

Four individual columns ranging from 2,000 mm to 3,500 mm in length were designed and filled with gravel to depths of 1,500 mm to 3,000 mm, to replicate typical media depths for aerated wetlands. The experimental columns were constructed in a workshop at Manchester Airport and positioned by a mezzanine floor to provide access to the top of the columns (Table 5.2, Fig 5.1a). The experiment comprised individual columns, sample ports, sample valves, ceramic disc diffusers and airlines. The columns were constructed from 220 mm internal diameter medium density polyethylene gas pipes which were sealed at the base with electrofusion couplings and bolted stainless steel end caps to prevent leakage (Fig. 5.1b). A drain was positioned at the base of each column (Fig. 5.1b). Fine bubble ceramic disc diffusers of 200 mm diameter were installed at the base of each column (Fig. 5.1c). Air was delivered into the columns through 10 mm tubing, using an Airmaster model 8/36, 1.5 hp, 24 L oil free compressor. A BOC 0 L min^{-1} to 15 L min^{-1} flow meter was positioned on the aeration line and used to adjust and regulate the air flow rate delivered into the columns. The four individual columns were cut to lengths of 2,000 mm, 2,500 mm, 3,000 mm and 3,500 mm respectively. Evenly distributed holes were drilled along the length of each column and two sample ports installed on both sides of each column opposite each other at elevations from the base of the column of 25 %, 50 %, 75 % and 100 % of the total media depth. Each sample port protruded into the column by approximately 20 mm, to avoid sampling water from the internal column wall (Fig. 5.1e). Following completion of bubble frequency and observation tests (Section 5.2.3), each column was filled with washed, 10 mm to 20 mm angular limestone gravel, to depths of 1,500 mm, 2,000 mm, 2,500 mm and 3,000 mm.

Table 5.2.
Details of experimental columns specifications used during standard oxygen transfer testing

Parameter	Column 1	Column 2	Column 3	Column 4
Total column depth (mm)	2,000	2,500	3,000	3,500
Total media depth (mm)	1,500	2,000	2,500	3,000
Media vol. (m^3) [(b)]	0.05	0.06	0.08	0.09
Water vol. (L) [(c)]	16	22	27	33
Media type	10mm - 20 mm washed angular limestone gravel [(a)]			
Sample locations	elevation from the column base of 25 %, 50%, 75 % and 100 % of the total column depth			
Aeration device	Airmaster 8/36, 1.5hp 24 L oil free compressor			
Diffuser type	200 mm fine bubble ceramic disk diffuser			
Aeration Vol. (L m^{-1})	1 – 3			

[(a)] Media porosity = 34.75 %,
[(b)] Media volume = π r^2 * depth,
[(c)] Water volume = π r^2 * measured media porosity * depth.

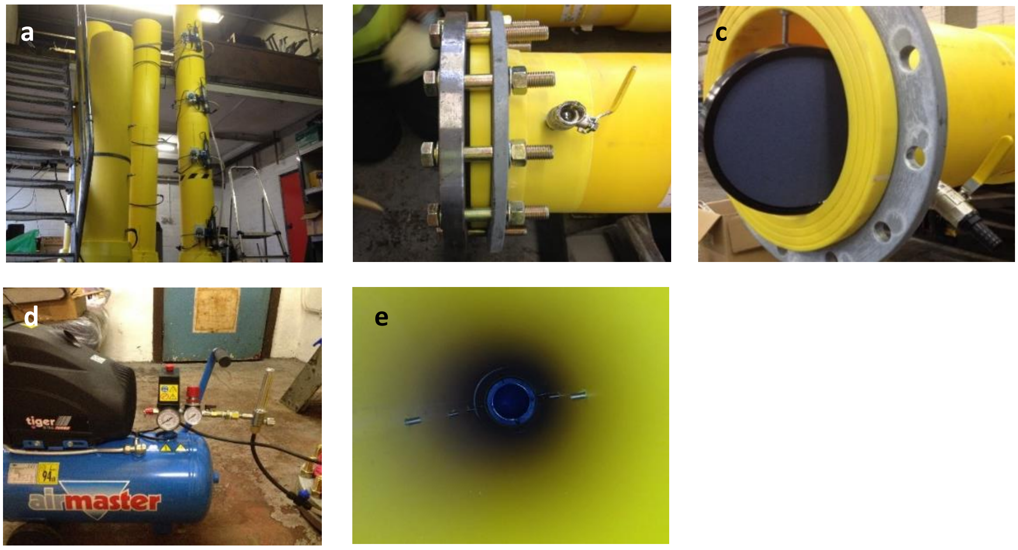


Figure 5.1. Components of experimental columns, (a) overview of four media-filled columns of 1,500 mm to 3,000 mm deep, (b) stainless steel base and outlet valve, (c) fine bubble disc diffuser, (d) air compressor and flow meter, (e) internal sample ports.

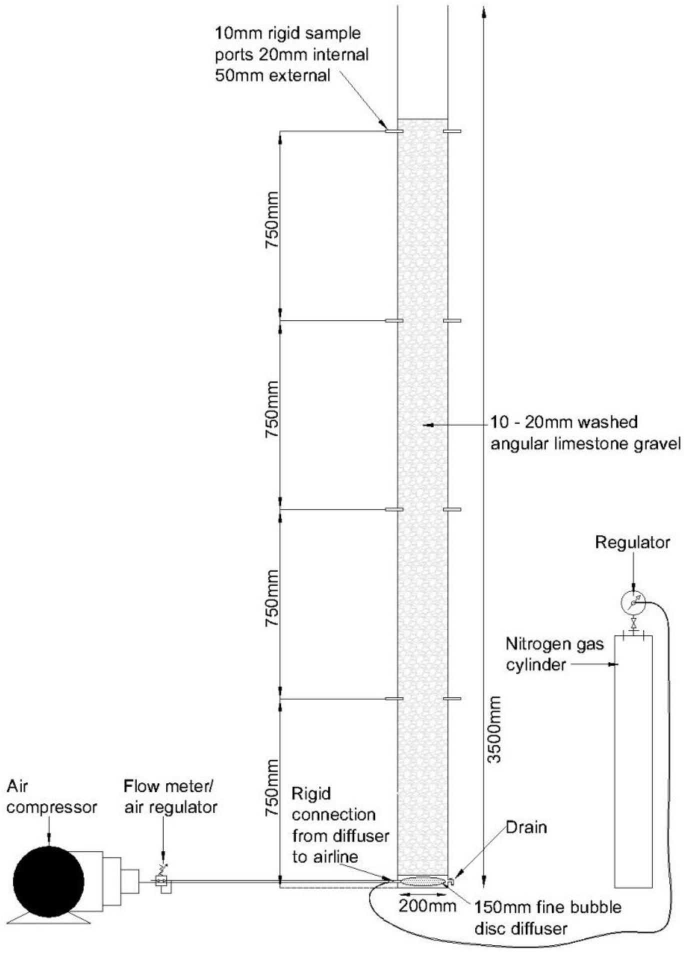


Figure 5.2. Example section view of experimental column design and equipment setup.

5.2.3. Bubble Diameter and Bubble Coalescence

Several methods of determining bubble diameter have been previously reported, including electro-resistivity measurements (Yasunishi et al., 1986), gas holdup and pressure measurements (Dobby and Finch, 1986), calculations using empirical or semi-empirical observations (Sada et al., 1978, Tsuge et al., 1981) and photographic techniques (Miller, 1985, Butterworth et al., 2013). The method used within this study was based on the photographic technique (Miller, 1985, Butterworth et al., 2013). This involved taking photographs of bubble plumes from the top of each column prior to and following the addition of media, to allow assessment of the effect of media on bubble frequency defined as the number of bubbles at the cross sectional surface of the column and to determine individual bubble diameters (Fig. 5.3). Photographs were taken using a 12.1 megapixel Panasonic Lumix G2 digital touchscreen camera equipped with a 14 mm to 42 mm optical image stabilisation (f/3.5 to 5.6) lens and ultraviolet filter capable of 3.2 frames per second. Each photograph was downloaded and printed, with the prints used to determine the frequency and diameter of individual bubbles within each column with and without media present. The number of bubbles were counted manually and measured individually for each photograph to assess whether increasing bubble diameter, interpreted as being the result of bubble coalescence, was observed as an effect of media presence. A tape measure was positioned within each column as a scale to ensure correct measurements of bubble diameters from the printed photographs. The process was repeated in triplicate for each test depth, with and without media, at air flow rates of 10 L m^{-1}, assuming that bubble plumes were at steady-state when the photographs were taken.

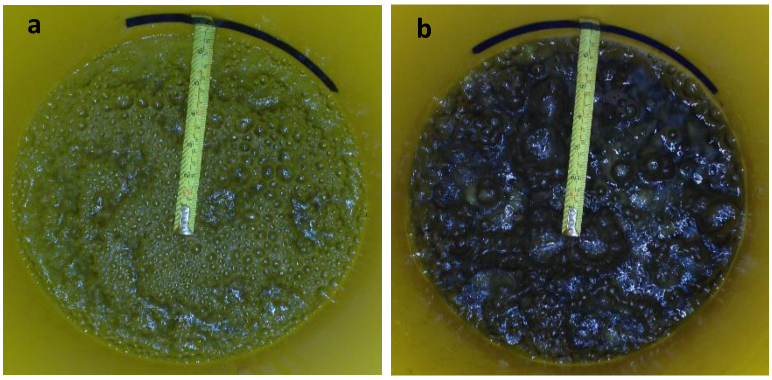


Figure 5.3. Example of bubble plumes within 1,500 mm deep aerated columns (a) without media and (b) with 10 mm to 20 mm angular limestone gravel media.

5.2.4. Standard Oxygen Transfer Efficiency Tests

Tests were conducted in media-filled columns only, following the procedures described within the ASCE standard, ASCE/EWRI 2-06 ‘Measurement of Oxygen Transfer in Clean Water’ (ASCE, 2007). The test involves the removal of DO from potable water, followed by reaeration to the steady-state saturation point. The DO concentrations were measured within the water column at four representative depths and at high resolution intervals of ten seconds throughout the reaeration process, from the point at which aeration begins to the steady-state saturation point. This data was subsequently analysed using the ASCE approved DOPar3-0-3 programme and non-linear regression model (ASCE, 2007). Three aeration flow rates (1 L min^{-1}, 2 L min^{-1} and 3 L min^{-1}) were tested within each of the four columns to assess the impact of air flow rate and total media depth on SOTE (Table 5.3). Tests were conducted between 15/11/2014 to 05/01/2015 at Manchester Airport and each test was repeated in triplicate.

Table 5.3.
Experimental variables for standard oxygen transfer efficiency tests in media-filled columns with total depths of 1,500 mm to 3,000 mm operating at airflow rates of 1 L min^{-1} to 3 L min^{-1}. n = 3 for each test

Test No.	Total depth of column (mm)	Air flow rate (L m^{-1})
1	1,500	1
2	1,500	2
3	1,500	3
4	2,000	1
5	2,000	2
6	2,000	3
7	2,500	1
8	2,500	2
9	2,500	3
10	3,000	1
11	3,000	2
12	3,000	3

Initially, deoxygenation was attempted through the process of sulphite oxidation by adding sodium sulphite anhydrous (Na_2SO_3) and cobalt ($CoSO_4$), as described in the ASCE standard (ASCE, 2007). Cobalt was dissolved in the column water body at concentrations of approximately 0.5 mg L^{-1} to act as a catalyst for the deoxygenation chemical reaction (Eq. 5.1). The column was aerated for 15 minutes following $CoSO_4$ addition to promote good mixing. Subsequently the aeration was turned off and 10 L of potable water containing Na_2SO_3 dissolved into the solution at a concentration of 120 mg L^{-1} was poured directly into the top of the column. The reaction which takes place as the DO concentration is reduced to 0 mg L^{-1} is identified in Eq. 5.1 as follows (Loehr, 1984):

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4 \qquad (5.1)$$

From the stoichiometry of this reaction, 7.9 mg L^{-1} of Na_2SO_3 is needed per mg L^{-1} of DO, although 10 % to 20 % excess is typically used (Sincero and Sincero, 2003, ASCE, 2007). However, the observed DO concentrations at the 4 sample location depths below the surface revealed poor mixing vertically through the system, likely due to the presence of the media, which reflects the design of the ASCE standard for open water systems. This resulted in the need to amend the procedures for media-filled columns. The method was subsequently adapted to resolve this issue by using nitrogen gas to deoxygenate the test water prior to each test, in line with the findings of previous studies which have determined that nitrogen gas can be used as a suitable alternative to Na_2SO_3 and $CoSO_4$ addition without having an effect on SOTE results (Ghaly and Kok, 1988). The addition of nitrogen gas was achieved by purging the nitrogen gas through the diffuser at a high flow rate, until DO concentrations decreased to <0.5 mg L^{-1} at each of the sample locations within the column, a process which took up to 60 minutes. The nitrogen supply was stopped following the deoxygenation process and the air supply was started at the pre-calibrated test flow rate.

Concentrations of DO were measured using four Smartroll optical RDO multi-parameter probes manufactured by In-Situ Inc. During testing the probes were positioned within flow cells, at each of the four sample locations. Water was pumped through the flow cell using a low flow peristaltic pump and tubing arrangement, forming a sealed, self-contained sample loop through which the test water was continuously circulated (Fig. 5.4). The low flow rate was considered insufficient to impact DO concentrations within the test water through agitation and the tubing was purged prior to each test to remove any trapped air resulting from the column filling or DO probe calibration procedures. To ensure accurate measurements of DO, each of the four probes were calibrated and installed into the appropriate flow cells prior to the beginning of each test. A two stage calibration procedure was used for DO which consisted of a calibration at saturation point within the atmosphere followed by a zero calibration using a solution of 1000 mg L^{-1} Na_2SO_3 and 1 mg L^{-1} $CoSO_4$. High resolution DO data was obtained at ten second intervals and the temperature, DO, redox (ORP), pH and total dissolved solids (TDS) of the test water were recorded prior to the start of each test.

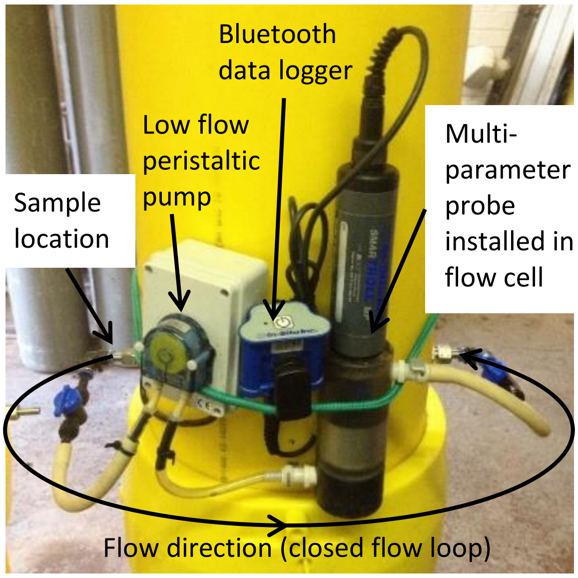


Figure 5.4. Photograph of an experimental column and the low flow recirculation pump, Smartroll RDO multi-parameter probe and flow cell arrangement setup to ensure a closed self-contained flow loop. This arrangement was replicated at each of the four sample locations during testing to obtain representative conditions at different depths within the column.

5.2.5. Determination of Oxygen Transfer from the Gaseous to the Liquid Phase

Oxygen transfer is defined as the process by which O_2 is absorbed from the gaseous to the liquid phase (Al-Ahmady, 2006) and is based on the principles of the two-film theory of gas absorption into water (Lewis and Whitman, 1924). Gas absorption can be determined experimentally using a simplified mass transfer model to determine the volumetric mass transfer coefficient (K_La) determined at an individual sample location and the steady-state DO saturation concentration (C^*_∞) following Eq. 5.2 (Stenstrom et al., 2006):

$$C = C*_\infty - (C*_\infty - C_0)\exp(-K_La^t) \tag{5.2}$$

where:

C = effective mean dissolved oxygen concentration in the liquid phase, mg L^{-1}

$C*_\infty$ = steady-state dissolved oxygen saturation concentration attained at infinite time, mg L^{-1}

C_0 = initial dissolved oxygen concentration at time zero, mg L^{-1}

K_La = volumetric mass transfer coefficient determined at each sample location within the column at infinite time, ^{t} and expressed as the mass transfer of O_2 per hour, L

A non-linear regression model was used fit to the DO profiles measured at each of the four column sample locations in order to calculate the parameters K_La and C^*_∞ during each test (Stenstrom et al., 2006, ASCE, 2007). The parameters K_La and C^*_∞ were then integrated into the calculation of the standard oxygen transfer rate (SOTR), which is defined as the mass of O_2 transferred per unit of time assuming that the starting DO concentration within the column was 0 mg L^{-1} and that standard conditions of 20 °C water temperature and barometric pressure of 1,000 mbar were maintained during testing under the specified air flow rate, test water volume, total system depth and power inputs (ASCE, 2007, Stenstrom, 2001). The SOTR is typically expressed in kg O_2 m^{-1} and is calculated in accordance with Eq. 5.3 as follows (Stenstrom et al., 2006):

$$SOTR = K_La^{20}(C*_\infty{}^{20})\,V \tag{5.3}$$

where:

SOTR = standard oxygen transfer rate, kg O_2 m^{-1}

K_La^{20} = volumetric mass transfer coefficient at water temperatures of 20 °C

V = liquid volume of the test water when aeration is turned off, m^3

$C^*_\infty{}^{20}$ = determination of steady-state dissolved oxygen concentration expressed as mg L^{-1} and corrected to 20 °C water temperature and standard barometric pressure of 1,000 mbar

The OTE refers specifically to the percentage of the mass of O_2 within the supplied air that is dissolved into the test water. The OTE can be further standardised to conditions of 20 °C water temperature and 1,000 mbar when the assumed starting DO concentration is 0 mg L^{-1}, to reveal SOTE which can be determined following Eq. 5.4 as follows (Stenstrom et al., 2006):

$$SOTE = SOTR \div W_{02} \tag{5.4}$$

where:

SOTE = standard oxygen transfer efficiency as a fraction,
W_{02} = the mass flow of oxygen in the air stream, kg s^{-1}

Two-way ANOVA and Tukey's-b tests were used to test for significant effects of the total media depth and airflow rate on OTE using IBM SPSS statistics 20 software. Significant effects were accepted at p=<0.05 for each test.

5.3. Results

Table 5.4 reports water quality characterises related to the potable water used during SOTE tests within the experimental columns. The mean water temperature recorded during tests one to twelve was 10.2 ± 1.3 °C and ranged from 9.2 ± 0.9 °C to 12.2 ± 0.5 °C (Table 5.3). The potable water used during testing was saturated with DO prior to testing, with mean DO concentrations of 12.2 ± 1.1 mg L^{-1} ranging from 10.8 ± 0.2 mg L^{-1} to 14.3 ± 4.2 mg L^{-1}. The test water was slightly alkaline prior to all tests, with a mean pH of 9.14 ± 0.32 ranging from pH 8.51 ± 0.21 in test one to pH 9.64 ± 2.14 in test two. The TDS concentrations were well within the ASCE standard specified test limits of 2,000 mg L^{-1} (ASCE, 2007), with mean concentrations of 67.3 ± 5.0 mg L^{-1} ranging from 58.5 ± 21.3 mg L^{-1} in test nine to 73.9 ± 7.8 mg L^{-1} in test eight. The mean barometric pressure prior to testing was 1,004 ± 11 mbar ranging from 979 ± 31 to 1,019 ± 0.3 mbar. Overall, the water quality characteristics within the test water were relatively constant throughout all 12 tests.

Table 5.4.
Summary of potable water characteristics recorded prior to the start of standard oxygen transfer efficiency (SOTE) tests one to twelve in media-filled columns (see Table 5.3). n = 3 for each test

Test No.	Temperature (^oC)	Dissolved oxygen (mg L^{-1})	pH	Total dissolved solids (mg L^{-1})	Barometric pressure (mbar)
1	12.2 ± 0.5	10.8 ± 0.2	8.51 ± 0.21	67.7 ± 2.6	1001 ± 4
2	11.5 ± 1.3	11.5 ± 0.3	9.64 ± 2.14	59.3 ± 3.2	1019 ± 0.4
3	9.6 ± 0.3	12.1 ± 0.4	8.99 ± 0.06	65.2 ± 3.8	1015 ± 3
4	10.3 ± 0.9	11.5 ± 0.1	8.81 ± 0.33	69.3 ± 9.9	1012 ± 2
5	10.7 ± 1.3	12.1 ± 0.6	9.16 ± 0.15	69.7 ± 5.2	1005 ± 8
6	9.7 ± 0.1	11.8 ± 0.4	9.22 ± 0.07	66.6 ± 3.7	1001 ± 0.7
7	9.2 ± 0.9	14.3 ± 4.2	9.01 ± 0.27	70.2 ± 4.8	994 ± 4
8	7.9 ± 0.9	12.0 ± 0.4	9.06 ± 0.30	73.9 ± 7.8	979 ± 31
9	9.0 ± 0.7	12.5 ± 0.6	9.57 ± 0.25	58.5 ± 21.3	1003 ± 0.9
10	9.7 ± 0.5	14.3 ± 3.1	9.37 ± 0.45	66.4 ± 4.7	1004 ± 2
11	11.8 ± 0.1	11.5 ± 0.2	9.21 ± 0.22	73.6 ± 1.7	997 ± 1
12	11.0 ± 1.4	11.7 ± 0.3	8.99 ± 1.84	71.1 ± 5.2	1015 ± 2
Mean	**10.2 ± 1.3**	**12.2 ± 1.1**	**9.13 ± 0.31**	**67.6 ± 4.9**	**1004 ± 11**

5.3.1. Effect of Media and Total Media Depth on Bubble Frequency and Bubble Diameter

Observations revealed that media presence or absence had a significant effect on bubble frequency (F(1,16) = 147, MSE = 1,380,001, p=≤.0001), with Tukey's HSD test revealing that a higher frequency of bubbles were observed at the surface of columns that were not filled with media compared to columns that were media-filled (Fig. 5.5a). For example, in media-filled columns, mean bubble frequencies were 242 ± 28, 244 ± 22, 237 ± 42 and 89 ± 11 at total column depths of 1,500 mm, 2,000 mm, 2,500 mm and 3,000 mm, compared to 831 ± 185, 661 ± 121, 655 ± 122 and 583 ± 91 respectively within columns of the same total depth but containing no media. The total column depth did not have a significant effect on bubble frequency in columns that were not filled with media, although a significant effect of column depth on bubble frequency was observed within media-filled columns (F(3,16) = 4.31, MSE = 40,518, p=.021). Post-hoc Tukey's HSD tests revealed that the bubble frequency increased significantly in media-filled columns with a total media depth of 3,000 mm in comparison to columns with total media depths of 1,500 mm, 2,000 mm or 2,500 mm which were not significantly different from one another.

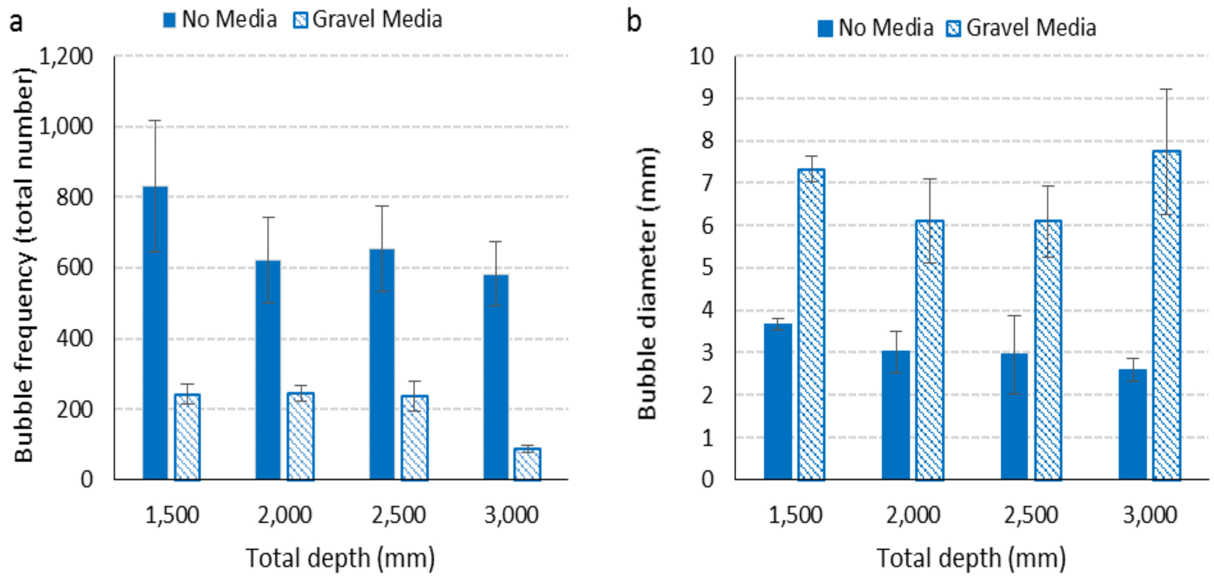


Figure 5.5. Results of tests to establish: a) bubble frequency; and b) bubble diameter within total column depths of 1,500 mm to 3,000 mm containing no media or gravel media respectively and aerated at 10 L min^{-1}. All tests were conducted in potable water and observations were made at the upper surface of each column. Columns represent the mean result for each column depth and error bars represent ± 1 standard deviation of the mean (n = 3).

No significant effect of total column depth on bubble diameter was observed in columns containing no media or in media-filled columns. Further, no significant effect on bubble dimeter was exerted by the interaction between column depth and media presence. However, the presence or absence of media had a significant effect on bubble diameter ($F(1,16) = 149$, $MSE = 84.86$, p=≤.0001). Post-hoc Tukey's HSD tests revealed that significantly smaller bubble diameters were observed in columns containing no media compared to media-filled columns, across the four column depths evaluated within tests one to twelve. For example, the mean bubble diameter was 3.1 ± 0.5 mm in tests where no media was present, ranging from 2.6 ± 0.3 mm to 3.7 ± 0.1 mm, in contrast to a mean of 6.8 ± 0.8 mm ranging from 6.1 ± 0.8 mm to 7.7 ± 1.5 mm in media-filled columns (Fig 5.5b).

Columns containing no media were characterised by a higher frequency and percentage of smaller bubbles, with 86 %, 94 %, 94 % and 95 % of bubbles having diameters of <5 mm in total column depths of 1,500 mm, 2,000 mm, 2,500 mm and 3,000 mm respectively (Fig. 5.6a). In contrast, media-filled columns were characterised by a much lower frequency of small bubbles, both in absolute and in relative terms. Compared to columns containing no media, a wider range of bubble diameters was also observed in media-filled columns, with 39 %, 55 %, 54 % and 30 % having bubble diameters of <5 mm and 49 %, 33 %, 34 % and 53 % within the 6 mm to 10 mm bubble diameter range in total gravel media depths of 1,500 mm, 2,000 mm, 2,500 mm and 3,000 mm respectively (Fig 5.6b). Overall, the maximum bubble diameter observed at the upper surface of the media-filled columns was 42 mm, which was 75 % larger than the maximum bubble diameter observed in columns without media (24 mm). The extent of the impact of media presence on bubble frequency is indicated by the difference between Fig. 5.6a and Fig. 5.6b in terms of y-axes scales, where media-filled columns have a considerably smaller frequency range than observed within columns containing no media. Further, the effect on bubble diameter is illustrated by the distribution of data on the x-axis where media-filled columns have a considerably greater distribution range than reported for columns containing no media.

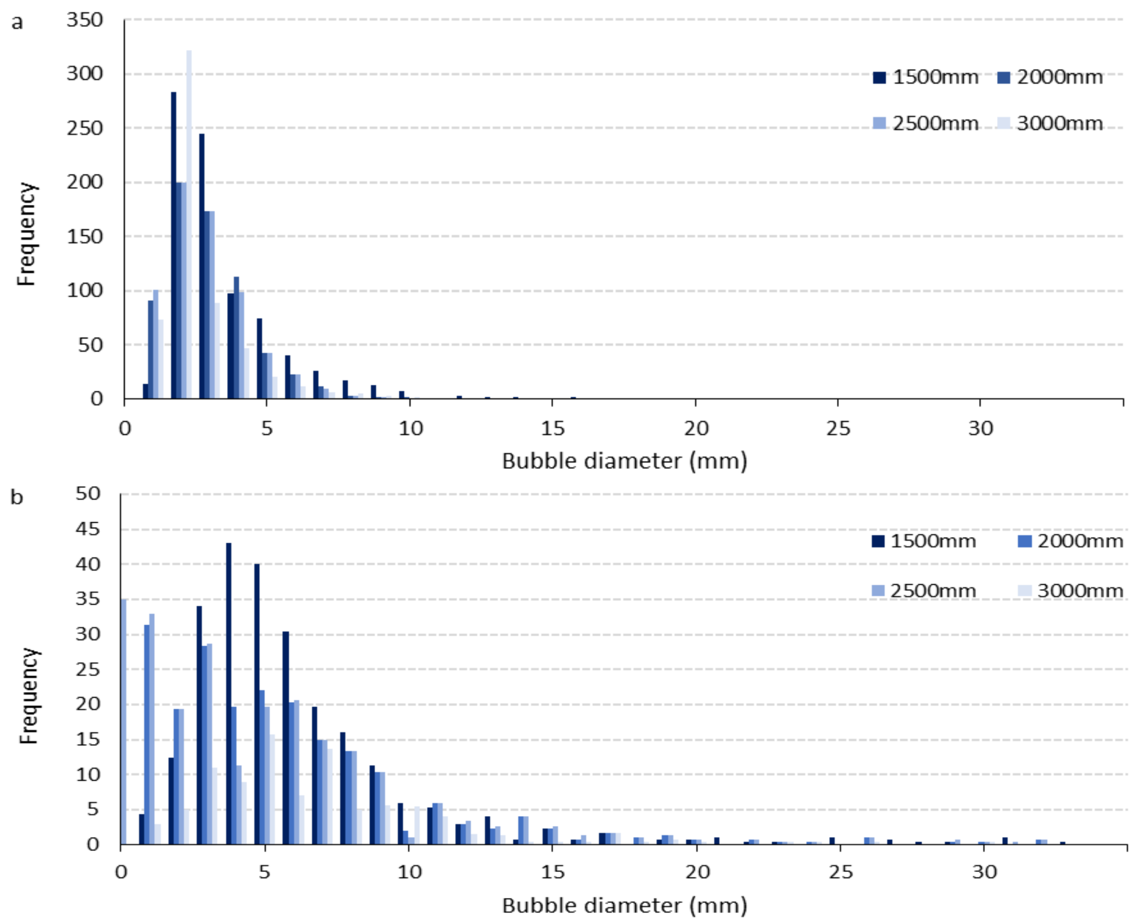


Figure 5.6. Bubble diameter frequency in: a) non-media columns; and (b) media-filled columns when aerated at 10 L min^{-1} in total column depths of 1,500 mm to 3,000 mm. Bars represent the mean, where n = 3 for each individual test.

5.3.2. Dissolved Oxygen Profiles during Standard Oxygen Transfer Efficiency Tests

The deoxygenation process through purging columns with nitrogen gas led to a declining DO concentration of < 0.5 mg L^{-1} DO within the test water of all tests. Following deoxygenation, the DO concentrations typically increased exponentially during the re-aeration process until DO saturation was reached at between 10 mg L^{-1} to 14 mg L^{-1}, or until the test was ended. Occasionally during testing, one or two of the four DO probes failed to respond during the re-aeration process and therefore saturation was not recorded at these sample locations, resulting in a test ending before all four of the probes had recorded steady-state DO saturation. This issue was assumed to be an instrument error and therefore the relevant DO profiles were omitted from the final results. The DO profiles for tests one to twelve presented in Table 5.3 are reported in Fig. 5.7 to Fig. 5.10. Three replicates for each of the twelve tests are presented as opposed to mean results, in order to illustrate the DO profiles used to determine the SOTE using the non-linear regression model, as discussed within Section 5.2.5.

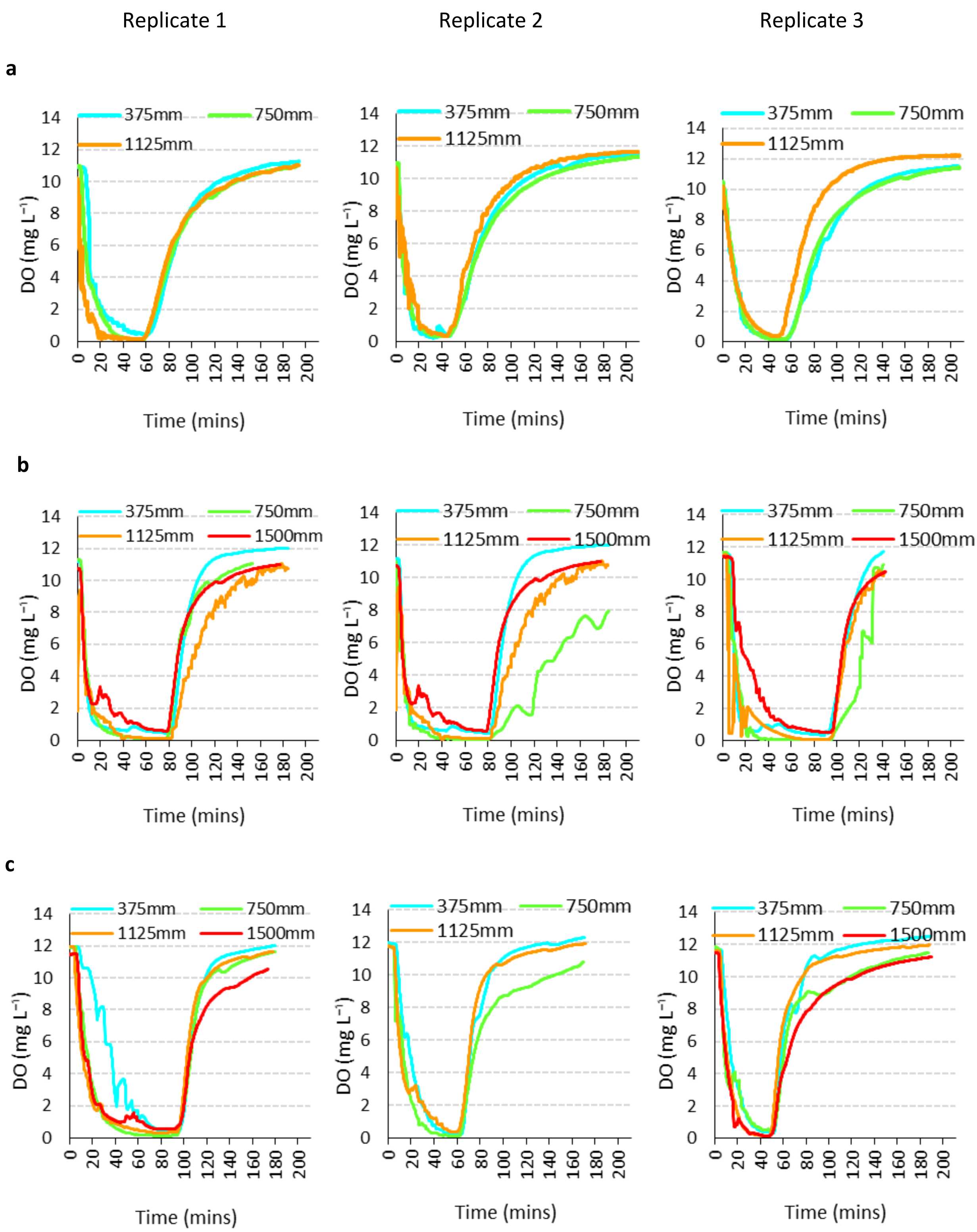


Figure 5.7. Dissolved oxygen profiles for tests conducted in 1,500 mm media-filled columns with sample locations at elevations, from the base of the column, of 375 mm, 750 mm, 1,125 mm and 1,500 mm and at airflow rates of (a) 1 L m^{-1}, (b) 2 L min^{-1} and (c) 3 L min^{-1} with each airflow rate tested in triplicate. Dissolved oxygen profiles have been omitted from the 1,500 mm sample location during 1 L min $^{-1}$ tests and from replicate two during 3 L min^{-1} test due to issues with the DO probe and the data retrieved at the time of testing.

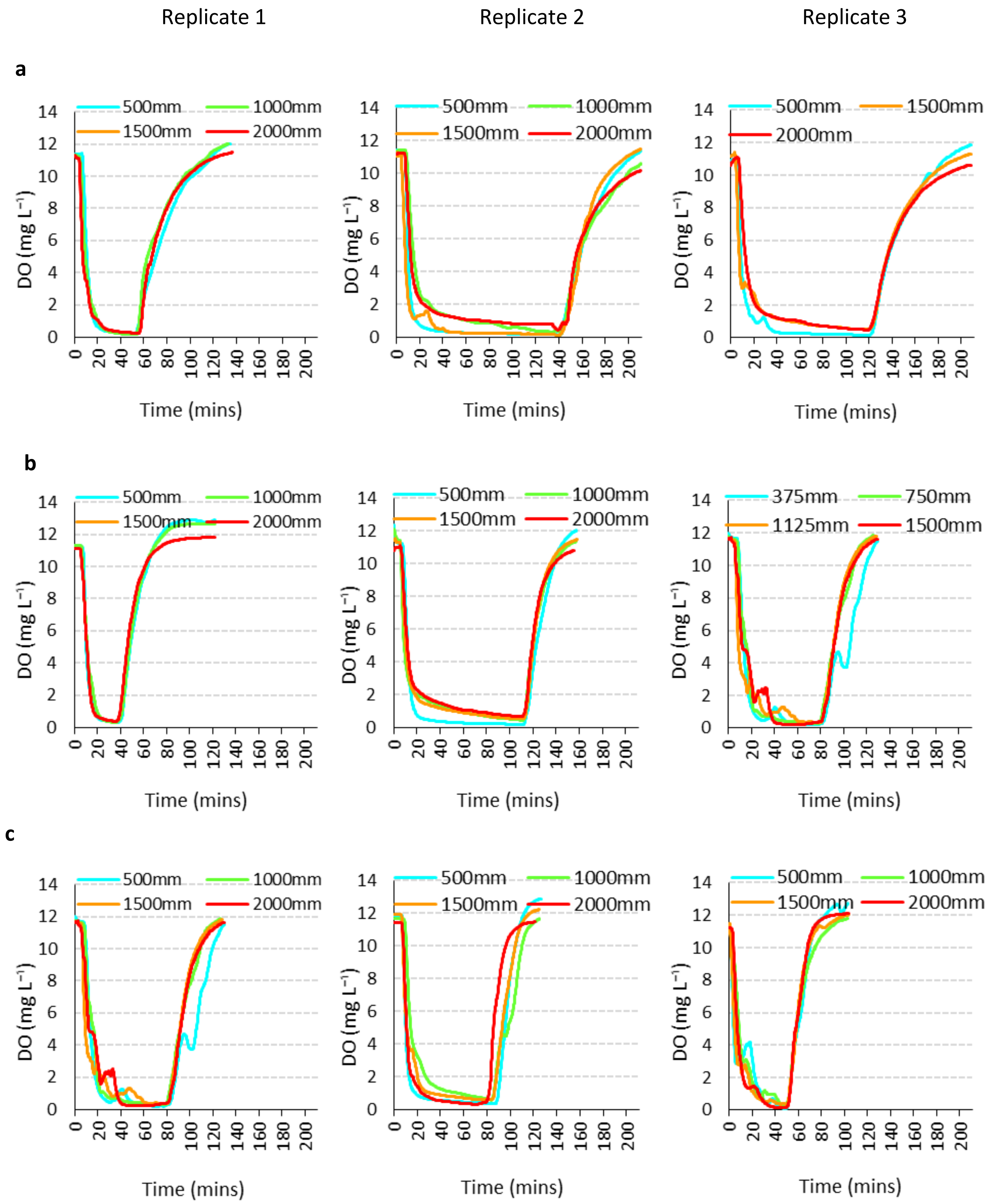


Figure 5.8. Dissolved oxygen profiles for tests conducted in 2,000 mm media-filled columns with sample locations at elevations, from the base of the column, of 500 mm, 1,000 mm, 1,500 mm and 2,000 mm and at airflow rates of (a) 1 L m^{-1}, (b) 2 L min^{-1} and (c) 3 L min^{-1} with each airflow rate tested in triplicate. Results from the 1,000 mm sample location have been omitted from replicate 3 of the 1 L min $^{-1}$ tests due to issues with the DO probe and the data retrieved at the time of testing.

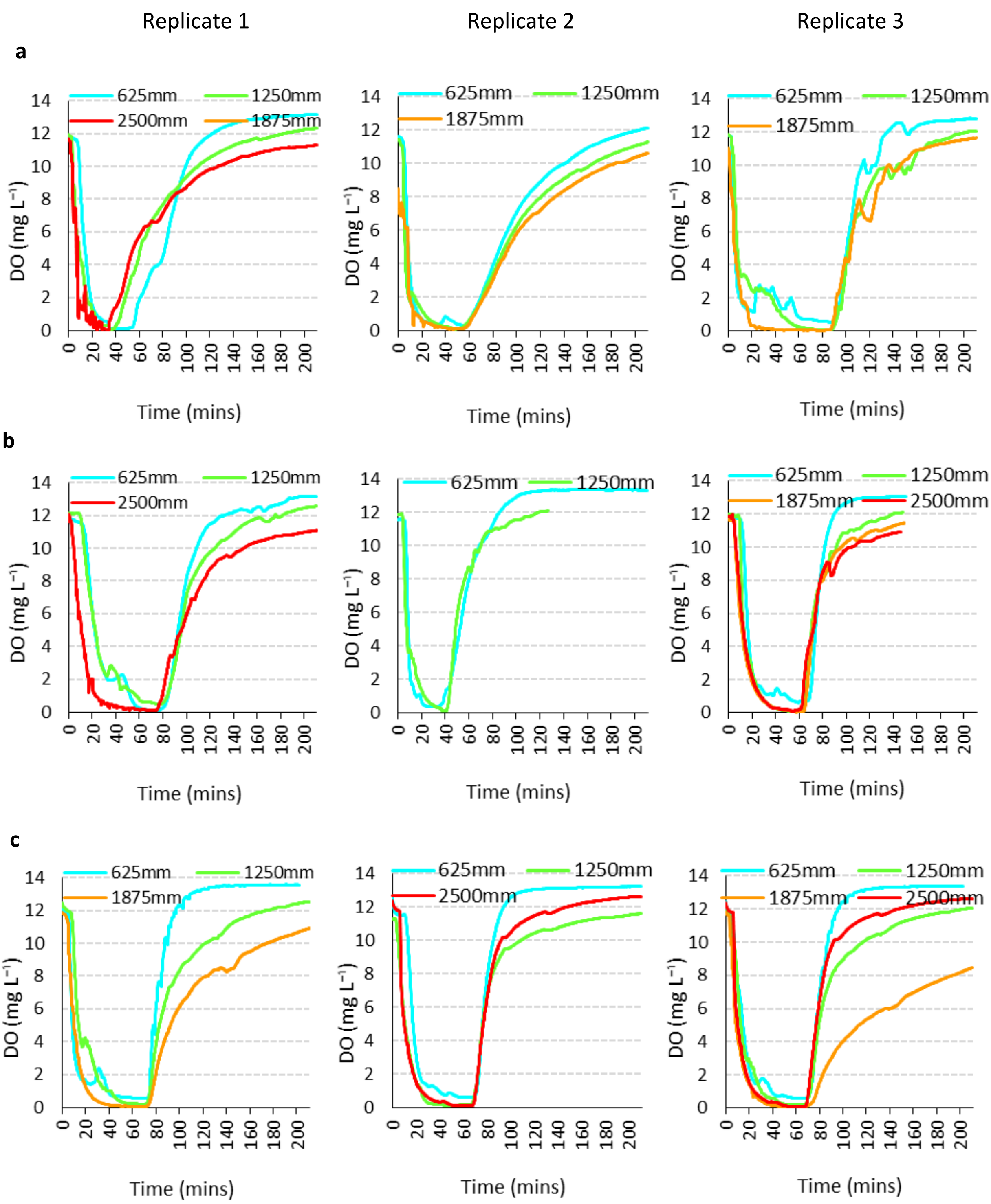


Figure 5.9. Dissolved oxygen profiles for tests conducted in 2,500 mm media-filled columns with sample locations, at elevations from the base of the column, of 625 mm, 1,250 mm, 1,875 mm and 2,500 mm and at airflow rates of (a) 1 L m^{-1}, (b) 2 L min^{-1} and (c) 3 L min^{-1} with each airflow rate tested in triplicate. Results from the 2,500 mm sample location have been omitted from replicate two and three of the 1 L min $^{-1}$ tests, sample locations 1,875 mm have been omitted from replicate one of the 2 L min^{-1} along with sample locations 1,875 mm and 2,500 mm from replicate two of the 2 L min^{-1} tests and sample locations 2,500 mm and 1,875 mm have been omitted from replicates one and two respectively during 3 L min^{-1} tests due to issues with the DO probe and the data retrieved at the time of testing.

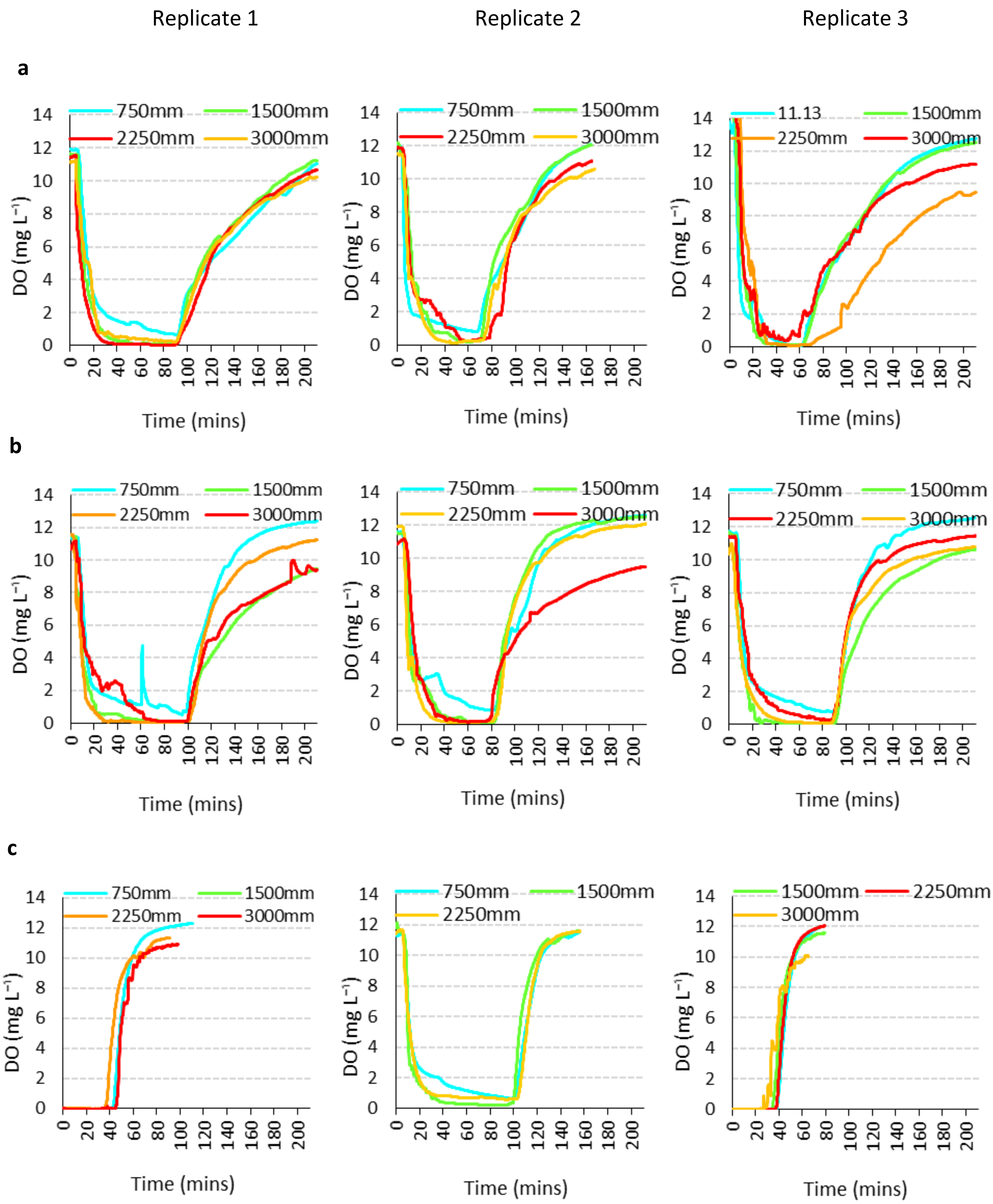


Figure 5.10. Dissolved oxygen profiles for tests conducted in 3,000 mm media-filled columns with sample locations at elevations, from the base of the column, of 725 mm, 1,500 mm, 2,250 mm and 3,000 mm and at airflow rates of (a) 1 L m^{-1}, (b) 2 L min^{-1} and (c) 3 L min^{-1} with each airflow rate tested in triplicate. Results from the 1,500 mm sample location have been omitted from replicate one, along with the 3,000 mm sample location from replicate two and 750 mm sample location of the 3 L min $^{-1}$ tests due to issues with the DO probe and the data retrieved at the time of testing.

5.3.3. Effect of Media Depth and Airflow Rate on Standard Oxygen Transfer Efficiency

Airflow rate had a significant effect on SOTE ($F(2,24) = 28.13$, $MSE = 14.10$, p=≤.0001). However, the effect of media depth on SOTE was not significant, nor was there a significant interaction effect between airflow rate and media depth. Post-hoc Tukey's HSD test revealed that airflow rates of 1 L min^{-1} resulted in significantly higher SOTEs compared to SOTEs observed under airflow rates of 3 L min^{-1}, with no significant difference compared to SOTEs at 2 L min^{-1} and no significant difference between SOTEs at airflow rates of 2 L min^{-1} compared to 3 L min^{-1}. Whilst there was no significant effect of media depth on SOTE, a clear trend in the data was observed with increasing media depth resulting in an increased SOTE for each of the three airflow rates tested (Fig. 5.11). For example, mean SOTE expressed as a percentage increased from 2.42 ± 0.10 %, 3.49 ± 0.29 %, 4.20 ± 0.84 % and 4.90 ± 0.74 % across 1,500 mm, 2,000 mm, 2,500 mm and 3,000 mm deep gravel columns respectively, when aerated at a rate of 1 L min^{-1}. Whilst SOTE results reported within this chapter are limited to media-filled columns only, results for SOTE for comparable standard experiments but in systems containing no media have been reported previously within the literature and have been used as a benchmark against which to compare the media-filled SOTE data, as discussed in detail within Section 5.5.2.

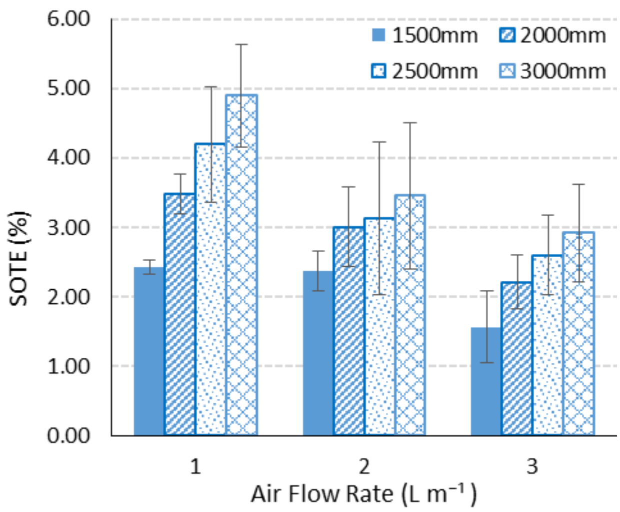


Figure 5.11. Standard oxygen transfer efficiency in gravel columns of 1,500 mm to 3,000 mm at airflow rates of 1 L min^{-1} to 3 L min^{-1}. Bars represent the mean standard oxygen transfer efficiency for each depth and each airflow rate, where n = 3 for each test. Error bars represent ± 1 standard deviation of the mean.

5.4. Discussion

The data reported within this chapter illustrates the importance of design criteria, including depth and airflow rate, on SOTE and therefore on the performance, cost-effectiveness and sustainability of media-filled systems, such as aerated wetlands. The research presented within this chapter supports the hypothesis that, by altering media depth and airflow rate, SOTE can be increased within aerated wetlands. It was shown that low airflow rates of 1 L min^{-1} compared to either 2 L min^{-1} or 3 L min^{-1} significantly increased SOTE in media-filled columns. Further, SOTE was shown to increase consistently with media depth, although the effect of media depth on SOTE was not statistically significant. Further, it was established that media presence had a significant effect on bubble frequency and diameter, with media-filled columns being associated with significantly fewer, although significantly larger diameter bubbles compared to columns containing no media.

5.4.1. Impact of Media on Bubble Frequency and Bubble Diameter

Research reported within this chapter demonstrates that bubble frequency decreases significantly in media-filled columns in comparison to columns containing no media for a given airflow rate (Fig. 5.5a), suggesting that bubble coalescence is a major issue within media-filled systems. In media-filled systems, the ascent pathways for O_2 bubbles are severely limited due to the presence of the media (Fig. 5.12). This results in preferential pathways and increased contact between individual bubbles, in comparison to open water systems (Fujie et al., 1992, Collingnon, 2006). Further, bubble velocity in media-filled systems is reduced by up to 2.5 times that of systems containing no media, as a result of bubble holdup within the pore space of the media (Fujie et al., 1992, Butterworth et al., 2013). This presumably results in newly formed bubbles becoming temporarily attached to or suspended within the media pore space until their buoyancy force or water flux forces causes them to move (Kellner et al., 2005). Subsequently, additional gas enters the same pore space, leading to bubble coalescence and to bubbles growing to a diameter whereby the buoyancy force exceeds the frictional drag forces exerted by the media surfaces, within the geometry of the media pore space. This mechanism can be seen within the results presented Fig. 5.5b, in which bubble diameter is significantly higher in the media-filled columns compared to the columns containing no media and in Fig. 5.6b where media-filled columns were characterised by lower overall bubble frequency and a wider distribution of bubble diameters, compared to columns containing no media. Previous research conducted in saturated peat soils suggested that if gas bubble diameters are smaller than the pore size, then bubbles would respond to water pressure changes as if they were in free water and therefore bubble holdup would not be expected (Kellner et al., 2005). In contrast, bubbles that coalesce and grow to sizes approaching the pore size become entrapped within saturated peat soils, resulting in significant bubble holdup which can block water flow and affect hydraulic conductivity (*k*) (Kellner et al., 2005). For example, a significant relationship between gas bubble coalescence and *k* has been observed within poorly decomposed peat soils (Beckwith and Baird, 2001) and quasi-saturated mineral soils (Faybishenko, 1995), whereby *k* decreased with increasing bubble coalescence as a result of larger bubbles blocking effective pore spaces. Therefore, the occurrence of trapped bubbles within saturated media based treatment systems, such as artificially aerated wetlands, could accelerate pore space clogging mechanisms through a reduction of *k*, increased sediment settling and enhanced biomass production due to enhanced availability of O_2 within pore spaces. These effects would adversely impact the hydraulic and pollutant removal efficiency of a treatment system. However, it is assumed that trapped bubbles are less of an issue for *k* within artificially aerated wetlands, due to relatively larger pore sizes compared with peat soils. The larger pore space would allow smaller bubbles to pass, have higher water through-flow rates and result in a greater mixing throughout the system resulting from additional pressures created by the delivery of air into the system, as opposed to conditions of natural gas formation within peat soils.

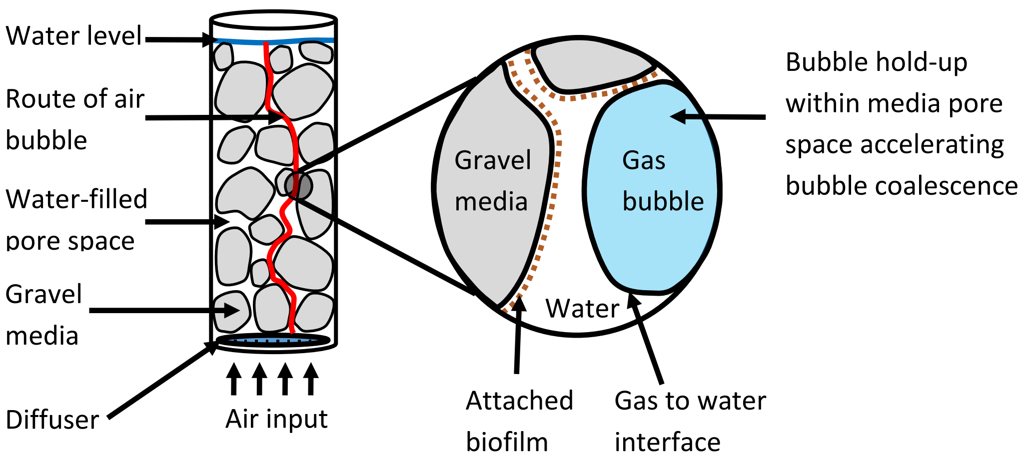


Figure 5.12. Conceptual diagram of bubble behaviour within the pore space of saturated media-filled systems. Adapted from (Butterworth et al., 2013).

5.4.2. Impact of Media Depth and Airflow Rate on Standard Oxygen Transfer Efficiency

Overall, the SOTE results for the media-filled columns within this chapter are below those reported for similar studies assessing SOTE in experimental systems containing no media, thereby representing conventional open water treatment processes such as activated sludge systems and aerated lagoons. For instance, mean SOTEs of 2.42 % and 4.90 % were observed within total media depths of 1,500 mm and 3,000mm respectively in 220 mm internal diameter experimental columns containing 10 mm to 20 mm angular limestone gravel of 34.75 % porosity during this study when aerated at 1 L min^{-1}. In contrast, previous research conducted in comparable experimental conditions consisting of 220 mm internal diameter columns containing no media and operating under air flow rates of 1 L min^{-1} reported SOTE results of 15.53 ± 0.12 % and 30.03 ± 0.51 % at depths of 1,500 mm and 3,000 mm respectively (Stenstrom, 2001) (Fig. 5.13).

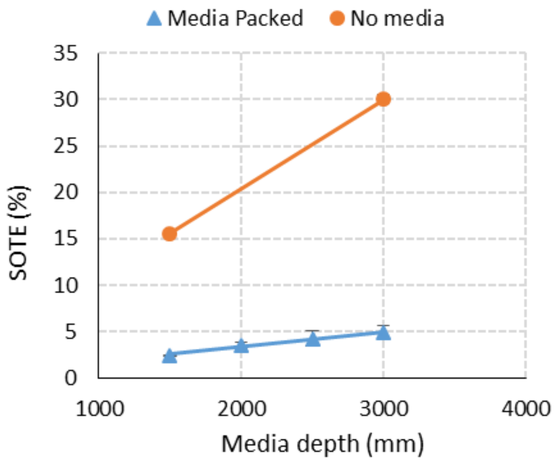


Figure 5.13. Comparison of standard oxygen transfer efficiency (SOTE) in experimental columns filled with media and containing no media, when aerated at 1 L min^{-1}. Columns of 220 mm internal diameter containing media were filled with 10mm to 20 mm angular limestone gravel media of 34.74 % porosity and are indicated by the triangle shaped blue data points. Results of 220 mm internal diameter columns containing no media are reported in previous research undertaken by (Stenstrom, 2001) and are indicated by circle shaped orange data points.

The reduction of SOTE in media-filled systems compared to systems containing no media is likely a function of the reduced ratio between bubble surface area and aeration volume, induced by larger bubble diameters due to the media presence resulting in greater bubble coalescence. This subsequently results in a reduced gas to water interfacial area within media-filled systems compared to open water systems, as discussed previously in Section 5.5.1. Although higher SOTEs are possible in open water systems, media-filled systems are often a more appropriate treatment solution for treating de-icer contaminated runoff from airports due to several other influencing factors. For instance, media-filled systems such as aerated wetlands typically benefit from below ground construction reducing bird strike risks at airports. Further, aerated wetlands offer reduced complexity and mechanical moving parts, low operating and maintenance costs and high resistance to temperature fluctuations for treatment of winter runoff in contrast to other treatment technologies. The presence of media also serves to provide a more stable microbial population due to the increased surface area provided by the media, which contributes to a more consistent pollutant removal and lower final effluent concentrations compared to conventional open water treatment systems such as activated sludge systems (Wallace, 2000, Wallace and Liner, 2011b, Freeman et al., 2015) (Table 2.4).

The effect of depth on SOTE in media-filled columns was not significant in this chapter, despite the mean SOTE increasing from 2.42 % to 4.90 %, 2.37 % to 3.45 % and 1.56 % to 2.92 % when column depth increased from 1,500 mm to 3,000 mm, for airflow rates of 1 L min^{-1}, 2 L min^{-1} and 3 L min^{-1} respectively (Fig. 5.9). Despite this statistical result, a clear trend was observed whereby SOTE more than doubled from 2.42 % to 4.90 % when column depth increased from 1,500 mm to 3,000 mm at airflow rates of 1 L min^{-1}. A very limited number of studies comparable to the results presented within chapter 5 have reported the effect of depth on SOTEs in media-filled systems. The increasing SOTE with depth trend reported in this chapter however generally concurs with the results of previous studies undertaken in open water systems which have reported significant increases in SOTE from 4.0 % to 4.6 %, under low water depths when a total diffuser depth increased from 0.24 m to 0.32 m within a laboratory-scale column of 240 mm internal diameter operating under airflow rates of 1.6 L min^{-1} (Zhen et al., 2003). Similar findings were observed during laboratory tests conducted within 300 mm internal diameter columns characterised by low water depths and air flow rates of 1 L min^{-1}, whereby SOTE increased from 3.9 % to 4.2 % when depth increased from 0.45 m to 0.60 m (Atta et al., 2011). Further, increased SOTEs, from 5.2 % to 7.9 %, were reported when depth increased from 1.5 m to 2.9 m in an open water pilot-scale system containing a full lift aerator, with diffuser orifice diameters of 0.14 mm and operating under airflow rates of 10 L min^{-1} (Ashley et al., 2008). Further, SOTE was reported to increase significantly from 1.8 % to 11.5 % when depths increased from 0.40 m within an experimental scale open water tank to 4.6 m within a full-scale activated sludge system (Al-Ahmady, 2006).

Manufacturers of diffusers typically provide performance estimates based on tank tests of three to five meters depth, which represents the depth of typical full-scale treatment systems (DeMoyer et al., 2003). However, reed beds and constructed wetlands are typically designed with relatively shallow depths, ranging from 300 mm to 1,200 mm, based on the principles of the vegetation root zone method, whereby the shallow depth improves the contact between the rhizosphere which delivers O_2 into the system and the effluent flowing through the system (Conley et al., 1991). In contrast, artificially aerated wetlands designed to treat de-icer contaminated runoff from airports are typically constructed between 900 mm to 1,500 mm deep, as these systems rely less on the drawdown of atmospheric O_2 through reeds and more on the SOTE of artificial aeration devices. For instance, the artificially aerated wetland at Buffalo Airport in the USA has been constructed with a

1,500 mm deep media fill (Wallace and Liner, 2011a, Higgins et al., 2010), with similar depths of 1,100 mm and 900 mm used within the upgraded designs of the Heathrow Airport system in the UK (Murphy et al., 2014) and the Edmonton Airport system in Canada. The results reported in this chapter, whereby SOTE more than doubled from 2.4 % to 4.9 % when media depth increased from 1,500 mm to 3,000 mm, suggest that a more efficient, cost-effective and sustainable operation could be achieved through increasing the media depth within existing and future artificially aerated wetland designs. Despite this, there remains several challenges to constructing artificially aerated wetlands at depths of up to 3,000 mm, including increased construction costs resulting from additional excavation and disposal costs where the excavated material cannot be reused on-site, health and safety issues surrounding the structural stability of excavations (HSE, 2016) and potential issues with groundwater levels which could create pressure below the system potentially damaging the impermeable liner. The additional health and safety and design issues of increasing aerated wetland depths from 1,500 mm to 3,000 mm would substantially increase capital costs therefore reducing the economic feasibility of implementing an artificially aerated wetland. Increasing the media depth to 2,000 mm would be a more achievable prospect without significantly incurring escalating capital costs associated with deeper excavations. This is further justified by the results presented in this chapter, whereby a 44 % increase of SOTE from 2.4 % to 3.5 % was observed when media depth increased from 1,500 mm to 2,000 mm at airflow rates of 1 L min^{-1}.

The experimental results reported within Section 5.4.3 and Section 5.4.4, suggest that airflow rate was one of the main factors affecting SOTE in media-filled columns. For example, SOTE decreased from 2.4 % to 1.6 % when airflow rates increased from 1 L min^{-1} to 3 L min^{-1}. The SOTE response to increasing airflow rate reported here is consistent with previous results reported for both media-filled and open water diffused aeration systems (Schmit et al., 1978, Butterworth et al., 2013, Ashley et al., 2008). For example, when airflow rates were increased from 0.4 L min^{-1} to 2.3 L min^{-1}, SOTE was reported to decrease from 23.6 % to 18.3 % within a full-scale oxidation ditch system located Milly la Forêt wastewater treatment plant in France and operating under extended aeration configuration. Further, SOTE decreased from 8.9 % to 7.1 % in a 1,500 mm deep system and 4.5 % to 6.0 % in a 2,900 mm system when airflow rates increased from 10 L min^{-1} to 40 L min^{-1} within an open water pilot-scale tank (Ashley et al., 2008). Airflow rate is known to influence the fluid dynamics of bubbles within open water systems whereby larger bubbles are produced when the airflow rate per orifice or diffuser is increased. This subsequently results in reduced bubble surface area and increased bubble rise velocity, with a net result of a smaller gas to water surface interfacial area and reduced bubble retention time and therefore reduced mass transfer of O_2 (Gillot and Héduit, 2000, Henze et al., 2008). The bubble terminal velocity also increases in line with bubble diameter, resulting in reduced bubble retention time within the liquid (Ashley et al., 2008). Further, bubbles are known to form more slowly at lower airflow rates in viscous liquids (Davidson and Schüler, 1997), presumably resulting in greater O_2 transfer during the formation of each individual bubble at the diffuser or orifice location (Ashley et al., 1991, Gillot and Héduit, 2000). There is also a greater distribution of bubbles released from the diffuser orifice under low airflow rates, resulting in a greater vertical distribution between bubbles rising through the water column. This serves to reduce bubbles coming into contact with one another in open water systems therefore reducing bubble coalescence (Ashley et al., 1991, Gillot and Héduit, 2000, Butterworth et al., 2013), although this maybe of less importance in media-filled systems where bubble holdup within the media pore space propagates bubble coalescence (Fujie et al., 1992, Collingnon, 2006, Butterworth et al., 2013). In practice, much higher airflow rates than would be practical to test within the experimental columns are used within full-scale treatment systems such as aerated wetlands, in order to ensure sufficient supply of O_2 to meet the BOD_5 of the influent, prevent biological fouling of diffusers, promote mixing and keep biological solids in suspension (Ashley et al., 1991). For example, airflow rates delivered to full-scale aerated wetlands are often within the range of 1.8 $m^3\ m^{-1}$ to 140 $m^3\ m^{-1}$ (Nivala et al., 2007, Envirodynamics Consulting, 2012). Despite the reality of higher air flow rates in full-scale systems, the results reported within this chapter nevertheless provide an important reference to the design of media-filled treatment systems such as aerated wetlands. For instance, when designing aerated treatment systems, the design BOD_5 load is typically predetermined through water quality monitoring programs providing the critical information needed to determine the required SOTE to meet the influent demand. Once this has been determined, the SOTE per day per unit volume of the aerated system becomes fixed and therefore can be readily calculated and scaled according to the depths tested (Al-Ahmady, 2006), knowing that 1 – 1.5 kg O_2 per kg BOD_5 is generally required to achieve efficient reductions of BOD_5 from the influent to final effluent (Henze et al., 2008).

5.5. Conclusion

Energy consumption and sustainability are coming under increasing scrutiny in many modern day operations including wastewater treatment systems. Further, treatment systems within the aviation industry such as artificially aerated wetlands face future challenges resulting from increased pollutant loads within surface water runoff, as a consequence of the increasing de-icer consumption required to meet the increasing demand for air travel and subsequent increasing aircraft movements during winter months (DFT, 2013, Freeman et al., 2015). Therefore the need arises to improve the operating efficiency of aeration devices within artificially aerated wetlands to ensure that optimal

SOTEs are achieved to maximise pollutant removal efficiencies, whilst at the same time minimise treatment costs, therefore improving the economic viability and long term sustainability of aerated wetlands.

The research reported within this chapter supports the hypothesis that SOTE can be increased within aerated wetlands by optimising the total media depth and airflow rates. This is justified firstly as the findings demonstrate that, whilst depth did not impact bubble frequency or bubble diameter, the SOTE can be increased within artificially aerated wetlands by increasing the media fill depth. Whilst the variation of SOTE with depth reported here was not statistically significant, SOTE was observed to more than double from 2.4 % to 4.9 % when the media fill depth increased from typical aerated wetland depths of 1,500 mm to 3,000 mm, although health and safety and design issues would significantly increase capital costs having a negative impact on the economic feasibility of implementing a system with a 3,000 mm depth. The results presented within this chapter would therefore suggest that media depths of 2,000 mm would be the optimal depth for aerated wetlands, given practical and economic constraints. However, further work to establish accurate costings for increasing the system depth is recommended as part of the economic feasibility process for any future aerated wetland design, to ensure that optimal designs are produced which maximise SOTE and minimise capital costs. Secondly, SOTE can be increased significantly by reducing the airflow rate being delivered into the system. Clean water tests complying with the ASCE standard (ASCE, 2007) presented here demonstrate that even at low airflow rates of 1 L min^{-1} and 3 L min^{-1}, the mean SOTE increases from 2.2 % to 3.5 %. Further work within any future aerated wetland designs to optimise the airflow rate and establish the O_2 requirements to meet the BOD_5 of the incoming wastewater is also recommended and can be achieved through water quality monitoring programmes such as that presented within Chapter 3.

Chapter 6

Discussion

6.1. Overview

This thesis is primarily concerned with the risks to surface water quality resulting from the specific characteristics of airport operations. In particular, this thesis considers how winter de-icer application, airfield catchment processes and pollutant transport ultimately define the challenge of managing and treating storm runoff from airport catchments. The risk to surface water quality associated with discharges of wastewater from airports is currently one of the key environmental challenges facing the aviation industry and is likely to remain so in the future (Turnbull and Bevan, 1995, Koryak et al., 1998, Ramakrishna and Viraraghavan, 2005, Corsi et al., 2009, Sulej et al., 2011a, Sulej et al., 2012a, Freeman et al., 2015). The thesis addresses this globally-relevant challenge through research and development of a novel, low cost and sustainable treatment strategy for de-icer contaminated storm runoff from airport catchments. This final chapter seeks to summarise and interpret the key findings reported throughout the thesis, describing how the results address the aims, objectives and hypotheses set out within Section 1.2. Further, this chapter places the findings and results of the thesis in the wider context of research and practical treatment options related to storm water runoff from airports, highlighting the relevance of the thesis to the challenges of de-icer management, safeguarding airport water quality and delivering sustainable wastewater treatment within the aviation industry.

A number of key findings have been presented in the preceding chapters to address the overall aim of the thesis which was 'to improve understanding of de-icer pollutant mobilisation, transport and fate within airport catchments and to develop and test novel, sustainable and low cost treatment systems for contaminated discharges'. Several objectives were established to structure the research within this thesis towards addressing this aim. These research objectives are reported within Section 1.2 and a concise summary of how the key thesis results address each objective is provided below. Further, a discussion of how the key thesis results advance knowledge and understanding within the specific research field of de-icer management and treatment of airport storm runoff is presented.

6.1. Synthesis of Existing Literature and De-icer Management Strategies

Following the introduction to the thesis within Chapter 1, which provided background information and an overview of the research field, Chapter 2 presented a literature review focused on establishing the current state of knowledge regarding de-icer contaminated storm runoff, management strategies and treatment options for this runoff at airports. Chapter 2 considered pertinent literature within the field of de-icer management, pollution control, sustainable aviation, low carbon and low cost sustainable treatment methods for the treatment of de-icer contaminated storm runoff. The literature provided the theoretical basis and framework for the key management issues associated with de-icer application within the aviation industry to be addressed within the thesis. The specific objective of Chapter 2 was to review catchment processes and aerated wetland literature, to improve understanding of the principles, processes and pathways of pollutant transfer to surface water systems, alongside how this ultimately impacts the treatment of airport runoff and the design and operation of treatment systems operating under these conditions.

The material within Chapter 2 led to the definition of gaps in knowledge for new research within the thesis. Chapter 2 highlighted the key water quality parameters of concern within storm runoff discharging from airport catchments contaminated with de-icers. Surrogate measures of de-icers are typically used, with COD, TOC and BOD_5 established as the most common measures of pollution within airport discharges. Chapter 2 reports relationships between the water quality parameters of concern within airport discharges (Fig. 2.4). These relationships address gaps in knowledge by introducing a methodology to improve the interpretation of monitoring data from within airport catchments, whilst also providing the statistical basis for converting real time TOC concentration data into COD or BOD_5 concentrations, the latter parameters being commonly stipulated on environmental permits to discharge. Therefore, these statistical relationships offer the basis for evidence-based management of storm runoff to ensure compliance with regulatory environmental permit to discharge limits.

Chapter 2 also demonstrated that winter operations, de-icer application, climate and catchment process combine in unique ways at individual airports, which has led to a wide range of bespoke DMS and treatment solutions being implemented across the global aviation industry. Despite this, many of the pollutant transport processes within airport catchments are more generally comparable across individual sites. These catchment and pollutant transport processes have been conceptualised to illustrate the key processes and mechanisms responsible for pollutant transfers into surface water systems and to illustrate how these processes are interrelated (Fig. 2.2.). It was established that the key processes and mechanisms for pollutant transfers to surface water systems include transport of de-icer mist droplets via wind during application, dissipation through jet blast and vehicle tracking, deposition on de-icing stands and taxi-ways and shear from aircraft onto runways during take-off. Once de-icers are deposited to ground they become ‘spent’, typically accumulating within a catchment until they are entrained within storm-induced surface water runoff. All of the de-icer applied to pavements and aircraft is ultimately deposited within the airport boundary through the various mechanisms of deposition during application, aircraft taxiing and aircraft take-off. Despite this, biodegradation on de-icing stands (Revitt et al., 2002) and within soils and groundwater (Evans and David, 1974, French et al., 2001, Nunes et al., 2011) typically results in only 2 % to 62 % of the applied pollutant load through de-icer application being measured at airport discharge locations during storm runoff events (Corsi et al., 2006b, ACRP, 2008). This discrepancy, between the loads applied and the loads measured within catchment discharges creates uncertainty regarding the fate of de-icers following application. This uncertainty complicates the management and containment of spent chemical de-icers, which is required to remain compliant with environmental permit to discharge limits for receiving waters. Further, biodegradation processes reduce the persistence of de-icers within the environment (Klecka et al., 1993, Gooden, 1998, Bausmith and Neufeld, 1999a, Jaesche et al., 2006). De-icer additives are however typically more resistant to biodegradation than the main ingredient within de-icer formulations, therefore persisting for longer periods of time and posing a more substantial environmental risk in regards to the contamination of soils and groundwater surrounding airport de-icing locations (Cancilla et al., 1998, Cornell et al., 2000, Cancilla et al., 2003b, Corsi et al., 2003, ACRP, 2008). The processes of biodegradation along with infiltration and percolation of spent de-icers to soil, water and groundwater have been captured within the conceptual model (Fig. 2.2.), to highlight the fate of spent de-icers within self-contained DMS. Further, the extent of pollutant mobilisation and transport is partly regulated by overnight temperatures (which typically determine the volume of de-icer applied) and precipitation events (which generate storm runoff), resulting in the highly variable discharge volumes, pollutant concentrations and pollutant loads typically observed within airport discharges.

Beyond the issues surrounding de-icer mobilisation, transport and fate within airport de-icing catchments, the literature review reported in Chapter 2 also identified several key challenges that face the treatment of de-icer contaminated storm runoff at airports. Firstly, the degree of temporal variability in discharge volume and pollutant concentration results in highly variable pollutant loads within airport discharges. This high temporal variability poses a challenge for microbial communities within biological treatment systems, which typically perform optimally under steady state conditions compared to highly variable conditions (Zhou et al., 2009). Secondly, the issue of high temporal variability of pollutant concentration and pollutant load (Fig. 3.8) has significant implications for the selection, design and sizing of suitable de-icer treatment technologies (ACRP, 2013b). Not all of the commercially-available, conventional treatment technologies identified in Chapter 2 (Table 2.4) have suitable capacity or flexibility to meet the varying treatment demand associated with storm runoff events from airport catchments. This is because many conventional treatment systems, such as rotating biological contactors or submerged aerated filters, have a fixed, compact footprint for convenience of implementation, but are consequently limited in terms of their potential to adapt to peak discharge volumes and pollutant loads during storm runoff events. Other technologies, such as aerated wetlands, have larger footprints which are typically sized to meet the bespoke treatment demands of the specific discharge quality and quantity, therefore providing greater capability to treat peak pollutant loads associated with storm runoff events. Whilst treatment system design and sizing are critical for the treatment of storm runoff from airport catchments, another key challenge that emerges from Chapter 2 is the robust quantification of storm event runoff water quality characteristics and, therefore, treatment requirements which are needed to underpin the treatment system sizing process. Despite the clear importance of determining water quality characteristics and treatment requirements, limited guidelines for monitoring the transport of de-icers across airport catchments and the impact that this ultimately has on surface water quality have been published to date.

Further, Chapter 2 establishes the current state of the art regarding de-icer management and treatment strategies, providing a synthesis of techniques used by airports across the globe to manage de-icer contaminated runoff (Table 2.4). The synthesis improves understanding of how existing treatment systems operate to meet the key challenges posed by storm runoff from airport catchments identified within Chapter 2 and summarised above. This synthesis provides a comparison of the performance, efficiency, pros and cons of each technology, to aid in the decision making process during the selection of the most appropriate technology for a given application. Further, Chapter 2 introduces the theory behind artificially aerated wetlands and provides a state of the art synthesis of the application of this technology for treating de-icer contaminated storm runoff at airports (Table 2.6). This ultimately provides the basis for further research and development of the aerated wetland technology to improve operating efficiency, reduce energy consumption, equivalent CO_2 emissions and operational costs associated with aeration devices and, therefore, to improve the sustainability of aerated wetlands for the treatment of de-icer contaminated storm runoff.

The concluding sections of Chapter 2 establish that sustainable aviation faces significant future challenges in response to expansion and development of airports which is required to meet the forecasted 1 % to 3 % increase in demand for aircraft movements up to 2050 in the UK (DFT, 2003, DFT, 2013), which will result in additional demand for de-icer application. Secondly, global climate change and the forecasted increased rainfall volume and intensity (Murphy et al., 2009, MAG, 2013) is likely to contribute towards increased runoff volumes, thereby placing pressure on existing infrastructure, storm water storage capacity, pollution prevention measures and posing a substantial risk to surrounding water quality and compliance with regulatory limits. In this context, the demand for novel, low cost, low carbon and more sustainable treatment technologies is highly likely to increase within the foreseeable future. To meet this demand, robust methods for monitoring the transport of pollutants from de-icing catchments to surface water systems, such as those established within Chapter 3, are needed to determine treatment requirements. Further, the need to optimise treatment systems such as aerated wetlands is apparent, to provide a more energy efficient, cost-effective, sustainable alternative to existing methods of managing de-icer contaminated runoff, such as the discharge of a trade effluent. The optimisation of aerated wetlands has been addressed within Chapter 4 and Chapter 5. The research priorities emerging from the literature review (Section 2.8) were subsequently used to identify gaps in knowledge for which research objectives were then formulated, forming the basis for the research reported within Chapters 3 to 5.

6.2. Fate, Transport and Water Quality Impacts Resulting from De-icer Application

The objective of Chapter 3 was to evaluate the fate of chemical de-icers following application within airport catchment areas, thereby establishing the risks of water quality degradation due to surface water runoff from airports. This objective was primarily addressed through field work involving a monitoring programme in which water quality data was collected from a catchment discharge location at the case study site of Manchester Airport in the UK. Data reported within Chapter 3 indicate that there is significant scope for storage of spent de-icers within airport catchments during dry weather periods. This was demonstrated by relatively low mean pollutant concentrations, of 222 mg L^{-1} BOD_5 and pollutant loads, of 2.6 kg d^{-1} BOD_5, measured within catchment C discharges at Manchester Airport throughout the 2013/14 and 2014/15 de-icing seasons (Table 3.8), despite significant volumes of de-icer being applied within the catchment area. However, across ten storm runoff events monitored at Manchester Airport during the 2013/14 and 2014/15 de-icing seasons, a mean of 55 % of the applied pollutant load was transported to the catchment discharge location (Table 3.9). Pollutant concentrations during the storm runoff events were typically characterised by a clockwise hysteresis, suggesting that de-icers are mobilised and transported to the catchment discharge location during the early stages of a precipitation event, thereby following the ‘first flush’ storm runoff characteristic (Fig. 3.11 and Fig. 3.12). Subsequently, catchment de-icer pollutant stores typically became depleted through the event, resulting in pollutant concentrations becoming diluted and returning towards typical base-flow concentrations on the falling limb of a storm hydrograph. In contrast to base-flow conditions, peak pollutant concentrations were 7,105 mg L^{-1} BOD_5, with pollutant loads up to 12,342 kg d^{-1} BOD_5, measured at catchment C discharge location, averaging 2,067 kg d^{-1} BOD_5 across the ten storm runoff events that were measured (Table 3.9). These results demonstrate that water quality deteriorates significantly during storm runoff events compared to base-flow conditions, resulting in significantly higher costs of trade effluent disposal during storm event conditions under the current management strategy of discharging a trade effluent to the water company sewer at Manchester Airport. Calculations established that when water quality deteriorated during storm runoff events, daily trade effluent discharge costs from catchment C alone increased from an average of £1,024 to £14,824 during the 2014/15 de-icing season at Manchester Airport (Table 3.11). The data reported within Chapter 3 establish that storm runoff generated by precipitation events is the major driver for the mobilisation and transport of spent de-icers from a de-icing location and into surface water systems. This emphasises the importance of managing and treating storm event runoff, in order to minimise the risks to the environment and particularly to receiving water courses following the potential export of de-icers from airports.

In summary, the results reported within Chapter 3 highlight a number of key challenges associated with managing airport catchment discharges, in particular the high temporal variability and storm event driven characteristics of surface water runoff. These characteristics should inform the design of sustainable management solutions, which Chapter 2 suggested will increasingly be required within the foreseeable future in order to mitigate the impacts of global climate change and the growing demand for air travel. The design of future solutions should therefore be based on robust and high resolution scientific evidence to ensure that they meet the requirements and characteristics of airport catchment discharges. The data reported within Chapter 3 were collected following a systematic methodology and approach for determining de-icer transport and the impact this has on the quality of storm event runoff discharging from airport catchments. Therefore, this chapter also provides an important future reference for practitioners involved in establishing the most appropriate technical and practical treatment solutions to meet the variability associated with event driven systems, such as airport catchments.

One of the most common management techniques for managing storm runoff from airports is to discharge contaminated water to the nearest public sewer as trade effluent (Fig. 6.1a), at a cost which ranges from 45 p m^3 to 82 p m^3 depending on the volume and strength of wastewater discharged (United Utilities, 2016) (Table 4.2). Chapter 3 established that airports have limited control over trade effluent costs, which are determined annually by industry regulators OFWAT in the UK (OFWAT, 2010). Further, the charging model used by water companies to determine trade effluent costs is highly dependent on discharge volume and pollutant concentration. Based on this charging model, the cost of airport discharges is likely to increase significantly within the foreseeable future, alongside increasing discharge volumes and pollutant concentrations that are forecast as a result of global climate change and increased aircraft movements and associated de-icer requirements. In this context, the use of treatment solutions such as aerated wetlands has potential as an alternative management method for airport discharges (Fig. 6.1b). Implementing an on-site treatment technology such as an aerated wetland would serve to reduce the volume and pollutant concentrations discharged as trade effluent, thereby minimising trade effluent costs. Some of the treated effluent would be of sufficient quality to discharge to receiving watercourses within environmental permit limits, further reducing the volume discharged as trade effluent and the associated cost. Typical treatment costs associated with operating aerated wetlands are approximately 17 p m^3, which is equivalent to a 62 % reduction in comparison to the minimum trade effluent costs of 45 p m^3. Research to optimise aerated wetlands for the treatment of airport storm runoff is therefore addressed within Chapter 4 and Chapter 5.

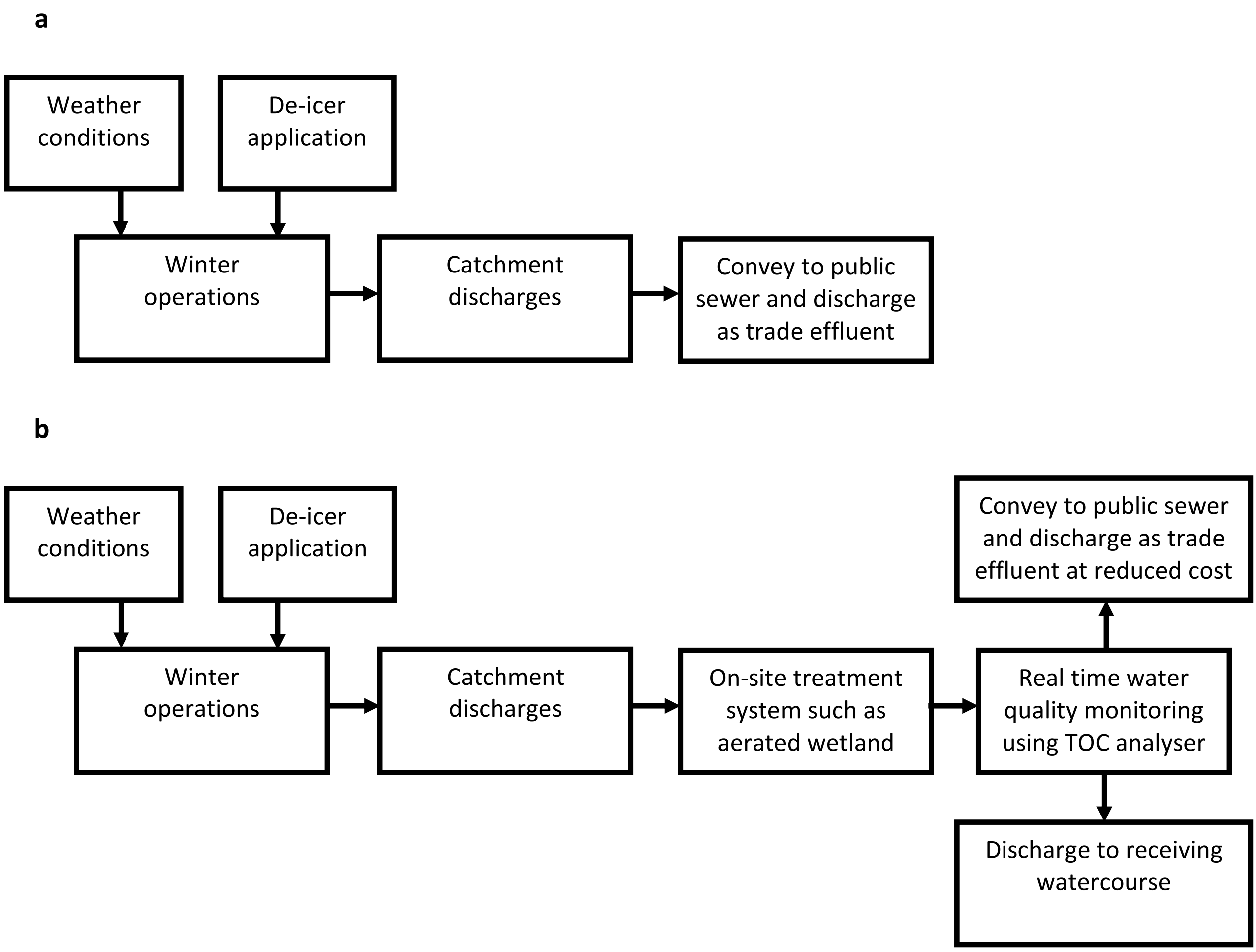


Figure. 6.1. Alternative conceptual methods for managing de-icer contaminated storm runoff, (a) typical de-icer management strategy of discharging contaminated storm runoff to the public sewer as trade effluent for treatment off-site, (b) implementation of on-site treatment system to improve water quality discharges to allow discharge to receiving waters within discharge permit limits or to minimise trade effluent discharge costs.

6.3. Development of Aerated Wetland Technologies for Treating Airport Storm Runoff

In Chapter 4 and Chapter 5, research and development of aerated wetlands for the treatment of de-icer contaminated storm runoff from airports was undertaken, to address a number of the research gaps that emerged from the literature review. Results reported within Chapter 4 are based on pilot-scale tests conducted under field conditions and designed to closely replicate conditions within a full-scale aerated wetland treating de-icer contaminated storm runoff. Further, tests to establish optimal loading rates for aerated wetlands are reported within Chapter 4. Experimental columns results are reported in Chapter 5, which sought to establish optimal design parameters such as media depth and air flow rates for aerated wetlands treating storm water runoff from airports.

6.3.1. Development of Novel Aeration Strategies

Research was undertaken to address the objective of determining the impact of altering aeration configuration on pollutant removal within pilot-scale artificially aerated wetlands, in order to identify novel aeration configurations for incorporation within aerated wetland design. A pilot-scale system located in the field and an experimental methodology were designed to test the hypothesis that the removal efficiency of organic pollutants in aerated wetlands could be improved by altering the spatial distribution of aeration inputs, in order to better match the supply and demand of O_2 throughout the treatment system. In this context, a phased aeration configuration provided up to 15 % greater COD removal efficiency in comparison to the more conventional uniform aeration approach to aerating wetlands and 53 % greater COD removal than the alternative of inlet-only aeration that was also tested (Fig. 6.2). Although the phased aeration approach has been used within other treatment technologies to optimise efficiency and reduce energy consumption, including the activated sludge process (McCarty and Brodersen, 1962), the research reported within Chapter 4 is the first to test phased aeration within aerated wetland systems for de-icer treatment. The theory behind phased aeration is that treatment within the inlet zone results in a higher O_2 demand, with O_2 demand typically decreasing exponentially through the system from the inlet towards the outlet, due to pollutant removal as water passes through the system (Fig. 2.6) (Kadlec and Wallace, 2009, Freeman et al., 2015). Therefore, to avoid under-aeration in the inlet zone and over-aeration in the outlet zone of a treatment system, the volume of air supplied artificially should be varied and increased within the inlet zone at the expense of aeration towards the outlet using a phased aeration approach.

Different approaches to aerating wetlands have been discussed within the literature, including continuous and intermittent aeration modes (Fan et al., 2013a, Fan et al., 2013b, Liu et al., 2013), O_2 concentration regulated aeration (Zhang et al., 2010), inlet-only aeration (Ouellet-Plamondon et al., 2006) and bottom, middle and surface aeration (Wang et al., 2015). However, these approaches do not appear to address the issue of decreasing O_2 demand from the inlet to the outlet with the same success as the phased aeration configuration tested within Chapter 4. In comparison to the other aeration approaches, including inlet-only and uniform aeration, phased-aeration has the advantage of better matching the input of O_2 to the O_2 demand compared to other configurations, thereby reducing unnecessary aeration and wasted energy associated with the blowers. Therefore, the findings within Chapter 4 offer an important reference to the future design of aeration systems within aerated wetlands. The increased COD removal efficiency reported within Chapter 4 with a phased aeration configuration, compared to the uniform aeration configuration, is significant because future designs for aerated wetlands implementing a phased approach could benefit from improved COD, BOD_5 and TOC pollutant removal efficiency. Further, implementation of a phased aeration configuration over alternative configurations results in a reduction in the energy consumption (and CO_2 equivalent) per kg of pollutant removed, thereby reducing treatment costs and improving the sustainability of operating aerated wetlands. This is an important finding in the field of aerated wetlands because enhancing pollutant removal per unit power input is one of the key factors for improving the cost-effective operation and sustainability of aerated treatment systems.

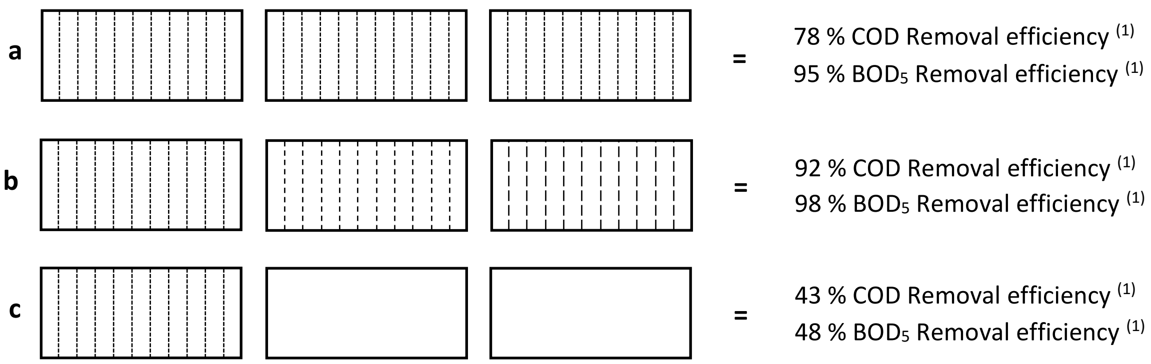


Figure 6.2. Alternative aeration configurations for aerating wetlands including pollutant removal efficiency results determined during testing, (a) uniform aeration configuration, (b) phased aeration configuration, (c) inlet-only aeration configuration. (1) Mean removal efficiency (n = 3 for each test) calculated as the cumulative removal from the influent concentration to the final effluent concentration following Equation 4.1.

6.3.2. Optimisation of Aerated Wetlands for Treatment of Airport Storm Runoff

Aerated wetlands were first invented in 2001 as a means to overcome low O_2 transfer within passive constructed wetlands and to provide a treatment solution for effluents with a high O_2 demand such as airport storm event runoff (Wallace, 2001). The aerated wetland technology is therefore relatively new in comparison to traditional approaches, such as the activated sludge process which has been used for over a century (Henze et al., 2008). Since 2001, aerated wetlands have been commercialised and implemented widely and within many wastewater applications (Ouellet-Plamondon et al., 2006, Gottschall et al., 2007, Nivala et al., 2007, Ong et al., 2010b, Dong et al., 2012, Nivala et al., 2013a) with over 40 currently operating within the UK and over 200 operating globally (Murphy et al., 2016). Some applications have proved more successful than others, with some systems requiring considerable research to understand and rectify operational issues, such as media pore space clogging and poor performance in regards to pollutant removal due to nutrient limitation of microbial communities with the wetlands. This has resulted in an increasing number of research projects which have subsequently improved our knowledge and understanding of the key processes that underpin successful operation of aerated wetlands. Despite this, there are currently only three full-scale artificially aerated wetlands operating within the aviation industry: at Buffalo airport in the USA; Heathrow Airport in the UK; and Edmonton Airport in Canada. There is no industry design standard, resulting in a level of inconsistency across system designs, which makes comparison of performance between systems challenging. Therefore the efficiency and optimal operating conditions for aerated wetlands, given the characteristics of de-icer contaminated surface runoff from airports, remain to be established, providing the context for the second specific aspect of the research reported within Chapter 4. A second objective to evaluate the removal of widely regulated pollutants within a pilot-scale aerated wetland operating under new aeration configurations and a range of hydraulic and pollutant loading rates was also addressed within Chapter 4. This objective sought to establish optimal operating conditions for aerated wetlands treating airport storm runoff. The results of the pilot study revealed that high levels (> 90 %) of pollutant removal for de-icer surrogate parameters COD, BOD_5 and TOC are achievable within aerated wetlands operating under phased aeration and mass pollutant loads of 0.23 kg d^{-1} m^2 BOD_5. However, based on the pollutant loads and HRTs tested within Chapter 4, it was established that MLR of 0.10 kg d^{-1} m^2 BOD_5 and HRTs of 1.49 d were optimal, delivering 98 % BOD_5 removal and final effluent concentrations that would meet stringent environmental permit limits to discharge of 23 mg L^{-1} BOD_5. The optimal operating conditions of 0.10 kg d^{-1} m^2 identified from the pilot-scale study is comparatively low when set against existing aerated wetlands treating airport runoff. For instance, MLR of 0.24 kg d^{-1} m^2 BOD_5, 0.18 kg d^{-1} m^2 BOD_5 and 0.25 kg d^{-1} m^2 BOD_5 have been reported to achieve environmental permit to discharge limits of 30 mg L^{-1}, 40 mg L^{-1} and 100 mg L^{-1} respectively for Buffalo Airport in the USA, Heathrow Airport in the UK and Edmonton Airport in Canada (Wallace and Liner, 2011a, Murphy et al., 2014, Dechanie, 2013). Although lower than existing full-scale systems, results indicate that the optimal loading rate of 0.10 kg d^{-1} m^2 BOD_5 established in Chapter 4 would be sufficient to achieve compliance with a more stringent discharge limit of 23 mg L^{-1} BOD_5. These findings therefore provide a reference for the design of future aerated wetlands to meet stringent regulatory permit to discharge limits. This helps to address the need to achieve low cost, energy efficient and sustainable operation of aerated wetlands, positioning the technology as an attractive alternative approach to managing de-icer contaminated runoff from airports. One of the key challenges of treating de-icer contaminated storm runoff emerging from Chapter 2 and verified within Chapter 3 is the high temporal variability in respect to volume, pollutant concentration and therefore pollutant load. Optimal pollutant removal can be achieved under steady state MLR, whereby microbial communities can acclimatise to the influent conditions. In practice, optimal operation of full-scale systems can therefore be achieved by carefully managing the influent by increasing and reducing influent volumes in response to BOD, COD or TOC concentrations to maintain a steady state daily pollutant load. Overall, the results reported throughout Chapter 4 provide evidence that aerated wetlands could play an important role in mitigating the future water quality impacts associated with increasing demand for air travel, airport expansion and increased use of de-icers. The wider issues of energy efficiency, operating costs and sustainability are further addressed through research to optimise the design of aerated wetlands in Chapter 5, as discussed below.

Following evaluation of novel aeration configurations and different loading conditions under these aeration configurations reported in Chapter 4, further research reported within Chapter 5 was undertaken to establish whether SOTE can be improved within aerated wetlands to further optimise the performance of these treatment systems. Specifically, Chapter 5 reports data that provides important insights into how media depth and airflow rates can be optimised within artificially aerated wetlands to improve SOTE and therefore the performance of a treatment system. Much of the existing research within the field of O_2 transfer to water has been undertaken within the context of open water systems, in an attempt to optimise the efficiency of conventional treatment processes such as activated sludge. However, these systems operate under different physical conditions compared to media-filled systems such as aerated wetlands. The net effect of media on the efficiency of aeration devices and SOTE remains unclear, due to the competing effects of DO concentrations in water on bubble coalescence, resulting from preferential bubble pathways through the media, versus increased bubble retention time within the media pore space. Further, as aerated wetlands are a relatively new form of media-filled treatment system, limited data exists regarding many of the key factors affecting O_2 transfer within these systems. An objective was therefore established to evaluate the impact of media depth and airflow rates on SOTE within media-filled aerated wetland systems. Further, bubble frequency and bubble diameters were investigated to improve understanding and interpretation of SOTE with media-filled and open water columns. To address the objective, a methodology was designed to test the hypothesis that SOTE can be increased within aerated wetlands by optimising media depth and airflow rates. The hypothesis was accepted based on data which indicated that SOTE more than doubled, from 2.4 % to 4.9 %, when media fill depths increased from 1,500 mm to 3,000 mm and that SOTE increased by a mean of 58 % when airflow rates were reduced from 3 L min^{-1} to 1 L min^{-1} at media fill depths of 1,500 mm. Further, bubble observations showed that the mean bubble diameter observed at the column surface significantly increased, by approximately 75 % from 24 mm in open water columns to 42 mm in media-filled columns (Fig.5.5b). This increased bubble diameter substantially reduces the gas to water surface area, thereby impacting SOTE in media-filled columns compared to open water columns and indicating that bubble coalescence is a major issue for SOTE in media-filled systems. This is further highlighted by lower SOTE that were observed for media-filled systems compared to open water systems (Fig 5.13). The data presented within Chapter 5 indicate that increasing media depth and minimising airflow rates are two methods to negate the issue of bubble coalescence and reduced SOTE in media-filled compared to open water systems. Therefore, these findings provide a reference and relatively simple solution for improving O_2 transfer within existing and future artificially aerated wetland designs. This is important because the aeration costs associated with the operation of aeration devices typically contributes between 45 % and 80 % of the total operational costs of wastewater treatment systems (Zhou et al., 2013, Stenstrom and Rosso, 2006, Gillot et al., 2005). Any improvements in the efficiency of aeration devices and O_2 transfer is therefore associated with reduced energy consumption, equivalent CO_2 emissions and operational costs, thereby improving the cost-effectiveness and sustainability of aerated wetland systems, not only in comparison to existing aerated wetland systems but also alternative treatment solutions such as trade effluent discharge.

6.3. Strengths and Limitations of the Research

The nature of the research presented within this thesis is such that both strengths and limitations exist. Overall, one of the major strengths of the research is the link to a large scale, real-world environmental issue faced by the aviation industry, namely to prevent detrimental impacts on surrounding water courses from winter operations and de-icer application. Whilst some of the research reported here focused on measuring and quantifying the risk to receiving waters from de-icer application, much of the research targeted the development and evaluation of a practical treatment solution with the potential for significant real-world impact and commercialisation. All of the research was underpinned by a good practical understanding of de-icer application at the case study site Manchester Airport, which helped to establish practical applications within the aviation industry for the research outputs. The close collaboration with the Manchester Airport Group presented opportunities to undertake field-scale experiments that were highly relevant to the aviation industry, as opposed to smaller scale microcosm and mesocosm experiments more commonly associated with PhD-level research. Inevitably there were some limitations to the research, as considered below.

One of the limitations of the research presented within this thesis is the lack of complete monitoring of de-icer inputs and outputs to airport catchment areas. This is evident in Chapter 3 whereby monitoring was only conducted at catchment C discharge location (Fig. 3.5). Questions therefore remain surrounding the export of de-icers applied within catchment C into other catchment areas, other than through the monitored discharge location. The pathways potentially responsible for this are established within Chapter 2 (Fig. 2.2) and include transport of de-icer mist droplets via wind during application, dissipation through jet blast and vehicle tracking, deposition on the de-icing stands and taxi-ways and shear from the aircraft onto the runway during take-off. However, monitoring all of these potential pathways would be impractical at airport sites. These processes are also responsible for transport of de-icer applied within other catchments into catchment C, creating some uncertainty surrounding the de-icer mass balance data presented within Chapter 3 (Table 3.9). In this context, the mean of 55 % of the applied load transported to catchment C discharge location during storm runoff events indicates significant transportation of applied de-icers to other catchment areas that were not monitored. This is an issue that could be reasonably addressed at other sites, by expanding monitoring programs to cover all catchment discharge locations across the site, thereby improving confidence in the mass balance. Despite this, monitoring of transport mechanisms such as wind and jet blast transport would remain difficult therefore some uncertainty within the mass balance calculations would still exist.

A second limitation of the research was the availability of high resolution analytical methods, which is more broadly a challenge within many environmental monitoring studies. In Chapter 3, some high resolution, real time monitoring was undertaken using a BIOX-1010 instrument which determines the O_2 demand at three minute intervals. However, this does not fully represent the BOD_5 analytical method which must be conducted over a five day period and this model of analyser is therefore being phased out at airports and replaced by TOC analysers. However, using the resources available and data from the BIOX analyser, results were converted to BOD_5 using a correlation derived from the linear regression model reported in Chapter 3 (Fig. 3.7) to help improve understanding of temporal variability of pollutant concentrations within storm event runoff. In future studies, real time TOC analysers combined with velocity sensors to calculate discharge volume could be installed into a catchment discharge location to provide more robust high temporal resolution data. This monitoring approach would provide a better understanding of the system in terms of transportation of de-icer loads from the catchment area to the catchment discharge location through improved resolution of pollutant load calculations.

A further limitation of the research is the timescale of which the water quality monitoring programme reported in Chapter 3 was undertaken. Data was collected over two winter de-icing seasons, with 2013/14 being very mild and 2014/15 more in line with typical UK temperatures and snowfall events. Further, monitoring using the real time remote TOC and velocity sensors as previously discussed would provide a more complete understanding of water quality characteristics that a treatment system may face. The higher frequency data from real time monitoring devices also serves to establish water quality characteristics across a comprehensive range of conditions including, temperature, rainfall, snowfall and de-icer application within the catchment area. Further, the results of the pilot study presented within Chapter 4 were somewhat limited by the length of the study, which was restricted to a six month winter period between February and June 2015. Such short studies are often limited in that they are conducted in infant or juvenile constructed wetland ecosystems, which have not had sufficient time to develop into the full suite of components and mechanisms which underpin pollutant removal processes within fully developed, mature wetlands (Kadlec and Wallace, 2009).

Another limitation of the research was maintaining a constant temperature during pilot-scale experiments. The pilot-scale study was located in the field and therefore testing of individual system configurations was undertaken during fluctuating ambient air temperatures. To reduce any impact of temperature variations between tests, each of the three treatment cells within the field-scale system was insulated. Temperatures within the system remained relatively constant during testing, in comparison to the fluctuating air temperatures and therefore any temperature fluctuations within the trial cells are considered insufficient to invalidate comparison between tests configurations. However, ideally, temperatures would have been constant during testing, although this would have been difficult to achieve given the size of the experimental system. Further, the temperature variations observed during testing are considered to replicate practical full-scale applications, which also operate under these fluctuating temperatures.

6.4. Priorities for Future Research within this Field

Six key priorities for further research and development of the aerated wetland technology for treatment of de-icer contaminated storm runoff have been identified, following the research reported within this thesis:

- Research to build on the mass balance results presented within Chapter 3 is required to quantify the amount of de-icer transported into and out of airport de-icing catchments, in order to improve understanding of de-icer mobilisation, transport and fate following application. It is recommended that future monitoring programmes are expanded to cover all catchment discharge locations in order to capture any transport or deposition of de-icers outside of the de-icing catchment. Specifically, at the case study site Manchester Airport, this would involve expanding the water quality monitoring programme at the catchment C discharge location in order to capture de-icer transportation at the discharge locations of the other drainage catchments A, D, E and R2 (Fig. 3.3). This would include the catchment areas containing taxiways and runways where it is hypothesised that de-icer losses from within catchment C are currently occurring. Building on the mass balance research at Manchester and other global airports would provide improved understanding of catchment processes, de-icer transport and fate following application, thereby providing robust data to establish treatment requirements. Without this initial work at sites, determining the feasibility of on-site treatment as an alternative management approach to discharging contaminated runoff as trade effluent remains a challenge.

- Data reported within Chapter 4 suggests that, although the phased aeration configuration enhanced pollutant removal efficiency in comparison to the other aeration configurations, the spatial distribution of the phased aeration inputs could have been further optimised in order to maintain a 0.6 mg L^{-1} to 2 mg L^{-1} DO concentration range within each treatment cell. Further research is therefore required in order to establish the optimal phased aeration configuration and aeration rates, to meet the O_2 demand along the length of an aerated wetland bed. It is envisaged that identifying the optimal phased aeration configuration and aeration rate will further enhance the pollutant removal efficiency per unit input of energy associated with aeration, therefore increasing the cost-effectiveness of aerated wetlands compared to existing applications. Further, research is required to understand the impact of altering aeration configuration on microbial communities within the wetland system. Increasing aeration volumes at the inlet zone of aerated wetlands could accelerate microbial growth and clogging of the media pore space as biomass increases in response to increased availability of DO that facilitates oxidation of organic carbon within the influent. Further investigation regarding clogging rates within artificial aerated wetlands operating under the novel phased aeration approach described within Chapter 4 is recommended. In addition, research to build upon the results presented within Chapter 5 and to establish accurate costings for increasing the media fill depth is recommended. This would be expected to form part of an economic feasibility assessment for any future aerated wetland design, to ensure that optimal physical designs are produced which maximise SOTE and minimise capital costs. Further work within any future aerated wetland design to optimise the airflow rate and establish the O_2 requirements to meet the BOD_5 of the incoming wastewater is also recommended.

- Storm runoff from airports is typically nutrient limited, because commercial de-icer formulations do not contain either N or P. Nutrients were therefore added to the aeration configuration experiments reported within Chapter 4 to prevent N or P from limiting the microbial community and the pollutant removal processes associated with this community. Whilst previous studies have reported nutrient dosing rates, questions still remain over optimal dosing rates and what impact nutrient addition has on final effluent and downstream water quality. One specific issue requiring investigation is the release of nutrients in the spring following the reduction of de-icer application and organic loads delivered to a treatment system. This is an important issue in nutrient limited systems and needs to be understood in more detail, due to the release of nutrients potentially causing downstream water quality issues such as the eutrophication of receiving waters. Further research to understand nutrient uptake and release within aerated wetlands systems is therefore recommended.

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