Modelling of Fine Chemical Manufacturing Effluent and Emissions: Implementation of Mathematical and Physical Models for Wastewater Management

Daniel Mullen

Biopharmaceutical Bioprocessing Technology Centre

School of Chemical Engineering and Advanced Materials

Newcastle University

A thesis submitted for degree of

Engineering Doctorate

December 2017

Abstract

This thesis consists of a portfolio of four projects that investigates, and addresses challenges faced by fine chemical and pharmaceutical manufacturers based in the UK to achieve greater control of effluent and air emissions in an environment of tightening legislation. In part one of this research, a mathematical model based on modified continually stirred tank reactor (CSTR) in series equations was created using MATLAB and deployed as a standalone tool with graphical user interface (GUI) to allow non-experts to predict the concentration of substances through a complex plant effluent system and activated sludge wastewater treatment plant (WWTP). The model showed an average prediction accuracy to within 9% of the true value on-site when validated against a tracer compound.

In Part two of the thesis, a 100 litre small-scale activated sludge wastewater treatment plant was designed and built to enable extended testing of treatment efficiency for potential new wastewater streams for a large-scale (2400 m^3 reactor) plant, to reduce the risk of breaching site effluent consent limits or large scale microorganism poisoning. Plant variables and conditions required to maintain equivalent wastewater treatment performance from the large-scale to the small-scale plant were researched and found to include temperature, pH, dissolved oxygen (DO) concentration, hydraulic retention time (HRT) and solids retention time (SRT). The resulting pilot plant matched performance of the large-scale plant to within 12.8% of effluent chemical oxygen demand (COD) concentration. Long term treatment efficiency testing of a methylene-blue dye containing wastewater was conducted and shown to be satisfactory after a period of microorganism acclimation, where equivalent short-term lab respirometry testing had previously shown no digestion of the blue wastewater.

In part three of this thesis, mathematical models were researched and developed in MATLAB to study prediction of the effluent chemical oxygen demand concentration of an activated sludge wastewater treatment plant. Existing methods of non-linear modelling using partial least squares (PLS) and artificial neural network (ANN) structures were investigated and compared against a newly proposed structure that replaces the linear inner regressor of the PLS algorithm with a combination of multiple neural networks (mNNPLS). The mNNPLS model showed an improved correlation coefficient (R^2) of 0.855 between observed variables and predicted effluent chemical oxygen demand. In the final section of the thesis, a methodology was created for conducting consequence and risk modelling using DNV's PHAST software to compliment the studies in parts one and two by allowing estimation of substance input concentrations to the effluent system from potential major accidents to aid emergency response planning and test the robustness of the effluent system. Sources for input data including individual and societal risk criteria are researched and presented along with techniques of scenario identification, results presentation and overall report format.

Acknowledgements

Firstly, I would like to express my sincere gratitude towards my academic supervisors, Dr Chris O'Malley and Sharon Joyce, for their continued support throughout the duration of my EngD study. Additionally, I'd like to thank my industrial supervisors, Jon Cummins and Helen Stephenson for all of their help whilst based in industry at Shasun Pharma Solutions.

Nomenclature

Symbol/ Abbreviation	Definition	Units
ALARP	As Low As Reasonably Practicable	
ARX	Auto regressive with exogenous inputs	
ASM	Activated Sludge Model	
CAS	Conventional Activated Sludge	
COD	Chemical Oxygen Demand	mg/l
COMAH	Control Of Major Accidents and Hazards	
DNNPLS	Dynamic Neural Network Partial Least Squares	
DO	Dissolved Oxygen	mg/l
DOC	Dissolved Organic Carbon	
EMS	Environmental Management System	
FANN	Feedforward Artificial Neural Network	
FIR	Finite Impulse Response	
GUI	Graphical User Interface	
HAZID	Hazard Identification	
HRT	Hydraulic Retention Time	
IAWQ	International Association on Water Quality	
IDLH	Immediately Dangerous to Life and Health	ppm
LC50	Lethal Concentration (50% mortality rate)	ppm
LTEL	Long Time Exposure Limit	ppm
MATTE	Major Accident To The Environment	

Symbol/ Abbreviation	Definition	Units
MIMO	Multiple Input Multiple Output	
MLSS	Mixed Liquor Suspended Solids	g/l
NIPALS	Non-linear Iterative Partial Least Squares	
NN	Neural Network	
PEC	Predicted Environmental Concentration	
PNEC	Predicted No Effect Concentration	
PHAST	Process Hazard Analysis Software Tool	
PLS	Partial Least Squares	
SRT	Solids Retention Time	
STEL	Short Term Exposure Limit	ppm
SISO	Single Input Single Output	
SS	Suspended Solids	mg/l
SSE	Sum of Squared Error	
WEL	Workplace Exposure Limit	ppm
WWTP	Wastewater Treatment Plant	

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Chapter 1. Introduction

1.1.Thesis Overview

The main theme of this thesis is the control of emissions from industry to the environment and helping to ensure that wastewater emissions generated from industrial operations do not exceed limits set by the regulatory authorities, which exist to make sure that waste disposal is sustainable and conducted in a safe and efficient as possible manner. This thesis contains a portfolio of projects each under this same theme and was developed in collaboration with Shasun Pharma Solutions, a company based in the pharmaceutical / fine chemicals manufacturing industry but this research can also apply to a much larger range of industries that have a focus on control and reduction of emissions at source.

To give an idea of the wide range of applicability of the research contained in this thesis, the chemical industry alone covers a broad range of manufacturing. This includes production of organic and inorganic chemicals, fertilizers, biocides, explosives and pharmaceutical products including intermediates. The chemical industry is large and competitive, therefore companies are always looking for ways to reduce operating costs in a manner that is sustainable.

Initially, to set the scene on why the research in this thesis is of importance to the chemical industry and why it is necessary to control emissions, the current legislation on the matter will be reviewed.

1.2. Literature review on Legislation for Controlling Emissions

In order to control industrial emissions, a general framework based on integrated permitting has been developed by the EU for member states (EC, 2010/75/EU). This framework lays down a set of rules to prevent and control pollution into the air, water and land and avoid generating waste from large industrial installations. Permits therefore have to take account of a plant's overall environmental performance as different approaches to controlling emissions into air, water or soil separately may encourage pollution migrating from one medium to the next. It is therefore necessary to provide an integrated approach which will also contribute towards creating a level

playing field by aligning environmental performance requirements for industrial installations. As always, pollution should first be prevented by reducing or eliminating at the source.

The legislation applies to a wide range of industrial activities and sectors, some of these include: energy, metal production and processing, minerals, chemicals, waste management, pulp and paper production, slaughterhouses and the intensive rearing of poultry and pigs (EC, 1999/1 3/EC). If covered by this directive, an installation must be in possession of a permit and must also follow the Best Available Techniques (BATs), efficient energy use, waste production and management and measures to prevent accidents and limit their consequences**.** Installations covered by these regulations must also be regularly inspected by the relevant competent authorities and the public must also be given every opportunity to participate in the permitting process. In regard to the public participation in decision-making, the public must be informed of the following matters early in the procedure for the taking of a decision for the following:

- The application for a permit, or proposal for updating a permit or permit conditions
- Where applicable, the fact that a decision is subject to a national environmental impact assessment
- Details relating to the proposal for updating the permit conditions
- The public concerned shall be entitled to express comments and opinions to the competent authority before a decision is taken.

The legislation also states that it is important to prevent accidents and incidents and limit their consequences and that liability regarding the environmental consequences of such accidents and incidents are a matter for relevant national law and where applicable union law. It also mentions that if the implementation of the best available techniques for controlling emissions would lead to disproportionately high costs compared to the environmental benefit, emission target values can be set that deviate from the original levels. Temporary emission target levels may also be set for the purposes of testing out new technology for the control of emissions. If any changes are made by an operator to an installation that may give rise to higher levels of pollution, affecting either human health or the environment, the operator must notify the competent authorities to assess the changes and impact on the status of the permit. To take account of developments in best available techniques or other changes to an installation, the permit conditions

should be reviewed regularly and where necessary, updated, especially where new or updated BAT conclusions are adopted.

To ensure that an installation does not result in the deterioration and quality of groundwater and soil, permit conditions should include measures to survey soil and groundwater in order to detect any contamination as soon as possible. The results of this surveying is compared against a baseline report to establish the original state of the soil and groundwater for future comparison, this baseline report will contain at a minimum information about the present and previous use of the site and information on soil and groundwater measurements. It is therefore important to have methods and procedures in place to prevent the occurrence of leaks, spills and incidents.

The use of organic solvents (something Shasun do on a daily basis) that can give rise to emissions of organic compounds into the air which can then contribute to the formation of photochemical oxidants, causing damage to natural resources and harmful effects on human health must be controlled. Therefore, there must be emission limit values set where other measures such as the use of low or solvent free products or techniques are not feasible. The legislation also refers to heavy metals and dioxins as significant environmental pollution and member states should lay down rules on penalties applicable to infringements and make sure that they are implemented. These penalties should be effective, proportionate and dissuasive.

In the event of an incident or accident that can significantly affect the environment or where permit conditions are breached, member states must take the necessary measures to ensure that the operator immediately informs the relevant competent authority, takes measures to limit the environmental consequences and ensure compliance is restored in the shortest time possible and to prevent further possible incidents or accidents.

Emission limit values shall apply at the point where the emission leaves the installation, any dilution prior to that point shall be disregarded. With regards to releases of polluting substances in water, the effect of a water treatment plant may be considered when determining the emission limit values of the installation concerned – provided that an equivalent level of protection to the environment as a whole is guaranteed. The legislation also states that member states shall prohibit the disposal of the following waste into any water body, sea or ocean:

- Solid waste

- Mother liquors arising from certain processes
- Waste from installations applying the chloride process containing more than 0.5% free hydrochloric acid and various heavy metals
- Emissions from installations into water and air shall not exceed the emission limit values for a range of particular substances

1.3. Review of UK Legislation

The UK environmental regulators include the Environment Agency (EA), Scottish Environmental Protection Agency (SEPA) and the Northern Ireland Environment Agency (NIEA). Their role is to administer the Pollution Prevention and Control Regulations (PPC) to implement the Industrial Emissions Directive.

The PPC Regulations apply to a wide range of activities, however in the manufacturing of pharmaceutical products for solvent emissions activity, the solvent consumption threshold (SCT) is 50 tonnes per year (EC, 2010/75/EU). Shasun exceed this limit and so these regulations apply to them directly.

After the review of the European legislation on industrial emissions in November 2005 by the European Commission, a new directive on industrial emissions was proposed. This proposal involved merging of seven existing directives including:

- Large Combustion Plant Directive (LCPD)
- Integrated Pollution Prevention and Control Directive (IPPCD)
- Waste Incineration Direcive (WID)
- Solvent Emissions Directive (SED)
- Three existing directives on titanium dioxide.

The Pollution Prevention and Control (PPC) regulations control many industrial activities that have the potential to pollute our environment. The regulations came into force on the 7th January 2013 in order the implement the Industrial Emissions Directive (IED) as well as building upon the previous revision of PPC 2000. These regulations apply an integrated environmental approach to the regulation of certain industrial activities (SEPA, 2013). Operation of installations that come under the PPC regulations must have a permit in place to allow continued operation. The conditions of these permits are set to ensure a high level of protection towards the environment as a whole and are based on the Best Available Techniques (BAT) to prevent and minimise

emissions and aim to balance the costs of the operator against the benefits to the environment where possible. The type of permit required is based on the type of activity taking place, this can either be classified as Part A or Part B activities. A Part A Permit represents the highest level of control under the PPC regulations.

The aim of the PPC regulations are to prevent or reduce emissions from installations. This is being done by placing the onus on the operators to take responsibility for finding solutions to potential environmental problems. This helps to promote and develop techniques that reduce the amount of waste produced and pollutants released overall.

1.4. Environmental System

In addition to the mandatory compliance with the Industrial Emissions Directive and Pollution Prevention and Control Regulations to maintain compliance with permit conditions and therefore license to operate, having an environmental management system (EMS) in place can help organisations identify, manage, monitor and control environmental issues in a "hollistic" manner. One such EMS is the International Standard of Environmental Management Systems: ISO 14001 (ISO, 2015). It requires an organisation to look at all environmental issues related to their operations including air pollution, water and sewage issues, waste management, soil contamination, climate change mitigation and resource use and efficiency. ISO 14001 includes the need for a company to show continual improvement of its management systems and approach to concerns for the environment. There are several reasons that an organisation should take this strategic approach to improving its environmental performance and users of this standard have reported the following benefits:

- Helps to demonstrate compliance with current and future statutory and regulatory requirements such as PPC
- Improves company reputation as well as confidence of stakeholders, this can lead to increased business
- Achieve strategic business aims by incorporating environmental issues into business management
- Provide a competitive and financial advantage through improved efficiency and reduced costs

Becoming certified to ISO14001 can also help an organisation signal to buyers, customers and suppliers that they meet regulatory and contractual requirements.

Over the past few years there has also been increasing attention paid towards the ethical, environmental and social dimensions of a business (Kolk, 2015). Companies can be expected to show a degree of social responsibility in terms of socially responsible behaviour in an ethical sense. This expectation has grown from increased awareness over the past several decades, especially due to negative environmental 'by-effects' of industrialisation and international production.

1.5. Environmental Regulations for Installations using Organic Solvents

As previously mentioned, Shasun undertake many activities involving organic solvents due to the nature of the pharmaceutical business and the chemical reactions that take place to manufacture these products. The following section will review the EU environmental legislations relevant to installations that use organic solvents.

Relevant activities involving the use of organic solvents can include the cleaning of equipment, manufacturing of pharmaceutical products: the chemical synthesis, fermentation, extraction, formulation and finishing of pharmaceutical products and, where carried out at the same site, the manufacture of intermediate products.

The solvent management plan is required for such installations and is used to verify compliance with article 62 of the Industrial Emissions Directive (EC, 1999/1 3/EC), to help identify future reduction options and enable provision of information on solvent consumption and solvent emissions. To ensure compliance, the average periodic measurements should not exceed the emission limit value and none should exceed the emission limit value by a factor of 1.5. The solvent management plan should list the inputs of organic solvents or their quantity in mixtures into an installation’s process and consist of a mass balance of each substance over the timeframe that it is used and also take into account the quantity of organic solvents that are recovered.

The outputs of organic solvents can include emissions in waste gasses, organic solvents lost in water, taking into account waste water treatment, quantity of solvent which remains in the product or residue in the process, uncaptured emissions of organic solvents into air (e.g. general ventilation in rooms where air is released to the outside via doors, windows and similar openings), fugitive emissions (e.g. flanges, drips and washes), organic solvents lost due to chemical reaction, organic solvents contained in collected waste, organic solvents contained in mixtures which are sold as commercially valuable products, organic solvents contained in mixtures recovered for re-use but not

input to the process or organic solvents released in any other way (EC, 2010). Table 1 shows a list of polluting substances for an example, as described in section 5 of the Scottish Pollution Prevention and Control Regulations (SEPA, 2013).

Table 1: List of Polluting Substances

Air	**Water**
1. Sulphur dioxide and other sulphur compounds.	**1.** Organohalogen compounds and substances which may form such compounds in the aquatic environment.
2. Oxides of nitrogen and other nitrogen compounds.	**2.** Organophosphorus compounds.
3. Carbon monoxide.	**3.** Organotin compounds.
4. Volatile organic compounds.	**4.** Substances and mixtures which have been proved to possess carcinogenic or mutagenic properties or properties which may affect reproduction in or via the aquatic environment.
5. Metals and their compounds.	**5.** Persistent hydrocarbons and persistent and bioaccumulable organic toxic substances.
6. Dust including fine particulate matter.	**6.** Cyanides.
7. Asbestos (suspended particulates, fibres).	**7.** Metals and their compounds.
8. Chlorine and its compounds.	**8.** Arsenic and its compounds.
9. Fluorine and its compounds.	**9.** Biocides and plant health products.
10. Arsenic and its compounds.	**10.** Materials in suspension.
11. Cyanides.	**11.** Substances which contribute to eutrophication (in particular, nitrates and phosphates).

12. Substances and mixtures which have been proved to possess carcinogenic or mutagenic properties or properties which may affect reproduction via the air.	**12.** Substances which have an unfavourable influence on the oxygen balance (and can be measured using parameters such as BOD, COD, etc.). E.g. the COD effluent limit for Shasun is 4000 mg/l.
13. Polychlorinated dibenzodioxins and polychlorinated dibenzofurans.	**13.** Substances listed in Annex X to Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for Community action in the field of water policy(1**).**

1.6. Current Techniques for Pollution Prevention

The BAT (best available technique) reference document (BREF) for the manufacture of organic fine chemicals describes the main findings and summary of an information exchange for the principal BAT conclusions and the associated consumption and emission levels (EC, 2006). This document is relevant for a wide range of activities but includes the production of pharmaceutical products and intermediates. The key environmental issues with the organic fine chemicals sector are the emissions of volatile organic compounds, waste waters with potential for large amounts of non-degradable organic compounds and large quantities of spent solvents and non-recyclable waste in high ratio to product produced.

1.6.1. Active Pharmaceutical Ingredients (API's) and Sources of Emissions

Shasun specialises in the contract manufacture of Active Pharmaceutical Ingredients (API's). API's consist of organic molecules that have been created and/or modified to provide medicinal products and makes up the vast majority of the segment of available drugs today. The variety of different drugs available on the market is huge.

API manufacture is normally required to follow the rules of current Good Manufacturing Practice (cGMP) and as such can require approval by a number of different agencies such as the United States Food and Drug Administration (FDA), European Medicine Evaluation Agency (EMEA) or the Medicines and Healthcare products Regulatory Authority (MHRA). This can create a large obstacle to process modification that would require approval from these agencies or even the end customer

of the product and therefore redesign of existing processes with the aim of reducing environmental impact can be very difficult. It may therefore be easier to design improved abatement systems that rely on a developmental process change. API manufacture can produce a lot of waste gas emissions. These emissions can be split into ducted emissions and non-ducted emissions (diffuse or fugitive). Table 2 gives an overview of the main sources and pollutants (SEPA, 2013).

Table 2: Summary of sources and pollutants for waste gas emissions

From process equipment	Exhaust gases from reaction vessels and condensers
	Exhaust gases from catalyst regeneration
	Exhaust gases from solvent regeneration
	Exhaust gases from storage and handling
	Exhaust gases from purge vents or preheating equipment
	Discharges from safety relief devices and accidental releases
	Exhaust gases from general ventilation systems
	Exhaust gases from diffuse or fugitive sources installed within an enclosure or building
Others	Diffuse emissions
	Fugitive emissions
	Pollutants
	Sulphur compounds SO_2, SO_3, H_2S, CS_2, COS
	Nitrogen compounds NOX, N_2O, NH_3, HCN
	Halogens and compounds Cl_2, Br_2, HF, HCl, HBr
	Incomplete combustion products CO, CxHy
	Volatile organic compounds
	VOC's
	Halogenated VOC
Particulate Matter	Dust, soot, alkali, heavy metals

Volatile Organic Compound (VOC) emissions come mainly from the use of solvents but also from volatile raw materials, intermediates, products and by-products **(EC, 2006)**.

Table 3 list the typical solvents that are used in the OFC sector and the limitations on emissions of volatile organic substances that applies to installations that consume over 50 tonnes of solvents per year (such as Shasun) **(EC, 1999/1 3/EC)**.

Table 3: Typical Solvents used in the Organic Fine Chemicals Sector

Solvent	Formula
Methanol	CH_4O
Toluene	C_7H_8
Acetone	C_3H_6O
Ethanol	C_2H_6O
o-chlorotoluene	C_7H_7Cl
Benzene	C_6H_6
Trichloromethane	$CHCl_3$
1,2 dichloroethane	$C_2H_4Cl_2$
Dichloromethane (methylene chloride)	CH_2Cl_2
Dimethylformamide	C_3H_7NO

A typical API manufacturing process involves charging raw materials to a batch reactor, some reactions and further chemistry takes place, followed by crystallisation of the product and then isolation by use of a filter. API manufacturing typically generates large quantities of waste liquids due to the fact that most of the chemistry takes place in the liquid phase. An overview of the sources of waste water streams, possible contaminants and relevant parameters are shown in Table 4 (EC, 2003). The vast majority of contaminant loads (approximately 90%) originate from mother liquors and the initial wash liquors following isolation of solid products on a filter, however, the volume of these waste waters only contribute to around 10-30% of the total. The toxicity/ inhibition and bioeliminability are key parameters to consider when assessing the suitability and performance in a biological treatment plant, such as the one Shasun have on their site in Dudley.

Table 4: Summary of the sources of waste waters, contaminants and relevant parameters

Sources
Mother liquors from processing products
Wash-water the from purification of products
Vapour condensates
Quench water
Wastewater streams from the treatment of exhaust gases or flue-gas treatment (scrubbers)
Wastewater streams from rinsing and cleaning
Contaminated water from vacuum generation
Boiler water blowdown
Pilot plants, filter washing, laboratory waste
Rainwater from contaminated ground (e.g. Bunded areas)
Parameters / Characteristics
COD/TOC, BOD, bioeliminability (organic load)
Toxicity, persistency, bioaccumulation
Inorganic load, Heavy metals, NH_4-N, inorganic N
Other P-total, N-total, pH, hydraulic load,
Temperature

With such large amounts of wastewater produced by manufacturing processes at Shasun, they have installed an on-site biological wastewater treatment facility to treat the wastewater in an economical manner. Biological degradation of a certain compound in a biological wastewater treatment plant is difficult to predict, there are many theoretical mathematical models and methods available but these, however still contain many uncertainties. There are rules of thumb that can be followed, for example: simple aromatic compounds are usually easily biodegradable, as are aliphatic compounds whereas compounds with functional groups such as $–NO_2$, NH_2, COOH and SO_3H decrease the degree of elimination due to higher water solubility (OECD, 2003).

To assess the suitability of a particular substance for treatment by biological means, readily biodegradability tests can be undertaken which are tests under aerobic conditions, where a high concentration of the test substance is used and the biodegradation rate is observed by measuring parameters such as dissolved oxygen concentration, chemical oxygen demand or biological oxygen demand. A positive result can be concluded from a rapid degradation rate. Methods for this type of testing include CO_2 Evolution, closed bottle and manometric respirometry. These tests, however don't

give the whole story when assessing a particular waste stream. There can be longer term or inhibitory effects on the biodegradation performance of a wastewater treatment plant when a particular waste stream is mixed with other streams or when the concentration of the test compound is much lower.

1.7. Summary of Environmental Requirements and Potential Issues for a Contract Manufacturing Pharmaceutical Company

Shasun are subject to an integrated Pollution Prevention and Control regulations that take an overall look at an installation's emissions and cover emissions to air, water and land. They must follow the best available techniques (BAT) for controlling emissions and keep emissions within strict emission limit values set by the Environment Agency who monitor these emissions and test groundwater and soil. In addition to following BATs, they must strive to ensure efficient energy use, employ waste management programmes and also reduce the number of accidents and limit their consequences. This is national law and failure to comply can result in enforcement notices and potential loss of license to operate, large fines and even imprisonment. Additionally, for any release of pollutant exceeding the allowed limits, they must notify the relevant authorities immediately. A significant event leading to damage to the environment can not only result in large fines but also result in poor public image which can be very damaging to the company's reputation.

Shasun is a large user of solvents and must have a solvent management plan in place. Strict emission limit values (the permissible quantity of a substance which may be discharged to the environment in a given period) provided by the regulatory authorities may never be exceeded by 1.5x at any one time. Ensuring this is the case can be difficult, especially where on-site wastewater treatment can be used as abatement prior to calculating a site's emission values. Nowadays the onus is on the operator of an installation to find solutions to potential environmental problems, additionally, by showing continual improvement with control of emissions Shasun can more easily demonstrate compliance with environmental regulations and comply with ISO14001 – something many customers of contract API manufacturers consider important. There is also a moral and social responsibility for Shasun to reduce their emissions wherever possible and a beneficial by-product of this will be improved public image.

1.8.The Research Problem

With controlling emissions being such an important aspect of the business for Shasun, the company is looking for ways to help ensure compliance. This can be difficult due to the nature of contract manufacturing where a new process can be implemented in a short amount of time. These new processes can range greatly in terms of the raw materials required, chemical reactions, hazards and equipment that's used and so management and disposal of the waste from these processes is important. This should be done with a quick and efficient process which involves evaluating likely emissions, the new wastewater treatability (and compatibility with their on-site wastewater treatment process), environmental effects and the potential recycling of substances generated and used in the process and of waste, where appropriate.

Where a new process that has significant process hazards or introduces hazardous or toxic substances to the site, consequence and risk modelling is required. A robust methodology of efficiently implementing a consequence and risk study and dissemination of this information throughout the company is also important. There is a need to prevent or reduce to a minimum the overall impact of the emissions on the environment and the risks to it, this involves preventing accidents and also minimising the consequences.

The objective of this research is to provide improved methods and tools to enable better control of wastewater emissions from Shasun's manufacturing site in Dudley. This will help Shasun maintain compliance with their environmental permit whilst reducing risk with the introduction of new processes.

By examining the current effluent system at Shasun's site in Dudley, it is theorised that a dynamic mathematical model can be created to better understand the effects of mixing, dilution and treatment of effluent as it is produced during active pharmaceutical ingredient (API) manufacture and works its way through the site's effluent system before arriving at the municipal wastewater treatment works in Howden. In addition to this model, both physical and mathematical models of the wastewater treatment plant itself (WWTP) will be created for further understanding of the WWTP's treatment capabilities of complex mixtures of wastewaters and its long-term effect on stability of the treatment process.

By creating a methodology for implementing consequence and risk modelling of processes on-site, it also is theorised that efficiency and dissemination of information can be improved resulting in time saved for the company whilst maintaining high standards of safety and reducing the risk of unplanned releases polluting the environment. The consequence and risk modelling will also help with determining potential accidental inputs of substances into the effluent system, which can be further modelled using the models created in chapters 2 and 3 for the purpose of enhanced environmental risk management

1.9.Thesis Outline

The research will begin with the wastewater treatment theme which directly includes the issues with understanding the effluent system and process of wastewater treatment. Following this section, potential methods for creating models of the system and wastewater treatment plant will be investigated and conclusion drawn from the research. In the next section, a method for determining the concentration of a particular substance in the entire effluent and wastewater treatment plant (WWTP) system will be derived and a method for assessing the long-term treatability of new wastewaters will be created and tested for accuracy. The potential for improving upon this new effluent system model and the potential for integrating a mathematical model to model the wastewater treatment in the bioreactor of the WWTP will also be investigated.

Finally, a methodology for efficient implementation of consequence and risk software and reporting will be created.

As this thesis contains a portfolio of different projects, albeit related under the same theme of controlling emissions, a review of literature will be undertaken in each section that is more directly related to the respective section's topic, this will complement the review of regulations and legislation found earlier in this chapter.

Chapter 2: Wastewater System Model and Graphical User Interface

2. Introduction

The purpose of this chapter is to describe the steps taken to create a solution to Shasun's problem of accurately predicting the concentration of substances leaving their site in the effluent system via their on-site wastewater treatment plant. This is necessary to allow maximum efficiency in wastewater treatment whilst ensuring compliance with environmental regulations as described in the first chapter of this thesis. This chapter begins with background information about the chemical manufacturing site at Shasun in Dudley, UK followed by a more in-depth definition and research of the problem, a review of current available solutions and then design, implementation and analysis of the proposed solution. A case study will then be conducted to validate the model, this will use small amounts of wastewater produced by a pilot scale production trial of a new potential process. This process produces wastewater containing a very strong blue dye coupled with a heavy metal, Zinc. Chapter 3 will also use this source of wastewater for studies on treatability by the on-site wastewater treatment plant.

2.1. A Background of Shasun Pharma Solutions

Shasun was incorporated in 1976 and is headquartered in Chennai, India. They are a global supplier of development and manufacturing services for active pharmaceutical ingredients (API's), their associated intermediate substances as well as final drug product formulations (into doses) to the Pharmaceutical industry. Their goal is to provide to their customers flexible and tailored solutions to ensure client's projects are executed at the highest level (Shasun, 2013)

The site in Dudley provides customers with contract research and manufacturing services (CRAMS). At a total of 169,900 square metres it was opened in 1969 by Sterling Drug who were purchased by Eastman Kodak in 1988. In 1994 the site was acquired by Sanofi, followed by ChiRex in 1996 and Rhodia in 2000 who formed Rhodia Pharma Solutions in 2003. In 2006, Shasun Pharma solutions was purchased.

The plant at Dudley is approved by the Medical Health Regulatory Authority and FDA and offers reactor capacities of up to 40 cubic meters, this enables manufacture of a very large range of materials at up to tonne-scale. Shasun advertise rapid entry for new products to full cGMP (current good manufacturing practise). The site also produces

material required for undertaking of clinical trials as well as commercial quantities of API's from grams to tonnes per annum.

The research and development facility employs 40 scientists that focus on process development and industrialisation with hazard evaluation capability. Three other main plant areas can perform demanding and aggressive chemistry such as hydrogenation, halogenation, Friedel-Crafts and cyanation.

There are many different processes run on site each producing their own respective waste streams and it is common for new process streams to be implemented from time to time. Disposal of the resultant wastewater streams can be costly and so an activated sludge wastewater treatment plant was constructed to biologically treat the wastewater produced on site, resulting in a comparatively low-cost wastewater disposal.

This biological treatment plant is integrated with their manufacturing facilities to provide a continuous system for treatment of process wastewaters. The facility uses a mixture of air and liquid oxygen to enable aerobic bacteria to reduce the organic content of the wastewater. The plant has three bioreactors giving it the ability to treat up to 1500 m^3 of wastewater per day, with treatment levels that regularly surpass a 90% reduction of the organic content in the wastewater.

When a new product is introduced, an environmental assessment takes place to ensure that the treatment facility is fully utilised in an effort to reduce the environmental burden related to the transport and disposal of waste at alternative facilities. The Shasun plant is also a registered wastewater management facility that is used regularly on a commercial basis by local businesses to provide a sustainable and cost effective alternative to incineration or other disposal techniques.

2.2. Problem Definition

The Shasun site in Dudley has a complex drainage system comprising process effluent, surface water and domestic wastewater systems (e.g. kitchen and toilet waste). The onsite biological treatment plant receives wastewater from the Shasun plant as well as external sources delivered by tanker (ranging from landfill leachate to high strength chemical waste) and currently, it is not well understood what the status of the wastewater plant is, in regards to the concentration of particular substances at any one time, from the series of feed tanks that supply the plant to the clarifiers and reactors. It is therefore difficult to predict the capacity of the plant for additional wastewater, as the

system is highly dynamic and so predicting what the quality of treated wastewater discharged to the effluent system will be when it leaves the site, arrives at the sewerage treatment plant in Howden and finally when it is discharged into the Tyne Estuary, is difficult.

If it is found likely that a wastewater will result in breach of environmental permit limits, it can be diverted to emergency holding tanks. It then becomes a challenge to predict at what rate this wastewater can be released into the wastewater treatment system to stay within the strict discharge limits. There is also the problem of emergency planning, if there is an unexpected release of a dangerous or toxic substance on-site that can end up in the effluent system or even a large storm which can result in excessive volumes of water passing through the effluent system, this can have a drastic effect on the wastewater treatment plant's efficiency and so a method of assessing the effects of these scenarios before and as they are occurring is required.

The ultimate goal of this project is to have the ability to say with confidence that the quality of wastewater leaving the site and reaching the Tyne estuary stays within strict environmental limits set by the regulatory authorities. This would enable Shasun to identify which process wastewaters and in what quantity in a given time period can be discharged to the effluent system. As well as reducing the environmental impact of the site, this project has the potential for decreasing costs through reduced use of less sustainable methods of wastewater disposal, such as transport of the wastewater off-site for treatment via third-party. It will also allow for an increase in the number of externally sourced wastewaters delivered by tanker, growing the profits of the biological treatment facility.

2.3. User Requirements

The solution to the problem needs to be easy to use and quickly provide an answer to a query. For this reason a mathematical model will be created using MATLAB and Simulink software to simulate the entire effluent system at Shasun's site in Dudley. The model needs to be used by several different people who do not have knowledge of how MATLAB or Simulink works. These customers include the bioplant coordinator, regulatory compliance manager, waste and effluent coordinator and environmental manager. There is also the potential for process engineers to use the software for estimation of the predicted environmental concentrations (PECs) of wastewater from processes run onsite. With a number of people with different backgrounds using the

model it must be a simple and straightforward as possible to use and so a graphical user interface (GUI) will be created to allow the user to change model inputs and retrieve results with ease. This graphical user interface along with the model that it manipulates must also have the ability to be deployed as a standalone system that does not require MATLAB to be installed on the users' computer, this is to reduce cost of implementation of the model whilst allowing multiple users on different machines.

2.4. Problem of Pollution

It has been known for a long time that there is a problem with substances originating from the production of pharmaceuticals, including the active pharmaceutical ingredients themselves, making their way into the environment and over the past few years this has been a subject of increasing importance, especially to the general public. Pharmaceutical products have been found in waters, soils and sediments and it is suspected that this has had a negative effect on the integrity of the ecosystem (Benoit Roig, 2009). Pharmaceuticals are used all over the world and can enter the environment through many different pathways including manufacturing and wastewater treatment plant (WWTP) discharges due to the fact that conventional urban WWTP's have a limited removal capacity for these contaminants (R. Moreno-Gonzales, 2014).

Current US and European regulatory guidance require new pharmaceuticals to undergo standard acute toxicity tests to algae, Daphnia magna and fish if the predicted environmental concentration (PEC) is greater than 10 ng/l. For compounds with a PEC that exceed these concentrations, a predicted no effect concentration (PNEC) must be calculated by dividing the $E(L)_{50}$ values (concentration resulting in acute toxicity to 50% of daphnia species) obtained from toxicity tests by an assessment factor of up to 1000. If the quotient between the PEC and PNEC is lower than 1, it is not necessary to assess further (Meritxell Gros, 2010).

The Water Framework Directive (EC, 2000) is increasing the range of pollution control measures that are needed to protect surface waters. The Environmental Quality Standards (EC, 2008) along with individual national regulators have defined concentration limits on many substances for satisfactory water quality. A clear understanding of the effectiveness of wastewater treatment processes in removing the substances of interest from effluent discharges is required. The UK Water Industry Research (UKWIR) has collaborated with the water industry and environment agency and other UK regulators to design a £25 million programme of investigations into the

management and control of a range of substances that may be present in wastewater treatment plant discharges. The programme is known as The Chemicals Investigation Programme.

2.4.1. Heavy Metals

Metals are not degraded or eliminated from the ecosystem and accumulate in organisms and sediments. However, some elements such as zinc, manganese, copper, iron and nickel are essential in low concentrations for the metabolism of aquatic organisms. There are however metals such as cadmium, lead and arsenic that are nonessential to organisms and are highly toxic. It must also be noted that even the essential metals can be toxic for biological activities of organisms at certain concentrations. For example, as fish find themselves high up in the aquatic trophic web, they accumulate many kinds of contaminants in their tissues including heavy metals. Fish can absorb these contaminants either directly from the water or from food. These contaminants pose a health risk to piscivorous birds, mammals and humans (Roberto Merciai, 2013).

This existence of heavy metals in sewerage effluents remains a concern due to their adverse effects on biota and sediments of receiving waters. In conventional wastewater treatment, heavy metal removal occurs during both primary sedimentation and secondary biological treatment. Removal during primary sedimentation is a physical process that is dependent on the settlement of precipitated metal. During secondary treatment, metal removal only occurs if the metal associates with settleable solids, which are removed from the effluent by gravity during secondary sedimentation (Crane, 2010). Metal removal can be classified into two types; settlement of insoluble metal, and adsorption of soluble metal or fine particulate metals by the sludge flocs. From time to time, Shasun run processes on site that use various heavy metals in the raw materials, these heavy metals can end up in the effluent discharged from the process and can be sent to the on-site biological wastewater treatment facility.

The wastewater system model should therefore be able to predict the concentration of these elements anywhere in the effluent and treatment system, at the point it reaches the microorganisms in the wastewater treatment plant (WWTP), as well as the effluent leaving the site at any one time. This will ensure that no toxic concentration level of heavy metals (or any other substance) will be able to poison the microorganisms in the WWTP and reduce its treatment efficiency as well as ensuring that the limits set by the Environment Agency are met. The results of the model can be used to determine is a

pre-treatment step is required before the biological process of a potential new wastewater.

2.5. Review of Literature

The problem stated in section 2.2 involves investigation into a mathematical model capable of predicting the concentration of various substances in the effluent system at Shasun at a given time and to test the effects of changes to the inputs of materials into the system and their effects further downstream (e.g. concentrations in the bioreactor of the on-site wastewater treatment plant). The topic of concern therefore involves a researching a system that can accurately calculate dilution through a dynamic system with multiple mixing streams and differently sized containment vessels. Such concepts have been studied on the very large scale, such as water balances in nature spanning several kilometres down to lab scale tracer experiments involving multiple stirred reactors connected in series.

These concepts will be studied and their relation to the problem at hand will be assessed. The author of this thesis could not identify work in literature with a direct relationship to the problem at hand and so the works with the closet match in concept will be studied. These works can be broken down into the following categories; water balances (such as for a drinking water supply network), residence time distribution and relatable studies involving changes in dilution and mixing with time in reactor vessels connected in a series configuration.

2.5.1. Water Balances

Knobloch studied approaches for establishing zonal water balances for a water distribution network to enable efficient planning and implementation of steps for water loss management (Knobloch, 2014). In this study a successful methodology for creating a water balance was described which involved firstly reducing the water distribution system to its bare elements such as sources, tanks, bulk meters and supply zones (consisting of pipes, consumers etc). Pumps and valves (as well as their state, open or closed) are also taken account of to determine whether or not a link between two particular elements in the system is open or not. The methodology later describes starting the model by calculating the flowrate of liquid into and out of the system as well as its constituents using measurements from flowmeters where available followed by investigating the unmeasured withdrawals from the systems (such as cleaning, pipe

flushing, construction and repair, and firefighting) using estimations based on a combination of operator experience and sound scientific principles. Additional variances that could arise were taken account of including bulk water meter inaccuracies, overflow and leaking of tanks or main lines and an estimation of water loss due to unknown damage. The results of this study described the model of having the ability of detecting failures in the water network with leak flowrates of just 0.5 m^3/hr in smaller zones of the water system which would represent approximately 2% of overall flow in that zone.

There are similarities between this work and the problem of creating an effluent system model at Shasun's plant. The work sets out a clear methodology of dividing the overall system down into zones including the layout of tanks, pipework, pumps and valves. The inputs and expected outputs of each zone are determined based on measured data, and where data is unavailable, sensible estimations are included to ensure that losses are accounted for. A similar methodology should be followed, with adaptations to suit the different system at Shasun to take account of its unique characteristics.

Plagnes describes creating a water balance model which would be used to predict the downstream water quality due to releases of uranium mill effluent (Plagnes, 2017). A methodology is presented and used to create a mathematical model to predict water volume (lake volumes) and quality downstream of discharge in large surface water bodies. The tool was used to optimise the management of the effluent throughout the life of the mill, enabling forecasting downstream water quality to mill activities. The approach taken for building the model describes taking a balance between model complexity and structure, a compartmental model was created based on the four main water bodies, where volume was calculated based upon time-dependant inputs/outputs. Additional variables taken account of include the surface water chemistry, elevation and flowrates between water bodies. Plagnes proceeds to create a mass balance model approach which involved estimated terms for values such as evaporation rates, rain and meltwater collection, seepage loss and groundwater input. Validation of the model was conducted using background measurements of Cl and SO4, with flowrates taken as an average value of measurements taken over a previous year. Although a statistical analysis of the accuracy of the model's predictions was not conducted, the predictions appear graphically to be reasonably accurate and assumptions such as perfect mixing in the large bodies of water did not appear to have adverse effects on the accuracy of the model. Although the work by Plagnes involves creating a system model on a far greater

scale that would be required for the work of this thesis, elements of the methodology can be used when creating the model for the effluent system at Shasun, this includes the creation of a mass balance, potentially the assumption of perfect mixing in unagitated containment vessels, awareness of model complexity and structure and validation using a detectable known compound found in the system.

2.5.2. Continuous Stirred Tank Reactors

Miyawaki studied the performance of continuous stirred-tank reactors connected in a series as a photocatalytic reactor system compared with a plug-flow reactor (Miyawaki, 2016). In this study, five lab scale stirred reactors were connected in series, the first reactor fed via a reservoir and pump, with flow to the subsequent reactors via gravity. The photocatalytic decomposition reaction took place in each of the reactors, with the overall conversion of the initial reactant increasing as flow moved throughout the system. Miyawaki successfully developed a mathematical model to predict the reduction in reactant concentration in each reactor with varying flowrate, this model was accurate when compared to the experimental results. A continually stirred tank reactor (CSTR) equation was derived (Equation 1) with terms describing the liquid volume and concentration in each reactor at a specific time and were derived as follows:

$$V\frac{dC_{b,i}}{dt} = \upsilon\left(C_{b,i-1} - C_{b,i}\right) - r_i V \quad (i = 1, \ldots, 5)$$

Equation 1: CSTR Equation for Predicting Reactant Concentration in a Series of Photocatalytic Reactors

Where V = Volume in each reactor (m3)

v = flow rate of an influent (m3/min)

C = Concentration of reactant (g/m3)

r = rate of photocatalytic reaction

i = Reactor number

This method of creating a mathematical model using the CSTR equations to describe the system in this work has proved accurate and similarities can be drawn towards the effluent system at Shasun, which consists of a number of tanks, the majority of which are stirred (or well agitated) connected in series. Difference exist however between the level control, which is not completely gravity fed (as this study was) and the physical

orientation of the storage vessels, where parallel systems which later connect in series as well as alternating modes of substance addition to the system exist. It can therefore be theorized that by creating a mathematical model based upon modified CSTR equations which have added terms to describe the specific characteristics of the effluent system at Shasun, an accurate model can be created. An example would be replacement of the rate of photocatalytic reaction created by Miyawaki (as shown in Equation 1) by a term describing the bio-decomposition of a particular substance in the bioreactor at Shasun's activated sludge wastewater treatment plant.

2.5.3. Residence Time Distribution

Following on from theory that the effluent system at Shasun could be represented and modelled accurately as a series of interconnected continuously stirred tank reactors whilst also introducing terms taking account for the specific characteristics of the system such as valves, pumps, storage level and a terms describing the removal of substances due to the bioreactor in the wastewater treatment plant, a study by Obonukut investigated the measured residence time distribution versus predicted of a tracer compound through a series of three CSTR's to determine the drift observed from theoretically ideal reactors (Obunukut, 2017). The residence time distribution (RTD) is defined as the probability distribution of time that a material stays inside a unit operation (in this case a stirred vessel) in a continuous flow system (Gao, 2012) and is therefore an important aspect of a model which would be used to determine the concentration of substances throughout the effluent system at Shasun over time, potentially enabling better management of the system. Obonukut mentions the limitations of such CSTR models (e.g. akin to Equation 1 above) that typically assume instantaneous perfect mixing as the inlet flow to the reactor contacts the bulk liquid, whereas in reality there will be areas of non-ideal mixing or stagnant zones due to the physical characteristics of a particular stirred vessel and it is therefore likely that deviations from the perfect RTD profile will be observed. The study conducted by Obonukut uses three lab scale stirred reactors (120 cm^3) in series, a pump to deliver liquid to the first reactor with the subsequent reactors fed via gravity, and Potassium chloride used as the tracer compound and calibrated conductivity meter for detection. The results showed that there was in fact a discrepancy between the ideal (theoretically perfect CSTR's in series) and the measured experimental results. This difference was relatively small however, the results obtained in the experiment with 3 CSTR's in series exhibited the performance of 2.61 theoretically perfect CSTR's in series. The

difference suggests either perfect mixing was not achieved (perhaps due the relatively high flowrate through the system compared with the reactor volume) or potentially due to the experimental procedure, such as the manual method of injecting the tracer compound with syringe and the location of doing so. Given the results presented by Obonukut, it is the opinion of the author of this thesis that the use of modified CSTR equations to describe the effluent system at Shasun would most likely present more accurate results than those obtained by Obonukut, due to the lower relative flowrate through the system compared to the volume of the storage vessels involved. The systems at Shasun also operates on a level-control system, rather than continuous flow which would allow more time for better mixing to occur earlier on in the effluent system, where concentrations of substances would be highest and therefore reduce the domino effect of errors early on in the system model.

2.6. Modelling the Effluent System

The steps taken to model the effluent system at Shasun will now be described. Following a review of literature, the model will be based on modified CSTR equations and begin with breaking the system down into component parts, defining the input and output variables, summarising the requirements of the model before development of the model's equations.

The effluent system firstly consists of a number of brick lined liquid holding "pits" connected directly to the manufacturing equipment (these are effectively sub-ground level rectangular storage tanks) followed by storage vessels for any other wastewater produced onsite. After these vessels, the wastewater is pumped into the wastewater treatment plant. Here, organic material is aerobically digested by microorganisms before being discharged to the municipal sewer. The sewer takes the wastewater off-site and to the sewerage treatment plant in Howden where is it treated and discharged into the river Tyne's estuary.

Figure 1 and Figure 2 show that the effluent system consists of 7 vessels of varying shape, volume and location. The effluent system begins with the 2 pits which collect wastewater from various different processes from the D1 and D2 production buildings. As these pits fill up, a high-level control switch is triggered, activating the pumps until the level is reduced to a set value. This control philosophy results in a periodic discharge of wastewater from the pits at a high flow rate. The wastewater is pumped into either of 2 holding tanks based on the anticipated chemical oxygen demand (COD);

wastewater with a high chemical oxygen demand is usually kept in holding tank B3066 whereas lower COD wastewater is kept in storage tank B3065. In addition to wastewater from the pits, commercial road tankers discharge wastewater into either of the holding tanks during the day.

The wastewater that enters the bioplant is a mixture from both of these holding tanks which allows for the COD to be controlled. By blending both the high and low COD wastewaters, a desired level of effluent treatment efficiency can be achieved. The wastewater is pumped from the holding tanks into the primary clarifier before flowing via gravity into the bioreactor (where organic content of the wastewater is reduced), secondary clarifier and then the municipal sewerage system. It should be noted that there the wastewater treatment plant can operate with up to three bioreactors in parallel and the number of bioreactors in operation depends on the organic load of the incoming wastewater stream. The wastewater then reaches the wastewater treatment plant in Howden before being discharged into the river Tyne's estuary.

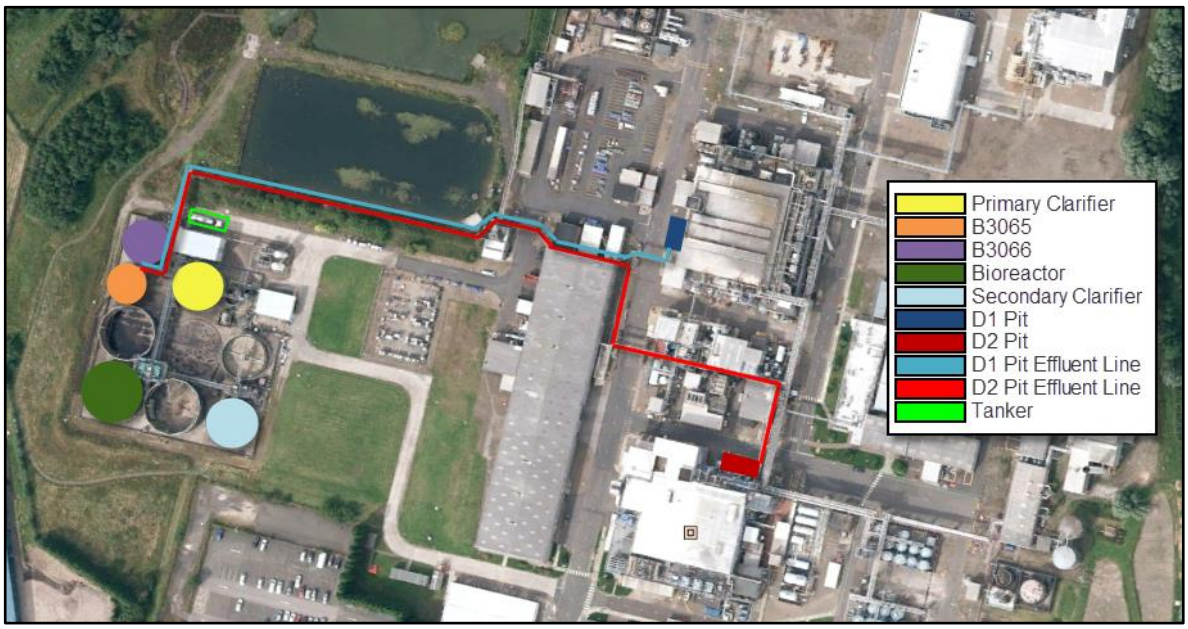

Figure 1: Birds-eye-view of the effluent system

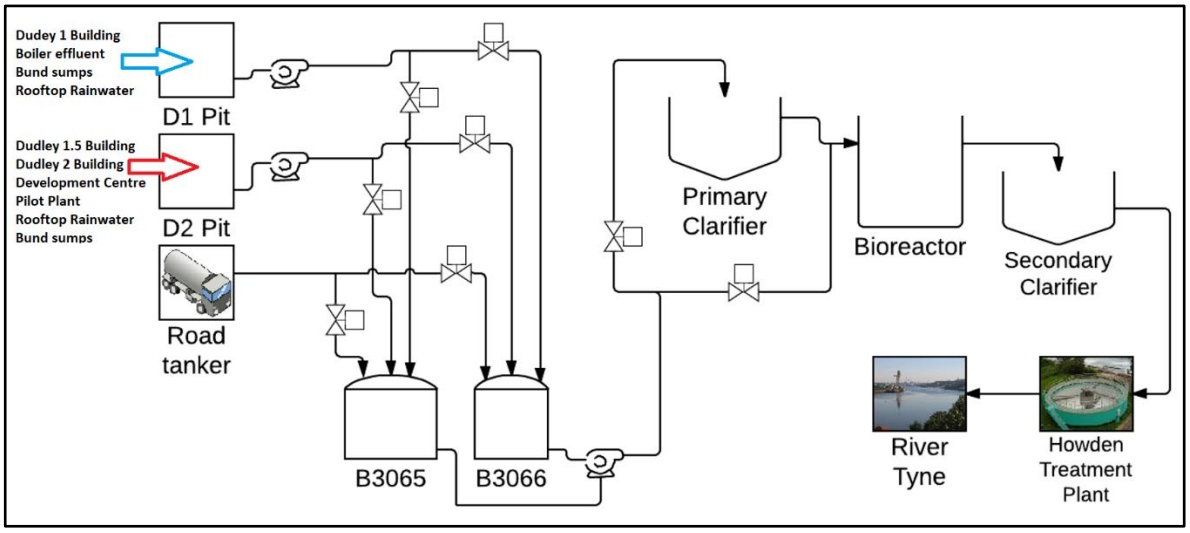

Figure 2: Effluent System Flow Diagram

2.6.1. Sources of Wastewater

The wastewater produced onsite at Dudley that is suitable for biological treatment is discharged into the effluent system. This wastewater can come from a number of different processes and can change with time due to demand of different products, or introduction of new ones.

The bulk of the wastewater produced onsite originates from three manufacturing buildings, Dudley 1, Dudley 1.5 and Dudley 2 buildings. Wastewater from Dudley 1 is directed into Dudley 1 pit, similarly wastewater from Dudley 2 is directed into Dudley 2 pit. Wastewater from Dudley 1.5 is directed into the smaller Dudley 1.5 pit, which is pumped directly into Dudley 2 pit when the level becomes too high.

There are several other sources of wastewaters that are suitable for biological treatment. These include the research and development centre, bunds, boiler house effluent and the pilot plant.

The bunds that contain liquid from areas containing large amounts of stored chemicals such as the flammable tank farm or drum parks drain into small localised sumps. When the liquid in these sumps reach a certain level, a pump is activated, this pumps the liquid into either Dudley 1 pit or Dudley 2 pit, typically whichever is nearest. Similarly, condensate from the boiler house collects in the boiler house effluent pit, which is pumped directly into Dudley 1 pit.

Wastewater from processes on the pilot plant is pumped into a nearby underground pit, which is periodically pumped into to Dudley 2 pit. Wastewater from the labs in the development centre is pumped into the development centre sump which is periodically pumped into Dudley 2 pit.

The way that the site effluent system is setup is such that it has the potential of capturing large amounts of rainwater, as any rainwater that falls in certain bunded areas or on the rooftops of the any building that handles chemicals will end up in either Dudley 1 pit or Dudley 2 pit. This can cause Shasun to exceed effluent discharge limits set by the regulatory authorities such as the maximum volume of wastewater discharged per day, amount of solids in the effluent or the maximum concentration of substances in the effluent leaving the site. A sudden increase in the volume of wastewater (e.g. from a storm) can have several negative effects on the biological treatment facility. To ensure that the effluent storage system does not overflow, the flow into the bioplant must be increased. This results in a faster flow of liquid in the primary and secondary clarifiers which can disturb the blanket of settled solids near the bottom of the vessels, this causes a large increase in solids in the effluent leaving the bioplant. Another effect is the reduction in the residence time of wastewater in the biological treatment plant and so reduces the amount of time that the microorganisms have to reduce the organic content of the wastewater and so the treatment efficiency is decreased.

Wastewater is also treated by the bioplant on a commercial basis, tanker loads of wastewater are driven to the site and discharged into either vessel B3065 or B3066 depending on the characteristics of that particular wastewater. These could be high or low chemical oxygen demand as well high ammonia (which can cause activated sludge settleability properties to deteriorate (Novak, 2001) resulting in decrease in plant treatment efficiency) or sulphate levels. Typically, the bioplant receives wastewater in the form of landfill leachate which usually has a chemical oxygen demand of 5000 mg/l. The chemical oxygen demand of wastewater from other off-site sources has been known to reach the 100,000's or even 1,000,000's, in which case it will be diverted to B3066 and fed into the bioplant at a controlled rate to ensure adequate dilution, this rate is currently based on a simple volume calculation and doesn't take into account the complex dynamics of the system and is something that the effluent system model should be able to calculate.

The COD of wastewater from Dudley 1 pit has typically ranged from 1000-25000 mg/l and the wastewater from Dudley 2 pit typically ranges from 1000-50000 mg/l.

Other sources of wastewater could be from intentional discharges from drums or intermediate bulk containers (IBC's) which are discharged directly into either B3065 or B3066 mixing/balancing tanks, or alternatively straight into the bioreactor. This often takes place when the wastewater contains a high level of solids (that would have settled out if discharged to Dudley 1 or Dudley 2 pits) or if the disposal of the wastewater by other means (e.g. off-site treatment by a third party) is too expensive even though it may not have a high level of biodegradability. There should therefore be the ability to model the effects of discharging a known volume of wastewater to different parts of the effluent system over a specified time period, separate from normal operation, to account for scenarios such as drum additions.

There may also be unintentional releases such as spillages from containers or leaks from other systems (e.g. glycol from the sites' vessel jacket services or even scrubber systems) that work their way into the effluent system and there should be a way of investigating these scenarios with the model.

2.6.2. Summary of Requirements

A summary of the customer requirements for the effluent system model is listed in Table 5 below. These requirements were obtained through meetings with Shasun staff involved with the site's wastewater management.

Table 5: Summary of Effluent System Model Requirements

No.	Description
1	Closely simulate the current effluent system dynamics
2	Produce an interface to allow easy use of the model
3	Ability to change and save all variables behind the model
4	Model addition of a new wastewater to the system with either a batch or continuous profile
5	Model tanker wastewater discharge into either holding tanks
6	Model drum discharge to holding tanks, primary clarifier or bioreactor
7	Model up to 5 components with different concentrations, treatment efficiencies, source and addition profile / rate at the same time
8	Ability to set wastewater route by opening / closing valves in the system
9	Simulate the concentration of a substance as it reaches the domestic wastewater treatment plant
10	Simulate the dilution of a substance into the Tyne's estuary
11	Ability to simulate the effects of excessive rain (flow) on the system

12	Ability to simulate unintentional releases to the system
13	Library of substances with associated environmental discharge limits and treatment efficiency e.g. Predicted No Effect Concentrations (PNEC[Note1])
14	Facility to display results of a simulation in both numerical and graphical ways for ease of interpretation
15	Simulate operation of the effluent system with either 1, 2 or 3 bioreactors in operation

Note 1: PNEC is the upper concentration limit of a chemical at which no observable adverse effects on the ecosystem are measured.

2.6.3. Vessel sizes and flowrates

The next sections of this chapter describe how the effluent system was characterized and a representative model created. Table 6 shows the dimensions and volume of each vessel in the effluent system and also show which vessels are continually agitated. D1 pit, D2 pit and vessel B3065 have mechanical stirrers and although vessel B3066 does not have a mechanical stirrer, a degree of mixing is achieved though the constant recirculation of the contents of the vessel by a nearby pump.

The primary and secondary clarifiers have no agitation as the function of these vessels is to remove solids by gravity settlement. The bioreactor is continuously well agitated by the force of a mixture of pure oxygen and air being blown into the bottom of the vessel as required by aerobic digestion of the organic content of the wastewater by the microorganisms that make up the activated sludge.

Table 6: Effluent System Tank sizes

Tank	**Agitated**	**Height (m)**	**Area (m^2)**	**Volume (m^3)**
D1 Pit	Y (Continually Stirred)	3.5	24	84
D2 Pit	Y (Continually Stirred)	5	30	150
B3065	Y (Continually Stirred)	6	133	800
B3066	Y (Recirc pump only)	6	200	1200
Primary Clarifier	N	n/a	n/a	800
Bioreactor	Y (Recirc pump & aeration)			2500
Secondary Clarifier	N	n/a	n/a	800

Table 7: Flowrates and concentrations entering the effluent system

Wastewater Source	Average flowrate (m^3/day)	Average COD (mg/l)
D1 Production building	133.13	2886.64
D2 + D1.5 Production buildings	99.23	9638.84
Road Tankers	112.14	7061.3
B3065 Dilution water	120	0
Total (m3/day)	510.46	
Total (m3/hr)	21.269167	

Table 7 shows the average flowrates and chemical oxygen demand of wastewater entering the effluent system; they were calculated by averaging data collected from the last 3 years. D1 and D2 pits collect wastewater from the whole site, this wastewater is predominantly sourced from D1, D1.5 and D2 production buildings. Other sources that end up in one of these pits include bunds across the site, development centre wastewater, pilot plant wastewater and boiler house condensate. The values in Table 7 are used for general case modelling, they are configurable and can be changed to reflect different circumstances on the site or for sensitivity analysis.

2.7. Equations for Modelling

The effluent system contains a series of mixing tanks, where one substance is poured into the tank at a flowrate of *Qin* (m^3/hr) and is mixed with another substance to form a mixture. This mixture is assumed to be 'well mixed' which is a term used to indicate that the fluid being poured into the tank is assumed to instantly dissolve into a homogenous mixture as soon as it enters the vessel. This well mixed solution then leaves the tank at a flowrate of *Qout*. Figure 3 shows a diagram of a mixing tank.

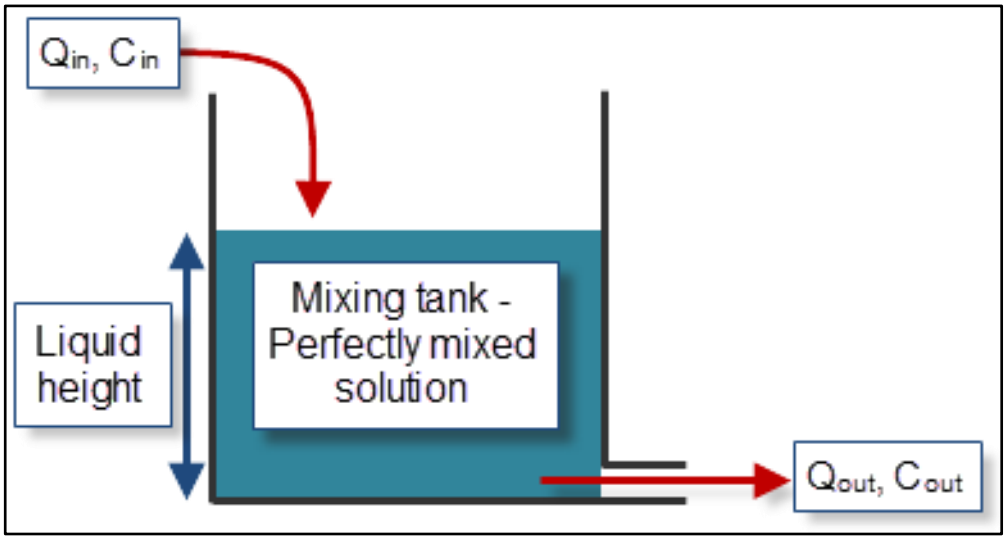

Figure 3: Mixing Tank containing a perfectly mixed solution (Continuously Stirred Tank Reactor, CSTR)

If the flowrate of liquid entering the tank is equal to the flowrate of liquid leaving the tank, the liquid height will stay the same. This is the case that is assumed for all the vessels in the effluent system except for D1 pit and D2 pit, which has pumps that activate when the level in the pit reaches a maximum height and deactivate when the minimum height is reached. The liquid level in the two storage tanks, B3065 and B3066, can also change if desired depending on the position of valves and pump flowrates.

C_{in} is the concentration of a substance in the solution being poured into the tank and C_{out} is the concentration of the substance in the mixture leaving the tank.

The two differential equations used to determine the liquid level and concentrations of substances in each tank are described in the following section.

2.7.1. Liquid Level

To calculate the change in liquid level in a tank with respect to time, the following equation was derived:

$$Change\ in\ tank\ level = Amount\ of\ liquid\ entering - Amount\ of\ liquid\ leaving + Accumulation\ of\ liquid (= 0)$$

$$\frac{dH}{dt} = \frac{Q_{in} - Q_{out}}{A}$$

Equation 2: Calculation of Liquid Level

Where: H = liquid level in tank (m),

Q_{in} = Volumetric flowrate of liquid entering the tank (m^3/s),

A = Cross-sectional area of tank (m^2),

Q_{out} = Volumetric flowrate of liquid leaving the tank (m^3/s).

2.7.2. Substance Concentration

To calculate the change in concentration of a substance, s, in the mixing tank with respect to time, the following calculations were made:

$$Change\ in\ amount\ of\ substance$$
$$= Amount\ of\ substance\ entering - Amount\ of\ substance\ leaving$$
$$+ Accumulation\ of\ substance\ (= 0)$$

$$\frac{dS}{dt} = C_{in}Q_{in} - \frac{S}{V}Q_{out}$$

Equation 3: Calculation of Substance Concentration in a Mixing Tank

Where: C_{in} = Concentration of S in liquid entering the tank (kg/m^3),

Q_{in} = Volumetric flowrate of liquid entering the tank (m^3/s),

S = Mass of particular substance, S, in the tank (kg),

V = Volume of tank (m^3),

Q_{out} = Volumetric flowrate of liquid leaving the tank (m^3/s).

Since there is assumed to be perfect mixing, there is no accumulation of substance, *S*, in the tank and so the mass of *S* in the tank is dependent on the concentration in the liquid entering the tank.

2.7.3. Model Assumptions

The following list describes the assumptions made and their rationale when creating the model:

1. **Each tank is perfectly mixed (CSTR)**

   This assumption was made to keep a balance of model complexity versus accuracy. It will eliminate the dependency of change in position in the vessel on the substance concentration. Additionally, five out of the seven vessels in the effluent and wastewater treatment system have agitation (Table 6) and the remaining two clarifier vessels are designed such that baffles reduce inlet velocity and prevent a direct path for incoming liquid to exit the vessel via the outlet. It has been assumed that due to the low velocity and relatively large volume, mixing has time to occur.

2. **The source flowrates of wastewater are an average over the last 3 years and do not change with time for the duration of the model**

   To provide an accurate background of wastewater flow through the system, an average flow over the past 3 years was taken. Any additional wastewater discharged into the model by the user will be added on top of this background flow.

   In the case that the user wishes to change the background flowrates, it can easily be done by changing the input variables for flowrate and chemical oxygen demand. If the user wishes to test changing background conditions during a model run to account for added variability, perhaps due to introduction of a new batch process or for sensitivity analysis, this is also possible by adding a new wastewater stream to the model inputs and selecting the characteristics of the stream.

3. **There is no transfer delay between tanks.**

   Since a typical simulated period by the model is over a month in length, the time it takes to transfer wastewater from one vessel to the next (a couple of minutes at maximum) is insignificant and will only add unnecessary complexity to the model.

   The exception is the time taken for wastewater discharged from the secondary clarifier to reach the sewerage treatment works in Howden, and then from there into the river Tyne's estuary. There is insufficient information to calculate the magnitude of this delay, and it may depend greatly on the flow of municipal

wastewater in the catchment area for Howden which could have significant variation. This time delay has therefore been excluded in favour of estimating the worst case scenario.

4. **Initial tank concentrations and levels are estimates.**

The initial chemical oxygen demand and levels in each vessel are estimates. The model is run for sufficient time in the background for equilibrium to be reached (based on the background wastewater flowrate and COD) in each vessel before any user input wastewater enters the system.

5. **There is no accumulation of substances in the tanks.**

Ignoring the accumulation of substances in each vessel has the advantage of keeping the model simple. Every couple of years each vessel develops a layer of sludge at the bottom and requires cleaning out, however since the model run time will most likely be approximately 4-16 weeks at maximum, the effect of a small continuous amount of accumulation of substances will be negligible.

The working volume of the tank and the concentration of substances will decrease by an extremely small amount per week resulting in no significant change in the models results.

6. **There are no reactions taking place that change the concentration (except in the bioreactor)**

D1 pit and D2 pit contain a cocktail of chemicals from various processes onsite which may result in chemical reactions that change such things as the chemical oxygen demand. This effect would be time consuming to account for in the model as processes can run at different times resulting in many different combinations of chemicals at any one time in the effluent system. Additionally, data collected on the typical characteristics of the wastewater found in D1 and D2 pits (e.g. COD measurements) are conducted routinely and as these vessels are constantly stirred, reactions can be assumed to have already taken place and variance due to these reactions is accounted for in the measurements. If there is a known reaction of a new wastewater being tested by the model with background wastewater, this change in composition can be calculated manually prior to entering the new wastewater

characteristics into the model. The effects due to reactions have therfore been excluded from the model.

2.8. Simulink Model

The effluent system model to predict the concentration of different substances with respect to time was created using MATLAB's Simulink software. A fixed step solver that uses the Bogacki-Shampine formula for integration (ODE3) was used to solve the differential equations in the model (Equation 2 and Equation 3 on page 32). This solver was used as it exhibits an even balance between accuracy and computational effort (to prevent the user from waiting more than a minute for results to be presented) and is also suitable for continuous system such as the one being studied (MathWorks, 2019) and can be compiled into a standalone executable file as per Shasun's requirements. This solver computes the next simulation time by adding a fixed-size time step to the current time. For each of these steps, the solver uses numerical integration to compute the values of the continuous states of the model. These values are calculated using the continuous states at the previous time step and the state derivatives at intermediate points (minor steps) between the current and previous time steps (MathWorks, 2014). In these simulations, a time step of 1 was used which represents 1-minute increments in time. This was thought more than adequate as model simulation-times are of the order of several weeks, so time steps of smaller than 1 minute do not provide the user with significant extra information but would increase the time taken to perform the calculations. The following sections describe how Equation 2 and Equation 3 were built into Simulink to produce a model that represents the effluent system at Shasun.

2.8.1. Overview of the model

Figure 4 and Figure 5 show an overview of the whole model in Simulink. This is the highest-level view of the model and shows the flow of data from the left hand side to the right hand side. To begin with, all of the input variables to the model need to be defined, this is done via the 8 blocks named D1_Pit_Variables, D2_Pit Variables, Drum_Discharge2_Variables, Drum_Discharge2_Variables, Valve_Variables, Vessel_Vols, Tanker_Variables and Vessel_Conc_Variables. Once in the overall model, the initial variables are fed to the relevant location by using the From or In-port Blocks and calculated results are forwarded to the required location using the Goto Block. A BusCreator (as shown in Figure 6) block was used to compile multiple

variable signals into one stream for transporting around the model and a BusSelector Block was used to select a specific variable from a stream containing several signals.

The model layout is set-up to represent the process flow diagram of the effluent system, i.e. starting with input material into D1 and D2 collection pits before transportation to the two storage vessels B3065 or B3066 (depending on valve positions in Valve_1 block), the signal then travels forward to the primary clarifier or straight to the bioreactor (depending on the valve position defined in the Pipe_Valve2 block). The bioreactor can receive wastewater input from several locations, directly from the primary clarifier, drum discharge point or from tanks B3065 or B3066 is the primary clarifier bypass valve is activated. Following the Bioreactor block, data is fed into the Secondary_Clarifier Block followed by Howden Sewerage Works Concentrations and Tyne Concentrations Blocks where the final concentrations and flows calculated by the model are calculated.

All the way through the different sections of the model where calculations for each vessel and tank are made, there are Outport blocks to ouput results from the model so that they can be analysed as results. This allows the user to track the concentration profiles of a substance as it changes through the effluent system.

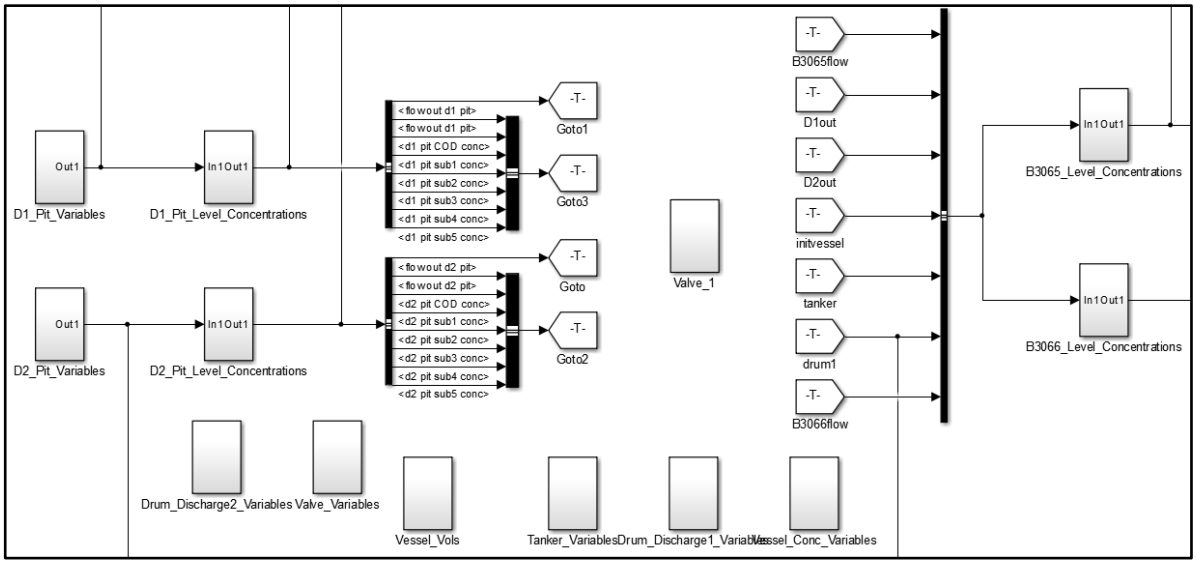

Figure 4: Overall Layout of the Simulink Model (part 1 of 2)

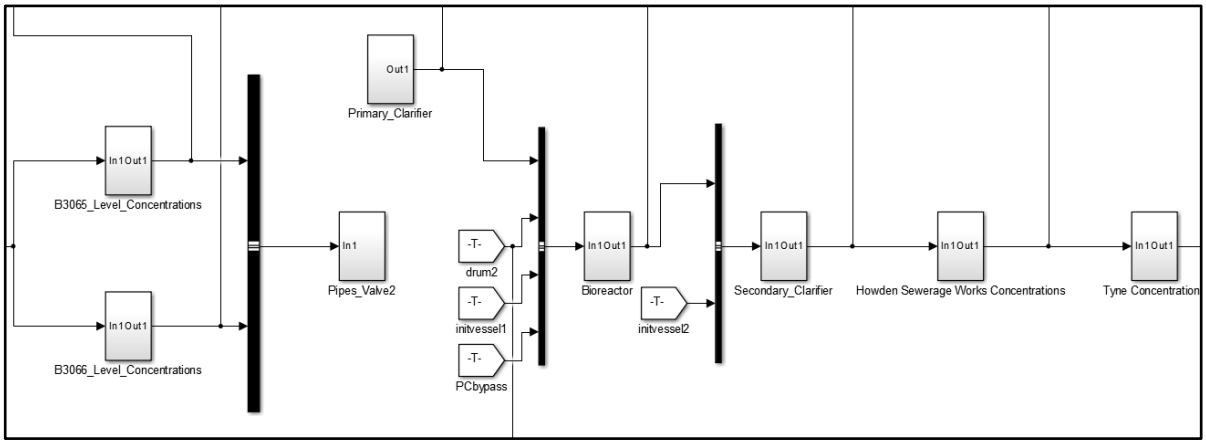

Figure 5: Overall Layout of the Simulink Model (part 2 of 2)

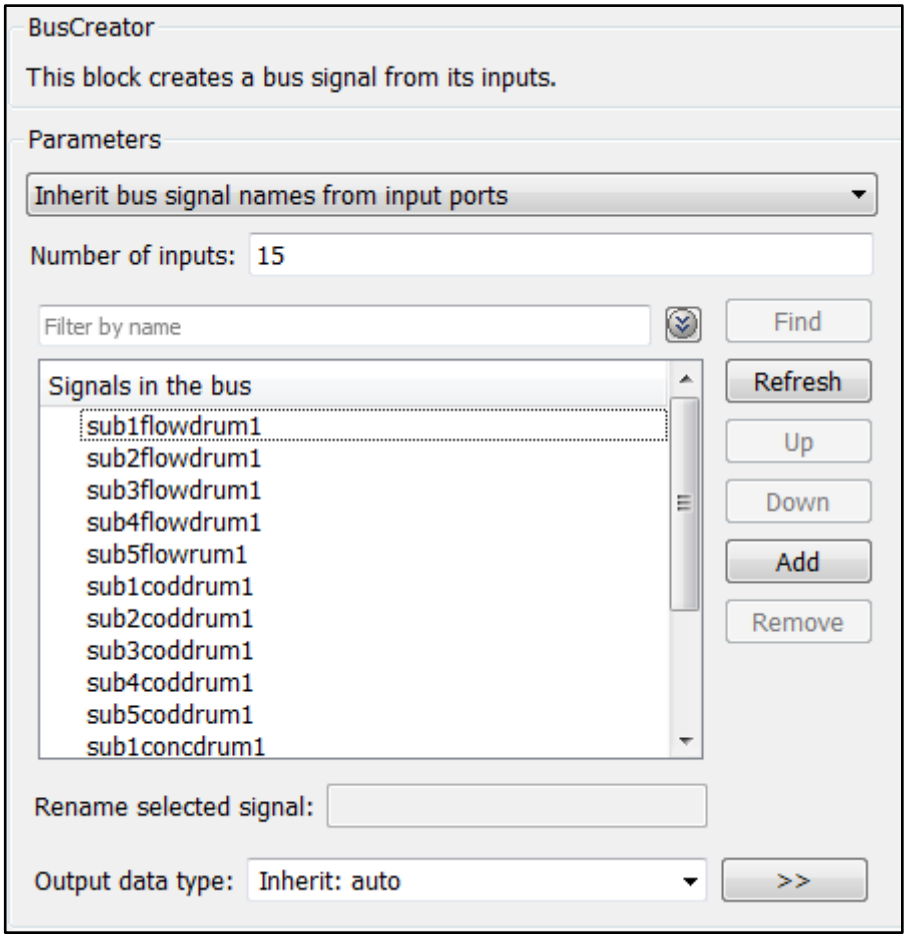

Figure 6: Bus Creator Block to combine signals into a stream

2.8.2. Input Variables

In order to input values into the Simulink model, there must be a defined block for a specific variable. There are two main types of input variables used in this Simulink model, these are Constants (Figure 7) which consist of a singular numerical value that doesn't change with time for the duration of a model simulation run (constant variables include tank areas and volumes, pump speeds and pump level control characteristics). The other type of variables are dynamic ones, the outputs of these variable can change with time and are represented by the pulse generator block in Simulink as shown in Figure 8 (e.g. Sub1flowd2) Figure 9. An example of a dynamic variable would be the flowrate of a substance that was added to the effluent system via the drum charging system directly to the bioreactors or storage tanks, B3065 and B3066. This addition can have different characteristics such as flowrate, duration of discharge and the time between additions if, for example, there was more than one drum or volume of wastewater to be discharged (e.g. 5 drums a week due to batch processing). The Amplitude, Period and Pulse Width value of the Pulse Generator Block in Simulink can be changed to achieve the desired type of flow. In the case that there are a finite number of batches where a substance is discharged to the effluent system, the signal resulting from the pulse generator block can be terminated after a certain period of time that relates to the number of batches that have occurred. To achieve this, a relay block and digital clock block shown in figures Figure 8 and Figure 10 (this tracks the time of the current simulation) is used which multiplies the signal from the pulse generator by zero once the specific time relating to the correct number of batches is reached and therefore stops the signal from transmitting any longer. This method of signal termination using a relay block is used throughout the model.

If the user of the model wanted to simulate different substances being discharged to the effluent system in the same simulation but at different times, the Transport Delay block is used (as shown in Figure 8) which allows the user to specify a time delay before the signal representing the flow of a substance becomes active in the model.

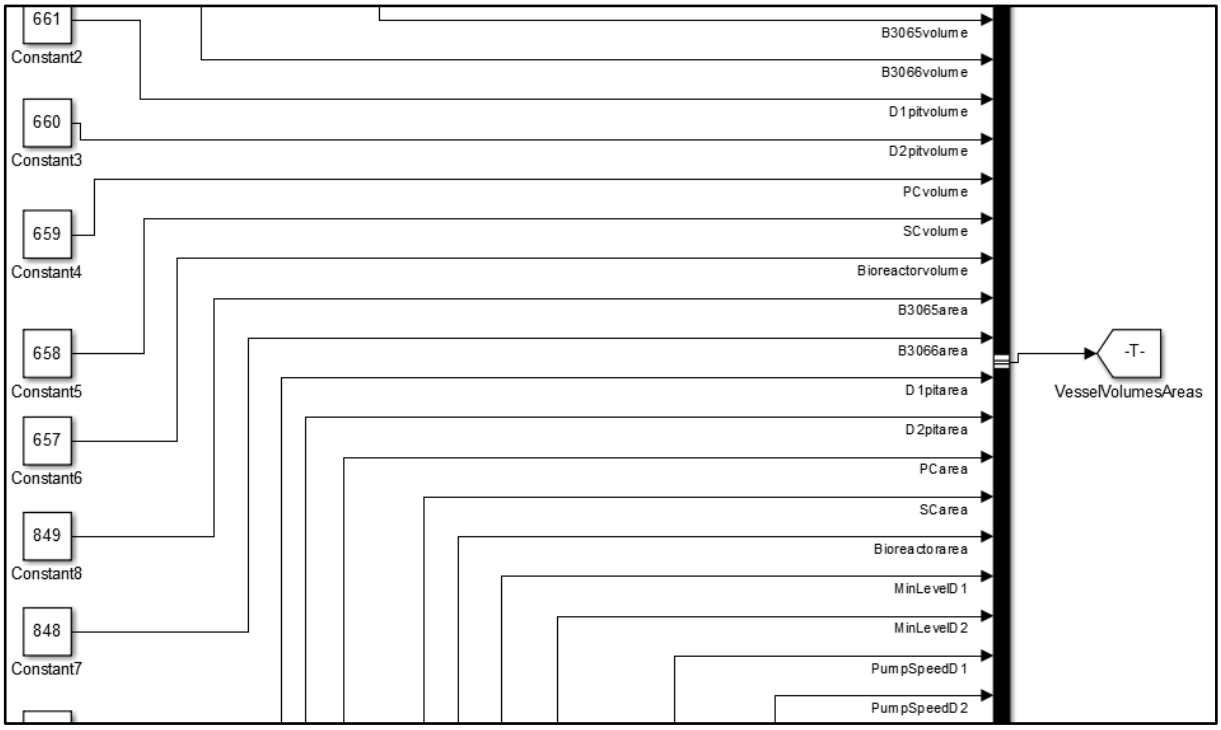

Figure 7: Input of variables with constant values

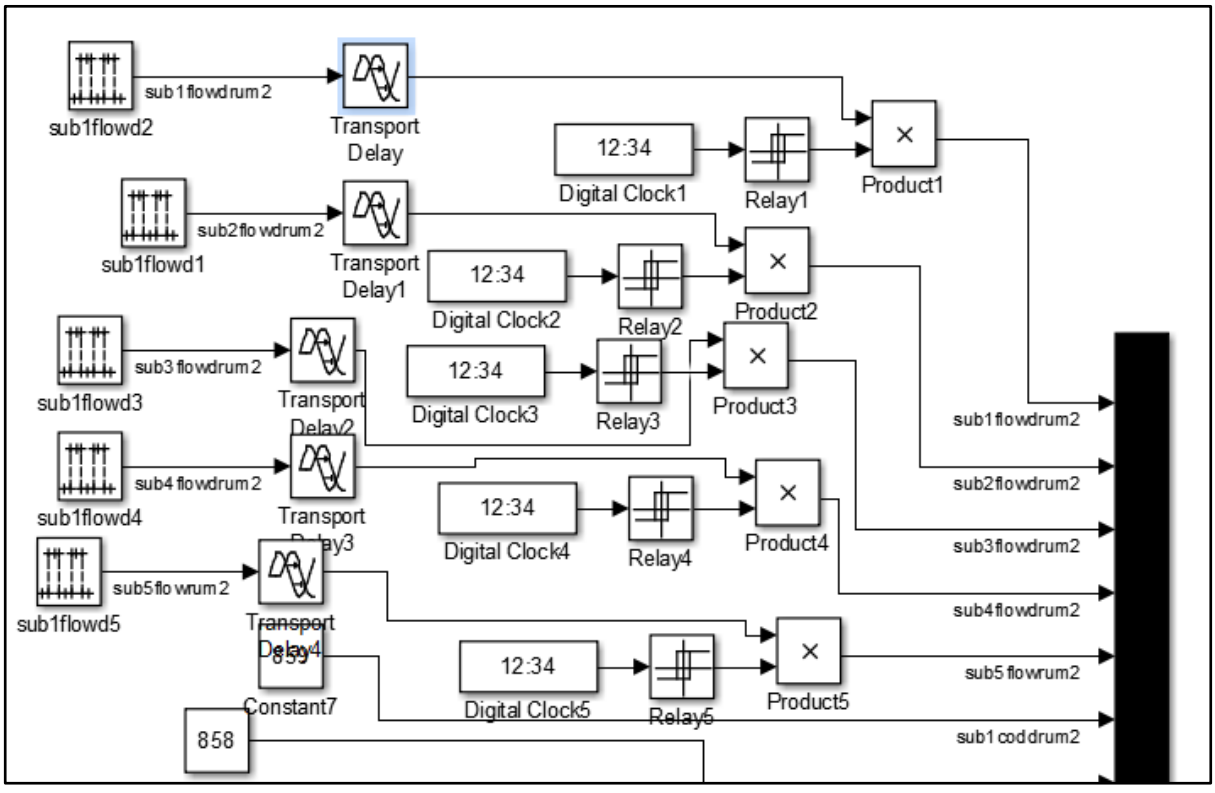

Figure 8: Input of Variables with time delay

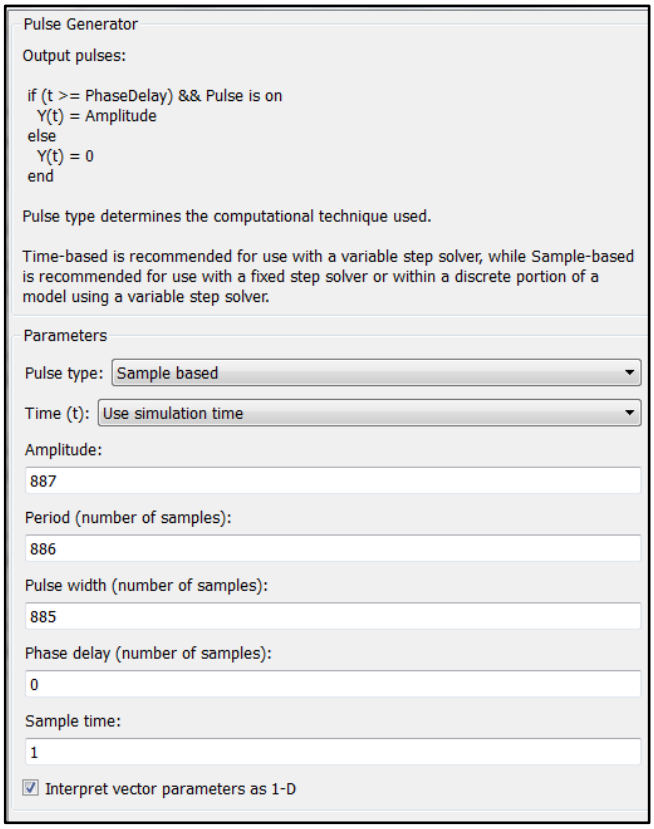

Figure 9: Use of Pulse Generators for Variables with Dynamic Values

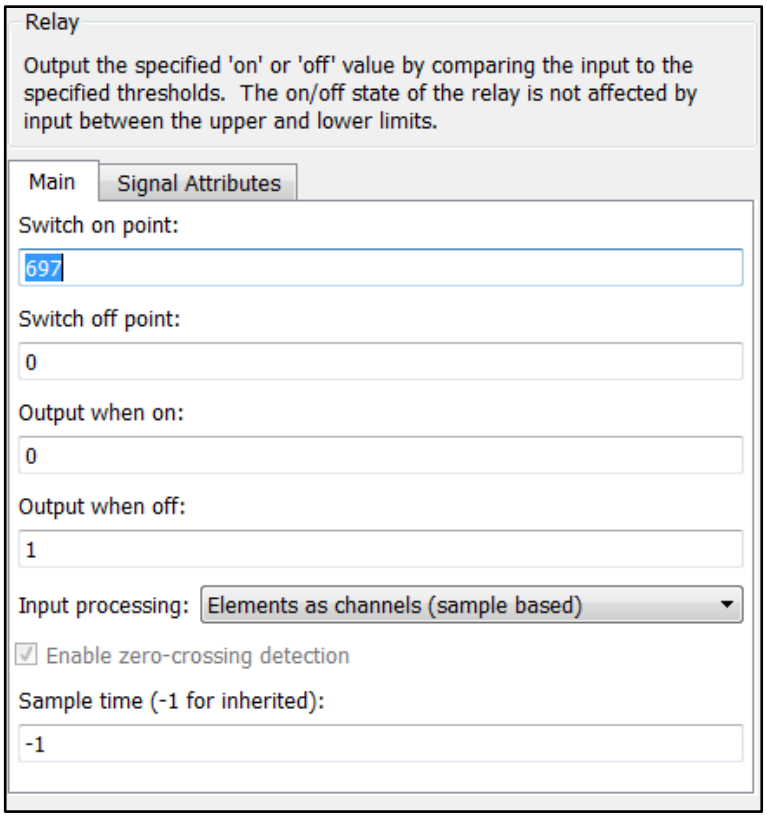

Figure 10: Relay Block to determine On / Off status of a variable or data stream

2.8.3. Tank Level Calculation

By clicking on one of the vessel system blocks in the overall high level view such as D1_Pit_Level_Concentrations (as shown in Figure 4 Figure 5) the following model set-up in Figure 11 below is shown. This is a high-level view of all the calculations for determining the liquid level and flow-out of a vessel as well as the COD concentration and substances 1 to 5 concentrations (as the model allows for simulation of up to 5 different substances at any one time). The main variables required for the calculation enter this part of the model via In1 (top left in Figure 11), the signal is diverted to each of the different calculation blocks (e.g. D1_Pit_Level). The resulting calculations from these blocks are diverted to a Bus signal or Goto block for use in the next section of the model.

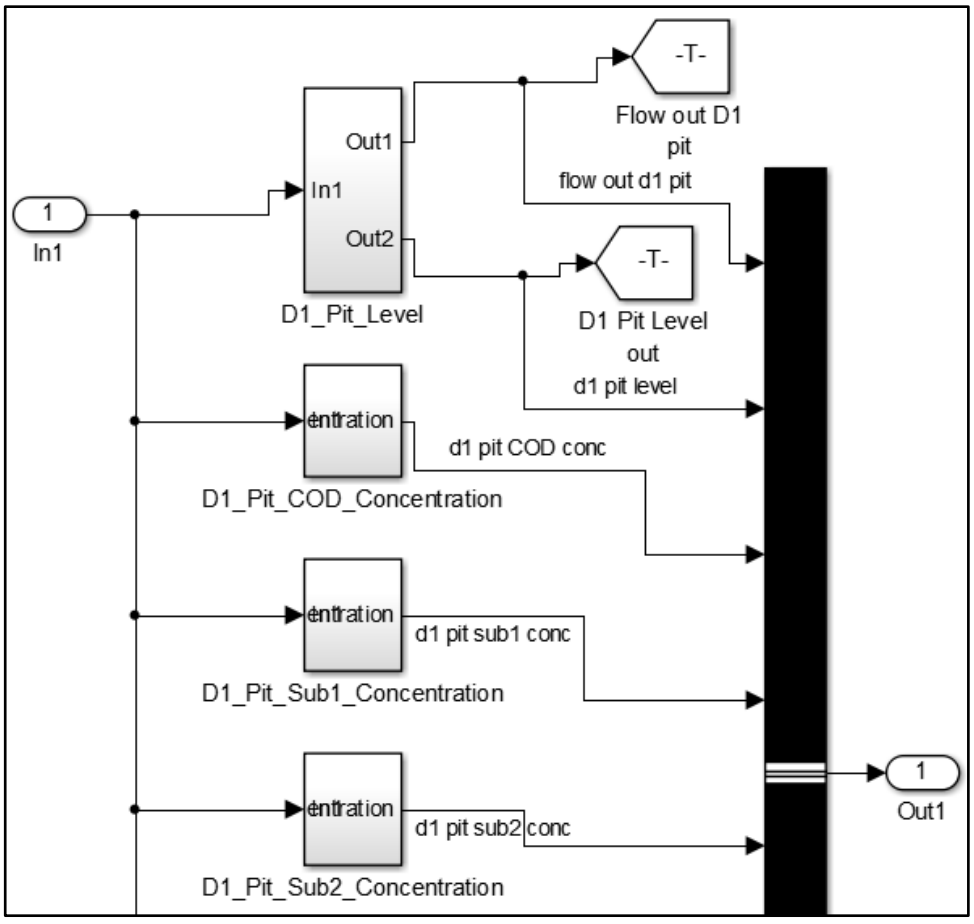

Figure 11: High Level View of Level and Concentration Values in a Vessel

Both D1 and D2 pits have pumps that are operated on level control. There is a maximum level, at which the pumps activate and begin emptying the pits and a certain flowrate until the liquid in the pits reach a minimum level, at which point they stop

pumping. This type of flow regime causes large spikes in concentrations of materials further down the effluent system.

The Simulink model that describes the change in liquid level in a storage vessel found in the effluent system is shown in Figure 12. This describes the level in D1 Pit and D2 Pit and is very similar to that of the calculation for the levels in B3065, B3066, the primary clarifier, bioreactor and secondary clarifier (except there is no representation of a pump in those calculations) and represents the differential equation for the change in level as shown in Equation 2 (page 32).

Figure 12 below shows how the level in D1 Pit is calculated, variables containing the pump speed, minimum level switch control and flowrate of regular background wastewater as well as any additional substances if present (substances 1 to 5, which exist depending on what chemicals the user of the model wishes to simulate in the effluent system) are input to the model. The flowrates are summed, divided by the area (gain block) to give a level in the vessel and then integrated with respect to time. This level height is then added to the minimum vessel level (the point when the pump switches off) until it reaches the level at which the pump switches on (defined by the relay block). This relay block then produces a signal value of 1, which multiplies with the PumpSpeedD1 variable and then becomes the flowrate out of the vessel. This flowrate out is used to subtract from the flowrate in and thus adjusts the level in the vessel accordingly over time until the minimum level in the vessel is reached.

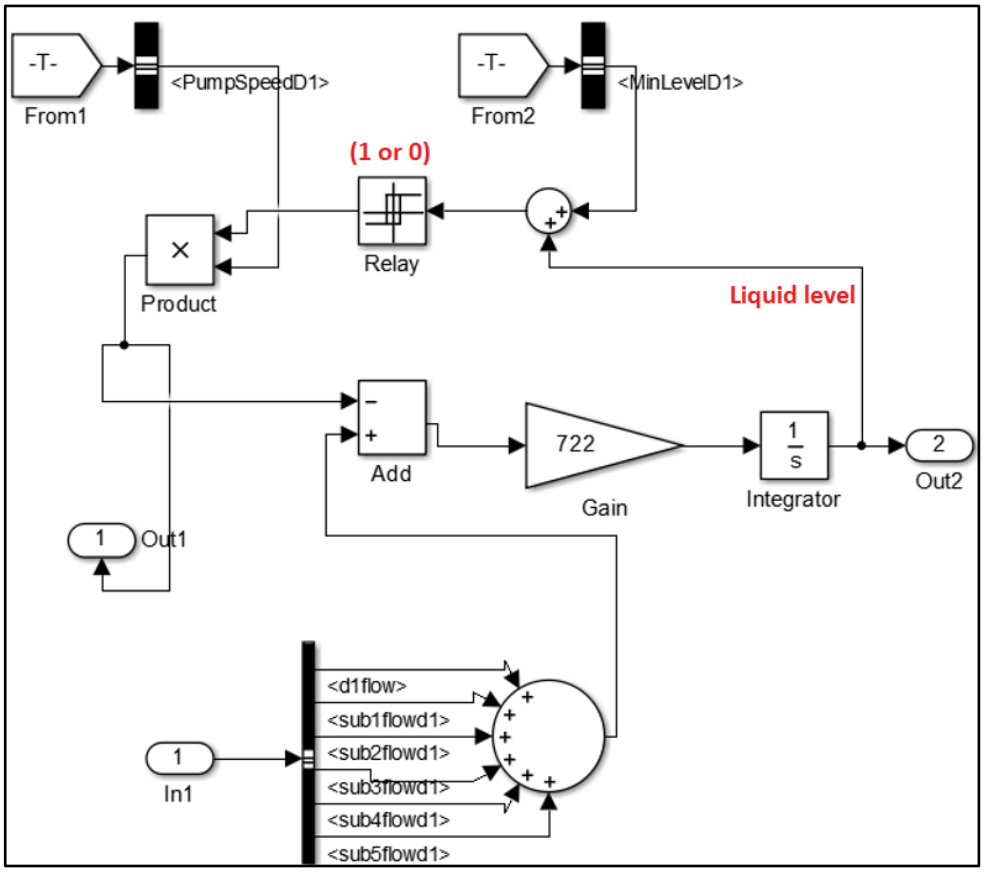

Figure 12: Simulink Calculation of Level in a Vessel

The COD and concentration of substance 1 to 5 in each of the vessels in the effluent system is calculated based on the Simulink model shown in Figure 13 below. In this case we are looking at the calculation for COD in D1 pit. The initial concentration at time 0 of the COD in the background wastewater and substances 1 to 5 are input into the Simulink model and multiplied by their respective flowrates to give a value in mass per unit of time going into the vessel. These values are summed to give a total mass of COD entering the vessel at a particular time step, integrated and then added to the initial amount of COD in the vessel at time zero. This total mass of COD is divided by the volume of liquid in the vessel (as determined by the previous liquid level model) to give an overall COD concentration in the vessel, this concentration is then used as the output from this part of the model and fed to the next vessel calculation. This concentration value is also multiplied by the flow out of the vessel and the resulting value used to subtract from the amount of COD entering the vessel at every subsequent time step so that the model properly describes Equation 3 (i.e. accumulation = in – out). As previously mentioned, the same general model is used for calculating the concentration in each of the vessels in the effluent system. There are small differences however depending on the vessel, the bioreactor for example, contains a term that reduces the

COD or concentration of a particular substance by a certain percentage depending on its biodegradability value which is a user defined input to the model. This can be seen in Figure 14, where the output of the blocks that calculate COD and concentration are multiplied by a factor (e.g. BioFactorCOD) relating to the biological treatment of that particular substance.

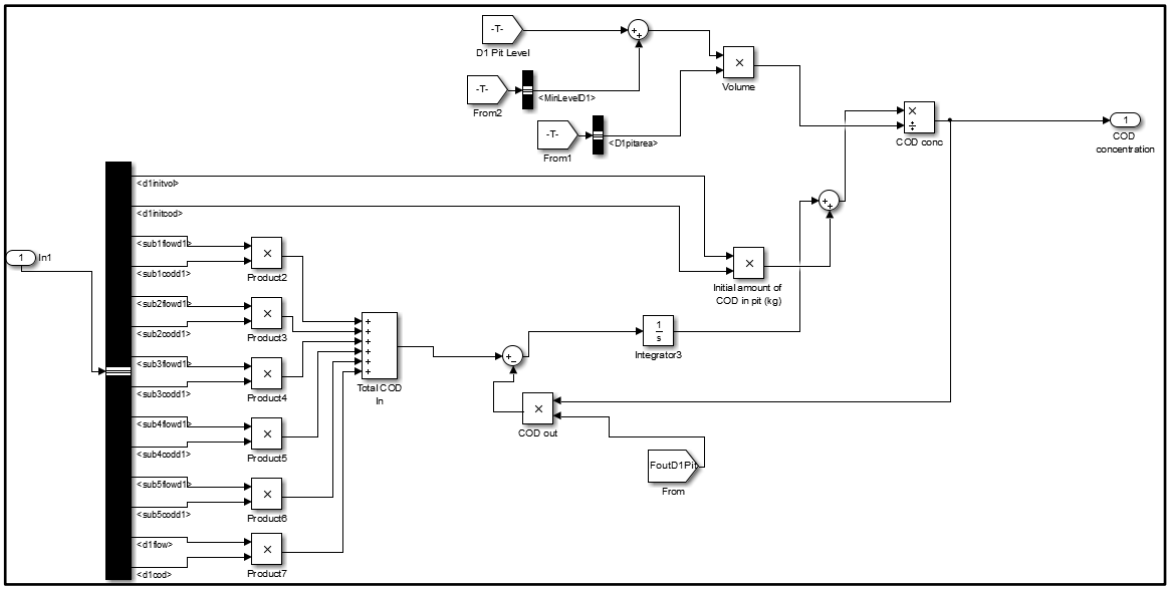

Figure 13: Simulink Calculation of Concentration in a Vessel

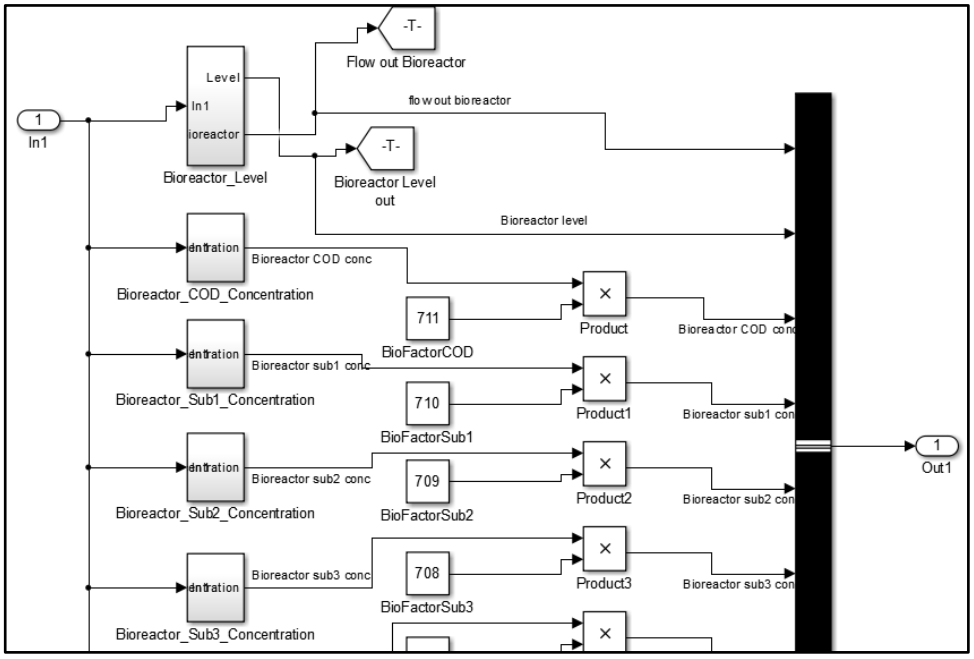

Figure 14: Simulink bioreactor high-level model view with biodegredation values

2.8.4. Simulation of Valves in the Effluent System

A similar concept to the level controls of the D1 and D2 pits were applied to the valves that determine the path of wastewater going into the large mixing tanks, B3065 and B3066, as well as whether or not to bypass the primary clarifier. The model set-up in Simulink is shown in Figure 15 Figure 16. Here the user of the model defines whether or not a specific valve is open or closed, which results in that particular valves input value to become either 1 or 0 by use of a relay block. The flowrate signal entering the large mixing tanks is then multiplied by this variable which determines whether the wastewater enters B3065 or B3066. The same principle was used for the primary clarifier bypass valve (as shown in Figure 17 Figure 18), which is activated when the primary clarifier is out of use due to maintenance.

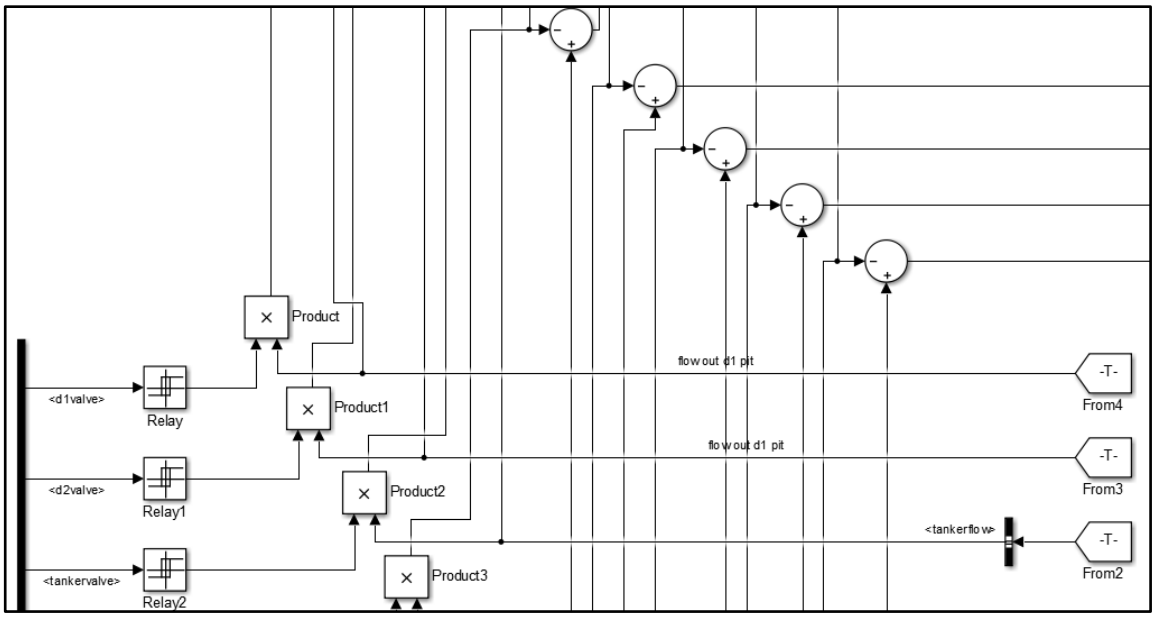

Figure 15: Simulation of Valves in Simulink (Part 1 of 2)

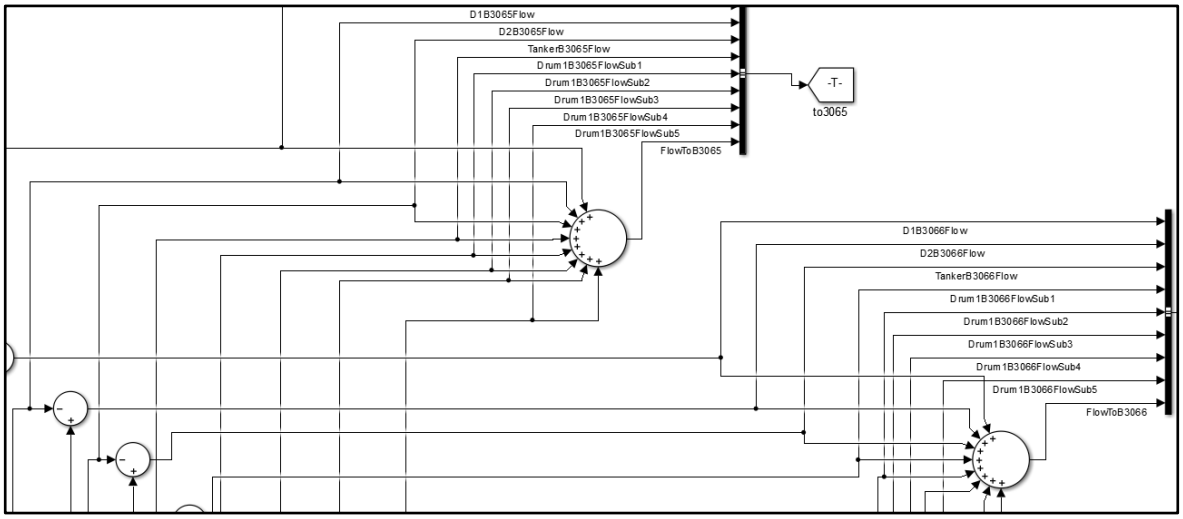

Figure 16: Simulation of Valves in Simulink (Part 2 of 2)

Figure 15 and Figure 16 show that if a valve is open or closed, its variable is 1 or 0 (relay output of on or off). This is multiplied by the flowrate of each stream and depending on the state of the valve variable, one of the streams leaving to the top of Figure 15 will have a flowrate. Figure 16 shows that these streams are recombined and are sent to tanks B3065 and B3066, thus redirecting flow depending on the state of the valve variables.

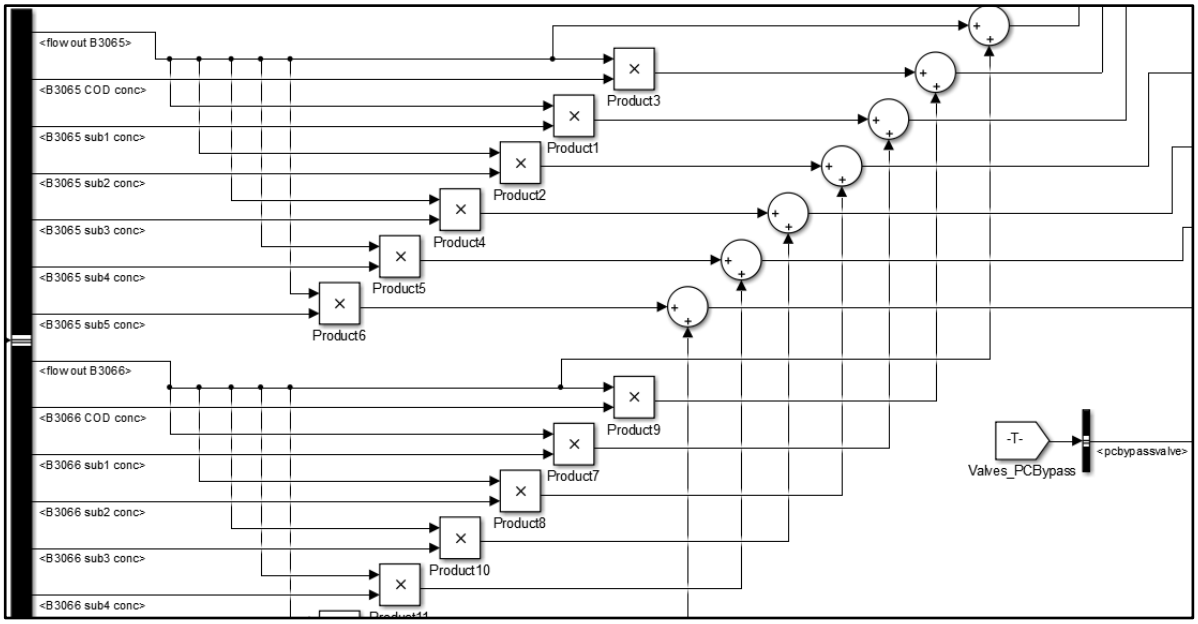

Figure 17: Simulink model of Primary Clarifier bypass valve (Part 1 of 2)

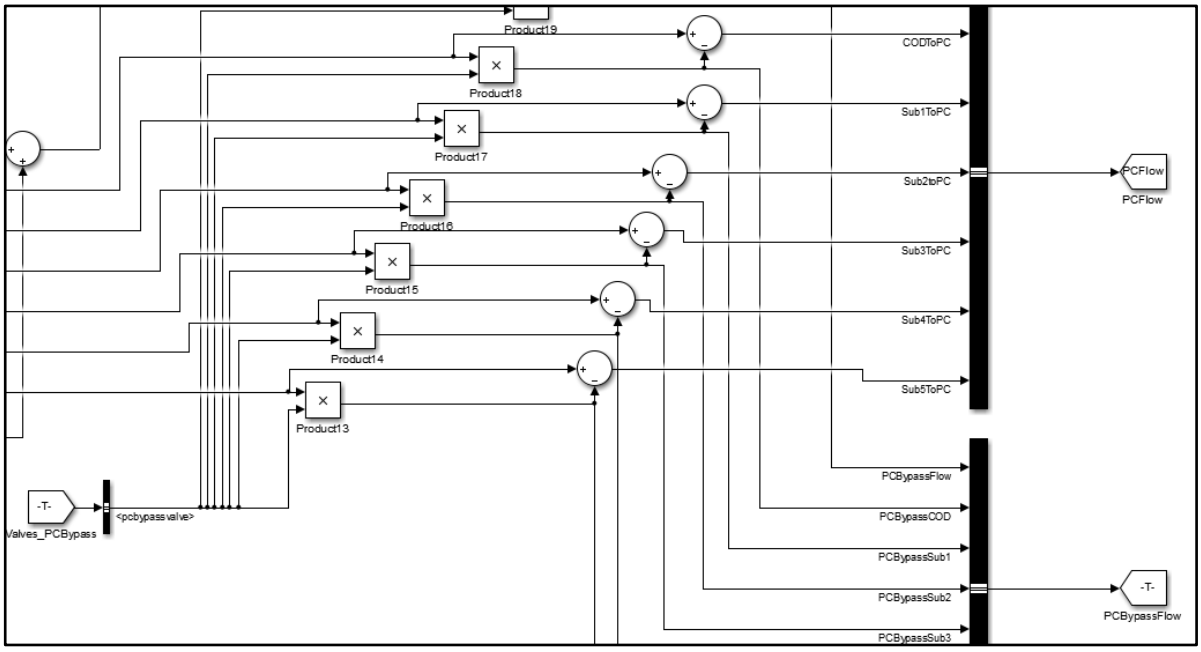

Figure 18: Simulink model of Primary Clarifier bypass valve (Part 2 of 2)

2.8.5. Dilution to Howden Wastewater Treatment Plant

The final part of the Simulink model is to calculate the concentration of a substance in the wastewater arriving at Howden WWTP and the Tyne Estuary, a simple dilution model was used based on the total amount of wastewater leaving the site per day, and the total amount of wastewater arriving at Howden WWTP. This results in a dilution of 460 times, this value was provided by the operator of the Howden Wastewater treatment plant, Northumbria Water. Similarly, the dilution of wastewater from Howden into the Tyne estuary is estimated at 25 times, this value was provided by Northumbria Water. Figure 19 below shows how this was achieved in Simulink:

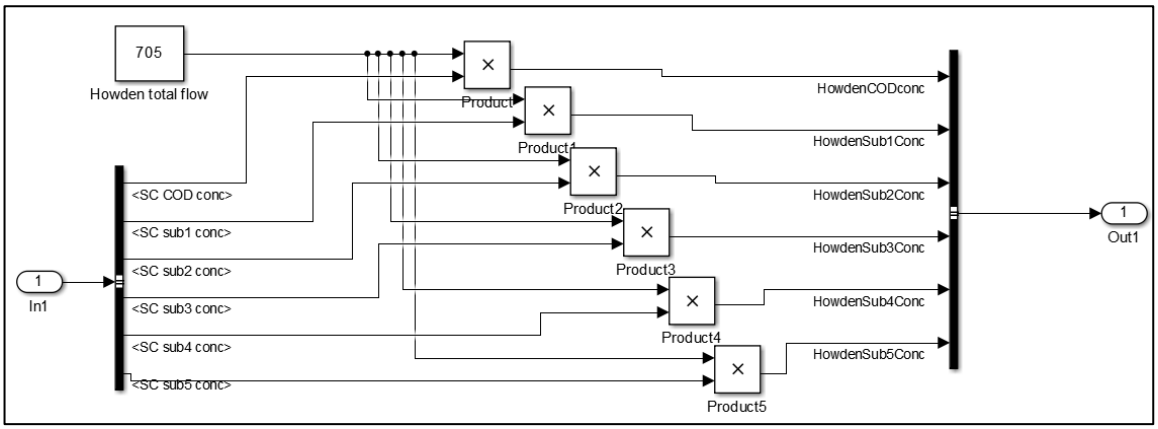

Figure 19: Dilution from secondary clarifier to Howden wastewater treatment plant

Variable 705 represents the total volumetric flowrate going into Howden wastewater treatment plant, this is multiplied with the concentration of COD and substances 1 to 5 (as up to 5 substances can be run in the model at any one time) by a factor of 1/460. The result of this multiplication becomes the respective concentration level leaving the Howden treatment plant.

2.8.6. Dilution into the Tyne Estuary

The dilution level into the Tyne estuary from the Howden wastewater treatment plant is calculated in exactly the same way as into the Howden wastewater treatment plant as described in the previous section. However, the level of dilution is different and so the concentration levels of COD and Substances 1-5 are multiplied by a different factor, the level of dilution into the Tyne's estuary is 25 times (this value was provided by the operator of the wastewater treatment plant in Howden, Northumbria Water) and so this new factor is 1/25.

2.9. Requirements of the Graphical User Interface

Now that the model for the effluent system has been created, it must be packaged in a way to make it easy to use. This is necessary due to the large number of input variables (136) and outputs (70) required to run the model, the complete list of variables can be seen in Appendix 2. This large number of variables has arisen due to high complexity of the model as there are lots of potential interactions between different sections in the model depending on what the user requires, for example, up to 5 different wastewaters on top of the standard "background" flow of wastewater can be simulated at the same time, each with different chemical characteristics (e.g. concentration, biodegradation),

flowrates, discharge location, number of batches, time of each discharge etc. This packaging of the model can be achieved through creation of a graphical user interface (GUI) to enable the user to easily input variables and view the results. There are several requirements needed by the user of the graphical user interface to allow for modelling of a wide range of scenarios. These include

1. Ability to change model settings:
    - This allows the user to change every single input and save these changes for use at a later date. Settings include valve positions, model run time, substance concentrations and chemical oxygen demand, background flowrates, tanker flowrates etc.

2. Background wastewater flowrates:
    - Allow the user to change the background water flowrate, this includes the wastewater produced on site and from commercial tankers.

3. Tank sizes, Pump flows, level control:
    - The plant can change, to keep the model valid it must allow for the change in tank sizes, number of bioreactors, and maintenance on equipment or even pump speeds and level controls.

4. Customised flow patterns for input wastewaters:
    - Inputs can come in 2 forms, batches (single or many) or continuous and the model must allow the user to easily select either.

5. Up to 5 different substances to run in the model simultaneously with varying entry times and flow patterns – compound effects:
    - This will allow the user to see compound effects of discharging several substances to the effluent system at the same time, or even at planned times in the future by selecting a substance flowrate start time in the model. The user could also use this feature to model different substances in the same solution of wastewater should it have multiple components of interest.

6. Different levels of biological treatment for each substance.

- No substance will behave the same in the bioplant and so a substance database that can easily be accessed must be included. Since there are several different users of the model, this database must be accessible and updateable by all. This was achieved by storing the materials database file on the central computer system at Shasun. The graphical user interface would call upon this database upon start-up and again during any changes made to the database.

7. Combination of substance concentration and chemical oxygen demand
    - Each wastewater can simultaneously have a chemical oxygen demand and a concentration of a substance of interest in that same wastewater. Each should be modelled to have different treatment levels in the bioplant.

2.10. Graphical User Interface: WasteModel

As previously described in Table 5: Summary of Effluent System Model Requirements, the goal of this project is to produce the graphical user interface to allow for easy use of the model. It was created by compiling the Simulink model as a rapid simulation target file written in C code, which allows it to be executed on any windows PC. The GUI was created in MATLAB, this GUI creates an input file containing every parameter of the model for the rapid simulation (rsim) target file. It then retrieves the results created when the rsim file has been executed and displays them in an easy to view manner. MATLAB compiler was used to generate a standalone GUI that just requires MATLAB compiler runtime to be installed on the users' computer.

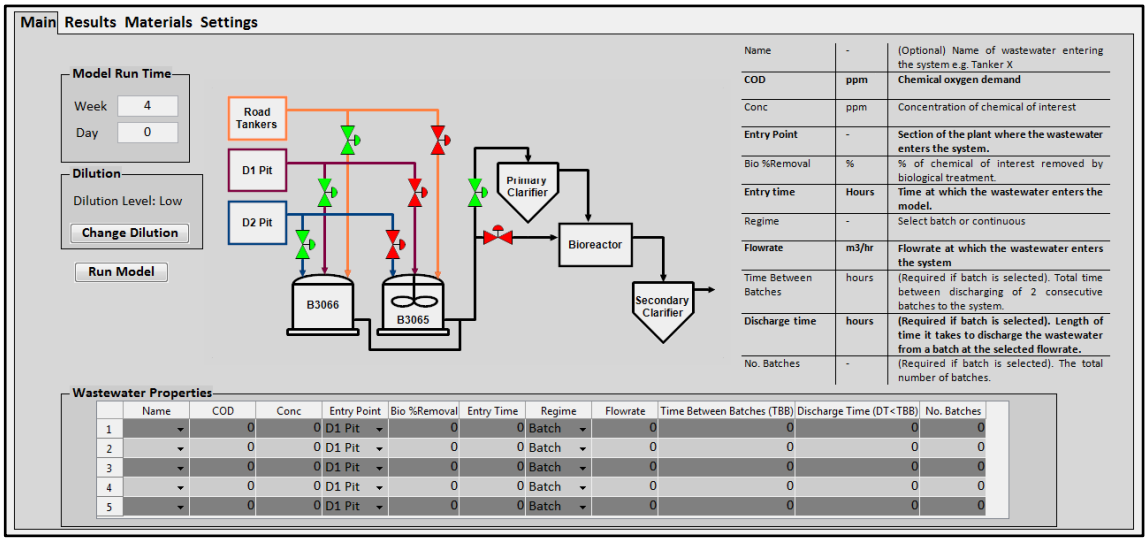

Figure 20: WasteModel Main tab

Name	-	(Optional) Name of wastewater entering the system e.g. Tanker X
COD	**ppm**	**Chemical oxygen demand**
Conc	ppm	Concentration of chemical of interest
Entry Point	-	**Section of the plant where the wastewater enters the system.**
Bio %Removal	%	% of chemical of interest removed by biological treatment.
Entry time	**Hours**	**Time at which the wastewater enters the model.**
Regime	-	Select batch or continuous
Flowrate	**m3/hr**	**Flowrate at which the wastewater enters the system**
Time Between Batches	hours	(Required if batch is selected). Total time between discharging of 2 consecutive batches to the system.
Discharge time	**hours**	**(Required if batch is selected). Length of time it takes to discharge the wastewater from a batch at the selected flowrate.**
No. Batches	-	(Required if batch is selected). The total number of batches.

A library of Bio %Removal values can be found in the software's materials tab as shown in Figure 23.

Figure 21: WasteModel Guidance Notes

Figure 20 shows the main menu of the GUI, here the user selects a valve position by simply clicking on the various valves and this creates an easy to understand visual representation of how the effluent system is set-up. Figure 21 shows the guidance notes found on the main tab of the GUI in more detail. The user then inputs parameters such as the name of the substance in the wastewater to be simulated in the effluent system model, this can be selected from a drop-down menu that lists all of the current substances in the database. Once the desired substance is selected, the chemical

characteristics of the substance such as its specific biodegradation value or LC50 (used for calculating the permitted concentration of that particular substance to be discharged to the environment) is automatically loaded into the model. The user then enters the chemical oxygen demand of that particular wastewater, the concentration (ppm) of the particular substance of interest in the wastewater being added, selects the entry point into the effluent system, the entry time, selects continuous or batch flow regime, model runtime and then clicks 'Run Model'. The user can also click the high dilution button, which will add an excess of water to the system automatically in the substance 5 slot. This simulates the effluent system when there has been a large amount of rainfall or if the operator of the wastewater treatment plant wishes to manually add water via hose to the bioreactor for dilution effects.

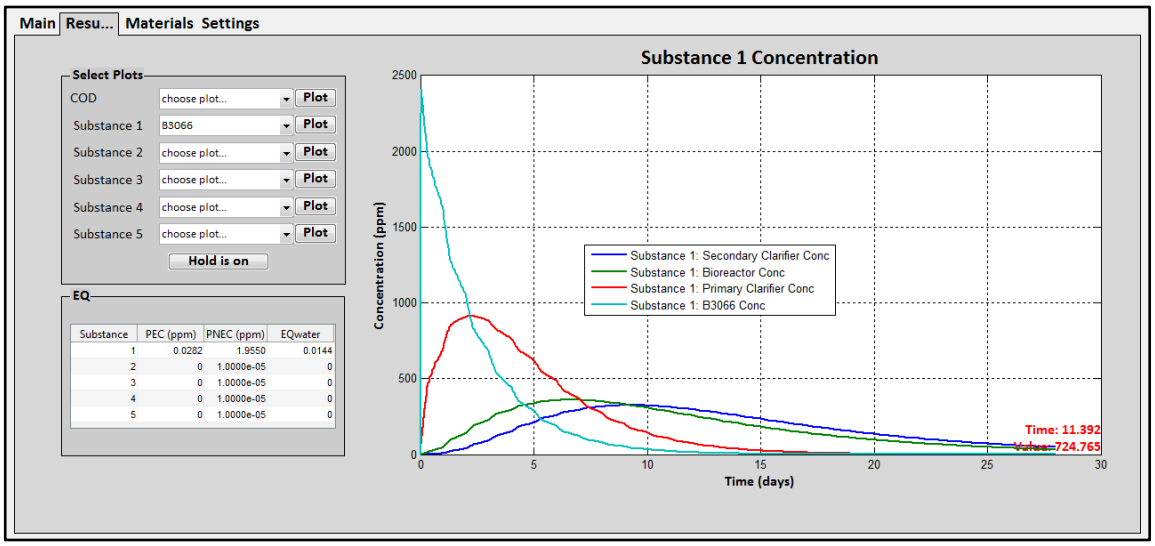

Figure 22: WasteModel Results tab

Figure 22 shows the results screen which graphically displays the results of the simulation based on the selected plot. The GUI also calculates an EQ (bottom left of Figure 22) which tells the user whether or not it is environmentally safe to discharge the wastewater as described in the main menu. This calculation is carried out by the GUI and simply takes the predicted environmental concentration (PEC) in the Tyne estuary as calculated by the model and compares this to the predicted no effect concentration of that substance which is calculated as the LC50/1000. An EQwater value below 1 indicates that the maximum allowable environmental concentration limit values are not exceeded, and it is safe to discharge the wastewater.

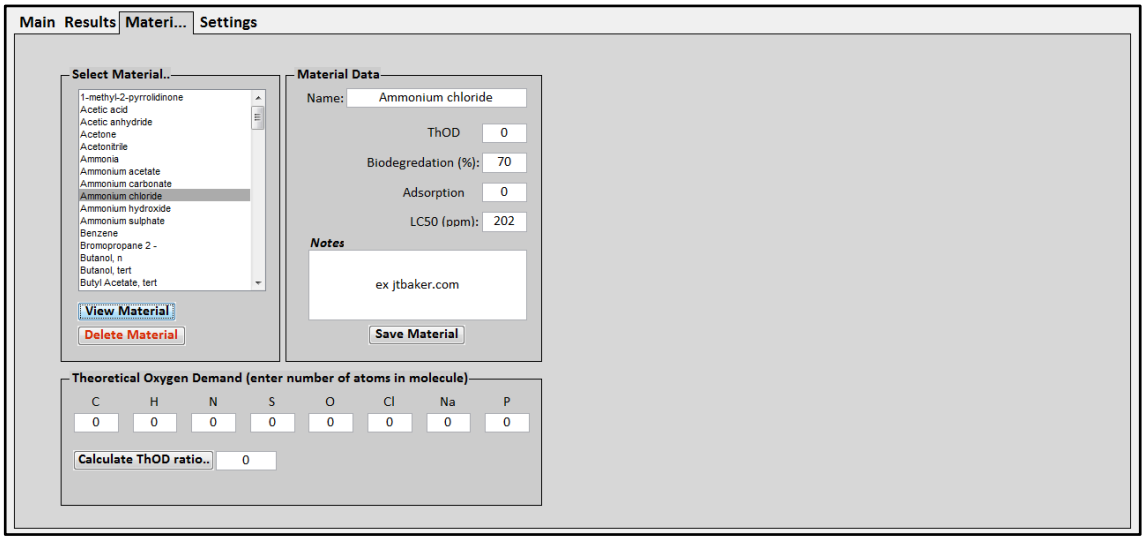

Figure 23: WasteModel Materials tab

Figure 23 shows the materials database interface. Here the user can view, edit, add or delete materials in the database located on Shasun computer servers. It gives you the option of leaving a note on where the data was found, and you input values such as the theoretical oxygen demand (to help calculate the chemical oxygen demand of the wastewater), the biodegradability of the substance in the bioreactor and the LC50 which is used in the EQ calculation. There is also a theoretical oxygen demand calculator at the bottom in case this information is not known, this can be used for calculating the chemical oxygen demand of the wastewater.

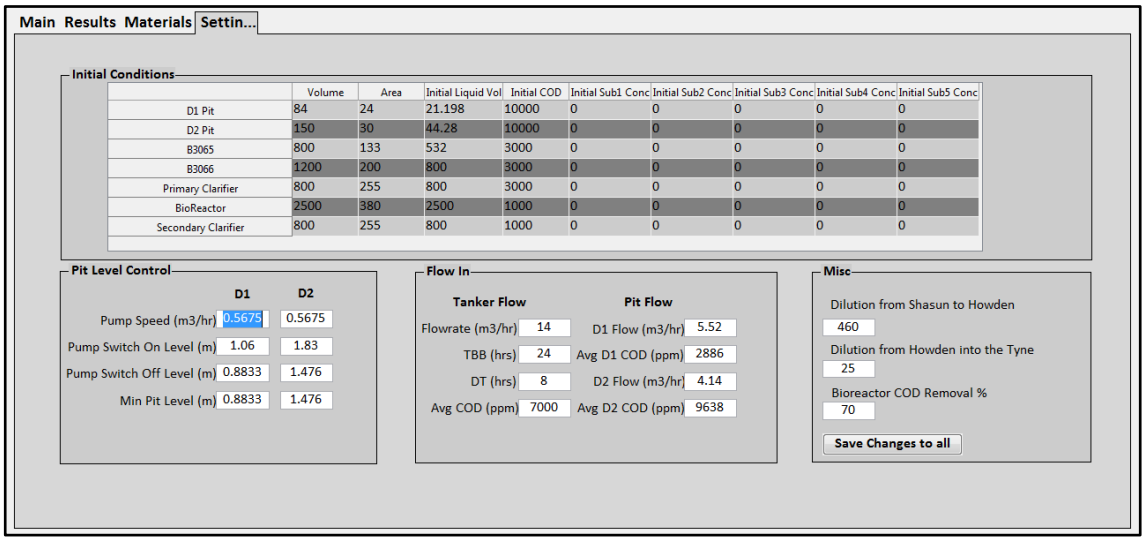

Figure 24: WasteModel Settings tab

Figure 24 shows how all the background settings can be changed such as tank volumes, background flowrates etc. There is also an option to save your changes for future use,

this saves to a database file in the same directory on the computer as the WasteModel executable file.

2.11. Uses of the Model

There are many potential uses of the model that have been identified. In summary, these uses for the software are shown in the list below:

- Predicting the effect of high strength COD wastewater from a plant shutdown.
- Predicting the dilution of inorganics through the system.
- Predict the concentration of materials in wastewater leaving the site and reaching the Tyne estuary.
- Schedule process batches to ensure wastewater compliance.
- Show effects of adverse weather on the wastewater system.
- Aid in process design (maximum size of process waste streams)
- Make quick decisions about the treatability of commercial wastewater and the volume and flowrate allowed.
- Risk management through understanding the effects of unintentional releases of substances to the wastewater system due to equipment failure.

2.12. Model Validation

In order to validate the model, a known substance that can be easily measured should be inserted into the effluent system. Samples at different locations and times in the effluent system are then taken and compared with the results predicted by the model.

Firstly, it is necessary to set the flow and strength of background wastewater in the system. This is done by taking measurements of chemical oxygen demand and flow in D1 and D2 pits as well as any other sources of wastewater, including Tanker delivery or drum discharge. The COD of the wastewater leaving the site is then measured which will give the correct factor for the model to use in terms of percentage COD reduction.

As the effluent system is always running and in a constantly changing dynamic state with regards to chemical oxygen demand of the wastewater. A new wastewater should be introduced that can be measured independently and accurately over time. The chosen wastewater originates from a new potential process that Shasun are considering for large scale production. This wastewater contains a very strong blue dye, the concentration of which can be measured directly via use of a photospectrometer.

4000 litres of the strong blue wastewater was added to D1 pit over 30 minutes and a single 100ml sample taken throughout the system at different times and locations (See Table 8) and analysed for its concentration using photospectrometry and the calibration curve show in Figure 39: Calibration curve showing Absorbance at 663nm vs % Concentration of blue wastewater (page 90), the experiment time was started as soon as all of the blue wastewater was added to D1 pit. The results are shown in Table 8 and show that the model predictions have an average discrepancy between predicted and measured values of 9%. Initially at 0.5 hours, the predictions are very accurate in D1 pit due to the good mixing through continuous stirring, accurate estimation of background wastewater flowrate and the effects of dilution combined with the pit emptying/filling due to activation of the pump at high level. As time progressed, the error in D1 pit grew larger (from 4.6% to 12.2%) due to fluctuations between supply of background wastewater from other sources into the pit as the model predicts a constant average inflow as opposed to "batch" flow consisting of short bursts at high flow into the pit. It is likely that differences in background wastewater flow into the pits exist between daytime and night-time shifts. This difference could be investigated and incorporated into the model for greater accuracy. Prediction error in the primary clarifier was found to be 28% after 12 hours, this error later reduced significantly to 2.9% after 192 hours. This difference is due to the lack of agitation and mixing in the clarifier, initially resulting in areas of high and low concentration. However, over time these errors reduce due to the extra time for mixing and diffusion to occur throughout the clarifier.

The results of the model are reasonably accurate for the vessels shown in Table 8, as an average difference in predicted concentration of 9% was observed, these vessels are prior to the bioreactor as the percentage of blue wastewater in the bioreactor would be too low due to high dilution effects to test for by the photospectrometry method.

Table 8: WasteModel Validation Results

Sample Location	Measured Conc %	Experiment Time (Hours)	Predicted % Conc	%Difference
D1 Pit	14.22	0.5	14.877	4.6
D1 Pit	1.44	12	1.602	11.3
D1 Pit	0.18	48	0.158	12.2
B3065	0.62	12	0.645	4.0
B3065	0.51	48	0.479	6.1
B3065	0.11	192	0.116	5.5
Primary Clarifier	0.05	12	0.064	28.0
Primary Clarifier	0.11	48	0.117	6.4
Primary Clarifier	0.07	192	0.072	2.9
			Average	**9.0**

Samples were taken via dipstick at the centre of the vessel for D1 Pit and Primary clarifier. Samples were taken from the outlet of B3065.

2.13. Potential Improvements

Additional work could be carried out to validate the model further, this could include selection of a different dye or molecule that is more easily measured at very low concentrations and that does not degrade in the bioreactor or react with chemicals likely to be found in the effluent system. This could also be measured as it reaches the wastewater treatment plant in Howden to gain information on the level of dilution and time taken to reach the plant. An investigation into the mixing dynamics of the clarifier and the flow dynamics of the background wastewater into D1 and D2 pits could further increase the accuracy of the model.

In the future, this work could be built upon to include a mathematical model that describes the function of the bioreactor and the ability of the microorganisms to treat a specific wastewater depending on its characteristics. This would require much greater complexity and integration with the plant and process operating conditions and is investigated later on in this thesis.

2.14. Conclusion

The overall goal of this project within the thesis was to provide a solution to Shasun's problem of predicting the quality of wastewater leaving their site in Dudley so they can be sure to stay within strict environmental discharge limits set by the regulatory

authorities. This problem can be broken down further into more detail; the requirement to optimise the use of the on-site wastewater treatment plant to use as much capacity as possible and reduce more costly and less sustainable alternative means of waste disposal such as transporting the wastewater off-site for treatment via third parties. This will also demonstrate to authorities and businesses a level of continuous improvement and give confidence towards Shasun's commitment to protecting the environment.

To solve the problem, a mathematical model that accurately represents the effluent system at Shasun's site in Dudley was created along with a standalone graphical user interface (GUI) that can be deployed on any windows PC, this allows for easy manipulation of the model's inputs and presentation of results.

This model and software delivered all the requirements for solving the problem and was also useful in other aspects of the business as well.

It can be concluded that the differential equations used in the model representing stirred tanks in series, accurately represents the complex effluent system and in addition to specific system characteristics (such as modes of operation, pump flowrates, control philosophies, bioreactor efficiency) this method of modelling can be repeated for other systems on different sites.

This model and software set-up have allowed for a number of additional benefits as mentioned in section 2.10. These include the ability to quickly simulate emergency scenarios to provide decisions on mitigation, this can include human error on plant resulting in an unexpected release to the effluent system or from failure of equipment. This software allows for the calculation of consequences in an environmental risk assessment which will help in process design to reduce the risk if necessary, ultimately providing greater protection towards the environment.

Chapter 3. Bioplant Pilot Rig

3. Introduction

As described in the previous chapter, Shasun have an on-site biological wastewater treatment facility for their wastewater. This receives wastewater from different areas and processes from across the site and reduces the chemical oxygen demand (COD) of the wastewater to within set limits before it leaves the site boundary via the domestic sewer system. The treated wastewater then makes its way through the domestic system to the biological treatment works in Howden and then treated again before discharge into the Tyne estuary. A problem that Shasun have encountered is their lack of ability to assess the treatability of potential new wastewaters over a large time-frame. Currently, the Best Available Techniques (BAT's) as per European Commission guidelines (OECD, 2003) involve readily biodegradability tests which are conducted under aerobic conditions, where a high concentration of the test substance is used and the biodegradation rate is observed by measuring parameters such as dissolved oxygen concentration, chemical oxygen demand or biological oxygen demand, a positive result can be concluded from a rapid degradation rate. Methods for this type of testing include CO2 Evolution, Closed bottle and manometric respirometry, which is the method used by Shasun. These tests, however, don't give the whole story when assessing a particular waste stream. There can be longer term or inhibitory effects on the biodegradation performance of a wastewater treatment plant when a particular waste stream is mixed with other streams or when the concentration of the test compound is much lower. The activated sludge in the wastewater treatment plant consists of a large soup of different types of bacteria, these bacteria are present in different amounts depending on the wastewater streams that feed the facility. The ability of the micro-organisms to successfully reduce the organic content of a particular source of wastewater can depend on the make-up of this soup and proportion of different micro-organisms present. This proportion will change when the composition of the feed wastewater changes due to the preference of the different bacterial types and so where there may only be a small number of a particular micro-organism that "prefers" a new wastewater stream initially, this type of bacteria will thrive and multiply, resulting in a greater ability of the bacterial soup to digest the new wastewater. This adaptation is a process that can take weeks to achieve the desired levels of treatment for a particular wastewater and therefore short-term respirometer tests will not account for this phenomenon and can also provide

results that suggest a new type of wastewater is completely incompatible with the wastewater treatment plant.

It is also possible to effectively poison the micro-organisms in an activated sludge wastewater treatment plant (WWTP) due to accumulation of a toxic substance in the micro-organism itself, such as heavy metal residues. REF Adsorption and toxicity of heavy metals on activated sludge, Soon-An Ong, Department of Applied Chemistry, Oita University, Japan, 2010. This can reduce the ability of the micro-organisms to degrade the substrates and result in killing them.

This scenario of killing off the activated sludge could be catastrophic for Shasun in terms of costs as an alternative means of treating the wastewater would have to be found whilst the micro-organism population is being rebuilt in the plant which can typically take several weeks. Additionally, there is the possibility of the poisoning of the activated sludge to go unnoticed for a number of hours which could result in Shasun discharging untreated wastewater, potentially in excess of 300 m^3, to the domestic sewer in breach of their environmental permit resulting in pollution of the environment, potential for poisoning of the sewerage treatment works in Howden and associated fines due to the breaches.

It is also important to have the ability to test wastewaters produced by a potential new process from additional business to the company. The ability to treat wastewater on-site at low cost (compared to alternative means such as off-site treatment by a third party) can have a great impact in the cost/benefit analysis when assessing new potential processes and business. To meet these testing requirements, a pilot scale wastewater treatment plant based on the one located at Shasun's site in Dudley, UK will be constructed with the aim of being fully representative of the large-scale plant for the assessment of new wastewater streams over an extended period.

This chapter describes the steps taken to design and test the pilot scale activated sludge wastewater treatment plant for the testing of new effluent streams for the treatability (or toxicity) in the main wastewater treatment plant.

3.1. The Activated Sludge Process

The activated sludge process was developed at the beginning of the 20th century to treat domestic wastewaters, and today it is used extensively to treat municipal and industrial wastewaters.

The activated sludge process involves the use of a large mass of microorganisms (normally these are bacteria) in order to treat wastewater aerobically. Microbial reproduction and growth require a carbon source and energy, this is found in the organic contaminants in the wastewater. The combination of the wastewater with the microorganisms is known as the mixed liquor, and air is blown into the mixed liquor in the aeration tank so that the organic matter can be converted into microbial cell tissue and carbon dioxide. The motion of the air also allows for thorough mixing of the tank. (Sustarsic, 2009). After a certain amount of time in the aeration tank, the mixed liquor flows into the secondary clarifier, where the sludge (microorganisms) is separated from the treated wastewater by gravity settlement. The treated wastewater is then sent directly to the municipal drainage systems.

The activated sludge wastewater treatment plant at Shasun, Dudley is used to treat organic chemical wastewaters of a high strength (COD: 3,000 to 10,000), the performance can vary depending upon the specific chemicals present and their concentrations in the wastewater due to the varying batch chemical processes run on site. Activated sludge treatment is not used for the removal of metals or dissolved/suspended solids; instead this is removed by a primary clarifier (gravity settlement) where the solids are separated and subject to further processing steps such as dewatering.

The site at Dudley combines weak wastewater streams such as rainwater or landfill leachate with the much stronger process wastewater to achieve the correct strength of feed for the bioreactor.

3.1.1. Treatment Processes

After primary settlement of the wastewater to remove suspended materials and oils, the wastewater is fed into the aeration tank where it forms the mixed liquor with the microorganism. The air agitates this mixture as well as transferring oxygen into the water. The air enters the aeration tank around the circumference of the bottom of the tank to ensure a high level of mixing and prevent any dead zones.

With certain wastewaters, this action of aeration can create a large amount of foaming, this is controlled by the addition of an antifoam solution when needed. The pH is kept between 6 and 8, this is controlled by the addition of either caustic or acid. During significant lengths of time where the wastewater entering the plant is too weak to sustain the microorganism (e.g. during a plant shutdown) it is necessary to add nutrients such as urea (for nitrogen) and phosphoric acid (phosphorus) (Sustarsic, 2009). The temperature of the aeration tank changes based on the ambient air temperature and can be roughly controlled by changing the strength of the wastewater entering the plant (this is achieved by use of equalisation tanks).

Following the aeration tank is the secondary clarifier, where the activated sludge is separated from the treated wastewater by gravity settlement and the use of mechanical scrapers. Most of the sludge is returned to the aeration tank whilst some is sent for dewatering using a centrifuge and sent to landfill, this helps to maintain the correct level of solids in the aeration tank and maintain the microorganism at a healthy age.

3.2. Literature Review

There are many different design layouts of activated sludge wastewater treatment plants such as those containing anoxic tanks, membrane bioreactors or additional secondary treatment processes (Arif, 2018) and so finding an example of a pilot plant study in literature identical to the large scale plant one found at Shasun in Dudley is unlikely. Therefore, a review of current literature on the various designs of pilot scale plants available and their effectiveness was conducted to provide useful insight towards designing an appropriate pilot scale plant for Shasun.

One common design of a large air-wastewater activated sludge reactor is the “channel” type. These consist of a very long channel compared to their width and depth, with the availability of space being a constraint to their design (Le Moullec, 2011). Reactor hydrodynamic have been shown to be important in wastewater treatment plant modelling, this means that mimicking the flow patterns of the large-scale plant into the small scale should be made a priority, this can be achieved through using the correct geometry. One example of a pilot scale plant design is shown in the Figure 25. This pilot scale reactor was based on a large-scale municipal wastewater treatment plant and was built mainly for the comparison of different mathematical models to assess prediction capabilities rather than being focused on exactly mimicking the large scale plant for the testing of new wastewater sources.

This gas/liquid reactor has a very long length compared to its height and width and in this type of reactor, water flows along the length of the channel whilst gas sparging occurs from beneath. The length of the rector channel is 3.6 m with the channel width at 0.18 m, the height of the reactor is 0.2 m. Stainless steel tubing with 1 mm holes drilled every centimetre was placed at the bottom of one side of the walls for the purposes of sparging. This pilot scale reactor has a mixed liquor suspended solids (MLSS) recycle line from the reactor outlet to back to the reactor inlet and a 0.88 m^3 settler used to clarify the sludge from the treated wastewater, the sludge was then partially recycled to the reactor inlet.

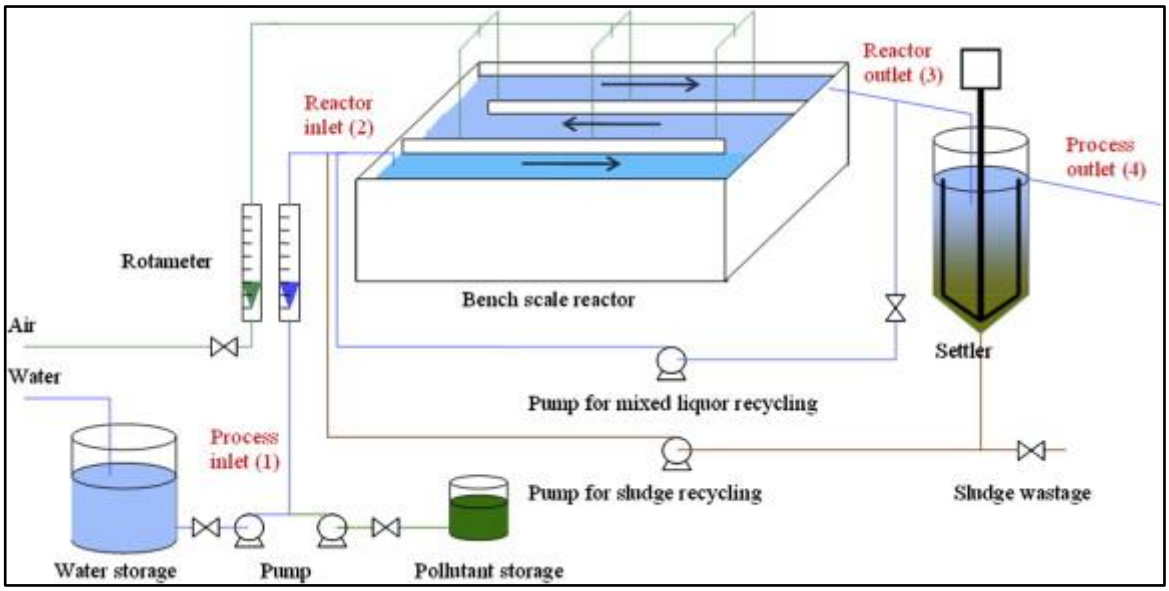

Figure 25: Channel-type Pilot Scale Activated Sludge Wastewater Treatment Plant Set-up

Due to handling issues, this study used a synthetic wastewater consisting of a mixture of sugar (glucose and saccharose), ethanol and acetate. Ammonium chlorine as ammoniacal nitrogen and potassium dihydrogenphosphate as a phosphate source were also added to the synthetic mix, it is stated that a typical real wastewater has a COD/N/P ratio of around 100/5/1 (this would be for domestic wastewater) the proportion used in this study with synthetic wastewater was a COD/N/P ratio of 100/15/1. The behaviour of the synthetic wastewater was tested using respirometric tests and compared with wastewater from the large scale WWPT in Nancy-Maxeville (France) after the sludge had acclimatized to the synthetic wastewater solution for one month and showed that the rate of reaction and total COD consumed was only 70% of the real wastewater COD consumption, however in this study this was accepted as a reasonable approximation given the difficulties described with handling issues of the real wastewater. During

experiments, the temperature of the reactor was equal to ambient (20 degC) and measurements of suspended solid concentration, nitrate, ammonium, soluble COD and oxygen concentrations were taken. The study itself fails to describe the key design characteristics of the pilot plant compared to the large-scale plant it is based upon. One design variable considered was the sludge retention time which was set to approximately 10 days, however it is unknown if this is based on the large scale plant. Although the purpose of this study was not to create a pilot plant that exactly matched the performance of the large-scale plant (it was designed for comparing different mathematical models) it highlights a number of consideration to take into account such as using the activated sludge microorganisms sourced directly from the large-scale plant and ensuring that the wastewater feeds are equivalent rather than using a synthetic source as this was shown to have a negative effect on the observed treatment efficiency in the pilot plant.

In another study (Aguilara, 2003), the behaviour of a conventional activated-sludge (CAS) process (such as the one at Shasun, Dudley) was compared to that of the membrane bioreactor (MBR) process by using two pilot scale rigs. The CAS unit consists of a 9 m^3 aeration tank basin with single clarifier, a 225 litre MBR was also used and both units were installed and run under real process conditions at a wastewater treatment plant in Evry, France. Key operating conditions were identified as the solids retention time (SRT) and the hydraulic retention time (HRT), it is suggested that the solids retention times (SRT) is important in defining the level of nitrification of the wastewater and that CAS systems can be prone to the wash-out of nitrifiers when operating at low SRT's or HRT's due to the low growth rates of autotrophic bacteria. To achieve full nitrification, SRT's of at least 12 to 15 days and HRT's of 18 to 24 hours are typical. During the experiments, a dissolved oxygen concentration of greater than 4 mg/l was used to ensure that oxygen availability was not a limiting factor and due to the relatively large size of the CAS unit, temperature was not regulated and so this ranged from 12.5 to 23.9 degrees Celsius, a mixed liquor suspended solids concentration ranged from 0.5 to 1.4 g/l. A number of additional variables were recorded during the experiments and these included: chemical oxygen demand on the inlet and treated wastewater, total suspended solids, dissolved oxygen, temperature, volatile suspended solids, ammonia, nitrate and Kjeldahl nitrogen. After set-up and seeding of the reactor, equilibrium was considered to have been achieved after three

SRT's (36-45 days) and a period of 2 weeks was used to assess the change in experimental operating conditions.

A separate study (Bakos, 2013) which looked at verifying if a down-stream nitrifying fixed-film reactor may effectively backseed an activated sludge (AS) system. The study consisted of using two pilot-scale AS systems set-up based on the wastewater treatment plant shown in Figure 26 below.

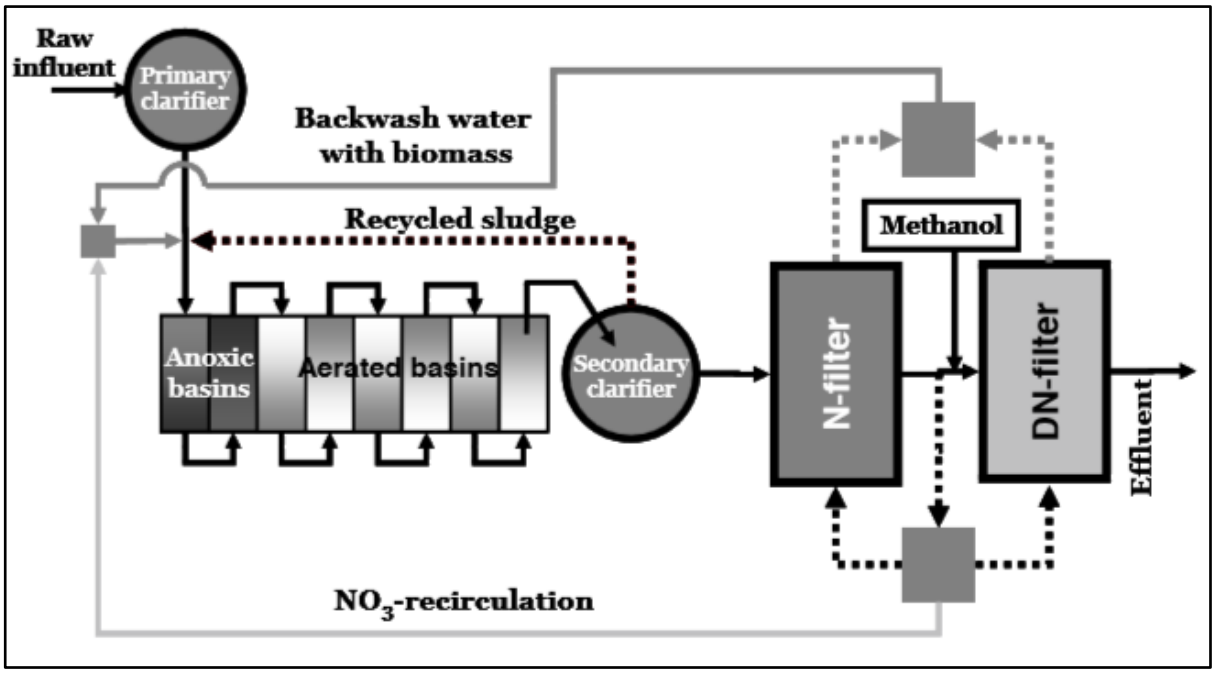

Figure 26: Schematic of large-scale wastewater treatment plant in Budapest

The pilot scale system was based upon the South-pest Wastewater Treatment Plant (WWTP) of Budapest, Hungary. The activated sludge reactors are divided into 8 equal volumes basins that are connected in series, four of the eight basins are equipped with both aerators and mixers and in general, the first 2 basins are operated in a non-aerated mode. The pilot scale systems were set-up assuring that the biological niche of each basin was similar to that of the large-scale system. Two experimental systems were divided into four reactors each with volumes of 0.9 l, 0.9 l, 1.8 l and 3.6 l respectively, the aim of this compartmentalisation was to adjust the concentration profiles of the occurring pollutants similar to those of the full-scale plant. The first two reactors represented the relative volumes of the first two reactors of the large-scale plant, the third reactor represented the third and fourth full scale basins whereas the fourth reactor represented the remaining 4 basins of the full-scale system. The pilot scale-system was set-up as shown in Figure 27.

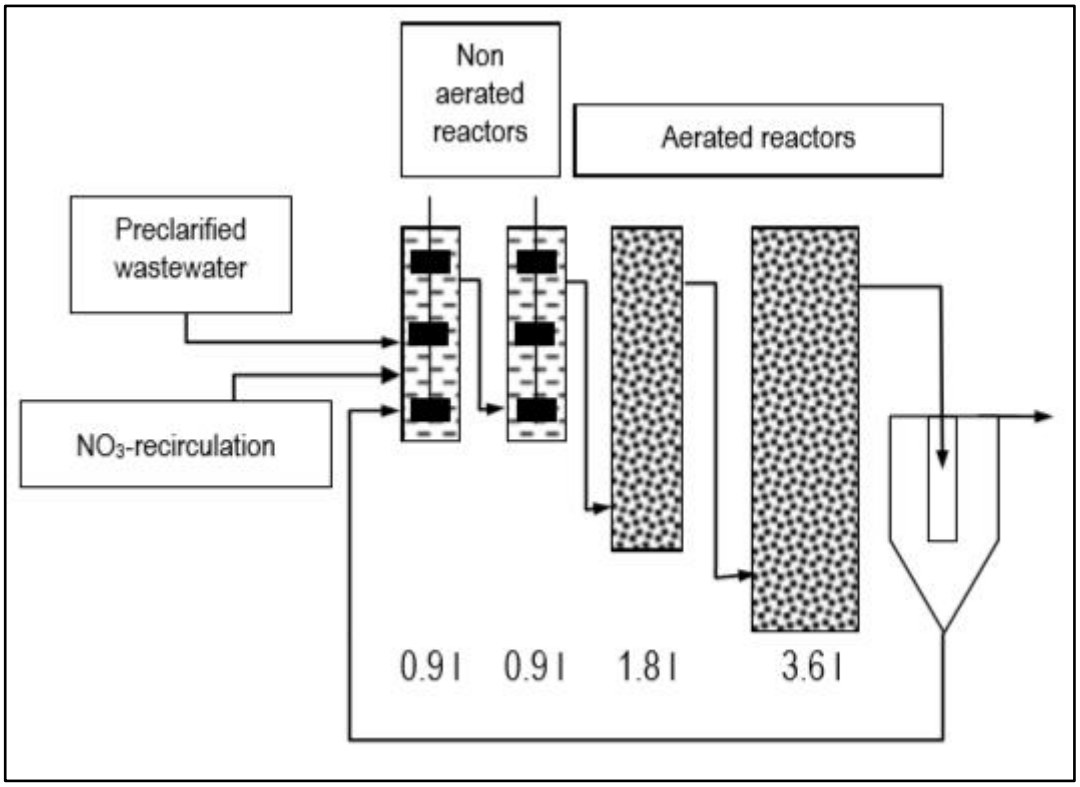

Figure 27: Schematic of Experimental Activated Sludge Reactors

In these studies, the pilot scale reactors were fed with pre-clarified influent from the full-scale plant and were temperature controlled in accordance with the temperature of the full-scale system. Key variables were again identified as the hydraulic retention time (HRT, 5.5 hrs) and solids retention time (SRT, 2 days) which were set to values that characterized the large scale plant. In addition to this, the mixed liquor suspended solids concentration was monitored and adjusted to stay in-line with the large-scale system. Where there was excess sludge, this was wasted from the last of the experimental AS systems, the flow rates and recycle rates were also representative of the large-scale system.

Based on a review of literature it's clear that there is no one-size fits all solution to creating a pilot scale activated sludge plant based on a full-scale system. It appears to be important to match the layout and geometry of the full-scale plant as much as possible whilst also considering variables such as the wastewater source and source and source of the microorganisms used to seed the reactor. Key variable to measure can include the dissolved oxygen concentration, temperature (and whether this should be controlled to match the large scale), influent feed rate, solids recycle rate, solids retention time, hydraulic retention time and mixed liquor suspended solids (MLSS) concentration. It is also important to consider and acclimation phase for the

microorganisms to adjust to their new environment and also the time between changing experimental operating conditions as to allow the true effects of the change to become apparent with time.

The following sections consist of a review of the large-scale plant at Shasun in Dudley followed by the steps taken to design a pilot scale rig to mimic the conditions found at the large scale to enable representative testing of new wastewaters.

3.2.1. Review of Activate Sludge Wastewater Treatment Plant Design Variables

As the purpose of this chapter is to design a small scale activated sludge wastewater treatment plant that accurately mimics the large scale, a review of literature into the design considerations and variables that affect treatment efficiency of the plant was conducted to ensure they are accounted for in the pilot plant design. The work is split into categories based upon the process condition or variable under review. These variables were found to be pH, temperature, dissolved oxygen concentration, hydraulic retention time (HRT) and solids retention time (SRT).

3.2.1.1. pH and Temperature

Xia studied the effects of pH on short-time aerobic digestion of wastewater in activated sludge treatment (Xia, 2019). It was reported that a suitable pH for the activated sludge system should be in the region of 6.5 to 8.5 as this allows high levels of microorganism activity and fast biodegradation rate of pollutants. Xia also reports that extreme conditions can cause cell lysis and the release of IPS which results in a reduction of microorganism activity and therefore number of living microorganisms available for the biodegradation of organic matter found in the wastewater. Painter also reported similar findings as well as that a 10 degrees Celsius rise in temperature provided an approximate three fold rise in growth rate, and therefore have a positive effect on the biodegradation rate of organic matter (Painter, 1983).

In the study Painter took activated sludge from a treatment works in Luton and investigated the effects of varying pH and temperature on the growth rate of the *Nitrobacter* and *Nitrosomonas* present in the sludge. In was confirmed that that a lower limit for growth was obtained at a pH of between 6 and 6.5, and the optimum was found at a pH of 8 although there was little difference between a pH of 7.5 and 8.5. Painter also mentioned that growth rates can be inhibited by the presence of substances such as

metals (e.g. copper and chromium) and organic substances such as certain amino acids or thiourea peptone.

This information is relevant to designing and operating a small scale model of an existing activated sludge wastewater treatment plant, as it shows the importance of pH and temperature on the growth rate of the bacteria found in the bioreactor and therefore the performance of the plant with its ability of digesting the organic content of the wastewater feeding the plant. It also highlights that it is important to use the same feed wastewater when operating the small scale rig compared to the large scale, as different wastewaters could potentially contain inhibitors that would affect the growth rate and provide different results when comparing the efficiency of the plant for treating a new substance.

3.2.1.2. Dissolved Oxygen Concentration

Li reports that fluctuation of process conditions in activated sludge systems such as change in influent water flow, seasonal climate variation and changes to dissolved oxygen concentration can cause instability of activated sludge conditions (Li, 2019). This is due to an effect on the microbial metabolism and results in problems such as sludge loss or deterioration of treatment plant effluent. Li also reports that limitation of dissolved oxygen frequently results in poor sludge performance due to poor settleability and deteriorated nitrifications. Li investigated the effects of low dissolved oxygen concentration on activated sludge using a laboratory scale reactor (10 litre volume) whilst maintaining key process variables such as pH, temperature, solids retention time and hydraulic retention time. A synthetic wastewater was fed to the reactor and the rate of respiration was observed with different levels of dissolved oxygen. Three operating conditions were tested, these include 7 days of normal dissolved oxygen levels (2-4 mg/l) followed by a 7 day period of low dissolved oxygen level (0.5 mg/l) and finally a third 7 day period with restored dissolved oxygen levels (2-4 mg/l) but under stress with NaClO addition. Throughout the experiment the respiration rates were observed for comparison. During the period of low dissolved oxygen, it was observed that the sludge settling ability had deteriorated and there was a decrease in the removal efficiencies of COD and therefore effluent quality after 3 days as the sludge had acclimatized to the low dissolved oxygen conditions.

These studies show that dissolved oxygen is an important process variable to take account of and it will be important to maintain the same levels of dissolved oxygen in

the small-scale pilot plant as compared to the large-scale facility. Li has shown that whilst small upsets in dissolved oxygen concentration typically occur in day to day operation of activated sludge facilities, prolonged exposure to low dissolved oxygen levels will results in poor plant performance and therefore the design of the small scale rig should involve monitoring and control of dissolved oxygen levels to ensure there is no decrease in respiration and COD removal efficiency as well as limiting the acclimation effect of the microorganism to low dissolved oxygen conditions which can have a long term negative effect on the wastewater treatment efficiency.

3.2.1.3. Hydraulic Retention Time (HRT)

Boonnorat investigated the effects of changes to hydraulic retention time (HRT) on micropollutant degradation of an activated sludge system treating wastewater derived from landfill leachate and agriculture wastewater (Boonnorat, 2015). Boonnorat measured the effects of three different hydraulic retention times (12hrs, 18hrs and 24hrs) over a period of 182 days and measured the effect on treatment efficiencies of organic compounds and nutrients. The results of this study show that there was a decrease in micropollutant degradation and effluent quality (COD) with decreased hydraulic retention time. The change in HRT caused the bacterial community to change, the bacterial abundance increased as HRT decreased. Under different hydraulic retention times, different groups of bacteria became dominant due to the changes in organic and nutrients loadings. This change influenced micropollutant degradation as different bacteria are capable of degrading different substances. Boonnorat also points out that retention time of micropollutants in the system with low hydraulic retention times is lower and therefore has less time for biodegradation to take place.

3.2.1.4. Solids Retention Time (SRT)

Clara describes the sludge (solids) retention time (SRT) as a parameter commonly used in the design of activated sludge wastewater treatment plant (Clara, 2005). This can be described as the average time the activated sludge solids are retained in the system and is expressed in days. Clara states that the SRT is a variable that effects the growth rate of the microorganisms as only the organisms able to reproduce in this time frame are retained in the treatment plant and therefore the SRT affects the diversity and treatment efficiency such as carbon removal. This is because the SRT is related to the reciprocal of the growth rate and therefore the treatment efficiency of a compound, as the microbial growth rate is dependent on the concentration of the substance sustaining its

growth and the ease of the substance to be metabolised. Clara conducted lab scale experiments to investigate the treatment efficiency of different substances with varying SRT's (1, 5, 13, and 26 days) and found that with increased sludge age, enhanced treatment was observed for most substances tested. One such substance was bisphenol-A, which showed treatment efficiencies at 3%, 78% and 91% at SRT's of 1, 5 and 13 respectively.

In addition to the pH, dissolved oxygen concentration and temperature, the hydraulic retention time and solids retention time have been shown to effect the treatment efficiency of different substances in an activated sludge wastewater treatment plant, these variables should therefore be considered in the design process for an accurate scale-down model of the wastewater treatment plant at Shasun.

3.3.Design of the Wastewater Treatment Plant (WWTP)

The Shasun wastewater treatment plant in Dudley consists of three 2400 m^3 aeration tanks (only 1 tank was in operation for the duration of this work), one primary clarifier, two secondary clarifiers (again, only 1 was in operation) and 2 mixing/balancing tanks. The plant serves both the adjacent production facilities as well as outside customers, receiving tankers containing landfill leachate on a daily basis. The stronger wastewater from the production facility is stored in an agitated tank whilst the weaker wastewater stored in the remaining 800m^3 tank, the wastewater is fed into the secondary clarifier from both sources to balance the strength. A few of the key design features of the bioplant are now discussed, starting with the hydraulic retention time.

The Hydraulic Retention Time (HRT) is defined as the aeration tank volume divided by the discharge rate and describes the amount of time it is expected for wastewater entering the aeration tank to be retained before leaving the aeration tank:

$$HRT\ (days) = \frac{V}{Q}$$

Equation 4: Hydraulic Retention Time

Where V = Volume of aeration tank (m^3),

Q = Discharge flowrate (m^3/day).

The Solids Retention Time (SRT) is also an important design factor for the bioplant. It provides a theoretical indication of how long the microorganisms remain in the aeration

tank. It is necessary to remove some of the microorganisms to prevent an overgrowth leading to a large build-up of sludge in the secondary clarifier.

The SRT is defined as a function of the aeration tank volume (m^3), the sludge wasting rate (m^3/day), the concentration of suspended solids in the mixed liquor of the aeration tank (g/L) and also in the recycle line (g/L):

$$SRT = (V \times MLSS_{aeration})/(W \times MLSS_{recycle})$$

$$SRT\ (Shasun\ Bioplant) = \frac{2400m^3 \times 9\ g\ litre^{-1}}{3m^3day^{-1} \times 72g\ litre^{-1}} = 100\ days$$

Equation 5: Sludge Retention Time

Where V = Volume of aeration tank (m^3),

W = Wasting flowrate (m^3/day),

$MLSS_{aeration}$ = Solids in the aeration tank (g/l),

$MLSS_{recycle}$ = Solids in the recycle from the secondary clarifier (g/L).

The HRT and SRT of the bioplant at Shasun, Dudley are 5 and 100 days respectively.

The recycle ratio, *r*, is also an important variable to consider in the design of an activated sludge wastewater treatment plant, as in combination with the wasting flowrate, this contributes to maintaining the solids concentration in the bioreactor. In a study by Hosseini, a higher sludge recycle ratio was also found to positively affect the treatment efficiency of an activated sludge wastewater treatment plant, however high recycle ratios were also found to negatively affect sludge settleability in the secondary clarifier (Hosseini, 2008) therefore risking significant loss of solids in the treated effluent stream. The recycle ratio is described in Equation 6 and is complimented by Figure 28: Diagram of Recycle Ratio.

$$r = \frac{q}{Q}$$

$$r\ (Shasun) = \frac{321.6\ m^3day^{-1}}{480\ m^3day^{-1}} = 0.67$$

Equation 6: Recycle Ratio

Where q = Recycle activated sludge flowrate (m^3/day),

Q = Influent wastewater flowrate (m^3/day).

The recycle ratio for the bioplant at Shasun, Dudley is 0.67 as calculated above.

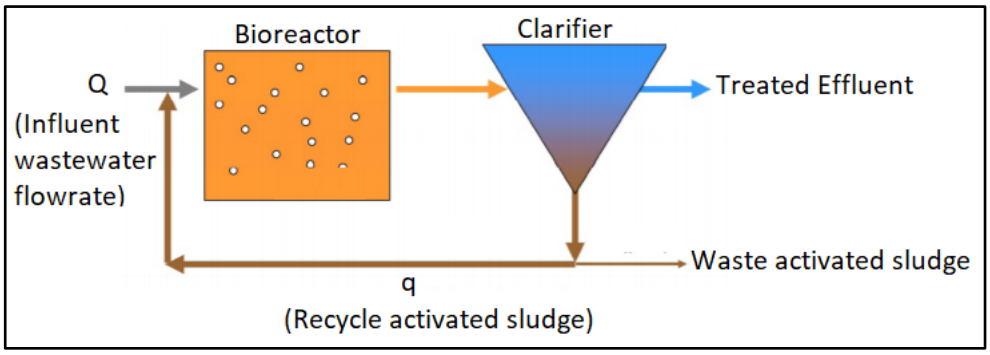

Figure 28: Diagram of Recycle Ratio

3.3.1. Aeration Tank Conditions

It is necessary to maintain the conditions required by the microorganisms in the aeration tank for healthy microbial activity. At Shasun, Dudley, these include a pH of between 6 and 8, a minimum of 2 g/l of dissolved oxygen and a temperature of between 15 and 30°C. Nitrogen and phosphorus is provided by the strong chemical waste from the production site.

3.3.2. Methylene Blue

The potential blue wastewater stream being tested contains mostly the basic dye, Methylene blue.

Dyes from wastewaters entering natural water bodies can cause aesthetic deterioration as well as harm to the flora and fauna in the natural environment (Lamia Ayed, 2011), the wastewater containing dye must therefore be treated before being disposed of into the environment. Some of the lowest cost biological processes for effluent treatment and decolourization are activated sludge based and are recognised for their ability to reduce the biological oxygen demand (BOD) and chemical oxygen demand (COD) by aerobic biodegradation (Jafarinejad, 2015).

3.3.3. Treatment of Dye with the Activated Sludge Process

It has been estimated that over 10,000 tonnes per year of dye is produced worldwide (Esther Forgacs, 2004) . Synthetic dyes can cause significant damage to the

environment they are also serious health-risk factors and the release of large amounts of synthetic dye causes public concern, legislation problems and are a difficult challenge to environmental scientists. There has been a wide range of methods developed for the removal of synthetic dyes from wastewaters and these involve adsorption on inorganic or organic matrices, decolourisation by photocatalysts, oxidation processes, microbiological or enzymatic decomposition.

The use of microorganisms for the biodegradation of synthetic dyes such as Methylene blue (The molecular structure of Methylene blue is shown in Figure 29) is an attractive option. This is because it is a simple and relatively cheap process compared with other methods of dye removal from wastewater. The operational costs are also comparatively low and the end products of complete mineralisation are non-toxic (Esther Forgacs, 2004).

The use of a range of different microorganisms can offer significant advantages over pure cultures, as individual strains may attack the dye molecule at different positions or may even use the decomposition products that are produced by a different strain for further decomposition.

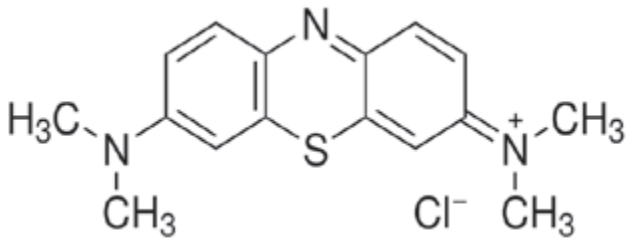

Figure 29: Methylene blue molecule

3.3.4. Effect of dye effluent on the environment

The presence of coloured industrial wastewaters in a natural body of water is an obvious indicator of water pollution which can also result in severe risk to the environment. The presence of dyes can inhibit photosynthesis as the dyes absorb and reflect sunlight, hence the growth of bacteria is inhibited. This absorption of light creates reactive oxygen species followed by photophysical processes of energy transfer in the presence of molecular oxygen can result in toxic effects towards the microorganisms (Miroslava

Smolinska, 2012). Additionally many dyes can form hazardous by-products through oxidation, hydrolysis or other chemical reactions.

Smolinska (2012) showed that bacteria which are found in activated sludge (*E. coli, P. aeruginosa, S. enterica and B, subtilis*) had reduced activity in the presence of methylene blue, the level of damage was shown to be dependent on the concentration of the dye. The inhibitory effect was found to be worse in the presence of visible light due to the generation of reactive oxygen species such as singlet oxygen. It was shown that methylene blue had an MIC (minimum inhibitory concentration) of just 4.86 g/l for *B. subtilis*. The results can be seen in Figure 30: Growth inhibition due to methylene blue on bacteria found in activated sludge, which shows that methylene blue was acting as a photosensitizer and is activated by visible light. This increase in inhibition of bacterial growth is explained by the generation of reactive oxygen species. It was also noted that the gram-positive bacteria (*B. subtilis*) is more sensitive to the dye than the gram-negative bacteria (*E. coli, P. aeruginosa* and *S. enterica*). This is due to the difference in structure and composition of the cell walls leading to varying adsorption of methylene blue onto the cells' outer surface as well as the penetration and uptake of the dye inside the cells (Miroslava Smolinska, 2012).

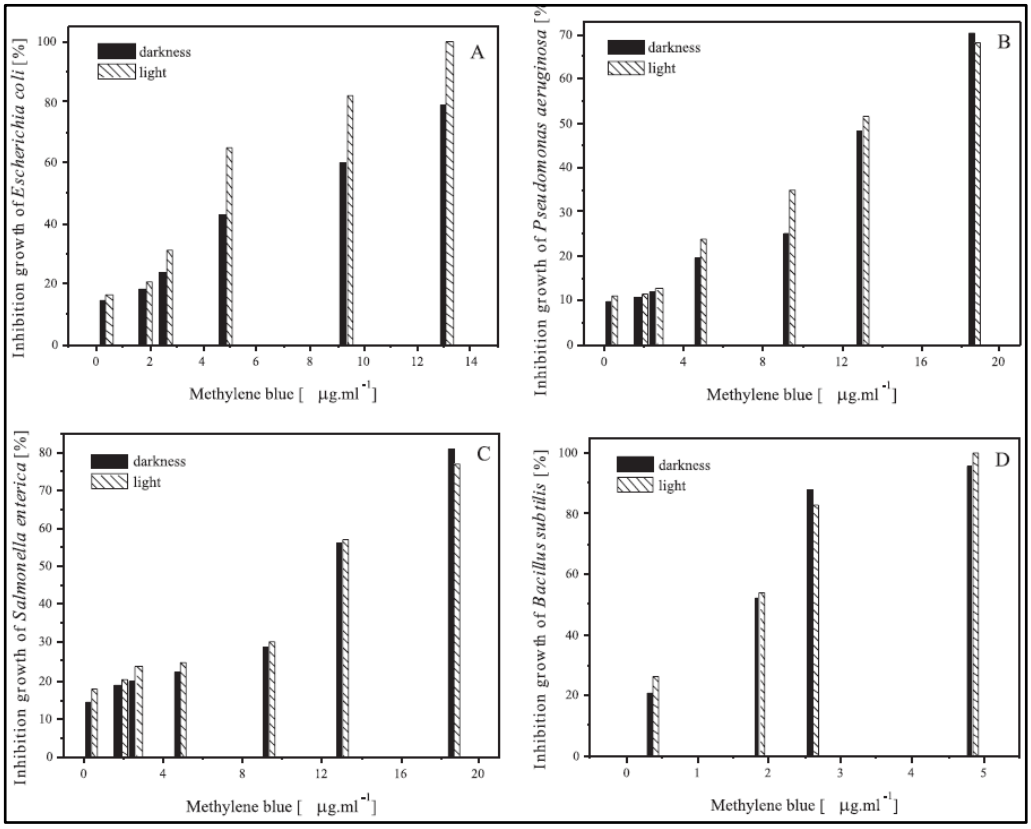

Figure 30: Growth inhibition due to methylene blue on bacteria found in activated sludge

3.3.5. Detection of Dye Removal

The degree of colourisation was measured visually as well as by a UV/Vis spectrophotometer (Hack DR2800). The wavelengths for measurement were chosen based upon the absorbance at the maximum peak of each chemical species of interest, these include Methylene blue, Azure A, Azure B and Azure C. Samples from the aeration tank and effluent leaving the clarifier were taken daily, whilst samples from the large scale plants' treated effluent and feed wastewater before addition of the blue wastewater as well as after were taken each time the feed tank to the pilot scale rig required filling up (3-4 days). Each sample was filtered before measurement.

Table 9 shows the wavelength used for each chemical species.

Table 9: Wavelength of maximum absorption for methylene blue and azure (Miller, 1957) (NCBI, 2013)

Species	**Maxima (nm)**
Methylene blue	663
Azure-A	620
Azure-B	652
Azure-C	616

3.4. Pilot Scale Rig Description

In normal laboratory circumstances, synthetic wastewater is used to carry out experiments as a steady composition is required for reproducible experiments, however the purpose of these experiments is to determine whether or not the blue wastewater can be treated by the wastewater treatment plant in constantly changing conditions with varying feed compositions and flowrates, and if treatable, find the maximum throughput of this wastewater whilst keeping the WWTP treated effluent within strict quality limits. It is therefore important to have as much equivalence between the pilot plant and large-scale plant as possible and therefore the same feed wastewater is used for the trials.

The reactor being studied is circular with an air sparging system in a ring configuration round the circumference at the bottom of the reactor. Due to manufacturing budget

constraints the pilot scale plant was constructed from plastic is rectangular in shape with a single circular air sparger in the middle of the bottom of the tank. In this case, a rectangular reactor was more cost effective to manufacture due to the labour costs. The experimental setup is shown in Figure 31, Figure 32 Figure 33. A settler (volume: 40 litres) was used to clarify the mixed liquor and return the activated sludge to the reactor. Peristaltic pumps were used to feed the system and to recycle biomass from the separator to the reactor

There are two deflection plates. The plate in the aeration tank is designed to prevent any fast-moving foaming liquid to enter the clarifier, and it has perforated sides to allow liquid through. The deflection plate in the clarifier is used to reduce the energy of incoming mixed liquor and allow it to properly settle and separate the treated wastewater from the sludge.

3.4.1. Acclimation of Microorganisms to Blue Wastewater

Adaptation is important for successful decolourisation, this is because individual strains of bacteria present in the biomass may attack the dye molecules at different positions or may use the decomposition products from a different strain (Lamia Ayed, 2011). Sufficient time should be allowed for acclimation to take place before altering the amount of blue wastewater in the feed.

3.4.2. Experimental Parameters

The conditions on the large scale bioplant were mimicked as closely as possible in the pilot scale rig in order to have a close representation of the treatment capability of the blue wastewater. Whilst the physical shape of the reactor is different (rectangular vs circular), the conditions including mixing (achieved through sparging), temperature, pH, mixed liquor suspended solids concentration (MLSS), dissolved oxygen concentration, hydraulic retention time (HRT), solids retention time (SRT) and recycle ratio which are described in the following sections are maintained.

The treated wastewater flowrate was controlled by a peristaltic pump and set to 833 ml/hour (this rate is derived in the following section) which represents that of the large scale plant, the dissolved oxygen, pH and temperature were measured using a handheld sensor (Hach Lange LCK014) in the corner of the aeration vessel where the concentration of dissolved oxygen is at its lowest. For each experiment, daily

measurements were taken (see Table 10: Pilot-scale Wastewater Treatment Plant Daily process measurements).

The temperature of the 100 litre reactor was kept between 22 and 23°C by use of two 250 watt aquarium heaters attached to the front and back sides of the aeration tank, just below the level of the liquid. The reactor was well agitated by the motion of air bubbles from the sparger at the bottom of the tank. The COD of the feed ranged from 1,000 to 10,000, and the pH kept at approximately 7.

Table 10: Pilot-scale Wastewater Treatment Plant Daily process measurements

New Blue Wastewater	Flowrate COD
Regular Feed	Flowrate COD
Treated Wastewater	Solids Colour COD
Reactor Conditions	Temperature Dissolved Oxygen pH Solids

3.4.3. Analytical Methods

Decolourization measurements were taken as the difference in absorption values of the filtered feed wastewater and the filtered treated effluent:

$$\%Decolourisation = \frac{F - E}{F} \times 100$$

Equation 7: Calculation of percentage reduction of decolourisation

Where F = Absorbance of filtered feed wastewater;

E = Absorbance of filtered treated effluent.

Similarly, the chemical oxygen demand (COD) removal was measured as the difference in feed wastewater COD and treated effluent COD:

$$\%COD\ removal = \frac{COD(F) - COD(E)}{COD(F)} \times 100$$

Equation 8: Calculation of percentage reduction in chemical oxygen demand

Where *COD(F)* = COD of filtered feed wastewater;

COD(E) = COD of filtered treated effluent.

The dissolved oxygen, pH and temperature and colour measurement were measured every day in the morning (excluding weekends and bank holidays).

3.4.4. Pilot Rig Design

An in-depth description of the design of the pilot scale rig is discussed in this section.

3.4.4.1. Diagrams

Figure 32 and Figure 33 show the way the pilot rig was constructed. Peristaltic pumps are positioned are positioned on the shelf at the side of the aeration tank for ease of access and the air sparger is located at the centre of the aeration tank to ensure uniform mixing of the mixed liquor. The three holes on the sides of the aeration tank and clarifier are used to select different tank volumes of 60, 100 or 140 litres.

There are two deflection plates, the plate in the aeration tank is designed to prevent any fast-moving foaming liquid to enter the clarifier, and it has perforated sides to allow liquid through. The deflection plate in the clarifier is used to reduce the energy of incoming mixed liquor and allow it to properly settle and separate the treated wastewater from the sludge.

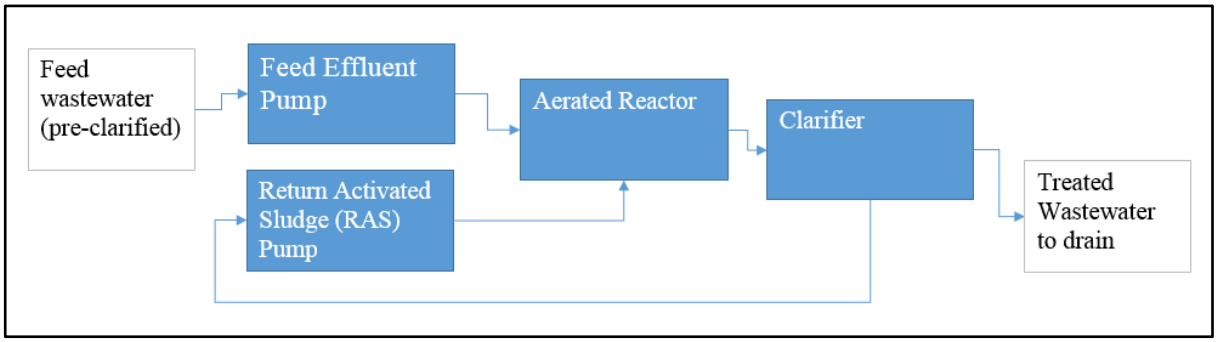

Figure 31: Pilot Scale Wastewater Treatment Plant Schematic

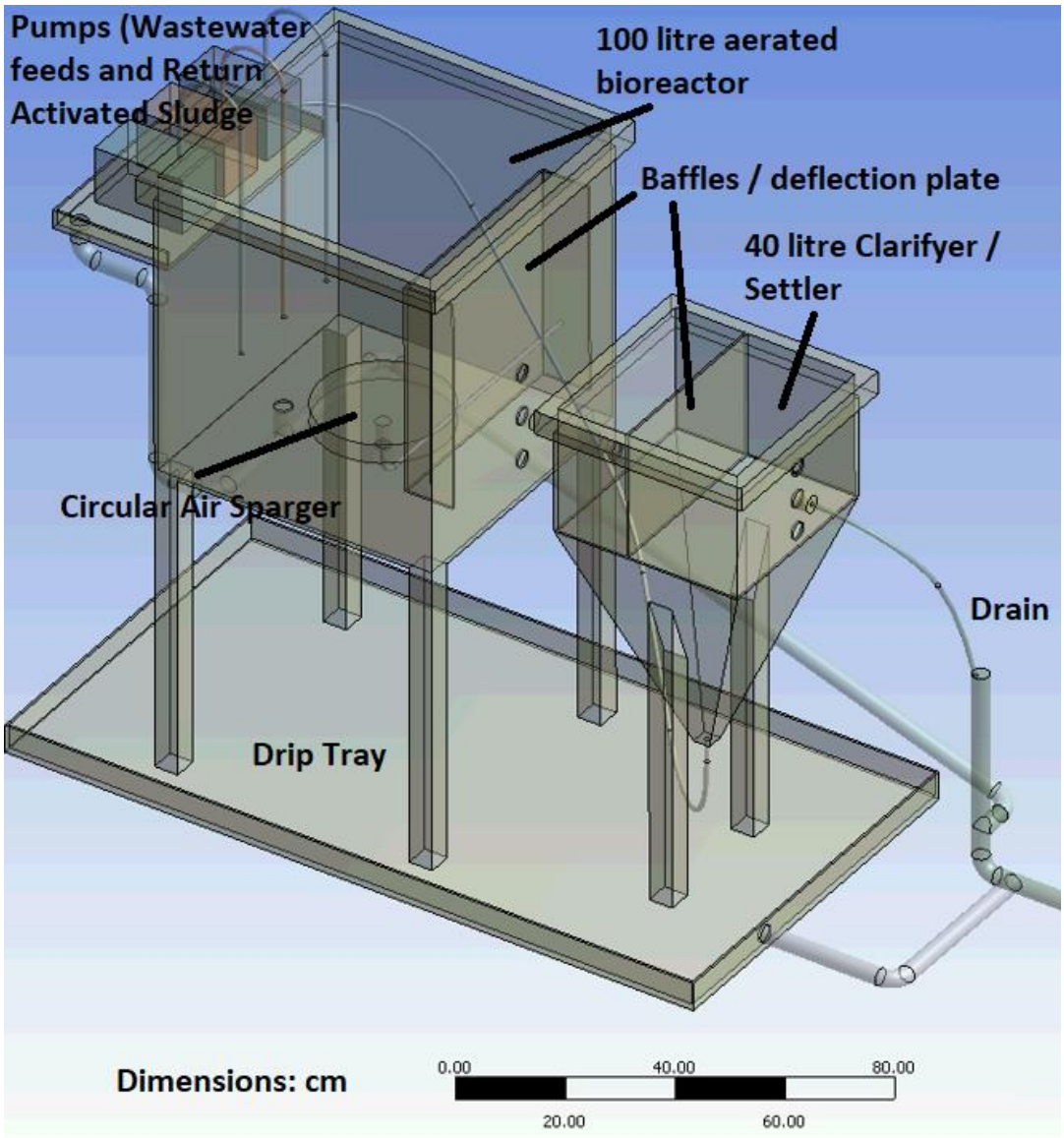

Figure 32: Transparent View of the pilot rig (scale in cm)

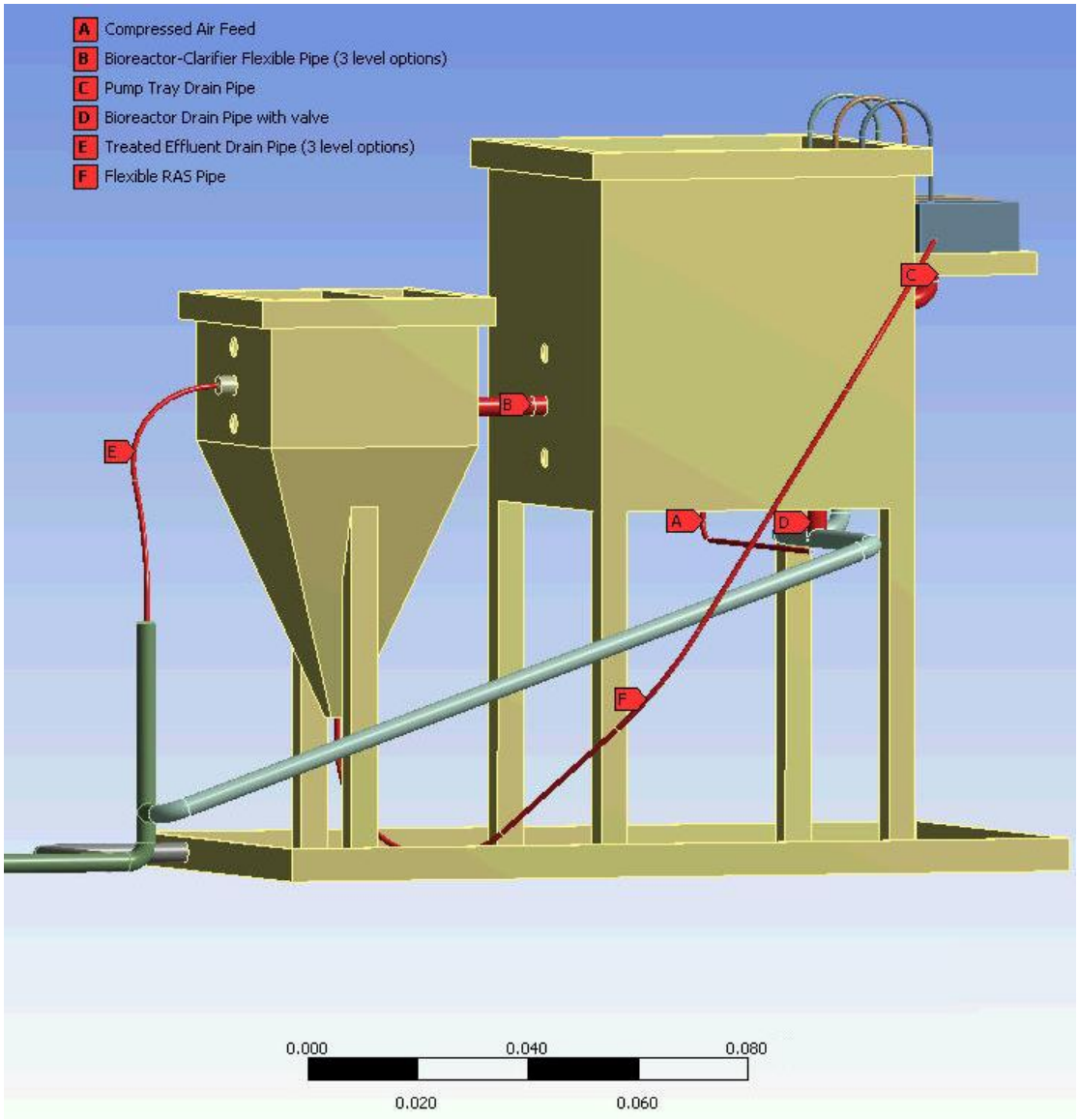

Figure 33: Rear View of the pilot rig (scale in cm)

3.4.4.2. Materials of Construction

The pilot rig was constructed using polypropylene; this is a material that is recognized for its high level of resistance to harsh chemical environments such as ones containing acids, bases and alcohols (BG, 2001). Polypropylene was also chosen for ease of manufacture of the rig due to its complicated shape.

The piping used by the peristaltic pumps are constructed out of Marprene, this material is also very chemical resistance to a wide range of chemicals including oxidising agents such as ozone or peroxides making it a suitable material to withstand chemicals likely to be present in the effluent system at Shasun. Marprene is also very durable and can last a

long time with continuous use (at least 6000 hours), negating the need to replace the pipe on a regular basis which results in plant down time (Marlow, 2013). A pipe diameter of 4mm was chosen to give the correct range of flowrates, these flowrates are calculated in the following sections.

3.4.4.3. Operation

The pilot rig has 3 peristaltic pumps (Wastson Marlow 120S/DV), two are used for feed (only one was used during these experiment, due to the very low flowrate of blue wastewater it was mixed in with the regular feed wastewater), and another pump was used for the return activated sludge from the clarifier. The greatest pump pressure of 2 bar is achieved with counter-clockwise operation and the motor speed ranges from 1-200 rpm.

3.4.4.4. Hydraulic Retention Time & Feed Rate

The large scale bioplant currently operates at an average feed flowrate of $20m^3$/hour when one 2400 m^3 bioreactor (aeration tank) is in operation, which results in a hydraulic retention time (HRT) of 5 days as per Equation 4. The pilot rig has a maximum volume of 140 litres but with these experiments being the first time the rig has been operated; 100 litres was chosen due to the possibility of excessive foaming. The pilot rig feed flowrate required to maintain the same HRT as the large scale is calculated by rearranging Equation 4 as follows:

$$Main\ Plant\ Average\ Feed = 20m^3/hour$$

$$Main\ Plant\ Reactor\ Volume = 2400m^3$$

$$Main\ Plant\ HRT = \frac{2400m^3}{(20m^3\ per\ hr \times 24\ hrs)} = 5\ days$$

$$Pilot\ Rig\ HRT\ (5\ days) = \frac{0.1\ m^3}{Daily\ flowrate}$$

$$Pilot\ Rig\ Flowrate = \frac{0.1\ m^3}{5} = 0.02\ m^3 day^{-1} = 0.833\ l\ hr^{-1}$$

After pump calibration with 4mm ID tubing, 0.555 ml of liquid was pumped for each revolution, and so for a target flowrate of 0.833 l/hour the pump must operate at a speed of 25 rpm.

3.4.4.5. Solids Retention Time & Return Activated Sludge Flowrate

The main bioplant has a mixed liquor concentration of 8-10 g/l in the aeration tank depending on the organic load of influent wastewater. The mixed liquor concentration can be augmented with return activated sludge from the large-scale plant when needed, however equations 4 and 5 will be rearranged and used to calculate the correct return activated sludge flow rate and solids wasting rate ensure equivalence. The clarifier suspended solids concentration is assumed to be the same as the large-scale plant, however if differences are discovered, the sludge wasting rate can be adjusted accordingly to maintain the same SRT of 100 days and recycle ratio of 0.67.

$$SRT\ (Pilot\ Rig) = \frac{0.1m^3\ \times\ 9\ g\ litre^{-1}}{Sludge\ Wasting\ Rate\ x\ 72g\ litre^{-1}} = 100\ days$$

$$Sludge\ Wasting\ Rate = \frac{0.1m^3\ \times\ 9\ g\ litre^{-1}}{100\ days\ \times\ 72g\ litre^{-1}} = 0.000125\ m^3day^{-1}$$
$$= 0.125\ litres\ day^{-1}$$

$$r\ (Pilot\ Rig) = \frac{Return\ Activated\ Sludge\ FLowrate}{0.02\ m^3day^{-1}} = 0.67$$

$$Return\ Activated\ Sludge\ FLowrate = 0.67\ \times\ 0.02\ m^3day^{-1} = 0.0134\ m^3day^{-1}$$
$$= 0.558\ l\ hr^{-1}$$

3.4.4.6. Food:Microorganism Ratio

The F:M ratio (also known as the process loading factor) describes the degree of starvation of the microorganisms. The F:M ratio of the large-scale plant should be maintained in the pilot rig. It is calculated as follows:

$$Average\ Feed\ COD = 5000mg/l$$

$$Daily\ feed\ flowrate = 24 \times 20m^3 = 480\ m^3/day$$

$$Food\ (F) = 480{,}000\ l\ \times\ 0.005\ kg\ l^{-1} =\ 2400\ kg\ COD/Day$$

With the mixed liquor suspended solids at a concentration of 10 g/l:

$$Microorganism\ (M) = 2400000\ (l)\ \times\ 0.01 = 24000\ kg\ of\ Microorganisms$$

$$F{:}M = \frac{2400}{24000} = 0.1$$

3.4.4.7. Weekend Operation

The pilot rig will be left unattended at weekends and so enough feed wastewater is required to last from Friday to Monday:

$$Operating\ hours = 72$$

$$Feed\ flowrate = 0.833\ l/hour$$

$$Amount\ of\ feed\ wastewater\ required = 60\ l$$

3.4.4.8. Blue Wastewater Flowrate

To begin with, an equivalent of 5 tonnes per week of blue wastewater entering the large-scale plant was mimicked in the pilot rig. After the pilot rig reaches steady state this will be increased by another 5 tonnes per week equivalent until the COD or colour of the treated wastewater exceeds the limits. There were 4 experimental runs ranging from 5 to 20 tonnes per week equivalent and the flowrate was calculated as follows:

$$Density\ of\ blue\ wastewater = 1248\ kg/m^3$$

$$Volume\ of\ blue\ wastewater = \frac{5000}{1248} = 4.01 m^3 = 4010\ litres\ per\ week$$

$$\frac{Volume\ of\ pilot\ rig\ reactor\ (l)}{Volume\ of\ large\ scale\ reactor\ (l)} = \frac{100}{2400000} = 4.17x10^{-5}$$

$$Blue\ wastewater\ flowrate\ in\ pilot\ rig = 4010x4.17x10^{-5} = 0.167\ l/week$$
$$= 23.9\ ml/day$$

Table 11 below shows the blue wastewater flowrate for the 4 experiments that were run.

Table 11: Flowrate of blue wastewater in the large-scale plant and the corresponding scaled down flowrates for the pilot rig

Tonnes equivalent	Blue wastewater flowrate (ml/day)
5	23.9
10	47.8
15	71.7
20	95.6

3.5. Description of Experiments

The experiments were carried out in 3 main stages:

1. The first stage was the initial setup of the pilot plant. To begin with, the reactor was loaded with biomass that was sourced directly from the Shasun wastewater treatment plant and then aerated. The reactor was then fed with the same clarified wastewater that entered the reactor from the large scale bioplant and run until operating conditions were stabilized and the level of wastewater treatment was closely comparable.
2. Phase 2 consisted of slowly feeding in small amounts of blue wastewater equivalent to 5 tonnes per week on the large scale until the level of treatment (removal of COD and change in colour) remained consistently close indicating acclimatisation. Phase two lasted approximately one week.
3. The previous phase was then repeated with increments of 5 tonnes per week equivalent until either the COD or colour of the effluent exceeded limits.

3.6. Results

Once the pilot rig had settled and reached steady state with the regular feed wastewater, the equivalent of 5 tonnes per week of blue wastewater was fed into the rig followed by increments of 5 tonnes equivalent until 20 tonnes was reached. The results from 60 days of continuous operation can be seen in Figure 34 which shows the total UV absorbance. The UV absorbance is correlated to the concentration of the blue wastewater in the effluent and is represented by the linear calibration curve shown in

Figure 39: Calibration curve showing Absorbance at 663nm vs % Concentration of blue wastewater. For example, an absorbance of 0.3 equates to approximately 0.075% concentration of blue wastewater in the effluent and 0.7 absorbance equates to 0.21% concentration of blue wastewater in the effluent.

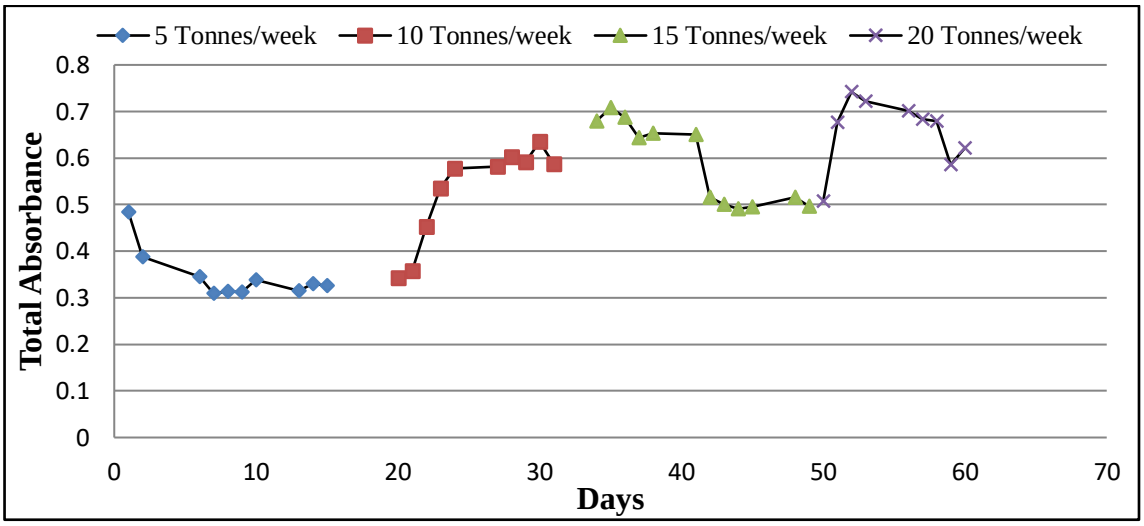

Figure 34: UV Photospectrometry measurements of total absorption in the filtered mixed liquor (sum of all 4 wavelengths)

A degree of acclimation is visible from the results, this is shown by the decrease in absorbance of the effluent over time once the concentration of blue wastewater in the influent has been increased (i.e. at the start of each of the four experiments denoted by different colours in Figure 34: UV Photospectrometry measurements of total absorption in the filtered mixed liquor (sum of all 4 wavelengths). Beginning with the 5 tonne per week equivalent, a large spike in absorbance during the initial feeding of blue wastewater material into the aeration tank of the pilot rig is visible. The concentration of blue wastewater in the feed at this stage is 0.12%, this correlates closely to the calibration curve-measured value of 0.13% in the filtered mixed liquor suggesting that none of the blue wastewater is being digested. The absorbance then reduces after 5 days and reaches a minimum absorbance of 0.309 (0.077% concentration) indicating a reduction of 41% of the blue wastewater in the filtered reactor mixed liquor. This pattern indicates that the microorganisms present in the mixed liquor are adapting to the changing feed wastewater conditions and those species capable of digesting the blue wastewater have multiplied. This pattern is repeated for both the 15 and 20 tonne experiments and is due to the further increase in population of microorganisms that favour the blue wastewater in the activated sludge. The 10 tonnes per week experiment does not follow the same pattern however. This maybe due to the fact that digestion of

the blue wastewater is already taking place, and significant population of microorganism exists that are capable of digesting the blue wastewater. A faster "response" to a step change increase is therefore possible and the peak concentration of blue wastewater was not actually observed due to the frequency of sampling and testing. This theory is supported by the fact that the concentration of blue wastewater in the feed at the introduction to the 10-tonne experiment was 0.24% vs an observed peak of 0.16%. This is also evidence that the molecules responsible for the blue colour in the wastewater can indeed be at least partially treated by the activated sludge and that the dye is not simply being diluted. The data collected for the 15 and 20 tonne experiments suggests that there exists longer term acclimation to the organic molecules in the blue wastewater as opposed to the first 5-6 days seen during the 5-tonne experiment. This is supported by the final observed concentration during the 20 tonne experiments of 0.17% blue wastewater in the pilot plant compared to a feed wastewater concentration of 0.48%, as these treated concentration levels are similar to those observed during the 10-tonne experiment.

A conclusion can therefore be drawn that in order to reduce the risk of accidental release of untreated blue wastewater into the municipal drainage system, it would be prudent to start with low input concentrations of the blue wastewater in the full-scale plant wastewater feed to allow time for the acclimation as observed during the pilot plant experiments before slowly increasing the concentration over several weeks or months until the maximum acclimation possible is achieved. If a large amount of the blue wastewater was fed directly to the large-scale plant without prior exposure of the microorganism, it's possible that very little to no digestion would occur as observed during the beginning of these experiments at the 5 tonne/week equivalent level.

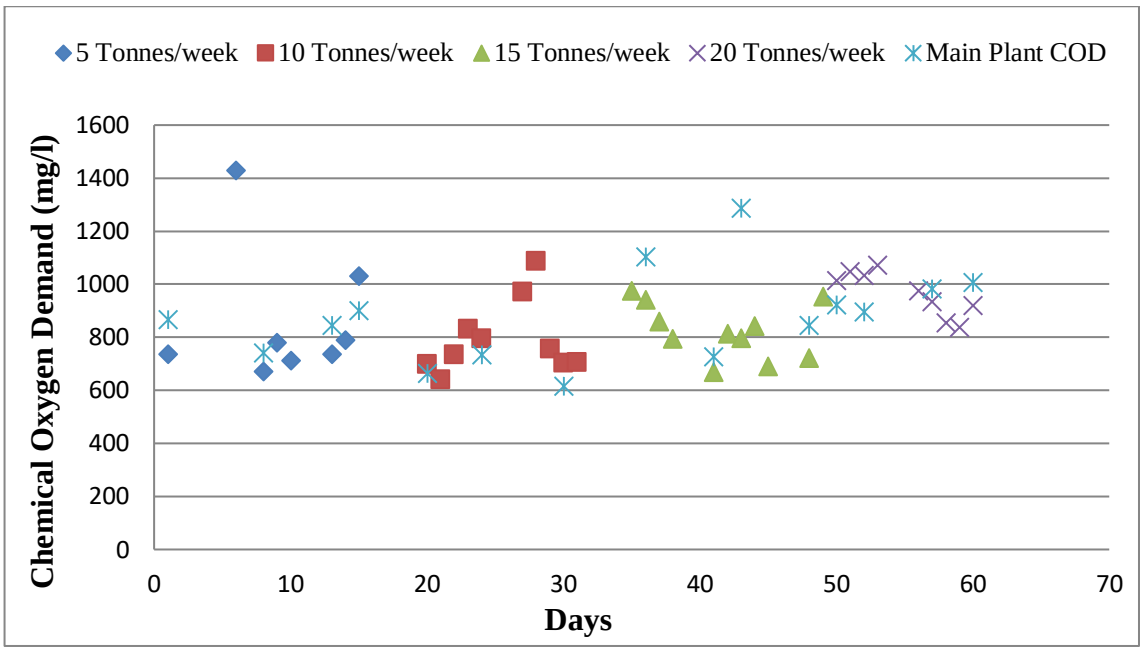

Figure 35: Measurements of chemical oxygen demand in the filtered mixed liquor

Figure 35 shows the chemical oxygen demand of the filtered mixed liquor over the 60 day period, the COD remains well below the maximum allowed by the site's effluent permit (4000 mg/l) and is comparable to the COD found on the full scale bioplant as shown by the "Main Plant COD trend" overlaid onto the graph. A vaguely similar pattern, albeit to a much lesser extent can be observed compared with the total absorption figures (Figure 34), where an increase in concentration occurs a short period of time after an increase in concentration of the blue wastewater (e.g. at beginning of the 5, 15 and 20 tonne experiments) and again this is due to the acclimation of the microbial soup in the pilot rig. This pattern does not occur during the 5-tonne experiment, an unexplained increase in COD to 1429 mg/l is observed and treated as anomalous as the COD is quickly reduced back down significantly and similar spikes are not observed for the remainder of the experiment.

Over the 60 day period measurements of pH, temperature, dissolved and dissolved oxygen concentration were taken and compared with that of the full scale wastewater treatment plant (see figures Figure 36, Figure 37 and Figure 38) found to mimic the large scale adequately. Average absolute difference between the temperature, dissolved oxygen concentration and pH of the small and large scale reactors over the 60 day period were calculated to be 0.79 degC, 1.6 g/l and 0.35 respectively. These were within normal target operating conditions of the plant as reported by the Plant Manager of 15-30 degC, minimum of 2 g/l dissolved oxygen and a pH between 6 and 8. Whilst the

temperature and pH were very close, the dissolved oxygen concentration showed greater variance with the large scale plant. This is due to the large scale plant having automated control (as demonstrated by the smoother line of results in figure Figure 37) and the small scale was manually controlled making it difficult for constant adjustments. By providing an excess of dissolved oxygen when compared to the large-scale plant, this variable was prevented from becoming a limited factor when considering treatment efficiency. Figure 35: Measurements of chemical oxygen demand in the filtered mixed liquor demonstrates similar COD concentrations in the effluent streams of the pilot and large-scale plant with an average absolute difference of 121 mg/l (average difference: 12.8%). Part of this variance between the plant can be due to the different number and timing of samples taken from each plant and the fact that wastewater feeding the pilot rig was taken from the large scale plant feed periodically (every few days as required) it is therefore possible for small differences in the feed wastewater to exist after a few days due to different batch processes being run by the sites manufacturing plants and the large scale plants constant feed from the manufacturing plant. This difference would be removed every time the feed wastewater to the pilot reg reached low level and was topped up with fresh feed.

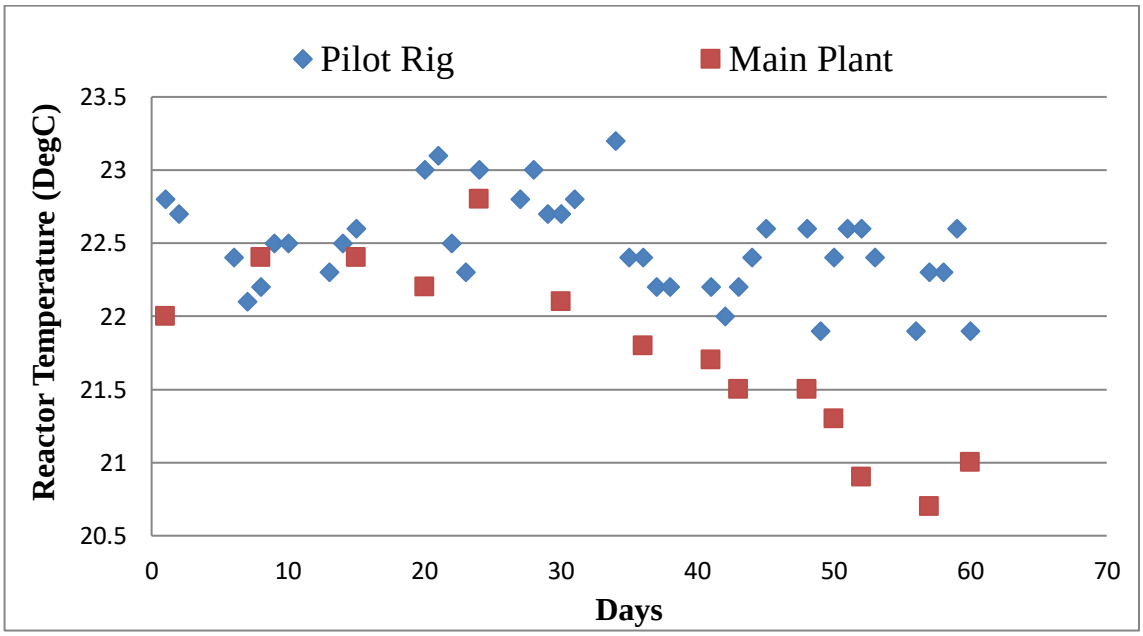

Figure 36: Comparison of Small Scale and Large-Scale Reactor Temperature

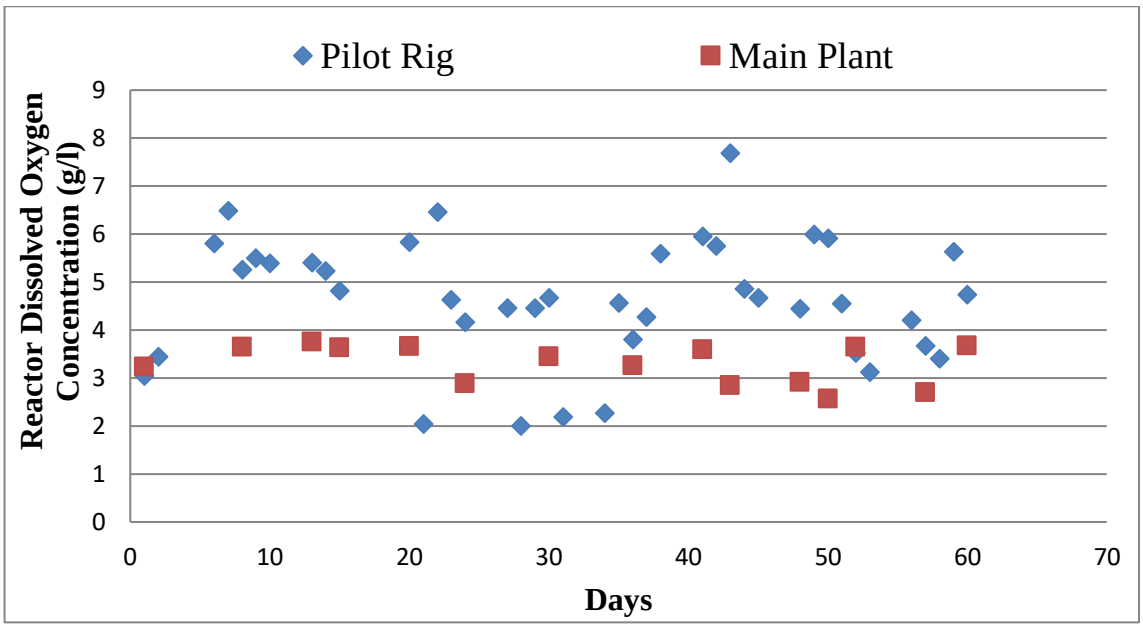

Figure 37: Comparison of Small Scale and Large-Scale Reactor Dissolved Oxygen Concentration

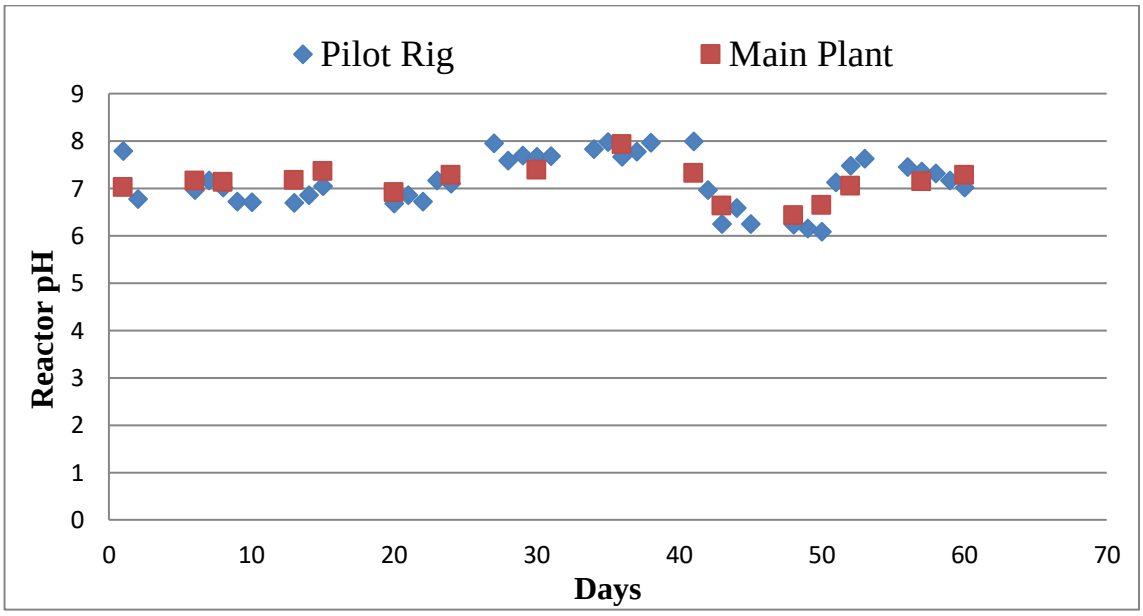

Figure 38: Comparison of Small Scale and Large-Scale Reactor pH

3.7. Case study: Using "WasteModel" to determine likely blue wastewater flowrate

The site effluent model developed in Chapter 2 was used to determine the likely concentration of wastewater from a new potential process as it reaches the wastewater treatment plant. This wastewater (from process: SPS3886) contains a strong blue dye that maybe of concern to the regulatory authorities and so tests are required to ensure that the effluent leaving the site is not considerably coloured. This concentration

calculated by the effluent model was then simulated in the bioplant pilot rig to investigate the treatability of the wastewater.

The purpose of these experiments is to determine whether or not the blue wastewater can be treated by the wastewater treatment plant and if treatable, find the maximum throughput of this wastewater whilst keeping the WWTP treated effluent within strict quality limits.

Currently, the projected number of batches of SPS3886 results in the production of 20 m^3 per week of this wastewater and for cost reasons it is preferred that the onsite bioplant treat this waste.

SPS3886 wastewater contains methylene blue and zinc, there is no criteria set by the regulatory authority about what colour the effluent can be, it is necessary to ensure that effluent leaving the site is not strongly coloured as its eventual destination is the River Tyne's estuary. There is also no limit on the amount of zinc allowed in the effluent, although regulation suggests (EC, 2008) that a concentration level 'not above background' should be maintained as the effluent reaches the watercourse.

3.7.1. Calibration Curve

In order to calculate the concentration of the blue wastewater in the treated effluent leaving the secondary clarifier of the pilot rig, a calibration curve was created using the photospectrometer. A number of solutions containing a known percentage of blue wastewater in regular treated effluent were created, these solutions ranged from 0 to 5%. This range was selected based on a judgement by eye on what the maximum acceptable level of blue colour in the effluent leaving the bioplant and entering the municipal drainage system could be.

The absorbance of these solutions at 660nm (maxima for methylene blue) were measured and a linear model was fitted. Figure 39 shows that the model is an excellent fit, with an R^2 value of 0.9984.

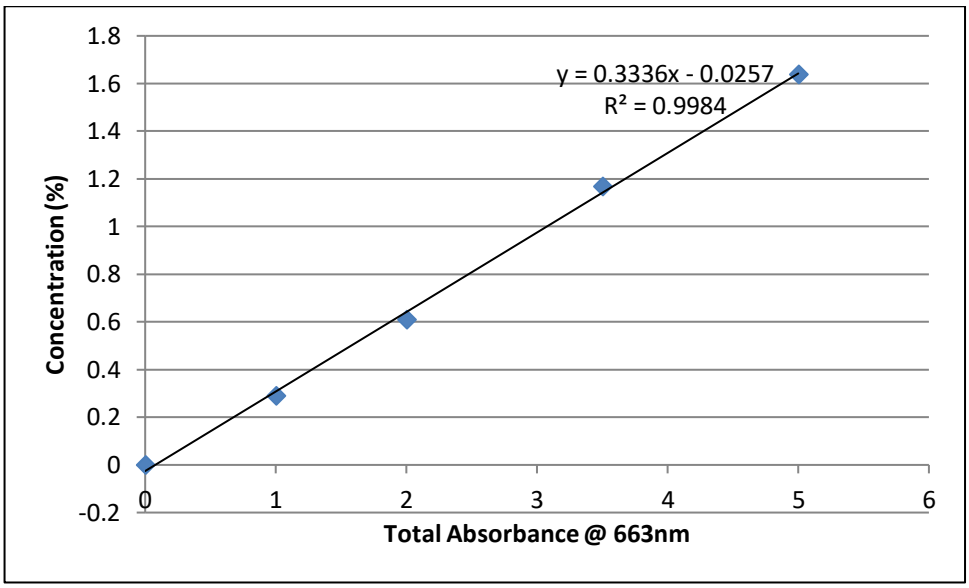

Figure 39: Calibration curve showing Absorbance at 663nm vs % Concentration of blue wastewater

$$\%Blue\ Wastewater = (Absorbance@663nm \times 0.3336) - 0.0257$$

Equation 9: Calculation of relative concentration of methylene blue containing wastewater

After several weeks in operation of the pilot rig with feed wastewater containing 4% of the blue wastewater, the absorbance (minus the baseline absorbance of 0.06) was measured as 0.228. According to Equation 9, this equates to a concentration of blue wastewater in the treated effluent leaving the pilot rig of 0.76%. This result suggests that the remaining 3.24% of the blue wastewater is being aerobically digested by the microorganisms in the bioreactor. It was thought that the microorganisms themselves could be absorbing or entrapping some of the colour, but after close inspection of the return activated sludge, there is no visual change in colour compared with microorganisms that have not had contact with the blue wastewater.

3.7.2. New Blue Wastewater Flowrate

The effluent model "WasteModel" developed in chapter 2 using MATLAB & Simulink was used to determine what the concentration of blue wastewater would be during full production at the projected number of tonnes of product per year. For the purposes of this simulation it was assumed that the bioplant was in full operation with 1 bioreactor running. The blue wastewater is discharged into Dudley 2 pit which is then directed into mixing/balancing tank B3065. The blue wastewater is discharged over a period of 8 hours with a total volume of 14m^3, an average flowrate of 14/8 = 1.75 m^3/hr is

therefore assumed, and a new batch is started every 2.5 days. This represents a flowrate equivalent to a 40 tonnes per week process which is the theoretical maximum amount of wastewater the site can produce, should the manufacturing process be run in anger. This flowrate is also higher than previously tested.

The concentration of blue wastewater leaving the primary clarifier will be used as the concentration of blue wastewater in the input to the pilot rig for these experiments. The following graphs generated by WasteModel (Figure 40, Figure 41 Figure 42) shows the concentration profile of the blue wastewater:

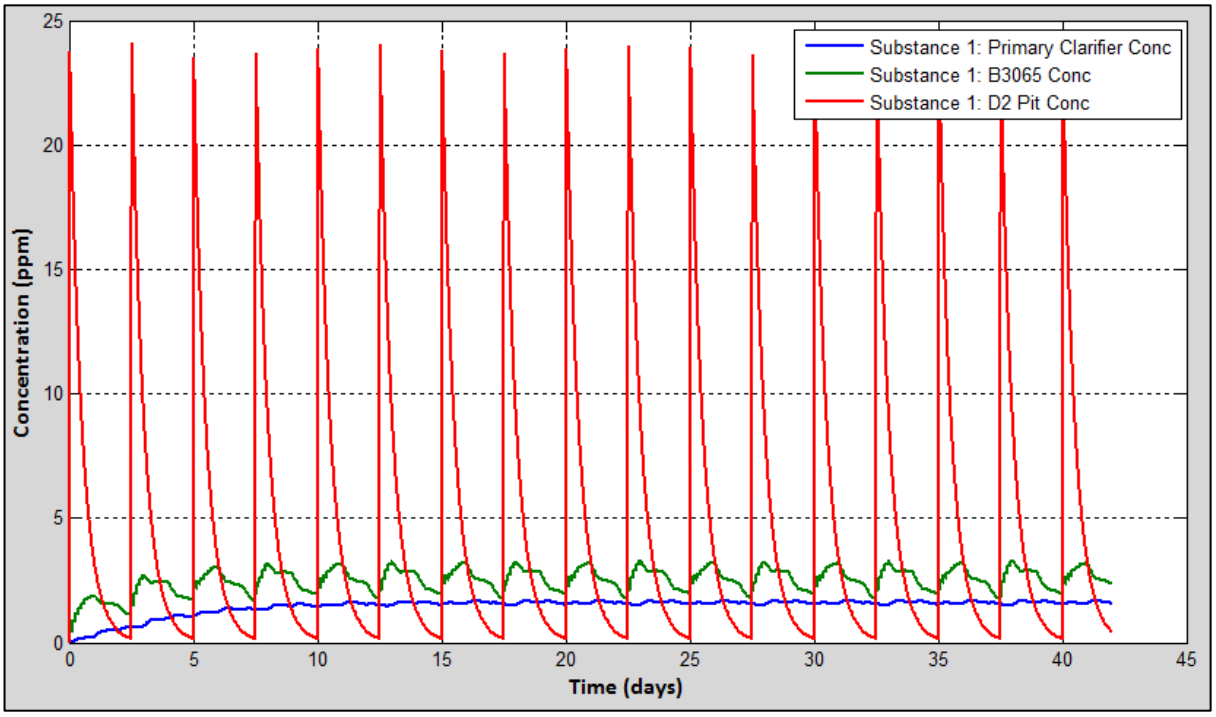

Figure 40: Concentration profile of blue wastewater from Dudley 2 Pit to the Primary Clarifier over time

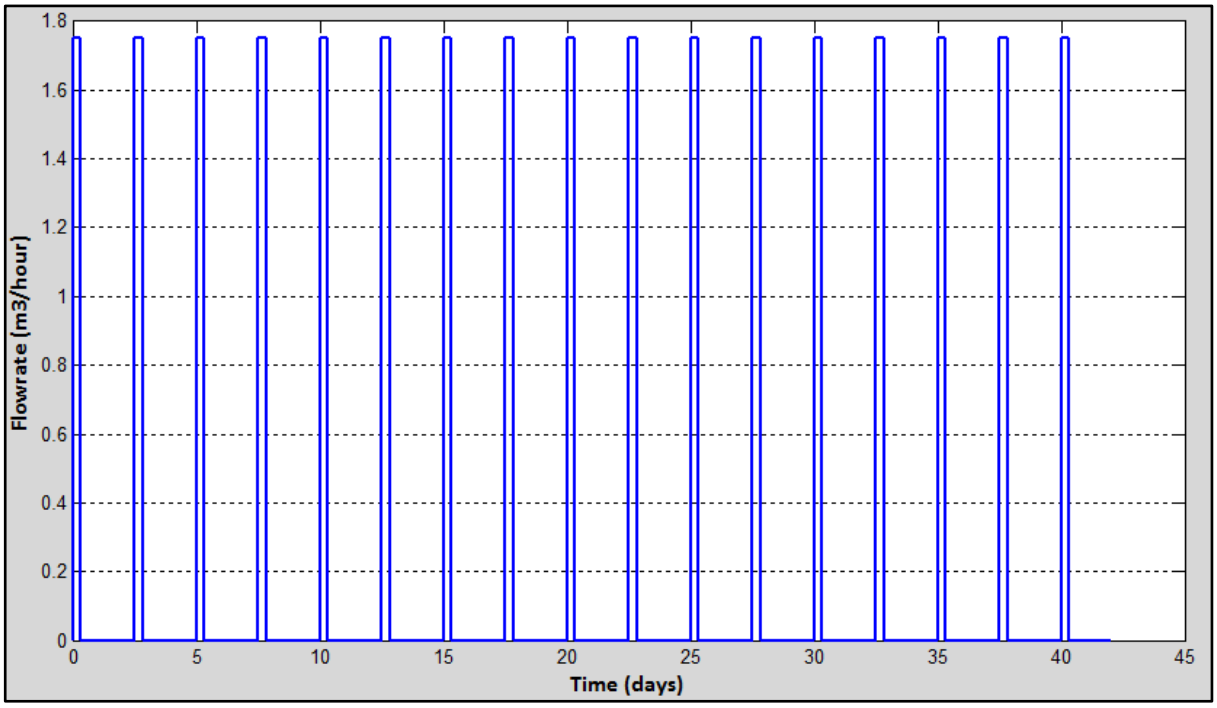

Figure 41: Change in flowrate of blue wastewater with time

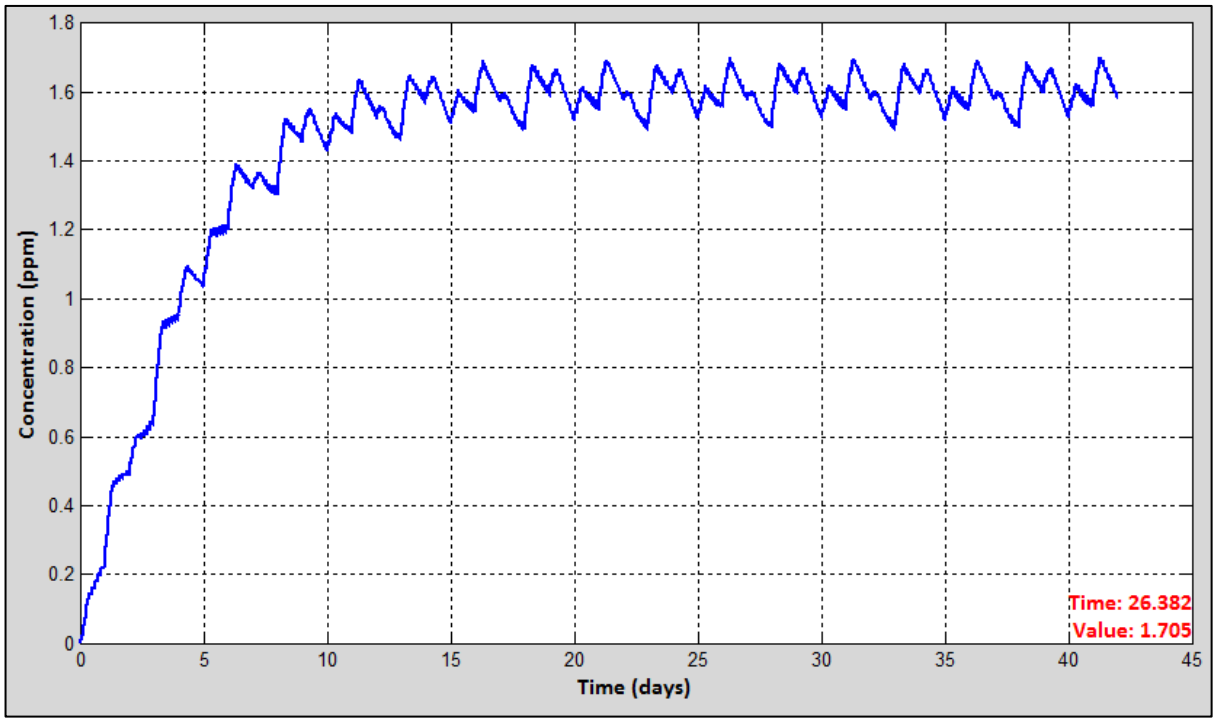

Figure 42: Concentration of blue wastewater in the primary clarifier

Figure 40 shows the simulated change in concentration of the blue wastewater due to dilution through the plant, up to and including the primary clarifier. Figure 41 shows the flowrate pattern of the blue wastewater, each batch occurs every 2.5 days and the

flowrate of the blue wastewater going into Dudley 2 pit is 1.75 m^3/hr for a period of 8 hours for each batch. After this verification of flow, Figure 42 shows a closer look at the concentration in the primary clarifier. It shows that the maximum concentration reached is 1.7% after a period of about 16 days, whereas using the previous method of calculating the inlet concentrations arbitrarily as detailed earlier in this chapter for the 5-20 tonne experiments, the concentration would have been calculated at 1.5%, representing a difference of 13%. The difference is due to the dynamics of the effluent system being taken into account, such as batch discharges.

To allow for variation in the flowrate of background wastewater such as the number of processes currently running on site or the number of commercial tankers visiting the bioplant and for ease in calculation, the concentration representing the worst case scenario for dilution of the blue wastewater in the feed to the pilot rig will be 2%.

3.7.3. Adjusted Experimental Procedure

The objective of this experiment is to determine if the wastewater treatment plant at Shasun is capable of treating the blue wastewater produced by a 40 tonnes per week process. The experiments were carried out in the phases described below:

1. Fill the pilot rig with mixed liquor from the main bioplant. This is a mixture of microorganisms and wastewater. Allow the pilot rig to reach equilibrium, this involves maintaining the same conditions as the large-scale plant (dissolved oxygen, temperature, suspended solids etc) whilst feeding in the same wastewater that the large scale receives.
2. Incorporate the blue wastewater into the regular wastewater feed at a concentration of 2% into the pilot rig. This concentration was calculated with the site effluent model.
3. Measure the absorbance of the mixed liquor to determine the concentration of blue wastewater over a period of at least 2 weeks.

3.7.4. Results

Once the pilot rig had settled and reached steady state (approx. 10 days) with the regular feed wastewater, the equivalent of 40 tonnes per week of blue wastewater (previously calculated at 2% blue wastewater in the feed) was fed into the pilot rig. The experiment was run for a total of 19 days (excluding the 10-day set-up). The following graphs show

the absorbance of the filtered mixed liquor and the chemical oxygen demand in the reactor.

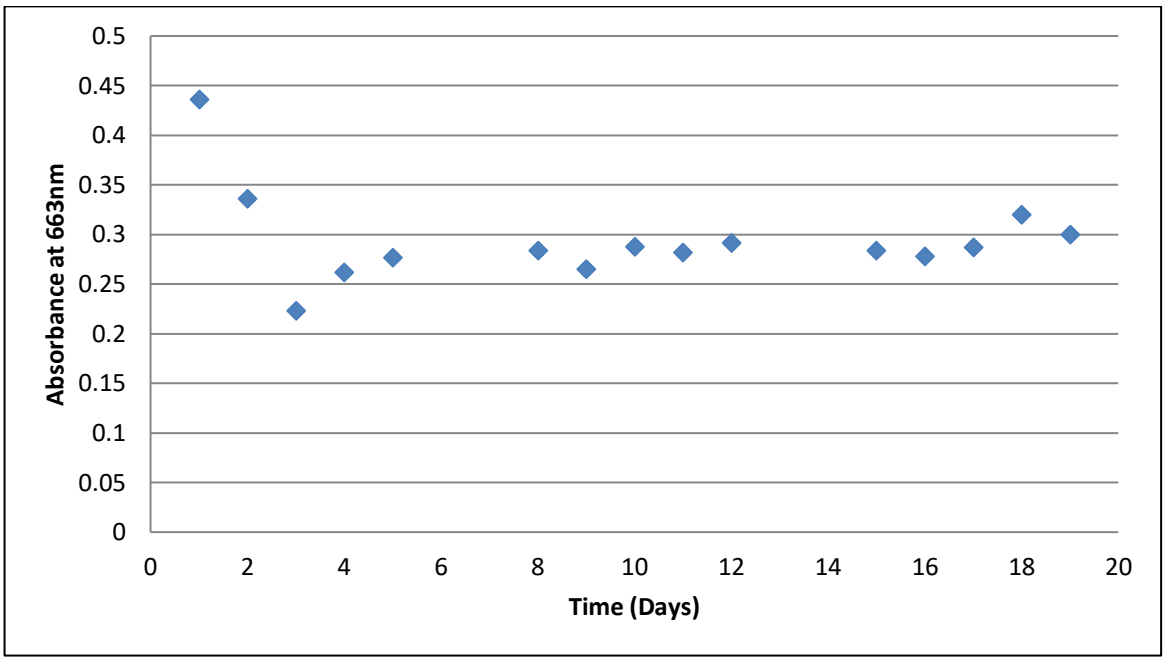

Figure 43: Graph of Absorbance of filtered mixed liquor vs time

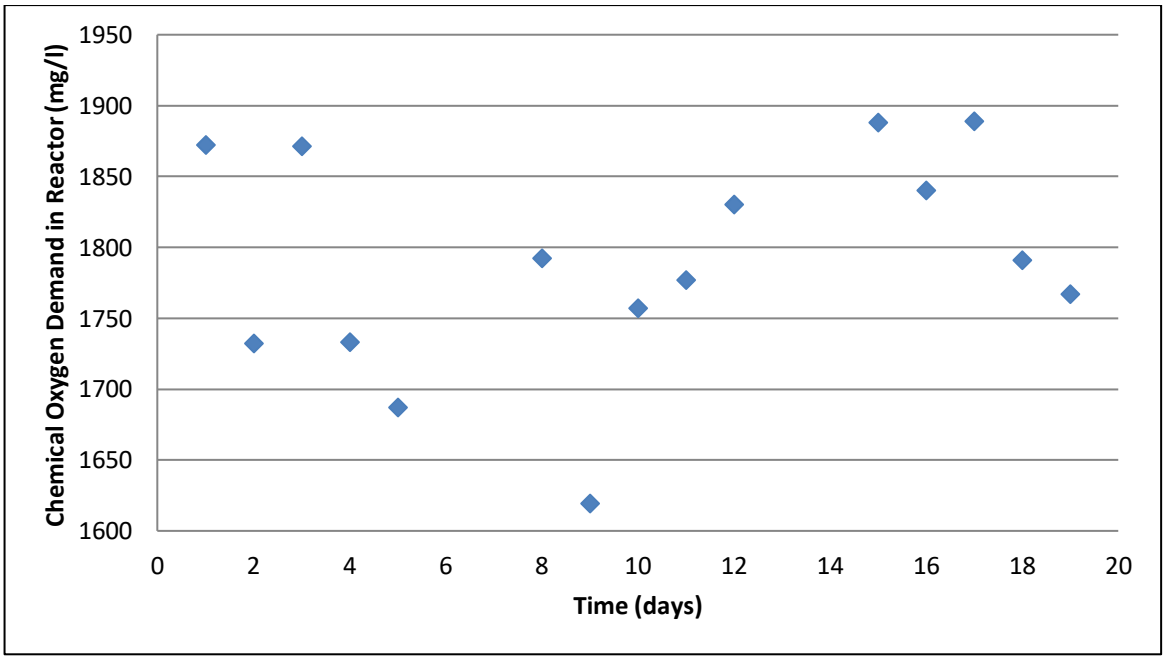

Figure 44: Graph of reactor COD vs time

As observed in previous experiments, a degree of acclimatisation is visible from the results. At the beginning, an increase in absorbance (Figure 43) during the initial feeding of material into the aeration tank of the pilot rig is visible. The initial absorbance reading at 2% blue wastewater feed was 0.64. The absorbance rapidly

decreases and remains constant at an absorbance of approximately 0.3, indicating a concentration of blue wastewater of 1.03% which represents a decrease of blue wastewater by 48.5%. This is comparable to earlier 5 tonne experiments where a decrease of 41% of the blue wastewater was observed. The difference in treatment efficiency is likely due to the significantly larger concentration of blue wastewater at the start of the experiment for the 40-tonne process when there are similar concentrations of microorganisms available to digest the wastewater.

Figure 44 shows the chemical oxygen demand of the filtered mixed liquor over the 19 day period, the COD remains well below the maximum allowed (4000 mg/l) and is similar to COD values found on the full scale bioplant at the time of testing. Based on these results it can be concluded that a significant portion of the blue wastewater can be digested in the large scale activated sludge plant.

3.8. Conclusions

This study has demonstrated the successful scale-down of the conventional activated sludge wastewater treatment plant found at Shasun. Key design criteria and operating conditions were identified that enable the same reactor conditions to be achieved and thus same level of wastewater treatment that allows for direct comparison when testing the treatability of new wastewater streams.

Chapter 4. Bioplant Predictive Modelling

4. Introduction

Research will now be conducted into the different modelling techniques available that would be suitable for the modelling of an activate sludge wastewater treatment plant. In the third chapter, the design needs of a pilot scale activate sludge wastewater treatment plant was discussed and a pilot rig is constructed for the testing of a newly available wastewater stream containing strong blue dye (methylene blue). Several experiments were conducted yielding results that determined whether or not the new wastewater stream can be treated on site. As well as having a physical model of the bioreactor system, a mathematic model that described the treatability of different wastewaters would be useful in predicting the concentration of substances in the wastewater leaving the site at Shasun. This model would complement the effluent system model developed in chapter 2, where it could replace the simple factors that are currently used that give an arbitrary percentage reduction in chemical oxygen demand (COD) and other substances as the wastewater passes through the bioreactor. The activity of microorganisms in an activated sludge wastewater treatment plant is difficult to predict and inherently non-linear, the current methods of modelling techniques thought capable of predicting this activity is reviewed in the following sections after a brief review of the wastewater treatment plant and its bioreactor at Shasun's site in Dudley, UK.

4.1. Review of Modelling Techniques

With advances in computing and instrumentation techniques, increasingly larger amounts of data from biological and chemical processes are available from which process performance and product quality can benefit through use of improved multivariate statistical process control (J.M. Park, 2006). The most widely used treatment for industrial wastewater is the activated sludge process; it is a difficult process for modelling due to the fluctuating composition and flow of wastewater influent as well as the time varying and non-linear reactions of the microorganisms (Dae Sung Lee, 2002). By increasing the understanding of this process via modelling a solid foundation to establish a control and optimisation strategy would be created.

4.1.1. Physical vs Mathematical Modelling

As shown in chapter 3 of this thesis, a small-scale physical model of the wastewater treatment plant and its bioreactor was successfully created. This allows for the testing of wastewater to determine its treatability in the plant, whilst providing very accurate and reliable results, it can take weeks to generate results. It would be useful to find out the short-term effects of changes in process operating conditions on the efficiency of the bioreactor in treating the wastewater feed in a much faster time, where results can be used to make quick decisions on how to operate the plant. For example, the bioreactor may be attempting to treat a wastewater with higher / lower pH than normal or in winter when the outside temperature is much lower than at other times of the year and so decisions on what type or strength of wastewater to send to the bioplant and in what quantities needs to be made. With the use of a mathematical model that describes the behaviour of the system in these changing operating condition, the user can quickly find out the effects of these changes an run the plant accordingly to stay within environmental discharge limit values whilst maximising output. The aim of this chapter is to determine an appropriate modelling technique that accurately represents the activity of the bioreactor in the wastewater treatment plant at Shasun given the current process measurements and data available so that the model could be implemented with minimal additional effort. The model will be assessed for its suitability for combining with the effluent system model developed in chapter 2 of this thesis. The following sections reviews different modelling techniques that are suitable for modelling the bioreactor given the data available and tests them to assess suitability.

4.1.2. Process Modelling

The industrial wastewater treatment plant (WWTP) at Shasun is a regular activated sludge unit (Figure 45), consisting of one primary clarifier, 3 activated sludge lines and 2 secondary clarifiers. Its purpose is to remove organic material from wastewater produced by a contract manufacturing pharmaceutical company. The treatment efficiency is calculated as the removal of dissolved organic carbon (DOC), sulphate and suspended solids. A list of measurements used to monitor performance of the plant can be seen in Table 12.

Table 12: List of regularly measured process variables on the bioplant

COD in
COD out
pH reactor
pH mixing tanks
Temperature reactor
Temperature ambient
Temperature effluent
DO reactor
Industrial wastewater flow rate
Return activated sludge flow rate
Specific oxygen uptake rate
Oxygen flowrate
Mixed liquor suspended solids
Sludge wasting flow rate
Tanker wastewater flow rate
Ammonia
Sulphate
Solids out

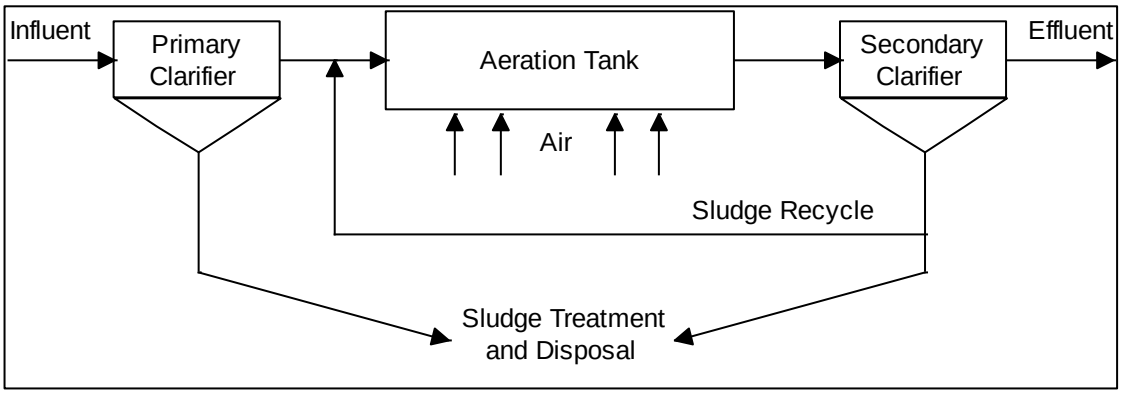

Figure 45: Flow diagram of the activated sludge wastewater treatment plant

Online measurements (pH, temperature, DO, flowrate) are monitored several times a minute whereas offline measurements (COD, SS, DOC, ammonia and sulphate concentration) are measured once per day, therefore daily totals and averages of the online measurements were combined with the daily offline measurements to provide a

whole data set to work with. The data used for the modelling was routinely gathered over a 12-month period. The following sections now investigate the different methods available for modelling of non-linear systems, the results of this investigation will determine which modelling techniques will be tested on the data gathered from the bioplant in an effort to give the best predictability of reduction in chemical oxygen demand of wastewater leaving the wastewater treatment plant.

4.2. Partial Least Squares

Partial least squares regression (PLS) is a type of multivariate analysis that uses the two block predictive PLS-model to model the relationship between two matrices, X and Y (S. Wold, 2001). PLS regression also models the 'structure' of X and Y, which produces better results than older multiple regression techniques.

Baffi (1999) mentioned that typically measurements from chemical processes are correlated, and so projection techniques such as principle component analysis (PCA) and partial least squares (PLS) have been shown to be suitable tools for the extraction of relevant information from correlated data, also PLS allows for the underlying structures of the process to be summarised as latent variables (linear combination of original variables). Linear regression models between these latent variable then relate the predictor and response variables.

In addition, PLS has been shown to be a great technique for regression where there is noisy data and only a limited number of observations. However, the inability of linear regression techniques to account for the nonlinearity and dynamics encountered in a wastewater treatment plant (WWTP) limits the effectiveness of this approach.

4.3. Neural Networks

Artificial neural networks have been used to successfully approximate continuous non-linear processes (Zainal Ahmad, 2009), however the name 'neural network' has not been exactly defined due to the large variety of network types and models and so the decision into which architecture of neural network to use for a given problem is a difficult one. Selection of the correct architecture involves picking smallest number of hidden units and connections suitable for decent approximation of the true function whilst noting that there is a trade-off between estimation bias and variability due to estimation errors (Ulrich Anders, 1999).

One of the most commonly used types of neural networks are feedforward neural networks (FANN), this is due to their simplicity and reliability (Zainal Ahmad, 2009). Figure 46 shows a diagram representing the structure of a multilayer feedforward neural network. It represents how information always travel forward in one direction; each initial layer represents an input value which is connected to each node of the next layer. Each connection has a specified "strength" described as the weights and with combination of layers and weight a function can be described that produces an output.

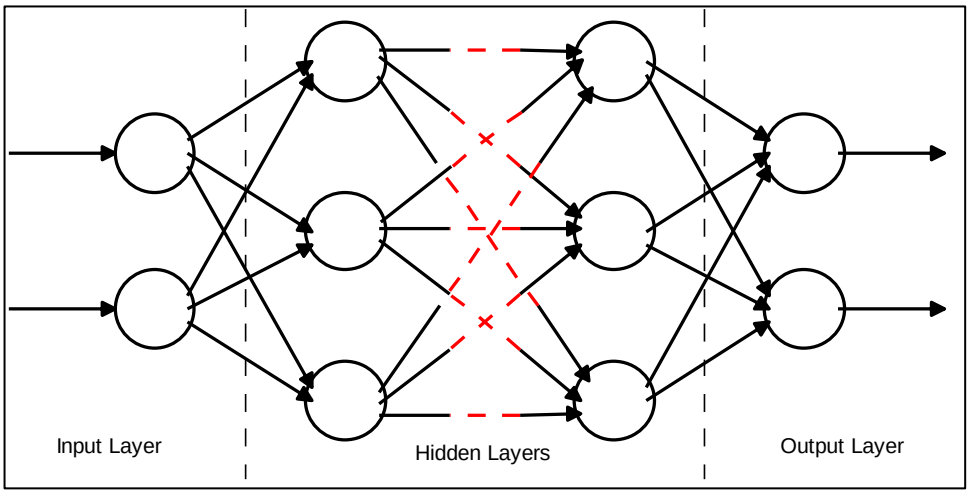

Figure 46: Multilayer Feedforward Neural Network

4.4. Multiple/aggregated Neural Networks

Multiple neural networks have become popular in recent times due to the phenomena of overfitting and underfitting, as well as the lack of generalization capability by single neural networks and the fact that it is probably impossible to develop a perfect single neural network. Although neural networks have a good ability at representing non-linear functions, an inconsistency of accuracy remains when dealing with unseen data and in any sort of advanced process control or supervision of an industrial process requires accurate process models (Zainal Ahmad, 2009). Combination of several 'imperfect' neural networks safeguards model predictions against the failure of individual component networks which could be due to a limited amount/overfitting of the training data set. The component networks are combined in a way that reduces the effect of the known errors of individual networks, increasing the generalization capacity of the model.

A commonly used way of building a multiple neural network model is the ensemble method. This involves the construction of several component networks where all input data is available to every component network resulting in networks present in the ensemble that reach a solution by different means. The output of all networks is then combined to form an ensemble output

There are a wide range of ensemble network combination methods, which can be grouped into linear, non-linear, Supra-bayesian and stacked generalization (Zainal Ahmad, 2009).

4.4.1. Stacked Neural Networks

This method involves training neural networks on different data sets, with different training algorithms and starting weights. All of these networks are then combined as shown in Figure 47. Each network shown in Figure 47 has been trained on a different data set (e.g. bootstrapped re-samples of the original data). The training algorithm and structure can also vary. When training neural networks, it is typical to apply data filtering and pre-screening methods such as mean-centring to reduce variability between different classes of data used for inputs, this ensures that a single particular variable is not preferentially used to explain the variance in the data when describing the output variable, where other variables may have useful correlations to extract.

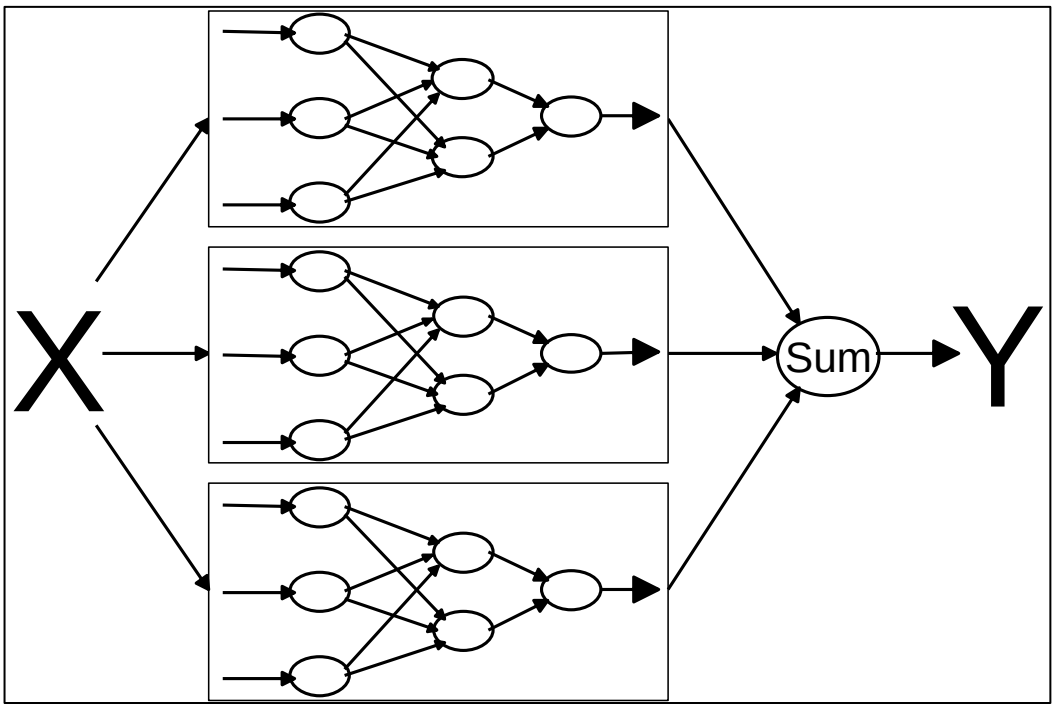

Figure 47: Multiple neural network (Zainal Ahmad, 2009)

4.4.2. Network Selection

Some neural networks may not be contributing positively to the multiple neural network output due to extreme overfitting of the training data or being too similar to other component networks and by doing so, representing the same information. A possible solution to this problem involves identifying and removing those networks detrimental to the overall output.

There have been many methods proposed for network selection such as forward selection and backwards elimination (Zainal Ahmad, 2009) which in essence combine those neural networks that significantly improve the generalisation of the model. Ahmad and Zhang (2009) showed that these network selection schemes are superior to other schemes such as combination of all component networks, the median of all networks, and the heuristic selective combination method where only the networks with lowest sum of squared error (SSE) on the training and testing data are included in the final model. There was shown to be little or no difference in the performance between forward selection and backwards elimination methods, however they showed that using networks with varying structures as opposed to fixed reduced the sum of squared errors of model long-range predictions on unseen validation data for both the modelling of a pH neutralisation process and modelling of reactant concentration in an irreversible exothermic reaction process.

4.4.2.1. Forward Selection

Forward selection involves adding networks one by one to the aggregated neural network (starting with the network with the lowest SSE on the training and testing data) until the aggregated network error on the original training/testing data cannot be further reduced.

4.4.2.2. Backwards Elimination

The backwards elimination method starts with all networks included in the aggregated network followed by gradual elimination of individual networks until the aggregated network error on the training and testing data cannot be further reduced.

4.4.2.3. Combination Approach

This approach begins with the forward selection method and in between each step of adding an additional neural network to the aggregated neural networks, backwards elimination takes place. This will systematically remove a particular neural network that now has a reduced performance in terms of contributing to reducing the overall SSE. This approach takes a little longer but finds a better combination of neural networks than one single approach alone.

4.5. Hybrid Residual Modelling

Neural networks are typically used for 'black box' modelling, i.e. no prior knowledge of the system is assumed. They can be used as estimators of unknown process parameters that are hard to model from first principles. This non-parametric learning can lead to overfitting (fitting both the function and noise), so therefore interest into developing ways to address these problems has been high in recent times.

One method to address this problem is to use a neural network to combine a known linear model with a non-linear neural network to model the non-linearities of the system and thereby creating a model that captures more complex dynamical information about the system than the linear model could achieve just by itself.

Psichogios (1992) successfully modelled a fedbatch bioreactor in this way. Bioreactors show a wide range of dynamic behaviours that are difficult to model due to the complex kinetic expressions that describe the growth of the microorganisms. It is difficult to derive expressions from first principles to relate process variables such as pH and temperature to state variables and control variables, and even more so during fedbatch operation where constantly changing conditions inside the reactor alter the microbial growth rate, making the system inherently non-linear (Dimitris C. Psichogios, 1992).

4.5.1. Activated Sludge Model no.1 (ASM1)

The activated sludge model no.1 developed by the International Association on Water Quality (IAWQ) has been considered one of the best models for carbonaceous and nitrogenous substrate removal processes (Nelson, 2009). However, it may not be suited to many plants due to the large number of stoichiometric and kinetic parameters required. Every plant has its own specific environmental operating conditions and processes of operation making it difficult to develop an accurate general model, it also

takes a considerable amount of time and effort to obtain these stoichiometric and kinetic parameters.

4.5.2. Combination of ASM1 with a non-parametric model

By combining a non-parametric model such as a neural network with the mechanistic model in a parallel structure it can become possible to make up for the non-idealities of the ASM1 by predicting its errors as shown in Figure 48.

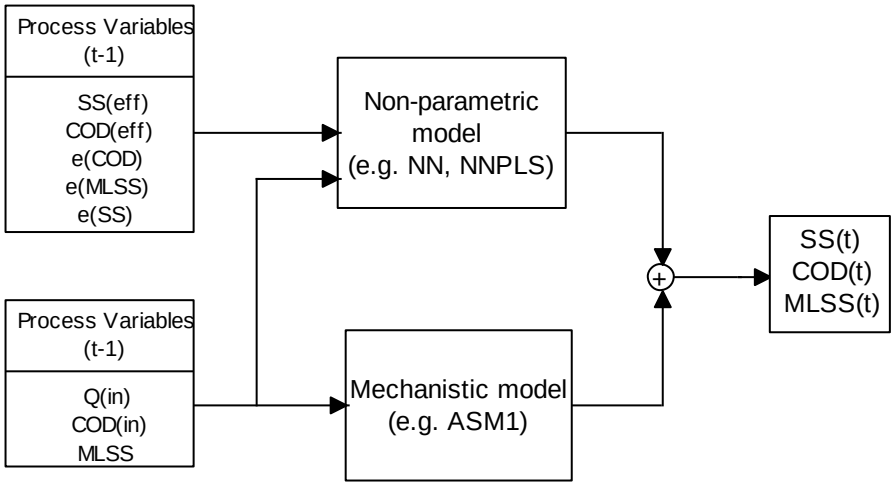

Figure 48: Parallel hybrid modelling structure (Dae Sung Lee, 2002)

With this parallel hybrid structure shown in Figure 48, it has become possible to combine to advantages of both model types; with ASM1 the basic dynamics of the required process variables are described, and with the non-parametric model representing the non-linearity of the system based on actual data correcting the imprecision of the mechanistic model (Dae Sung Lee, 2002).

4.6. Quadratic Partial Least Squares

Originally suggested by (S. Wold, 2001) a non-linear (polynomial) PLS algorithm that retains the framework of the linear PLS algorithm but instead, the relationship between the predictor and response latent variables is replaced with a non-linear one (quadratic). In addition to the proposal, Wold also suggested updating the weights of the input outer relationship by use of a Newton-Raphson linearization (first-order taylor series expansion solving with respect to the change in weights) of the quadratic inner relationship. This algorithm is fairly complex and can be slow to converge when the data lack structure, and so an evolutionary technique known as Differential Evolution (DE) has been successfully used to solve the non-linear programming (NLP) problem

of calculating the optimal input weights and parameters of the inner relationship (Xiaodong Yu, 2007). He demonstrated the use of this modelling technique on the prediction of diesel oil solidification points on a real crude distillation unit that is known to be highly complex with 12 variables chosen as inputs (mainly pressures, temperatures and flowrates). The system is also non-linear and showed an impressive decrease (~43%) in the sum of squared error of the predicted output of 200 samples compared with a linear PLS model.

Within the algorithm, the relationship between the scores vectors, t and u, is known as the inner relation, which in the standard PLS algorithm is linear:

$u = f(t) + r$ Where r = residuals.

Wold proposed replacing the linear inner relation with a non-linear quadric one, further to this work Xiaodong (2007) considered the weights updating procedure as a nonlinear programming problem with the objective function shown below. This procedure is less complex and computationally demanding than the Newton-Raphson linearization on the inner relation as proposed by Wold. The optimal weight and coefficient values that minimised the objective function whilst staying within the constraints were calculated.

$\min\{(u - \hat{u})^T(u - \hat{u})\} \qquad s.t. \|w\| = 1$

Where:

$\hat{u} = [1\ t\ t^2]^T \qquad c, t = X.w$

Xiaodong also noted that this algorithm is robust, simple and easy to implement, making it a prime candidate for testing on the data gathered from the waste water treatment plant.

4.7. Neural Network Partial Least Squares

As discussed earlier, the regular PLS regression technique is not suitable for modelling non-linear systems due to its linear nature and so a more complex regression approach is required. (G. Baffi, 1999).

Baffi, Martin and Morris (1999) built upon the non-linear PLS algorithm first proposed by Qin and McAvoy (1992) which replaced the linear inner regression model with a non-linear feed-forward neural network whilst retaining the outer mapping of the linear

PLS algorithm by developing an error-based input weights updating procedure for a neural network PLS algorithm.

Qin and McAvoy (1992) suggested that the universal approximation abilities of neural networks meant that their NNPLS algorithm is generic for non-linear modelling as no prior knowledge to a functional relationship is required when building the inner PLS models.

A big advantage of the NIPALS (non-linear iterative partial least squares) algorithm is that each pair of input-output latent variables is uncorrelated with respect to the others, and so a different network topology can be used for approximating the non-linear relationship between each pair of input-output scores without affecting or being affected by other networks (G. Baffi, 1999).

Since PLS focuses on maximising the covariance structure between the input and output variables, it can be used to remove variable correlations affecting the input data set making the combination of neural networks as the inner regressors a viable decision. This is important because neural networks have been shown in practise to be affected by variable correlations, resulting in a failure to deliver a robust solution. In the case that correlations between input variables exists, there can be lots of different combinations of network weights that can minimise the training error to provide very similar output values and so the optimisation algorithm may not succeed in finding the optimal solution. This can lead to increased variance of the noise in the predictions, especially from data collected from industrial processes where there are large numbers of variables monitored on the same process unit (G. Baffi, 1999).

An advantage of the NNPLS over the direct neural network approach is the reduction in complexity of the neural networks themselves, i.e. from Multiple Input Multiple Output (MIMO) to Single Input Single Output (SISO) networks. This will result in a reduction in the number of network weights required, and hence avoid the problem of over-parameterisation that affects networks with numerous inputs and outputs as well as reducing the number of local minima making an optimal solution more likely to be found. Baffi (1999) came to the conclusion that the NNPLS approach is more robust, has less variance in the model predictions and a reduced sensitivity to variable correlations (thanks to the PLS framework) compared with the direct single neural network approach. The neural network partial least squares algorithm is shown in Table 13 below.

Table 13: Neural Network PLS Algorithm (G. Baffi, 1999)

(0) $Mean\ centre\ and\ scale\ \boldsymbol{X}\ and\ \boldsymbol{Y}.$

(1) $Set\ output\ scores\ \boldsymbol{u}\ equal\ to\ column\ of\ \boldsymbol{Y}.$

(2) $w' = \frac{u'X}{u'u}$

(3) $w'_{new} = \frac{w'_{old}}{\|w'_{old}\|}\ (normalization)$

(4) $t = \frac{Xw}{w'w}$

(5) $Train\ centred\ sigmoidal\ neural\ network\ between\ \boldsymbol{t}\ and\ \boldsymbol{u}.$

(6) $Calculate\ non-linear\ prediction\ of\ \boldsymbol{u}\text{:}\ \hat{\boldsymbol{u}} = \omega_2.\sigma(\omega_1.\boldsymbol{t} + \beta_1) + \beta_2$

(7) $q' = \frac{\hat{\boldsymbol{u}}'Y}{\hat{\boldsymbol{u}}'\hat{\boldsymbol{u}}}$

(8) $q'_{new} = \frac{q'_{old}}{q'_{old}}\ (normalizaion)$

(9) $u = \frac{Yq}{q'q}$

(10)

$Compute\ new\ input\ weights\ updating\ parameters\ \Delta\boldsymbol{w}\ as\ shown\ in\ section$ 4.1.

(11) $\boldsymbol{w} = \boldsymbol{w} + \Delta\boldsymbol{w}$

(12) $w'_{new} = \frac{w'_{old}}{\|w'_{old}\|}\ (normalization)$

(13) $t = \frac{Xw}{w'w}$

(14) $Check\ convergence\ on\ \boldsymbol{t}.\ \ If\ yes, go\ to$ 15 $else\ go\ to$ 5.

(15) $p' = \frac{t'X}{t't}$

(16) $Train\ centred\ sigmoidal\ neural\ network\ between\ \boldsymbol{t}\ and\ \boldsymbol{u}.$

(17) $Calculate\ non-linear\ prediction\ of\ \boldsymbol{u}\text{:}\ \hat{\boldsymbol{u}} = \omega_2.\sigma(\omega_1.\boldsymbol{t} + \beta_1) + \beta_2$

(18) $E_h = E_{h-1} - t_h p'_h;\ X = E_0$

(19) $F = F_{h-1} - \hat{\boldsymbol{u}} q'_h;\ Y = F_0$

For additional components, repeat the procedure with E and F replacing X and Y respectively.

4.7.1. Weights Updating Procedure

The use of a non-linear model between the scores vectors of the inner relation affects the computation of the weights vector, **w.** This is because **w** represents the association among variables of **X** and **u**, and will be closely related to the covariance values only if the non-linear mapping between latent variables is monotonic and slightly non-linear, but if this is not the case then an update of the weights vector is required (Rosipal, 2009). The non-linear function (neural network) is assumed to be continuous and differentiable with respect to the input weights **w** and that this non-linear mapping can be approximated by a Newton-Raphson linearization (Taylor-series expansion) of the non-linear function. This weights updating procedure takes place at each iteration in the NIPALS algorithm and replaces the step 10 in Table 13Table 14 which calculates the input weights.

The whole mathematical proof of the taylor series expansion of a centred sigmoidal neural network with respect to the input weights is shown by Baffi (1999). Table 14 shows the resulting equations required for the weights updating procedure used by the Neural Network PLS algorithm in Table 13 for step 10.

The error-based updating procedure begins with defining a matrix $\mathbf{Z}=[\mathbf{Z}_k]$, where each column of $\mathbf{Z}_k$ is equal to:

$$(1)\ Z_k = \frac{\partial f(\boldsymbol{t})}{\partial W_k} = \frac{1}{2}.\omega_1.\omega_2.\left(1-\sigma^2(\omega_1.\boldsymbol{t}+\beta_1)\right).\boldsymbol{X}_k$$

Where: $$\sigma(z) = \frac{1-e^{-z}}{1+e^{-z}} = tanh\left(\frac{z}{2}\right)$$

$$\omega_1, \omega_2 = Weights\ of\ hidden\ and\ output\ layer$$

$$\beta_1, \beta_2 = Biases\ of\ hidden\ and\ output\ layer$$

The mismatch between the value of **u** (step 9) and $\widehat{\boldsymbol{u}}$ provided by the neural network model is given by equation 2:

$$(2)\ \boldsymbol{e} = \boldsymbol{u} - \widehat{\boldsymbol{u}} = \boldsymbol{Z^T}.\boldsymbol{e}$$

The PLS outer input weights, **w**, can then be updated using the following parameters:

$$(3)\ \Delta\boldsymbol{w} = (\boldsymbol{Z^T}.\boldsymbol{Z})^{-1}\,\boldsymbol{Z^T}.\boldsymbol{e}$$

Table 14: Weights Updating Procedure (G. Baffi, 1999)

4.8. Multiple Neural Network Partial Least Squares

Following the research conducted in the previous section of this chapter, a potential improvement to the neural network PLS algorithm proposed by Baffi is described.

Through initial testing of the NNPLS (neural network partial least squares) algorithm, which replaces the linear inner regressor of the standard PLS algorithm with a non-linear one (centred sigmoidal neural network) modifications will be proposed to improve robustness in predictions.

Neural networks can suffer from a lack of robustness from over-fitting and poor generalisation of the models. The combination of multiple neural networks has been shown to be effective in tackling this problem (Zainal Ahmad, 2005). It is proposed that predictions can be further improved by integrating multiple neural networks and using an average value of predictions from these networks as the replacement to the linear inner regressor of the standard PLS algorithm to provide a more robust prediction.

The new algorithm is presented in Table 15. Table 16 and Table 17 shows the updated weights updating procedure and method for making predictions using the new algorithm.

Table 15: Multiple Neural Network PLS Algorithm

(0) *Mean centre and scale* $\boldsymbol{X}$ *and* $\boldsymbol{Y}$.

(1) *Set output scores* $\boldsymbol{u}$ *equal to column of* $\boldsymbol{Y}$.

(2) $w' = \dfrac{u'X}{u'u}$

(3) $w'_{new} = \dfrac{w'_{old}}{\|w'_{old}\|}$ $(normalization)$

(4) $t = \dfrac{Xw}{w'w}$

(5) *Generate n replication of* t *and* u *using bootstrap resampling* $\{t_{(1)}u_{(1)}\} \dots, \{t_{(n)}u_{(n)}\}$

(6) *Develop a neural network on each replication. Denote the prediction of the* i^{th} *network on the original data set as* $\widehat{\boldsymbol{u_i}}$.

(7) *Calculate combined non* $-$ *linear prediction of* $\boldsymbol{u}$ *for all networks*:

$$\widehat{\boldsymbol{u}} = \frac{1}{n}\sum_{i=1}^{n} \widehat{\boldsymbol{u_i}}$$

(7) $q' = \dfrac{\widehat{\boldsymbol{u}}' Y}{\widehat{\boldsymbol{u}}' \widehat{\boldsymbol{u}}}$

(8) $q'_{new} = \dfrac{q'_{old}}{q'_{old}}\ (normalizaion)$

(9) $u = \dfrac{Yq}{q'q}$

(10) *Compute new input weights updating parameters* $\Delta \boldsymbol{w}$ *as shown in the section below.*

(11) $\boldsymbol{w} = \boldsymbol{w} + \Delta \boldsymbol{w}$

(12) $w'_{new} = \dfrac{w'_{old}}{\|w'_{old}\|}\ (normalization)$

(13) $t = \dfrac{Xw}{w'w}$

(14) *Check convergence on* $\boldsymbol{t}$. *If yes, go to* 15 *else go to* 5.

(15) $p' = \dfrac{t'X}{t't}$

(16) *Repeat steps* $5 - 7$ *to calculate a new* $\widehat{\boldsymbol{u}}$, *store the network weights and bias' for prediction*

(17) $E_h = E_{h-1} - t_h p'_h;\ X = E_0$

(18) $F = F_{h-1} - \widehat{\boldsymbol{u}} q'_h;\ Y = F_0$

Table 16: Weights Updating Procedure for the Multiple Neural Network PLS Algorithm

The error-based updating procedure begins with defining a matrix **Z=**[$\mathbf{Z}_k$] for n neural networks, where each column of $\mathbf{Z}_k$ is equal to:

(1) $Z_{k,n} = \dfrac{\partial f(\boldsymbol{t})}{\partial W_{k,n}} = \dfrac{1}{2}.\omega_{1,n}.\omega_{2,n}.\left(1 - \sigma^2\left(\omega_{1,n}.\boldsymbol{t} + \beta_{1,n}\right)\right).\boldsymbol{X}_k$

Where: $\sigma(z) = \frac{1-e^{-z}}{1+e^{-z}} = tanh\left(\frac{z}{2}\right)$

$\omega_{1,n}, \omega_{2,n} = Weights\ of\ hidden\ and\ output\ layer\ for\ network\ n.$

$\beta_{1,n}, \beta_{2,n} = Biases\ of\ hidden\ and\ output\ layer\ for\ network\ n.$

The mismatch between the value of **u** (step 9) and $\hat{\boldsymbol{u}}$ provided by the combined neural network models is given by equation 2:

(2) $\boldsymbol{e} = \boldsymbol{u} - \hat{\boldsymbol{u}}$

The PLS outer input weights, **w**, can then be updated using the following parameters:

(3) $\Delta \boldsymbol{w}_n = \left(\boldsymbol{Z_n}^T . \boldsymbol{Z_n}\right)^{-1} \boldsymbol{Z_n}^T . \boldsymbol{e}$

(4) $\Delta \boldsymbol{w} = \frac{1}{n} \sum_{n=1}^{n} \Delta \boldsymbol{w_n}$

Table 17: Method of making predictions with the mNNPLS algorithm

Predictions using new $\boldsymbol{X}$ *data can be made as follows*:

(1) $\boldsymbol{w_i^*} = \prod_{j=1}^{i-1} (I - w_j p_j^T) w_h$

(2) $Y = \frac{1}{n} \sum_{n=1}^{n} \omega_{2,n} q_i \left(\left(\omega_{1,n} . \boldsymbol{X} \boldsymbol{w_i^*} + e \beta_{1,n}{}^T \right) \right) + \beta_{2,n} q_i{}^T$

Where i = Number of latent variables,

n = Number of neural networks for the corresponding latent variable,

I = Identity matrix

4.9. Dynamic Models

Now that a number of non-linear modelling techniques thought suitable for modelling an activated sludge wastewater treatment plant have been investigated, the implementation of dynamics to model time series will be investigated. This section provides a brief look at three different methods of implementing dynamics into a model. Dynamic models are required for process control (Shasun are effectively looking to control the performance of their wastewater treatment plant), with most methods requiring a considerable increase in the dimension of the input matrix, as this is where lagged values are found. The presence of these lagged values may result in models that are difficult to manipulate (Olufemi A. Adebiyi, 2003) but provide extra data inputs that

can give more accurate predictions of the target variable.. Three very commonly used methods are shown below:

4.9.1. Finite Impulse Response (FIR)

This method involves using a large number of lagged input values of the input variable in the input data matrix.

4.9.2. Auto-Regressive Moving Average (ARMA)

This is similar to the Finite Impulse Response method except lagged values of both the inputs and output variables are used in the input data matrix for predictions.

4.9.3. Auto-Regressive with Exogenous Inputs (ARX)

This method involves the model relating the current value of the time series to both the past values of the same series and current and past values of the input variables data, through initial testing on sample data of a pH neutralisation process, this method was found to give the best results in terms of minimising the mean squared error of predicted results on unseen data.

4.10. Data Gathering

A list of measurements made available for modelling are shown in Table 18. Online measurements are recorded hourly with offline measurements such as COD are recorded once daily. To account for the difference in the amounts of data between the online and offline measurements a daily average/total was taken. Variable such as reactor pH, temperature and dissolved oxygen were taken including values for flowrates and chemical oxygen demand in the main storage tanks that feed the bioreactor (e.g. D1 Pit). The final predicted value is the chemical oxygen demand of the treated wastewater leaving the plant and going to the municipal sewerage system.

The performance of the microorganisms in the activated sludge unit is known to be temperature dependant (Shahzad, 2015). The wastewater treatment plant manager informs that greater performance is achieved in the winter, contradicting conventional thought. The wastewater treatment plant is located in the north east of England with typical outside temperatures ranging from around 0°C in the winter to 20°C in the summer. For this reason, a minimum of 12 months of data is required to cover the seasonal fluctuation of temperature. For testing the models 15 months of data (one

value of each variable per day) was used in total, the first 12 was for training the models and the final 3 months used for testing and validation.

Table 18: Input and Predicted Variables in data used for testing predictive models

Input Variables (X)
Reactor pH
Reactor Temperature (DegC)
Reactor DO (mg/l)
Ambient temperature (DegC)
Return Activated Sludge flowrate (m3/hr)
Return Activated Sludge Density (kg/m3)
Raw Effluent pH
Treated Effluent pH
Treated Effluent Temperature (degC)
Dudley 1 Pit COD (mg/l)
Dudley 1 Pit Flowrate (m3/hr)
D2 COD (mg/l)
D2 Pit Flowrate (m3/hr)
Pilot Plant COD (mg/l)
Total Flow per Day (m3)
Total COD In (kg)
Predicted Variable (Y)
COD Out (mg/l)

4.11. Model Testing

The most promising model types that were investigated and these include the multiple neural networks and neural network PLS in addition to the new proposed method of multiple neural network PLS. These were compared with a standard PLS model to show how unsuitable a linear model would be in predicting a highly non-linear model such as this one. Testing on hybrid residual modelling (Neural network with the Activated Sludge Model 1) did not take place during the studies conducted in this thesis due to the lack of measurements and information available that is required by the model, such as stoichiometric and kinetic values. It should, however, be studied for comparison in future research as promising modelling results have previously been obtained (Dae Sung Lee, 2002). Each model tested used the auto-regressive with exogenous inputs (ARX) method of implementing process dynamics into the input data matrix as this was found to give the best results in terms of prediction accuracy.

4.12. Comparison of Results

Table 19 shows the results of testing 5 different types of model investigated in this chapter on the wastewater treatment plant data described in section 4.10, mean squared error on the respective model's predictions on unseen data was used as a measure to determine which modelling technique is the best for this bioreactor system. The type of model, model structure and values of overall mean squared error for predictions on unseen two weeks worth of bioplant data are shown in the table. Two weeks of future predictions was selected as this represents adequate time to foresee process upsets and apply correcting measures when this model is to be used for process control. The types of model tested using MATLAB are the standard partial least squares model (PLS), a single feedforward neural network, multiple aggregated neural networks which uses a combination of forward selection and backwards elimination to select the best combination of neural networks (an average value of the predicted variable was used for the aggregated neural networks), the neural network PLS (nnpls) model proposed by Baffi and the multiple neural network PLS model proposed in this thesis.

All of the models were combined with autoregressive with exogenous (ARX) inputs which included the previous Y value and 2 previous X values, the data was also mean centred and scaled prior to testing. 3 latent variables were used for PLS, and 2 for NNPLS/mNNPLS as this was found to give the best results and also helps maintain a level playing field when comparing the different techniques. The neural networks were trained 10 hidden neurons and used the Levenberg-Marquardt training method using mean squared error for evaluation of performance.

In the mNNPLS model, the simple average prediction of 10 neural networks per latent variable were used.

Table 19: Mean squared error of different model types on 2 weeks of unseen data from an activated sludge wastewater treatment plant process

Model	Structure	MSE	R^2
PLS-ARX	LV=3, Nx=3, Ny=1	7.538	0.270
NN-ARX	1 Network (Feedforward)	3.565	0.488
mNN-ARX	FS/BE from 100 Networks	1.022	0.602
NNPLS-ARX	SISO FBNN, LV=2, Nx=3, Ny=1	0.644	0.729
mNNPLS-ARX	SISO FBNN, LV=2, Nx=3, Ny=1, 10 Networks per LV	0.342	0.855

The results show that the predictions by a linear method (PLS) are very poor when compared with the non-linear methods which is as expected – as previously mentioned, the activity of the microorganisms in an activated sludge wastewater treatment plant is highly non-linear. The best results on unseen data can be seen using the two NNPLS algorithms, this is due to the robust PLS framework and ability of neural networks to model highly non-linear processes. By combining multiple neural networks for use as the PLS model's inner regressor the robustness can be further improved, this is also evident when comparing the single neural network with the multiple neural network model.

4.13. Conclusion

The aim of this research was to determine an adequate technique for predictive modelling of the on-site wastewater treatment plant at Shasun. A number of techniques were investigated and the best one found to be the multiple neural network PLS (mNNPLS) algorithm which replaces the linear inner regressor of the standard PLS algorithm with an aggregate of several neural networks to maintain the robustness of the overall algorithm whilst maintaining the ability to model highly non-linear data. This technique builds upon the neural network PLS algorithm described in section 4.7 and provides good predictions compared to the other modelling techniques tested as shown by the reduced values of mean squared error and R^2 of 0.855. This can be further compared to similar studies found in literature for prediction of effluent chemical oxygen demand concentration of activated sludge wastewater treatment plants such as an R value of 0.795 (Moral, 2008) which was achieved using artificial neural networks. This study however used data derived from a municipal wastewater treatment plant which typically have less variance of organic compounds in incoming waste streams when compared to a contract batch process manufacturer of fine chemicals. Additionally, this R value of 0.795 was obtained by using an effluent parameter (total suspended solids in the effluent (T_{eff}) as an input to the model which is unusual and not applicable if the model is to be deployed as a method of system control. When removing T_{eff} from the input matrix, the next best R value achieved by this study was 0.658. This value can be compared to the R value of 0.488 achieved in this study using neural networks alone, it is possible that the difference can be due to varying model architecture, quality of data, or perhaps increased non-linearity from the treatment of wastewater streams with different characteristics (municipal vs batch chemical manufacturing).

In the future the mNNPLS model should be compared with mechanistic models such as ASM1 and the possibility of integrating the model into the effluent system model described in chapter 2 of this thesis should be investigated as this would introduce the ability to test the effects of treating wastewater under different plant operating conditions to give more accuracy in the prediction of reduction in chemical oxygen demand of the treated wastewater leaving the site.

Chapter 5. Consequence Modelling

5. Introduction

The Shasun site in Dudley is a top tier COMAH facility due to its high inventory of dangerous and toxic substances such as hexane or bromine, and for this reason risk assessments need to be carried out to satisfy COMAH and PPC regulations to protect and reduce the risk to the environment and to people. It is important to take a pro-active approach as there is a growing trend for requirement of environmental consequence and risk assessment. The overall aim of this thesis has been to improve the predictions of emissions generated by a fine chemical manufacturing site to enable greater control of those emissions and planning of the processes that generate them to ensure environmental consent limits are not breached. Chapters 2-4 have created both physical and mathematical models to improve these predictions of emissions via the effluent system and wastewater treatment plant at Shasun. The volume and concentration of effluent generated on a day to day basis via regular batch processes can easily estimated by mass balances, difficulty arises however when estimating emissions due to unexpected releases such as catastrophic failures of equipment. The effluent system as Shasun is complex, with multiple areas such as tank bunds, drains and drum storage areas which drain to the main storage pits that supply the effluent system. Consequence and risk modelling can therefore aid in calculation of the likely volumes, concentration and location of accidental releases of substances on-site and provide valuable information as to the worst case scenarios of accidental releases into the effluent system, so that they can be assessed using the models developed in chapters 2, 3 and 4. In addition to predicting the possible releases of substances to the effluent system (e.g. from the extent of liquid pools from equipment failures, or evaporation and rain out of more volatile compounds) consequence and risk modelling has the added benefit of estimating emissions to the atmosphere, contributing to the overall view of the site's environmental footprint.

Given the nature of Shasun's business, a fast and robust method of consequence and risk assessment (historically these are known to be very large are time consuming pieces of work) for contract manufacturing is required as well as the efficient dissemination of the results of such assessments. Within contact manufacturing, the speed of manufacture can be a key aspect to customer requirements as well as company

reputation and so methods to reduce the time it takes to introduce a new product are important to the business from a commercial sense. Consequence and risk modelling requires lots of data gathering from different sources and knowledge of how to apply this data in the models (provided by Software packages such as DNV's PHAST) as well as identification of scenarios and how to report the results of the study and feedback to all required customers effectively can be a challenge. To begin this chapter, a review of the current literature and regulations around the requirements for risk assessments in regards to safety and the environment shall be conducted.

5.1.Requirements for Risk Assessments

There is an ever-growing requirement to construct formal methods for the identification of hazards towards the environment and assessment of the associated risks. This is particularly relevant to the Control of Major Accidents and Hazards (COMAH) safety report and Pollution Prevention and Control (PPC) application (Calder, 2004). Many companies have developed environmental risk methods that are based on simple risk matrices, but to increase accuracy and understanding of risks to people and the environment, a more detailed and quantitative risk assessment is required. Until recently, the requirement for undertaking a formal risk assessment for the environment has not been formally written in the regulations until recently. In particular the COMAH and PPC regulations and the Environment Agency has produced guidance on how to undertake the required assessments. However, even with this guidance, the environmental risk work undertaken in support of COMAH safety reports often does not meet the requirements (Calder, 2004). The general approach recommended for such risk assessments are as follows;

1. What can go wrong
2. How often
3. What gets out and how much
4. Where does it go
5. What are the consequences
6. What are the risks
7. What risk management is required on the basis of ALARP (As Low As Reasonably Practicable)

Under the Pollution Prevention and Control (PPC) regulations, there is currently a requirement to produce an Accident Management Plan, an example structure of this plan is as follows;

No.	Release Event	Cause	Initial Consequence Loss and Pathway Affected	Eventual Consequence	Freq.	Controls to Prevent /reduce Event Freq.	Actions Planned to Mitigate Effect of Event
1					Yr^{-1}		

The goal of a COMAH environmental risk assessment is to identify any environmental hazards created by an operation and then provide an assessment to find out whether or not these hazards can produce a major accident to the environment (MATTE), the guidance states that these MATTEs must be identified, irrespective of what controls are in place to mitigate the risk. Where a MATTE is identified, the risks can require further assessment to work out whether or not the frequency or consequence can be reduced so that the residual risks are considered as low as reasonably practicable (ALARP). According to COMAH guidelines, the approach taken for the risk assessment must include the following points;

1. The MATTE must involve a dangerous substance (as defined by COMAH regulations), this may not necessarily be a direct route. For example, one particular dangerous substance can result in a fire that causes another substance not defined as "dangerous" to be released into the environment. It is therefore important to correctly identify the direct and indirect consequences of releases of all dangerous substances.
2. A qualitative assessment of the risks may be undertaken initially and due to the complexity or scale of a particular risk, an assessment in greater detail may be necessary.
3. MATTEs that have a frequency of less than $1x10^{-6}$ yr^{-1} (this is less than once in a million years) can be discarded and do not require ALARP demonstration so that focus may be on the most significant risks.

There are however a number of issues and problems with environmental risk assessments. Currently COMAH guidelines acknowledges that the amount of accuracy and detail for an environmental risk assessment is not a high as that of a safety risk

assessment, this is due to a lack of data available to find out if a MATTE is actually likely and so sometimes subjective judgement is needed. Examples of issues and problems with the current situation are described below:

1. Details of the most sensitive environmental receptors are unknown.
2. Information of pollutant concentrations likely to cause an adverse effect of the receptors identified – dispersion or other modelling can help identify the concentrations at particular times and distances.
3. Dispersion modelling to establish consequences can be expensive
4. Consequence assessments tend to err on the side of caution which may result in much larger costs involved to mitigate the risk.
5. It's not always clear on the exact approach and where to get information from for consequence and risk modelling (this can include information on population areas, traffic, risk values and acceptance criteria).
6. Companies not always willing to share information to maintain a competitive advantages

There is however a practical approach that can be adopted for use in COMAH risk assessments, this is described as follows;

1. Conduct a hazard identification (HAZID) to provide a list of potential hazards to people and the environment and exclude events with low consequence
2. Select the hazards with the worst case where there may be similar events.
3. Undertake detailed quantitative consequence assessment work and identify whether the event has the potential to cause a MATTE.
4. A list of MATTEs are identified and then assessed to find out whether or not the risk is ALARP.

A HAZID study typically involves meetings between a number of site personnel such as EHS Advisor's, process and process safety engineers, plant managers, maintenance and reliability engineers and operators. During the meeting, a series of predefined guide-words such as "Utility failure", "Storage tank failure" or "Material corrosion" will provoke thought about possible scenarios for releases. A judgement on consequence and frequency is then made and events can be shortlisted for more in depth analysis.

Events resulting in accidental releases will normally require more detailed assessment in the form of dispersion modelling which can be undertaken with software packages such as ADMS or PHAST (COMAH, 1999). It can be more difficult for accidental emissions to effluent and drainage systems and accurately predict the concentration of the dangerous substance as it reaches the environment can be a challenge due to varying infrastructures at different installations, for example, there could be dilution or treatment effects by the on-site wastewater treatment plant. DNV's PHAST software can be used to assess the risk of an event and its consequences, it can also predict rain-out of materials from a release which could end up in the sites effluent system and this can be a starting place for calculating the eventual environmental concentration of the released substance in the environment for software such as WasteModel described in chapter 2.

For Shasun, it is necessary to conduct a risk assessment in the early stages of a project or use as a screening tool when assessing the feasibility of a potential project from both a cost and safety point of view. By undertaking a risk assessment in the early concept stages, one can ensure that the project or process is delivered in full and meets the required safety and environmental regulations and reduces the risk of dangerous exposure of materials to on-site and off-site personnel and the environment. Additional benefits include minimising the risk of damage to equipment and increase the reliability and availability of plant, therefore time spent early on with risk assessments will most likely be greatly beneficial to the company in the long run. By understanding the worst-case consequence of different types of events, the front-end engineering design (FEED) of a potential product can be changed to minimise the risk by designing in control measures. It can also be necessary to find out if a potential project can cause a significant off-site risk, planning guidance for the risk of fatality of-site should be below $1x10^{-6}$ yr^{-1} outside of the site boundary, this can be determined by looking at risk contours, these contours are drawn on a map and do not consider areas for their occupancy of vulnerability but assume that a person is present and at risk (Fearnley, 2011). By undertaking a study such as this it can become clear what the main risks are and where effort should be focused on to reduce the risk. This can give an indication of the total cost and feasibility of a project in its early stages where cost implications are likely less severe.

A report following the structure of the templates shown in HSG65 and HSG190 would have resulted in a very repetitive, lengthy and hard to read report (Ennis, 2003). It would be more useful to generate a more applicable report structure to the business.

For Shasun to maintain their license to operate, they need to continue to comply with COMAH and PPC regulations for protecting people and the environment, the source of site accidents and emissions are not always obvious and can be unexpected / unforeseen.

It is also important to complete safety and risk assessments early in the project proposal process to properly assess the costs and time involved in delivering a new project such as introduction of a new process. Delays and extra costs to a contract pharmaceutical API manufacturer can result in scenarios such as breach of contractual terms with the customer or reduced profit from the business as design changes can prove very costly if implemented a long way down the line in the project delivery stage for example. By enabling the undertaking modelling in an early stage by using a quick and robust method, the costs involved in implementing a new process can be accurately determined giving better insight into the overall cost-benefit analysis (Fearnley, 2011).

The overall issue that Shasun wish to address is how can they implement consequence and risk modelling quickly and disseminate the information so that individuals from a non-technical background can also understand the results. The aim of this project is to create a methodology and structured approach to applying consequence and risk modelling in a timely fashion to help satisfy COMAH and PPC regulations when introducing new manufacturing processes to Shasun's site in Dudley.

By forming a structured approach to consequence and risk modelling it is hypothesized that the time taken to complete a consequence and risk study on new and existing processes on the site will be reduced. The structured approach will also help users in other sites and industries with a resource for locating the required information to set up a model in PHAST, select the appropriate scenarios and draw conclusion from the results in a timely manner.

This chapter will begin with a review of the current situation at Shasun, the consequence and modelling software they use, a method of collecting all of the information required to set-up the model followed by some case-studies and how best to carry out the studies and report the results.

The methodology used involves collecting the requirements of the customers for these consequence and risk reports, which involved asking a series of questions to those who need to read the report and determining the best way to present the results in an easy to understand way. Methods for gathering information for the modelling software itself are explored, as well as for identifying scenarios, setting risk criteria and structuring of the report. There are two different types of reports for modelling of different substances, those with a fire risk and those with a toxic risk, although a single report can consist of the fire and toxic risks represented by the same chemical such as Methanol.

5.2. Summary of Chapter Layout

This chapter focuses on the effects of potential unintentional releases of chemicals at Shasun's site in Dudley. Use of a hazard analysis software tool (DNV's Phast) allows for the likelihood and consequence of an unintentional chemical release ranging from leaks in flanges to catastrophic ruptures of large storage vessels to be calculated. This information can be used in conjunction with the previously created waste model from chapter 2 to give an overall picture should a release make its way into the wastewater system.

Shasun requires a methodology that can be followed to quickly gauge the effects of a potential release to the atmosphere or effluent system, this methodology will be created in the following sections. The effects on the wider population as well as the environment need to be assessed to ensure regulatory compliance; a reliable and structured method of calculating and presenting these results can be indispensable when making business decisions regarding potential changes to plant equipment, layout, chemical inventory or processes when considering production of new products.

This chapter provides detail on how this methodology was created with the use of DNV's PHAST consequence modelling software including how key information needed for the setup of consequence and risk models were calculated.

5.3. DNV PHAST

PHAST is a hazard analysis software tool created by DNV GL. It is used to analyse situations that present hazards to life, property and the environment, and the ability to quantify their severity (DNV, 2014). The software allows the user to observe the

progress of an incident from the start of the release to far-field dispersion. This includes pool spreading, pool evaporation, flammable and toxic effects. The software uses DNV GL's proprietary Unified Dispersion Model as well as models for radiation effects, jet fires, pool fires and explosions. Explosion models include the Baker Strehlow, TNO Multi-Energy and TNT explosion. Toxic hazards for a release can also be calculated for both indoor and outdoor.

The software can consider releases from leaks, pipe ruptures, relief devices, vessel ruptures and venting. The results from the analysis are presented in tabular and graphical format.

Phast has also been designed to meet the requirements of the UK HSE regulations.

5.4. Data Gathering

Phast requires input data describing the local area for which the releases are modelled in. This includes the frequency of failure of process equipment, material characteristics, population data, weather data, transportation data and other ignition source locations. The following section describes the steps that were taken to gather this information and present it in the required format.

5.4.1. Failure Frequencies

The failure frequencies are key pieces of information, they allow the user of Phast to calculate the frequency per year of a release to allow for risk calculations to take place, frequencies for different equipment can be hard to find or there may be several different frequencies for the same type of equipment. As the Shasun site is located in Dudley, UK the Health and Safety Executive (HSE – UK) is the governing body for control of major accidents and hazards (COMAH). It is therefore preferable to use failure frequencies provided by the HSE wherever possible in the document titled 'Failure Rate and Event Data for use within Risk Assessments' (HSE, 2012). When this document does not contain the required information two alternative sources have been used; 'Classification of Hazardous Locations' (Cox, 1990) and 'Process Equipment Leak Frequency Data for use in QRA' (DNV, 2013).

5.4.2. Material Characteristics

It is necessary to know what concentration of a particular material the user of the software is looking for, this is so that contours for concentration against distance can be

plotted on a map following simulation of a release. These concentrations are typically at values related to specific occupational exposure limits (OEL's) and the associated adverse health effects. This will provide information for such things as evacuation time and distances. The different concentrations and their description are listed below:

Workplace Exposure Limits (WELs): These are the concentrations of a hazardous substance in the air, averaged over a specific period of time, referred to as a time-weighted average (TWA). Two time periods are used:

- Long Term Exposure Limit (LTEL): 8 hours
- Short Term Exposure Limit (STEL): 15 minutes

Data are taken from published HSE guidance EH40.

Immediately Dangerous to Life and Health (IDLH) published by the National Institute for Occupational Safety and Health (NIOSH). This limit refers to an exposure duration of 30 minutes and are defined as the maximum concentration from which escape is possible without permanent damage.

Emergency Response Planning Guidelines (ERPG) developed by the American Industrial Hygiene Association (AIHA).

- **EPRG 1** – is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or without perceiving a clearly defined objectionable odour.
- **EPRG 2** - is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.
- **EPRG 3** - is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing life threatening health effects.

10 Minute LC50: Concentration at which death will occur in 50% of the population if exposed for 10 minutes.

5.4.3. Population Data

The population of the Shasun site and local community and their location relative to the hazardous material is required by Phast Risk to calculate societal risk values.

The change in population levels at different times of the day and week have also been estimated (see notes below) and are included in the model. This allows the model to estimate Societal Risk more accurately.

The values have been collated from a number of sources and are summarised in Table 20.

Table 20: Population Data

Time	Population Category	Number of People	Proportion indoors/ outdoors	Data Reference
Weekday Day	Dudley Business Centre	250	0.9	Shasun Survey carried out in 2009 and updated in 2011.
	Northumberland Business Park	600	0.9	Shasun Survey carried out in 2009 and updated in 2011.
	Packaging Plant	40	0.9	
	Dudley & Fordley	3300	0.9	UK Population Census (2001) (note 1)
	Cramlington (South)	4500	0.9	UK Population Census (2001) (note 1)
	Shasun Site	190	0.9	Average site role call number.
Weekday Night	Dudley Business Centre	20	0.9	
	Northumberland Business Park	100	0.9	
	Packaging Plant	4	0.9	

Time	Population Category	Number of People	Proportion indoors/ outdoors	Data Reference
	Dudley & Fordley	5800	0.9	UK Population Census (2001) (note 1)
	Cramlington (South)	6500	0.9	UK Population Census (2001) (note 1)
	Shasun Site	40	0.9	Average site role call number.
Weekend Day	Dudley Business Centre	50	0.9	
	Northumberland Business Park	100	0.9	
	Packaging Plant	40	0.9	
	Dudley & Fordley	3400	0.9	UK Population Census (2001) (note 1)
	Cramlington (South)	4900	0.9	UK Population Census (2001) (note 1)
	Shasun Site	40	0.9	Average site role call number.
Weekend Night	Dudley Business Centre	20	0.9	
	Northumberland Business Park	100	0.9	
	Packaging Plant	4	0.9	
	Dudley & Fordley	5800	0.9	UK Population Census (2001) (note 1)
	Cramlington (South)	6500	0.9	UK Population Census (2001) (note 1)
	Shasun Site	40	0.9	Average site role call number.

Note 1 – Base population values have been taken from the UK Population Census (2001) for Dudley, Fordley and Cramlington (South). These values have been amended in an attempt to take into account the movement of the population in and out of the area e.g. the proportion of the Cramlington (South) population who have a job are all assumed to leave the area during weekdays as this part of Cramlington is almost exclusively residential.

5.4.4. Weather Data

Weather data is required by Phast to calculate the amount of dispersion and the direction. This determines both the concentration of a substance released at a certain distance downwind and where the release is likely to end up.

Shasun have a weather station on site that measures and records the wind direction and the speed. The data is recorded every second and stored electronically, this was analysed and converted into average wind direction and velocity every hour, enabling the associated probabilities to be calculated.

5.4.5. Weather Class Selection

The scenarios that will be identified will be modelled by Phast Risk using the weather conditions for both day time and night time. These are defined according to their Pasquill stability class (Table 21) and wind speed and are summarised in Table 22 below:

Table 21: Pasquill Stability Classes

Pasquill Stability Classes	
Stability Class	**Definition**
A	Very unstable
B	Unstable
C	Moderately unstable
D	Neutral
E	Moderately stable
F	Stable

Table 22: Weather Class Selection

Day Weather		
Speed (m/s)	Pasquill Stability	Description
2	D	Neutral – little sun and high wind or overcast/windy night
5		
Night Weather		
Speed	Pasquill Stability	Description
2	E	Moderately stable - less overcast and less windy than D
5		

Of the weather conditions summarised above, 2/E is considered the worst case for dispersion. This is because a relatively low velocity of 2 ms^{-1} and higher level of atmospheric stability reduces turbulence and mixing, resulting in a chemical release maintaining a higher concentration over further distances downwind where there may be potential for greater numbers of people to be residing.

5.4.5.1. Weather Direction and Probabilities

The hourly weather data recorded onsite over the last 7 years used by the Phast Risk model is summarised in Table 23 and Table 24 below. These tables show the wind direction split into 8 segments between 0 degrees and 360 degrees and the percentage of time that the wind is blowing in these directions at a specific range of wind speed as shown in the left hand column (e.g. 0.5 to 1 m/s). These tables summarise the probable wind speed and directions for 99.7% of the entire time in a year.

Table 23: Day Weather Data for Shasun, Dudley

Wind Speed (m/s)	Night time Wind Direction (degrees) and Probability (%)								Weather Total
	337.5°-22.5°	22.5°-67.5°	67.5°-112.5°	112.5°-157.5°	157.5°-202.5°	202.5°-247.5°	247.5°-292.5°	292.5°-337.5°	
0 to 0.5	1.61%	6.70%	5.30%	14.97%	16.14%	38.57%	16.03%	0.69%	49.17%
0.5 to 1	4.47%	9.68%	5.08%	19.36%	8.53%	37.03%	14.96%	0.88%	5.62%
1 to 2	5.09%	9.75%	4.48%	17.00%	7.36%	37.18%	17.36%	1.77%	10.53%
2 to 3	5.46%	8.94%	4.49%	15.76%	6.50%	41.25%	16.03%	1.57%	10.93%
3 to 4	5.39%	8.06%	3.56%	14.94%	5.79%	45.85%	15.08%	1.34%	7.69%
4 to 5	4.49%	5.80%	2.73%	12.91%	7.57%	50.46%	14.62%	1.42%	6.68%
5 to 6	4.30%	3.90%	2.40%	10.39%	6.29%	55.04%	15.58%	2.10%	3.81%
6 to 7	3.61%	2.28%	2.85%	7.98%	5.32%	62.36%	14.07%	1.52%	2.00%
7 to 8	3.15%	3.39%	1.21%	6.30%	4.60%	66.10%	14.53%	0.73%	1.57%
8 to 9	2.27%	0.57%	2.84%	6.25%	3.98%	65.34%	17.05%	1.70%	0.67%
9 to 10+	1.47%	0.74%	0.74%	2.57%	3.68%	75.00%	14.34%	1.47%	1.03%
								Total	99.70%

Table 24: Night Weather Data for Shasun, Dudley

Wind Speed (m/s)	Night Direction (degrees) and Probability (%)								Weather Total
	337.5 - 22.5°	**22.5-67.5°**	**67.5-112.5°**	**112.5-157.5°**	**157.5-202.5°**	**202.5-247.5°**	**247.5-292.5°**	**292.5 - 337.5 °**	
0 to 0.5	1.61 %	6.70 %	5.30%	14.97%	16.14%	38.57%	16.03%	0.69 %	49.17%
0.5 to 1	4.47 %	9.68 %	5.08%	19.36%	8.53%	37.03%	14.96%	0.88 %	5.62%
1 to 2	5.09 %	9.75 %	4.48%	17.00%	7.36%	37.18%	17.36%	1.77 %	10.53%
2 to 3	5.46 %	8.94 %	4.49%	15.76%	6.50%	41.25%	16.03%	1.57 %	10.93%
3 to 4	5.39 %	8.06 %	3.56%	14.94%	5.79%	45.85%	15.08%	1.34 %	7.69%
4 to 5	4.49 %	5.80 %	2.73%	12.91%	7.57%	50.46%	14.62%	1.42 %	6.68%
5 to 6	4.30 %	3.90 %	2.40%	10.39%	6.29%	55.04%	15.58%	2.10 %	3.81%
6 to 7	3.61 %	2.28 %	2.85%	7.98%	5.32%	62.36%	14.07%	1.52 %	2.00%
7 to 8	3.15 %	3.39 %	1.21%	6.30%	4.60%	66.10%	14.53%	0.73 %	1.57%
8 to 9	2.27 %	0.57 %	2.84%	6.25%	3.98%	65.34%	17.05%	1.70 %	0.67%
9 to 10+	1.47 %	0.74 %	0.74%	2.57%	3.68%	75.00%	14.34%	1.47 %	1.03%
								Total	99.70%

According to these tables, the most probable wind speed during the day is 0 to 0.5m/s (this will be the case 49.17 % of the time in any given year) and the most likely wind

direction during these conditions (38.57% of the time when the wind speed is actually 0-0.5 m/s) is from 202.5-247.5 (Approx. Southwest).

5.4.6. Transportation Data

Although some chemicals are not flammable, for model completeness the following ignition source data (Table 25) was used in the program in case the appropriate hazardous materials are introduced into the model.

Included in the model are the major transportation routes surrounding the site for both road and rail. An estimation of the traffic flow at different times of the day have also been included in the model. Transport routes are viewed by the model as potential ignition sources and their location relative to the site together with the flow of traffic using them allows the model to estimate Individual and Societal Risk more accurately.

Table 25: Ignition Data

Road	Traffic Per Day	Density Day (cars per hour)	Density Night (cars per hour)	Speed (m/s)	Count Point ID
A189N	37400	2026	1091	26.82	80780
A189S	15514	840	452	26.82	26760
A19E	22375	1212	653	26.82	36093
A19W	25754	1395	751	26.82	8463
A19 Average	**24065**	**1303**	**702**	**26.82**	
B1319	2000	108	58	13.41	*
B1319 South	2000	108	58	13.41	*
A1171	15638	847	456	17.88	18120
A190	9114	494	266	22.35	8136
A1068	16000	867	467	22.35	7499
A1068 South	2250	122	66	22.35	*
Train Line	192	4	4	22.35	**

*Estimates calculated as 10% of traffic from adjoining A roads.

** The total number of passenger train movements has been estimated from the timetables of the rail companies using the main East Coast Rail Line north of Newcastle. These companies are East Coast, Cross Country and Northern Rail. In addition to these companies there are also a number of freight train movements. The total estimated number of trains per day has been divided by 24 to give an average number of trains per hour. This value is used in the model.

The amount of traffic per day was found from data collected by the Department for Transport at the specified Count Point. 65% of the daily traffic was estimated to occur during the daytime (8am-6pm) and the remaining 35% at night.

5.4.7. Ignition Sources

In addition to the traffic, other sources of ignition that have been included in the model are the high voltage power lines that run along the side of the site, parallel to Sandy's Letch (a small stream to the north side of the site) as well as the high voltage line along the main east coast rail line to the west of the site. The site itself is also included as a general ignition source.

5.4.8. Map of the Area

Google maps was used as a source for an aerial map of the Shasun site as well as the surrounding area. This map is used by Phast to display information on releases such as dispersion characteristics or risk contours.

A map with high resolution is preferable in order to allow the user to identify features such as individual vessels for increased accuracy of results. Google maps provide a high level of zooming over the area required, by overlaying several maps at different levels of zoom a large area can be represented whilst maintaining a high amount of detail in the required areas.

5.4.9. Muster Points Locations (Risk Ranking Points)

Risk ranking points are points on the map that are used for calculation of the risk to an individual at that specific location. The risk ranking points consist of the muster points located on-site (indoor areas where individuals seek refuge during a toxic release – (first

8 locations in Table 26) as well as some off-site areas. The locations of the risk ranking points are shown in the following table:

Table 26: Risk Ranking Point Locations

Risk Ranking Point
Main Office
Restaurant
Dudley 1
Dudley 2
Development Centre
Pilot Plant Control Room
Bioplant Control Room
QC Labs Corridor
Nearest Residential Dwelling
Local Schools

5.4.10. Individual Risk

Individual risk is the annual risk of fatality to which specific individuals are exposed, the HSE risk criteria is shown in Table 27. Individual risk does not, however, completely describe situations where a single accident could kill or injure large numbers of people; this is described by societal risk.

Table 27: UK HSE Individual Risk Criteria (HSE, 2001), Adjusted for individual PHAST Risk studies

	Workers	**Public**	**Notes**
Maximum Risk Tolerable	$1x10^{-4}$ /yr	$1x10^{-4}$ /yr	Unacceptable risk above this level

ALARP Tolerability level	$1x10^{-6}$ /yr	$1x10^{-6}$ /yr	Broadly acceptable risk below this level

Individual risk in this context refers to the risk of fatality. The HSE have suggested that the upper bound for individual risk for an individual at work should be $1x10^{-3}$ per year, so for Major Hazard Events where other potential risks of fatality exist for most employees, the upper bound of $1x10^{-4}$ is suggested. The lower bound of risk which is considered to be broadly acceptable is generally considered to be $1x10^{-6}$ per year, although low cost risk-reduction measures should always be implemented where possible. The intermediate region is known as the ALARP region, 10^{-4} to 10^{-6} per year. In this region further risk reduction measures should be considered to ensure that the residual risk is 'As Low As Reasonably Practicable'. This is shown diagrammatically in Figure 49.

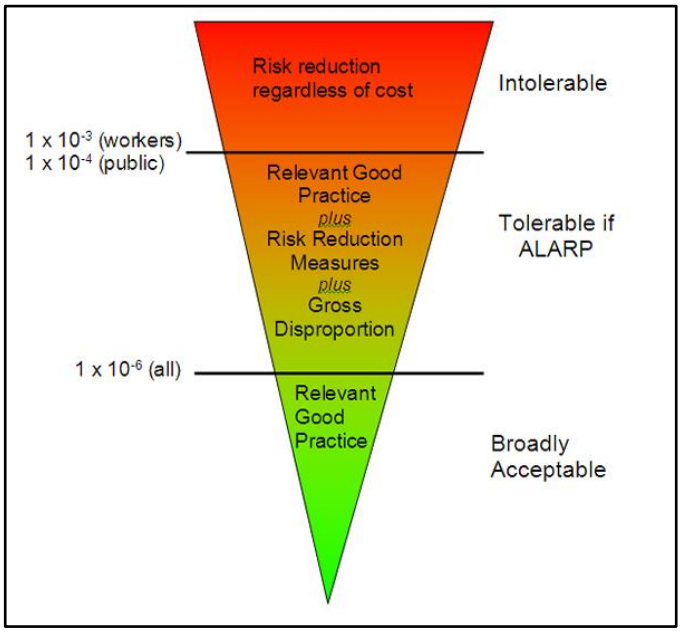

Figure 49: Types of ALARP Demonstration (HSE, 2012)

5.4.10.1. Risk to the public

Individual risk of fatality due to an onsite accident should be maintained in a region less than $1x10^{-6}$ per year. Based on HSE guidance (HSE, 2001), this level of risk is broadly acceptable as it is comparable with the risk the general public experience during their daily lives e.g. car accident.

5.4.11. Societal Risk

Societal risk can be explained as the relationship between the probability of a catastrophic incident, expressed as the average frequency per year with which it can be expected to occur, and its consequences. It is a measure of the possibility of a single outcome simultaneously affecting more than one person and requires an estimate of the location and number of people at risk; this can be represented as a curve on an FN graph.

The societal risk criteria are shown in Table 28 and are based on the HSE COMAH Societal Risk criteria. Since we are only considering risk from one facility/equipment at a time (e.g. Bromine storage tanks) it has been adjusted by a factor of 10 to allow for other major hazards that may occur from the site.

Table 28: UK HSE COMAH Societal Risk Criteria (HSE, 2004), Adjusted for individual PHAST Risk studies

Number of fatalities (N)	1	100	**Notes**
Maximum Risk Tolerable	$1x10^{-4}$ /yr	$1x10^{-7}$ /yr	Unacceptable risk above this level
ALARP Tolerability Level	$1x10^{-6}$ /yr	$1x10^{-9}$ /yr	Broadly acceptable below this level

5.4.12. Assumptions

- PHAST assumes a flat surface when calculating dispersion, i.e. buildings and the landscape are not modelled.

5.5. Identification of Release Scenarios

In order to maintain a consistent result from PHAST modelling it is necessary to follow the same methodology for identification of release scenarios from different sets of equipment.

5.5.1. Methodology

Many of the potential major accidents and hazards are due to the bulk storage of a dangerous substance. A number of different phases can then be identified:

- Transfer of substance into the bulk storage vessel
- Storage of the substance in the vessel
- Transfer of the substance out of the vessel

Each phase can have different conditions and different potential routes for release. In general there can be a catastrophic rupture of a vessel or a leak from the vessel or attached equipment.

5.5.2. Catastrophic Rupture

This can be described as complete and instantaneous loss of containment of a storage vessel. For example if a tank located at a height of 2 meters was subject to catastrophic rupture, Phast would model this release as though the walls of the tank suddenly disappeared and the entire bulk of the liquid stored in the tank spilling in all directions from the specified height.

5.5.3. Leaks

Alternatively and more commonly, leaks occur from pipes, flanges, and storage vessels and are calculated based on characteristics such as materials, hole size, pressures and environmental conditions.

5.6. Report Structure

The report structure was generated and demonstrated by using a case study on a large bromine storage tank at Shasun's site in Dudley, this report can be found in appendix 1 of this thesis. The report structure went through many iterations to achieve one that allowed for easy dissemination of the information to the required people. It begins with a high-level executive summary followed by an introduction to the problem and requirements of the study, description of the equipment, process and associated hazards. A summary of the release scenarios is described followed by a summary of the results and a conclusion. The more detailed calculations and descriptions of the model are found in the report's appendices as these will only need to be viewed for auditing purposes.

5.7. Discussion

A methodology for generating a robust consequence and risk modelling report has been generated, this can help with the early assessment of a potential new process or project and ensures that Major Accidents and Hazards (MAH) are identified. This can also help

with improvement to emergency planning by ensuring the consequences of a MAH are well understood and help ensure better communication with local authorities.

Previously, a significant amount of time was required by a range of individuals with different expertise in preparation of these reports and where a smaller company with limited resources may be involved the quality of such reports may suffer. A large cost may be involved where a lack of resource or expertise may result in using external consultancy businesses, for example the cost of preparing a COMAH report for a top tier COMAH site which includes consequence and risk modelling may be in excess of £200,000 (DETR, 1999) which can make up a large portion of a smaller company's annual profits. For comparison, the time taken to generate the report found in appendix 1, based on the structure and methodology presented in this thesis was 24 man hours which includes input from team members and managers.

5.8. Conclusions

Consequence modelling is an important part of the COMAH compliance process and is valuable in identifying what the biggest hazards on a site or new process may be. It can be very time consuming and expensive to produce these reports and with the methodology produced in this chapter, this time can be reduced whilst also providing a resource for difficult to find data required to set up the complex PHAST models. A cost/benefit analysis towards the savings in time and capital expenditure vs improvements in the reduction in safety and environmental incidents would be difficult to produce and take considerable time to become apparent especially if one considers the acceptance or rejection of a potential project based on the identified risks and consequences given that a risk is subject to probability and as such, the consequence and associated potential damage to life or the environment may never be realised. However, it will be possible to assess the reduction in time required to generate a model and report from scratch and assess the ability of its customers to understand its contents and draw conclusions to assist in business decisions.

Chapter 6. Conclusions and Further Work

This chapter will now present the main conclusions from the studies conducted in this thesis and provide a description of further work that can build upon this research. The conclusions are presented in order from the work in Chapter 2 through to Chapter 5.

6.1. Wastewater System Model and Graphical User Interface

The aim of this research was to create a model that can predict the concentrations of substances in the effluent system at Shasun's chemical manufacturing plant in Dudley to enable greater control and planning of wastewater discharge from the site. Previous work by Knoblock outlined a useful methodology which was adapted for breaking down a complex water system into blocks and component parts for building a mathematical model (Knobloch, 2014). A successful study by Miyawaki used CSTR equations to describe a series of photocatalytic reactors (Miyawaki, 2016). In agreement with the study by Miyawaki, modified CSTR equations were then used to create a model that represented the effluent system at Shasun. The mathematical model was created using MATLAB & Simulink and deployed as a standalone tool with graphical user interface (GUI) to predict the concentration of substances through a complex plant effluent system and activated sludge wastewater treatment plant (WWTP). It takes into account the system characteristics including modes of operation, pump flowrates, control philosophies and bioreactor efficiency. The model was validated using a blue tracer compound and showed an average prediction accuracy to within 9% of the true value on-site. The discrepancy between the predicted and measured values are due to differences in background wastewater flowrate between the model (constant average flow) and real world (dynamic, batch processes) and low mixing in the clarifier.

The model and software set-up have allowed for several additional benefits as described in section 2.10. These include the ability to quickly simulate emergency scenarios to provide decisions on mitigation, for example due to human error on plant resulting in an unexpected release to the effluent system or from failure of equipment. This software allows for the calculation of consequences in an environmental risk assessment which will help in process design to reduce risk, ultimately providing greater protection towards the environment.

Further work could be carried out on validation of the model, with repeat experiments to gain greater confidence of model accuracy. This could include selection of a different dye or molecule that is more easily measured at very low concentrations and that does not degrade in the bioreactor or react with chemicals likely to be found in the effluent system. An investigation into the mixing dynamics of the clarifier and the flow dynamics of the background wastewater into D1 and D2 pits could further increase the accuracy of the model.

Additionally, this work could be built upon to include a mathematical model that describes the function of the bioreactor and the ability of the microorganisms to treat a specific wastewater depending on its characteristics. This would require greater complexity and integration with the plant and process on-line sensors.

6.2. Bioplant Pilot Rig

The aim of this research was to create an accurate scaled down pilot plant model of the large-scale activated sludge wastewater treatment plant at Shasun to enable extended testing of treatment efficiency for potential new wastewater streams and reduce the risk of breaching site effluent consent limits or large-scale microorganism poisoning.

An investigation into previous studies on operation and designs of activated sludge plants in general and pilot-scale models was conducted. It was found that process variables including pH, temperature, Dissolved Oxygen (DO) concentration, Hydraulic Retention Time (HRT), recycle ratio and Solids Retention Time (SRT) have a significant effect on the treatment efficiency of an activated sludge plant. These variables were calculated and maintained in the scaled down model.

A 100-litre pilot plant was designed and built which matched performance of the large-scale plant to within 12.8% of effluent chemical oxygen demand (COD) concentration during experiments. The difference is potentially due to the slight variation in feed wastewater compositions as the pilot-scale plant did not have a direct line to the main feed wastewater pipe and instead was periodically fed in batches. Additionally, manual control of oxygen flow into the pilot-plant bioreactor was used which resulted in greater excess of dissolved oxygen concentration in comparison to the main plant, this could have resulted in a change of treatment efficiency.

Long term treatment efficiency testing of a methylene-blue dye containing wastewater was conducted and shown to be satisfactory at the concentrations tested (48.5%

reduction in blue colour) after a period of microorganism acclimation, where equivalent short-term lab respirometry testing had previously shown no digestion of the blue wastewater.

Additional improvement and testing work could be carried out on the pilot-scale plant by introducing a live wastewater feed and automated dissolved oxygen control. This will enable the conditions in the large-scale plant to be more closely matched, resulting in better comparable treatment efficiencies.

6.3. Bioplant Predictive Modelling

In Chapter 4, mathematical models were researched and developed in MATLAB to study prediction of the effluent chemical oxygen demand concentration of an activated sludge wastewater treatment plant. The aim of this research was to determine an adequate technique for predictive modelling of the on-site wastewater treatment plant at Shasun to enable better wastewater management.

Previous studies on modelling of the activated sludge process were investigated and demonstrated the activity of the microorganisms in an activated sludge wastewater treatment plant is highly non-linear. Existing methods of non-linear modelling using partial least squares (PLS) and artificial neural network (ANN) structures were then investigated and compared against a newly proposed structure that replaces the linear inner regressor of the PLS algorithm with a combination of multiple neural networks (mNNPLS). The mNNPLS model showed an improved correlation coefficient (R^2) of 0.855 between observed variables and predicted effluent chemical oxygen demand.

This can be compared to similar "black box" modelling studies found in literature for prediction of effluent chemical oxygen demand concentration of activated sludge wastewater treatment plants such as an R^2 of 0.658 (Moral, 2008) which was achieved using artificial neural networks only.

In future work, the mNNPLS model should be compared with mechanistic models such as ASM1. Testing in a hybrid-residual structure with ASM1 (mNNPLS would predict the errors of ASM1) should also be conducted as there is potential for improved predictions over the 0.855 R^2 discussed earlier. The possibility of integrating the model into the effluent system model described in Chapter 2 should be investigated as this would introduce the ability to test the effects of treating wastewater under different

plant operating conditions to give more accuracy in the prediction of effluent chemical oxygen demand.

6.4. Consequence Modelling

In Chapter 5, a methodology was created for conducting rapid and robust consequence and risk modelling using DNV's PHAST software. The purpose of this work is to compliment the studies in Chapters 2 and 3 by estimating substance input concentrations to the effluent system from potential major accidents to aid emergency response planning. Sources for input data including individual and societal risk criteria are researched and presented along with techniques of scenario identification, results presentation and overall report format. A consistent and robust methodology was created through voice of the customer and stakeholder meetings, allowing for faster studies to take place which a key requirement for Shasun where speed of manufacture of new processes.

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APPENDIX 1 - Consequence and risk modelling report structure. Case study on a bromine storage vessel located at Shasun's site in Dudley, UK

PHAST Risk Consequence Modelling

Bulk Bromine Storage Tank B2-D5 (R3316)

REFERENCE NO:	PH001 Rev 0
REVISED:	April 2015
REVIEW PERIOD:	5 years (unless superseded)

Prepared by:	Date
Reviewed by:	Date
Reviewed by:	Date
Approved by:	Date

EXECUTIVE SUMMARY

This report provides information on the consequences/extent of release scenarios identified during the hazard study on the bulk bromine storage facility. Computer modelling with PHAST Risk software is used to quantify the consequences for foreseeable release scenarios from the entire bromine installation. The PHAST Risk computer model calculates the associated individual risk of fatality for both workers on site and the public. It also assesses the societal risk where there may be a number of fatalities.

The individual risk of fatality is graphically represented on a contour map (section 6.1). Societal risk is graphically represented on an FN curve (section 6.5) with relation to intolerable and broadly acceptable risk criteria. This is followed by a conclusion, detailed descriptions of each scenario and diagrams that show the dynamic development of the release and dispersion contours across the site and surrounding area.

It must be noted that this analysis does not take into account safety measures such as the water deluge system, or the water layer in the bund around tank B2-D5 (R3316), this is due to the inability of PHAST Risk to model such safety features.

The results obtained from this analysis can be summarised as follows:

- The **individual risk** of fatality to off-site residential populations within the vicinity of the site is less than $1x10^{-8}$ per year. This represents an extremely low level of risk that is well below the broadly acceptable level of $1x10^{-6}$ per year. See the contour map in section 6 for more information.

- The maximum **individual risk** of fatality to on-site population is of the order 10^{-5} per year. This level of risk is confined to a small area of a 10m radius in the middle of non-flammable drum park no. 5. The area that carries a risk of $1x10^{-6}$ /yr or greater covers approximately one third of the site. This includes the whole of non-flammable drum park no. 5, Dudley 1.5 and Dudley 2 manufacturing buildings and the west side of warehouse no. 2. The risk of fatality in these areas lies in the bottom region of the ALARP triangle between 1×10^{-5} per year and 1×10^{-6} per year. The risk level beyond these areas is considered to be broadly acceptable (i.e. less than $1x10^{-6}$ per year).

- The individual risk of fatality at the muster points where an individual would seek refuge during a release has been assessed. The workers at the muster point in Dudley 2 are most at risk from the bulk bromine storage facility. This muster point has an overall risk of fatality of 2.19×10^{-6}/yr, most of this risk is due to scenarios 2 and 3 (small/large hole in base of bulk bromine tank) and scenario 17 (hole in flange in line between bulk storage tank and header during transfer). For more details see table 6 (section 6).

- The **societal risk** due to the bulk bromine storage facility lies in the tolerable region on the FN curves between the bounds of the broadly acceptable and intolerable. Many of the scenarios listed in table 5 have the potential to cause fatalities to off-site populations; dispersion diagrams for each scenario are available in appendix 3.

  The scenario with the highest risk frequency of causing a fatality (making up 21% of the total risk from all scenarios) is scenario 2 – Small hole (13mm) in the base of the bromine tank and the corresponding rate of fatality from this scenario is 9.25×10^{-6} per year.

  The scenario that can cause the greatest number of fatalities is number 5 – Over-pressurisation of the bulk tank (no lagging) due to road tanker fire. The maximum possible number of fatalities from this scenario is 18 and the average number is 1.64, this scenario has a very low frequency of 1×10^{-9} per year. This can be compared to scenario 6 where the tank is lagged, this reduces the maximum possible number of fatalities to 9 and the average is also reduced to 0.89. The societal risks for the remaining scenarios are detailed in section 6.

Table of Contents

Figures/Tables

1.0 INTRODUCTION

This document contains information about the hazards and risks associated with the bromine storage facility B2-D5 (R3316). The key hazard with bromine is toxicity and the assessment only considered the toxic effects of bromine on people on and off site. The main body of the report consists of a description of the bulk bromine storage facility, a summary of the identified scenarios, followed by the results of the PHAST Risk model and conclusions.

A more detailed description of the scenarios considered by this study as well as details about the overall PHAST Risk 6.7 model setup such as population and weather data can be found in appendices 2 and 3 respectively. Appendix 3 contains diagrams and dynamic descriptions of each scenario during a release.

It must be noted that the results and conclusions from this report are only valid for the exact conditions specified and any change in these conditions may require new results to be obtained.

1.1 INDIVIDUAL AND SOCIETAL RISK CRITERIA

Individual and societal risks of fatality are the key measures of risk acceptability for this study. This includes the individual risk of fatality for both workers on site and the public in nearby towns.

Individual risk is the annual risk of fatality to which specific individuals are exposed. Individual risk does not, however, completely describe situations where a single accident could kill or injure large numbers of people; this is described by societal risk.

Societal risk is expressed as the relationship between the probability of a catastrophic incident, expressed as the average frequency per year with which it can be expected to occur, and its consequences. It is a measure of the possibility of a single outcome simultaneously affecting more than one person and requires an estimate of the location and number of people at risk; this can be represented as a curve on an FN graph. Use of a FN curve is standard methodology of the HSE for analysis of societal risks [5].

This study uses the sites individual risk criteria which can be found in procedure GMP020C.

The societal risk criteria are shown in table 1 and are based on the HSE COMAH Societal Risk criteria [6]. This study only calculates the risks from the bromine facility; therefore it is prudent to adjust the societal risk criteria by a factor of 10 to allow for other major hazards that may occur on site (see R2P2 - Tolerability limits [6]).

Number of fatalities (N)	1	100	**Notes**
Maximum Risk Tolerable	$1x10^{-4}$ /yr	$1x10^{-7}$ /yr	Unacceptable risk above this level
ALARP Tolerability Level	$1x10^{-6}$ /yr	$1x10^{-9}$ /yr	Broadly acceptable below this level

Table 1: UK HSE COMAH Societal Risk Criteria [6], Adjusted by a factor of 10 for individual PHAST Risk studies (see above)

2.0 SUPPORTING DOCUMENTS

Data and assumptions were taken from the following procedures:

- SOP011A/151 - Rev 6, *Transfer of Bromine from B2D5 to A1551, including blow back procedure,* 24 October 2012.
- SOP11A/647 – Rev 2, *Bromine Goslar Discharge Procedure*, 04 April 2014.
- SOP011A/227 Rev 4, *Bromine Protocol*, 24 October 2012.

3.0 DESCRIPTION OF EQUIPMENT

Bromine is stored in tank B2-D5 (R3316) as a liquid at ambient temperature under a nitrogen pressure of 2-5 psig. Tank, B2-D5, is a horizontal and glass-lined vessel with a typical inventory of 7mT. Tank, B2-D5 (R3316), and ancillary equipment (catchpot, pump and scrubber system) are located within a concrete bund, which is large enough to contain the entire contents of the tank. The bund also contains 6” of water to reduce the evaporation of bromine in case of a leak and the vessels are surrounded by a water deluge system. However PHAST Risk is not capable of modelling these safety features; therefore these safety measures will be ignored for the purpose of this study.

The bulk bromine storage tank is located at the west side of the non-flammable drum park no. 5 and is connected by a long transfer line to the header, A1551, in Dudley 1.5.

Bromine is transferred from the bulk tank to the header, A1551, 6 times over a 1 month period every year for use in Doxazocin stage 1 process. The site takes delivery of bromine once per year, which consists of two goslars with each one containing 3500kg of bromine. Details of the bromine bulk installation can be seen below in figure 1:

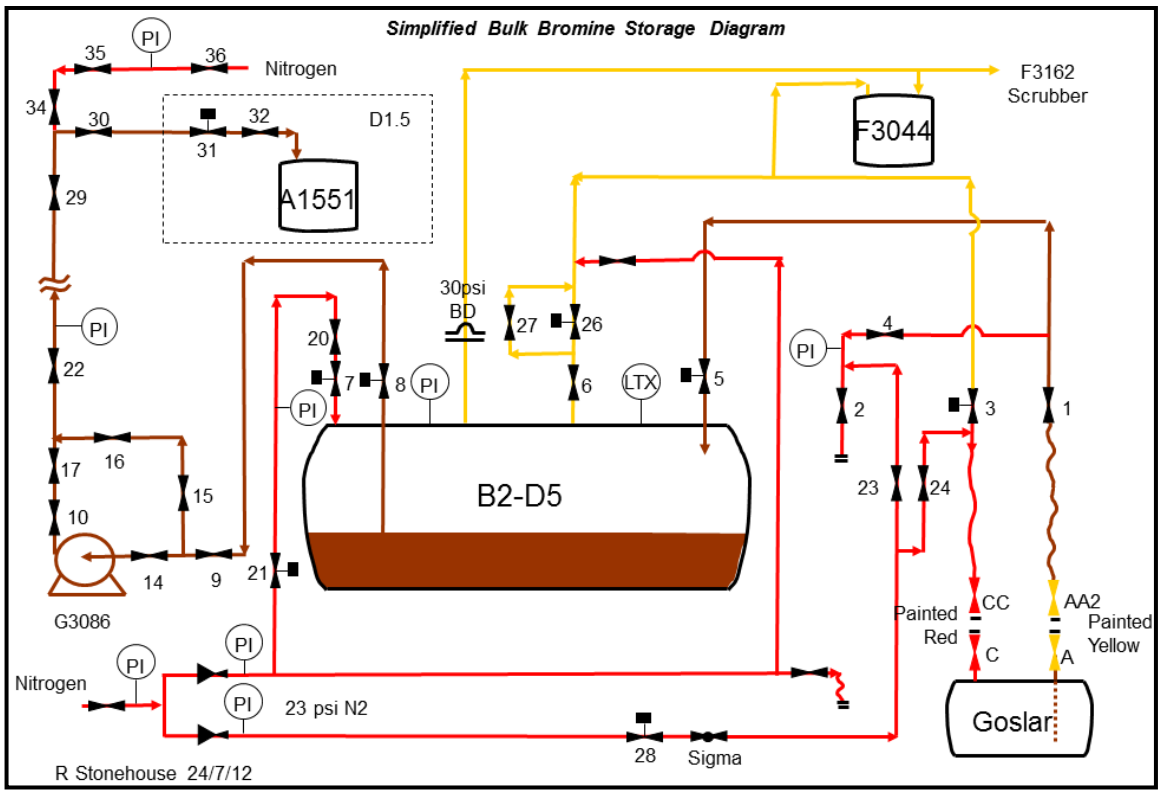


Figure 1: Bulk Bromine Storage Diagram

4.0 BROMINE TOXICITY

The following sections consist of an assessment of the Dangerous Toxic Load (DTL) for the Specified Level of Toxicity (SLOT) and Significant Likelihood of Death (SLOD) from a potential release of bromine. The next two tables summarise the toxicity data used by the PHAST Risk model, a description of each term can be found in appendix 1.

Material	CAS No	n	SLOT $ppm^n.min$	SLOD $ppm^n.min$
Bromine	7726-95-6	2	2.5E05	8.67E05

Table 2: Dose levels for Bromine

	ppm
Odour Threshold	0.05-3.5
Short term exposure limits (STEL)	0.2
Long term exposure limits (LTEL)	0.1
IDLH	3
EPRG 1	0.1
EPRG 2	0.5
EPRG 3	5
10 minute LC50 [4]	208

Table 3: Bromine Toxic Limits (see appendix 1 for definitions)

5.0 RELEASE SCENARIOS

Credible release scenarios that were derived from hazard and operability studies are listed in table 4. A detailed description of each release scenario can also be found in appendix 2.

No.	Scenario	Consequence	Frequency
1	Catastrophic rupture of bromine bulk storage tank (B2-D5).	Immediate release of entire contents of tank (7000kg) into bund.	4.0×10^{-6}/yr
2	Small hole (13mm) in base of bromine bulk storage tank (B2-D5).	Steady continuous release of liquid bromine (7000kg) into bund.	1.0×10^{-5}/yr
3	Large hole (50mm) in base of bromine bulk storage tank (B2-D5).		5.0×10^{-6}/yr

No.	Scenario	Consequence	Frequency
4	Failure of flange (10mm) on top of the bulk storage tank (B2-D5).	Vapour release of 5kg of bromine.	1×10^{-4}/yr
5	Over pressurization of bulk storage tank B2-D5 (no lagging) due to external fire.	Operation of bursting disc followed by flow of bromine vapour (3.82 kg/s) to scrubber.	1.87×10^{-6}/yr
6	Over pressurization of bulk storage tank B2-D5 (lagging present) due to external fire.	Operation of bursting disc followed by flow of bromine vapour (1.37 kg/s) to scrubber.	N/A – used only for comparison with scenario 5
7	Leak from gaskets on Kynar/PFA lined mild steel pipe or flexible during transfer. Transfer from Goslar with 25psig over 60 minutes.	Spill of bromine liquid to unbunded area (during working hours only). Leak size = 10mm. No intervention by the operator.	5.71×10^{-9}/yr
8	Leak from gaskets on Kynar/PFA lined mild steel pipe or flexible during transfer. Transfer from Goslar with 25psig over 60 minutes.	Spill of bromine liquid to unbunded area (during working hours only). Leak size = 10mm. 5 minute release considered.	2.28×10^{-8}/yr
9	Catastrophic rupture of Goslar.	Spill of whole tank inventory (3500kg bromine) to unbunded area.	2.2×10^{-8}/yr
10	Small hole (13mm) in base of the Goslar.	Spill of whole tank inventory (3500kg bromine) to unbunded area.	5.48×10^{-8}/yr

No.	Scenario	Consequence	Frequency
11	Large hole (50mm) in base of the Goslar.	Spill of whole tank inventory (3500kg bromine) to unbunded area.	2.74×10^{-8}/yr
12	Failure of transfer line between bulk storage tank (B2-D5) and header (A1551) on Dudley 1.5 during transfer.	Spill of 800kg to unbunded area.	5.67×10^{-6}/yr
13	Catastrophic rupture of header (A1551) while full of bromine.	Spill of 660Kg Bromine to unbunded area in Dudley 1.5.	3.33×10^{-7}/yr
14	Small hole (13mm) in header (A1551) while full of bromine.	Spill of 660Kg Bromine to unbunded area in Dudley 1.5.	8.33×10^{-7}/yr
15	Large hole (50mm) in header (A1551) while full of bromine.	Spill of 660Kg Bromine to unbunded area in Dudley 1.5.	4.17×10^{-7}/yr
16	Rupture of the pump used to transfer liquid Bromine from the bulk storage tank (B2-D5) to the header (A1551).	Spill of 800kg into the bund around tank (B2-D5). .	3.0×10^{-5}/yr
17	Hole in flanges in line between bromine bulk storage tank (B2-D5) and header (A1551) during transfer.	Steady continuous release of liquid bromine on to the road outside Dudley 1.5.	5.33×10^{-5}/yr
18	Hole in connection on bottom of header (A1551).	Steady continuous release of bromine liquid inside Dudley 1.5.	1.67×10^{-6}/yr
19	Hole in connection on top of header (A1551).	Rapid release of 1kg of bromine vapours inside Dudley 1.5.	2.5×10^{-6}/yr

No.	Scenario	Consequence	Frequency
20	Hole in man-way cover on top of the bromine bulk storage tank (B2-D5).	Rapid release of 5kg of bromine vapours to atmosphere around tank (B2-D5).	5×10^{-6}/yr

Table 4: Credible Release Scenarios – Summary

6.0 RESULTS

Figures and tables are presented in appendix 3 for each set of results; these provide a dynamic description of the change in size, concentration and location of the release. They are presented with the wind blowing in the most likely direction (south westerly) at a speed of 2 m/s, representing the worst case scenario. The following sections provide a summary of the data obtained from the PHAST Risk computer model.

6.1 INDIVIDUAL RISK CONTOURS FROM TOXIC CASES

The individual risk contour plot (figure 2) shows the distribution of risk in the local area due to the release scenarios listed in section 5. This gives the risk of fatality experienced by a person continuously present, **outdoors** and is based on the toxic dose received by the individual from the release.

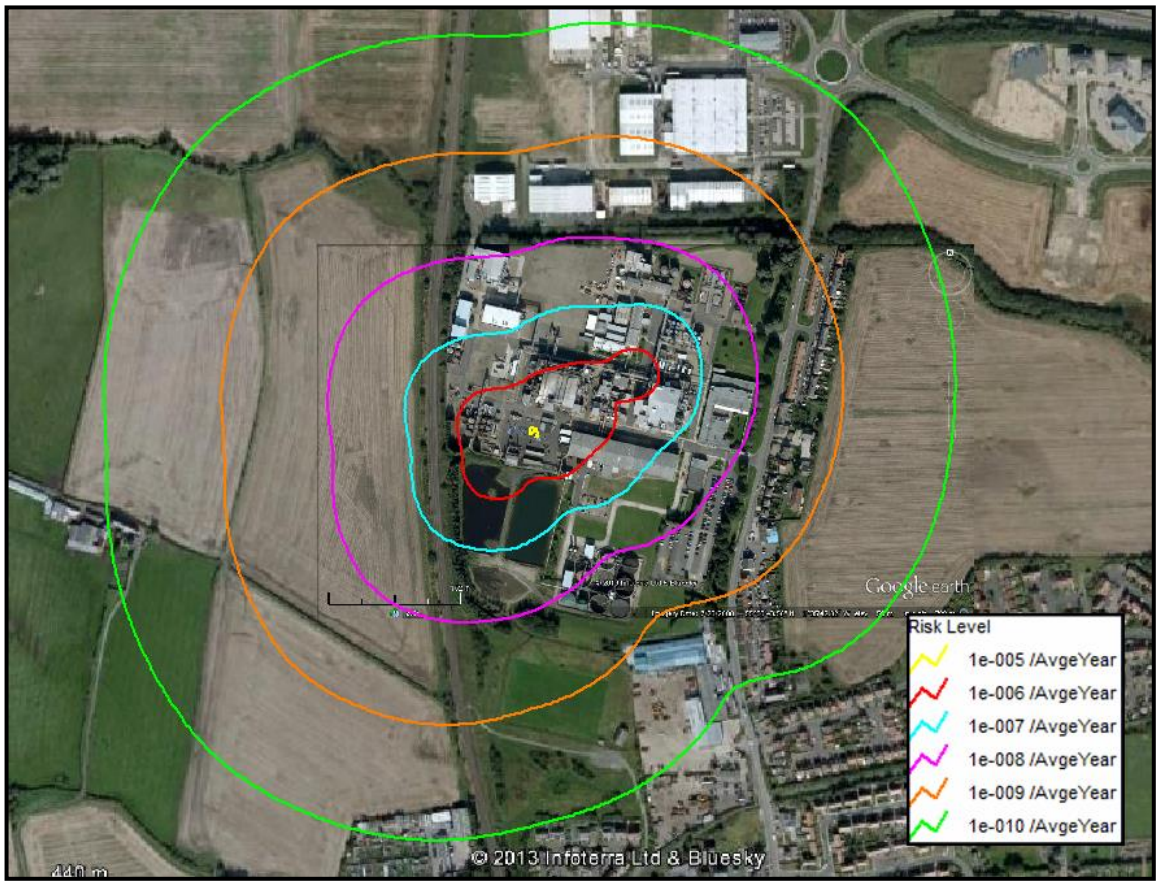


Figure 2: Individual risk contours

6.2 INDIVIDUAL RISK TO THE PUBLIC

By looking at Figure 2, it can be seen that the risk contour of 10^{-6}/yr (in red) does not reach residential populations indicating that the individual risk to the public is broadly acceptable. The 10^{-7}/yr risk contour (blue) below the broadly acceptable risk level includes the East Coast main railway line to the west of the site. The 10^{-9}/yr risk contour (in orange) contour reaches the residential area to the east side of the site, however the risk of fatality is broadly acceptable since it is less than 10^{-6}/yr. It must be noted that the land to the west of the site is considered to be only used for farming and therefore only include transient populations.

6.3 INDIVIDUALRISK TO WORKER

The area that carries a risk of $1x10^{-6}$ per year or greater (in red) covers approximately one third of the site. This includes the whole of the non-flammable drum park no. 5, Dudley 1.5, Dudley 2 buildings and the west side of the warehouse no. 2. The risk of fatality in these areas lies in the bottom region of the ALARP triangle between 1×10^{-5}

per year and 1×10^{-6} per year. The individual risk of fatality on site beyond these areas is considered to be broadly acceptable for a worker (i.e. less than $1x10^{-6}$/yr).

6.4 INDIVIDUAL RISK RANKING REPORT

The following table shows the muster points that are subject to the greatest risk from the bromine storage facility. They are in order of frequency of fatality per year for an individual continuously present **indoors** at that muster point. The cases that contribute to the majority of the overall individual risk for each muster point are listed. Table 5 shows that an individual seeking refuge at Dudley 2 muster point will be subject to the greatest risk of fatality due to the scenarios described in section 5, most notably scenarios 2, 3 and 17, however the risk is still regarded as broadly acceptable.

Muster point	**Relevant Scenario**	**Risk**	**%Total individual risk of fatality for this location**
Dudley 2	2	7.01×10^{-7}/yr	32.06
	3	4.60×10^{-7}/yr	21.02
	17	2.92×10^{-7}/yr	13.34
	Total point risk	**2.19×10^{-6}/yr**	-
QC Labs	18	3.40×10^{-7}/yr	39.90
	14	1.97×10^{-7}/yr	23.10
	15	9.85×10^{-8}/yr	11.60
	Total point risk	**8.53×10^{-7}/yr**	-
Dudley 1	18	1.83×10^{-7}/yr	40.4
	14	1.12×10^{-7}/yr	24.59
	15	5.59×10^{-8}/yr	12.31
	Total point risk	**4.54×10^{-7}/yr**	-

Table 5: Individual Risk - Muster Points

6.5 SOCIETAL FN CURVE

Societal risk is a measure of the possibility of a single outcome simultaneously affecting more than one person and requires an estimate of the location and number of people at risk; this can be represented as a curve on an FN graph.

The following FN graph (figure 3) shows the number of fatalities and its corresponding frequency for all cases described in section 5. The graph plots a set of points representing increasingly serious events relating to the numbers of persons potentially affected (N) to the frequencies (F) of the events. The green and yellow lines represent the UK HSE guidance criteria described in the document GMP020C, whilst the blue line shows the total risk from all release scenarios. The graph shows that the frequency of fatalities is below the maximum risk criteria and lies in the ALARP region. The maximum number of fatalities is 18 with a corresponding frequency of $3x10^{-8}$ per year.

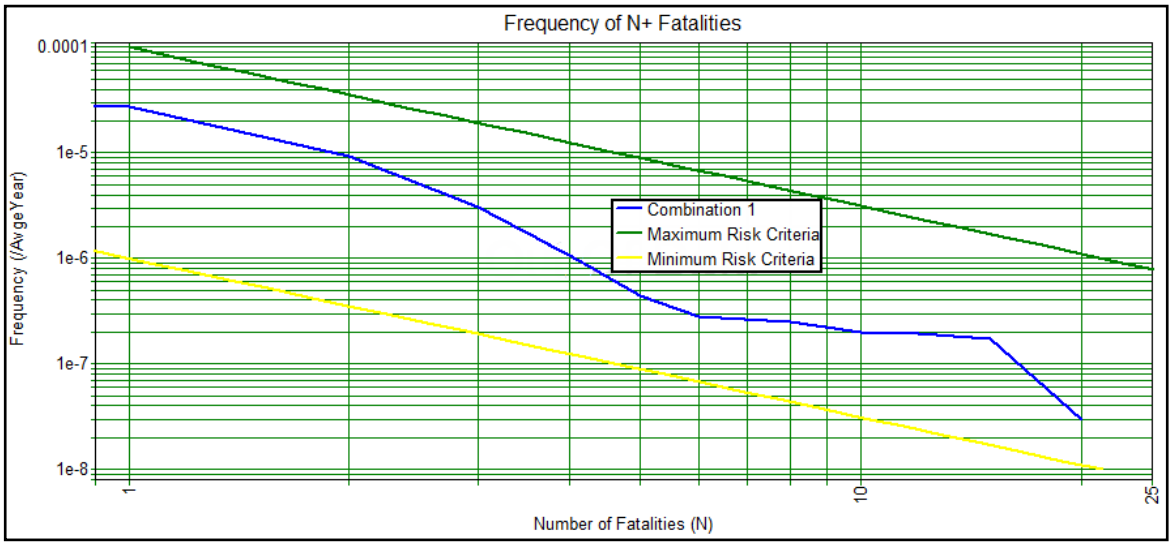


Figure 3: Societal FN Curve

6.6 SOCIETAL RISK RANKING REPORT

The table below lists all the scenarios by their rate of fatality; this is the frequency per year of a fatality due to that scenario. The worst scenario is number 2 - Small hole (13mm) in the base of the bromine bulk storage tank which contributes to 21% of the overall risk from the bromine tank. It can also be seen that the scenario that has the potential to cause the largest number of fatalities is scenario 5 (over pressurisation of bulk tank due to road tanker fire – unlagged), with 18 fatalities and this scenario also has a fairly significant portion of the total risk at 9.1%.

Scenario	Rate of Mortality	%total risk	Average no. Deaths	Maximum Deaths
2	**9.25E-06**	**21**	0.71	2.56
17	8.08E-06	18.3	0.31	1.93
16	7.57E-06	17.2	0.19	1.37
3	5.23E-06	11.9	0.8	3
1	4.12E-06	9.4	0.79	2.72
5	3.99E-06	9.1	**1.64**	**17.47**
18	2.50E-06	5.7	1.15	3.78
14	1.39E-06	3.2	1.28	4.29
15	6.94E-07	1.6	1.29	4.29
13	5.54E-07	1.3	1.28	4.28
12	5.26E-07	1.2	0.22	2.02
10	8.10E-08	0.18	1.24	8.47
11	3.93E-08	0.09	1.1	8.36
9	3.26E-08	0.07	1.14	8.59
7	9.04E-09	0.02	1.22	9.27
8	4.39E-09	0.01	0.15	1.04
6	N/A	0	0.89	8.94

Table 6: Societal Risk - Summary

7.0 CONCLUSION

The FN curve and risk contours show that for all credible release scenarios of bromine, both the societal and individual risks are within the maximum allowed risk criteria defined in section 1.1.

The area on site that carries an individual risk of fatality (located outdoors) that is greater than that considered broadly acceptable (> $1x10^{-6}$ per year) but less than 1×10^{-5}/yr is defined by the red contour in figure 2.

The individual risk of fatality at the muster points where an individual would seek refuge during a bromine release has been assessed. An individual seeking refuge at the muster point in Dudley 2 is most at risk from a bromine release. This muster point has an overall risk of fatality of $2.19x10^{-6}$ per year; this is a low risk, which lies in the bottom region of the ALARP triangle.

The scenarios with a potential for causing a fatality to off-site populations have a very low probability of occurring and the associated risk estimated at less than $1x10^{-6}$ per year, which is small enough to be considered as broadly acceptable.

8.0 APPENDIX 1 - GLOSSARY OF TERMS

Workplace Exposure Limits (WELs): These are the concentrations of a hazardous substance in the air, averaged over a specific period of time, referred to as a time-weighted average (TWA). Two time periods are used:

- Long Term Exposure Limit (LTEL): 8 hours
- Short Term Exposure Limit (STEL): 15 minutes

Data are taken from published HSE guidance EH40.

Immediately Dangerous to Life and Health (IDLH) published by NIOSH. This limit refers to an exposure duration of 30 minutes and are defined as the maximum concentration from which escape is possible without permanent damage.

Emergency Response Planning Guidelines (ERPG) developed by the American Industrial Hygiene Association (AIHA).

- **EPRG 1** – is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects.
- **EPRG 2** - is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.
- **EPRG 3** - is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing life threatening health effects.

10 Minute LC50: Concentration at which death will occur in 50% of the population if exposed for 10 minutes.

9.0 APPENDIX 2 - DETAILED DESCRIPTION OF SCENARIOS

The following section includes a detailed description of each release scenario listed in section 2.

9.1 Scenario 1: Catastrophic rupture of bromine bulk storage tank

The catastrophic rupture of the bromine bulk storage tank resulting in the immediate release of 7000kg bromine into the bund. The bund is large enough to contain the contents of the tank and does not fail or leak. The bund usually contains an amount of water, which would be expected to reduce the rate of bromine evaporation. The Phast Risk model cannot simulate this effect and therefore its presence has been ignored by the model in all of the scenarios. The pool of bromine, confined by the bund, steadily evaporates resulting in a large release of Bromine vapour downwind of the bulk tank. The pressure in the vessel prior to the catastrophic rupture is 5 psig.

The frequency of the catastrophic failure of the bulk tank has been taken as $4x10^{-6}$ per vessel year [1].

9.2 Scenarios 2 and 3: Small/Large hole in base of bromine bulk storage tank

A small hole (d=13mm) or a large hole (d=50mm) in the bromine bulk storage tank develops, resulting in the steady continuous release of liquid bromine to the bund. The bund is large enough to contain the contents of the tank and does not fail or leak. There is assumed to be no intervention to stop the flow of bromine during the model run time. The pool of bromine, confined by the bund, steadily evaporates resulting in a release of bromine vapour downwind of the bulk tank. The pressure in the vessel prior to the leak is 5 psig.

1. Frequency of a small hole = $1x10^{-5}$ /yr [1]
2. Frequency of a large hole = $5x10^{-6}$ /yr [1]

9.3 Scenarios 4: Hole in flange on top of the bromine bulk storage tank

A hole (10mm) in one of the 20 flanges on the top of the bromine bulk storage tank develops, resulting in the fast release of 5kg of bromine vapour to the atmosphere. There is assumed to be no intervention to stop the flow of Bromine vapour during the model run time. The bromine vapour disperses downwind of the bulk tank. The

equivalent hole size is calculated as the area formed by the distance between 2 bolts and the gasket thickness:

1. Frequency of a large hole = ($5x10^{-6}$) x 20 = $1x10^{-4}$ /yr [1]

The pressure in the vessel prior to the leak is 5 psig.

9.4 Scenario 5: Over pressurization of bulk tank (without lagging) due to external fire

The over pressurisation of the bulk tank without lagging occurs due to an external fire (road tanker fire) located on the site roadway adjacent to Dudley 2 building. This results in the operation of the bursting disk followed by a flow of bromine vapour to the scrubber. The maximum number of road tankers on the stretch of road outside Dudley 2 containing flammable liquid is expected to be 170 per year. The stretch of road that passes Dudley 2 and is in-line with the bromine bulk tank is 50m in length.

The release rate for this scenario is calculated as follows:

(50% bulk tank area) x (heat output from tanker fire outside Dudley 2 –calculated by Phast Risk)

11 m^2 x 60W/s = 660 kj/sec

Operation of the bursting disc was then simulated with ChemCad which calculated that the flowrate of bromine out of the tank would be 3.69 kg/sec.

The frequency of this release was calculated as follows:

1. Serious accident rate per km: $2.2x10^{-7}$ [1]
2. Total length travelled = 170 x 50 = 8500 m = 8.5 km/yr
3. Total frequency = $2.2x10^{-7}$ x 8.5 = 1.87 x 10^{-6} /yr

9.5 Scenario 6: Over pressurization of bulk tank (with lagging) due to external fire

The over pressurisation of the bulk tank with lagging occurs due to an external fire (road tanker fire) located on the site roadway adjacent to Dudley 2 building. This results in the operation of the bursting disk followed by a flow of bromine vapour to the scrubber. This scenario was not included in the risk calculations as it is for comparison purposes with scenario 5 to investigate the benefit of lagging on the tank.

The release rate for this scenario is calculated as follows:

(50% Bulk tank area) x (heat output from tanker fire outside Dudley 2 –calculated by Phast Risk)

11 m^2 x 60W/s = 660 kj/sec

Operation of the bursting disc was then simulated with ChemCad which calculated that the flowrate of bromine out of the tank would be 3.69 kg/sec. Applying 0.3 factor due to lagging reduces this flowrate to 1.1 kg/sec.

9.6 Scenario 7: Leak from gaskets on Kynar/PFA lined mild steel pipe or Flexi during transfer.

A leak from the gaskets on the Kynar/PFA lined mild steel pipe or flexible develops during transfer of bromine from the Goslar resulting of the spillage of bromine liquid to the unbunded area. There is expected to be no intervention and the release will continue until the Goslar is empty. The hole size is calculated as the distance between 2 bolts and the gasket thickness which is 10mm for a pipe with a diameter of 100mm. The frequency is calculated as $5x10^{-6}$ [1] per flange, with 25 flanges in total the overall frequency is $(5x10^{-6})x25 = 1.25x10^{-4}$. Since the Goslar takes a maximum of 1 hour to transfer, and there are 2 transfers per year with a pressure test immediately before each transfer, the overall frequency is calculated as $(1.25x10^{-4})$ x (2/8760) = $2.85x10^{-8}$. This frequency is adjusted for the likelihood of no operator intervention occurring as follows:

1. p(no intervention) = 0.2.
2. Total scenario frequency = 0.2 x $2.85x10^{-8}$ = $5.71x10^{-9}$ /yr

9.7 Scenario 8: Leak from gaskets on Kynar/PFA lined mild steel pipe or Flexi during transfer.

A leak from the gaskets on the Kynar/PFA lined mild steel pipe or flexi develops during transfer of Bromine from the Goslar resulting of the spillage of Bromine liquid to the unbunded area next to B2-D5 (R3316). The release is expected to last 5 minutes due to intervention from the operator. The hole size is calculated as the distance between 2 bolts and the gasket thickness which is 10mm for a pipe with a diameter of 100mm. The frequency is calculated as $5x10^{-6}$ [1] per flange, with 25 flanges in total the overall frequency is $(5x10^{-6})x25 = 1.25x10^{-4}$. Since the Goslar takes a maximum of 1 hour to

transfer, and there are 2 transfers per year with a pressure test immediately before each transfer, the overall frequency is calculated as ($1.25x10^{-4}$) x (2/8760) = $2.85x10^{-8}$. This frequency is adjusted for the likelihood of operator intervention occurring as follows:

1. p(intervention) = 0.8
2. Total scenario frequency = 0.8 x $2.85x10^{-8}$ = $2.28x10^{-8}$ /yr

9.8 Scenario 9: Catastrophic rupture of a Goslar

The catastrophic rupture of a Goslar resulting in the immediate release of the entire inventory (3500kg) of bromine into an unbunded area next to B2-D5 (R3316). A frequency of $4x10^{-6}$ [1] is used which is based on the median value for the catastrophic failure frequency of a general purpose pressure vessel. Since there can be 2 Goslars on site for 1 day during the year the overall frequency is calculated as:

1. 2 x ($4x10^{-6}$) x (1/365) = $2.2x10^{-8}$ /yr

The maximum pressure in the vessel prior to the catastrophic rupture is 20 psig.

9.9 Scenarios 10 and 11: Small/Large hole in the base of a Goslar

A small (13mm) or large (50mm) hole in the base of a Goslar develops, resulting in the steady continuous release of Bromine to an unbunded area next to tank B2-D5 (R3316) up to a maximum of 3500 kg of bromine. There is assumed to be no intervention to stop the flow of bromine during the model run time. The release frequency is calculated as follows:

1. Frequency of a small 13mm hole = $1x10^{-5}$ [1]. Since the Goslar is on site for 1 day during the year, and there can be 2 Goslars in one delivery the overall frequency is ($1x10^{-5}$) x (1/365) x 2 = $5.48x10^{-8}$ /yr.
2. Frequency of a large 50mm hole = $5x10^{-6}$ [1]. Since the Goslar is on site for 1 day during the year, and there can be 2 Goslars in one delivery the overall frequency is ($5x10^{-6}$) x (1/365) x 2 = $2.74x10^{-8}$ /yr

9.10 Scenario 12: Failure of transfer line between bulk tank (B2-D5) and header (A1551) on Dudley 1.5 during transfer

Rupture of the transfer line between the bulk storage tank and the header (A1551) on Dudley 1.5 develops during the transfer of liquid bromine, resulting in the steady

continuous release of liquid bromine on to the road. The pool of bromine on the road steadily evaporates resulting in a release of bromine vapour downwind of the bulk tank. The line is 178m long (110m of which is in constant view of the operator) with an internal diameter of 43mm. A failure rate of $1x10^{-6}$ [2] per meter of pipe per year is used.

The time it takes for bromine to reach the header from the bulk tank at the beginning of a transfer is 3 minutes, if after 3.5 minutes bromine has not reached the header the operators are instructed (SOP011A/151 REV6) to terminate the transfer and walk the line to check for leaks. This means that the maximum length of time for the pipe rupture is 3.5 minutes, additionally if a rupture occurs in the pipework that is in constant view of the operators, the transfer will be stopped immediately, so only the 178-110 = 68m of unseen pipe is considered for this scenario.

The event frequency is calculated as follows:

1. Total frequency of pipe failure = 68m x ($1x10^{-6}$ /m) = $6.8x10^{-5}$
2. Pipe usage factor = Campaign length totalling 1 month per year = 1/12
3. Total frequency = ($6.8x10^{-5}$) x (1/12) = $5.67x10^{-6}$ /yr

9.11 Scenario 13: Catastrophic failure of header (A1551) while full of Bromine

The catastrophic rupture of the header tank (A1551) whilst full of bromine resulting in the immediate release of 660kg of bromine into the unbunded area at Dudley 1.5. A frequency of $4x10^{-6}$ [1] is used which is based on the median value for the catastrophic failure frequency of a general purpose pressure vessel. Bromine is only present in the header tank during a batch of Doxazocin Stage 1. A conservative estimate of the time bromine is present in the header tank (A1551) is 1 month per year (2 batches). The overall frequency is adjusted as follows:

Overall frequency: ($4x10^{-6}$) x (1/12) = $3.33x10^{-7}$ /yr

9.12 Scenarios 14 and 15: Small/Large hole in header (A1551) while full of Bromine

A small (13mm) hole or a large hole (50mm) in the bromine header tank (A1551) on Dudley 1.5 develops, resulting in the steady continuous release of liquid bromine (maximum 660 kg) into Dudley 1.5 plant area. There is assumed to be no intervention to

stop the flow of bromine during the modelling run time. The pool of bromine steadily evaporates resulting in a release of bromine vapour downwind of Dudley 2. Since bromine is only present in the header tank for a maximum of 1 month per year, the release frequency is calculated as follows:

Total frequency of a small hole (13mm): ($1x10^{-5}$ [1]) x (1/12) = $8.33x10^{-7}$ /yr.

Total frequency of a large hole (50mm): ($5x10^{-6}$ [1]) x (1/12) = $4.17x10^{-7}$ /yr.

9.13 Scenario 16: Rupture of the pump used to transfer liquid Bromine from the bulk storage tank to the header (A1551)

Rupture of the pump used to transfer liquid bromine from the bulk storage tank to the header (A1551) on Dudley 1.5. The pump is located in the bund next to the bulk tank and its rupture results in the contents of the transfer line (800kg) draining back into the bund. The bund is large enough to contain the contents of the transfer line and does not fail or leak. The pool of bromine, confined by the bund, steadily evaporates resulting in a large release of bromine vapour downwind of the bulk tank.

Frequency of a pump rupture = $3x10^{-5}$ /yr [1]

9.14 Scenario 17: Hole in unseen flanges in line between bromine bulk storage tank and header during transfer

A hole (d=10mm) in a flange or valve on the transfer line between the bulk storage tank and header (A1551) on Dudley 1.5 develops during transfer of liquid bromine, resulting in the steady continuous release of liquid bromine in the area between the warehouse and Dudley 1.5 (unmonitored area). The pool of bromine generated steadily evaporates resulting in a release of bromine vapour downwind. The maximum length of time for the bromine transfer is 10 minutes and the system pressure is the sum of pressure in the vapour space of the bulk bromine tank as well as the head generated by the pump. The transfer time is based on the time is takes to transfer 660kg of bromine from the bulk tank to the header given a leak being present from the start until the finish of the transfer (as calculated using PHAST Risk).

The frequency of a hole in a flange or valve is taken as $5x10^{-6}$ [1]. There are 128 flanges and valves in the line, 90 of which are in constant view of the operators, and if a leak

occurred in these flanges or valves the transfer would be terminated immediately. The remaining 38 flanges and valves are out of view and it would not be known if these were leaking during the transfer and therefore will be the focus of this scenario.

The frequency of a leak in a flange or valve is calculated as $(5x10^{-6})$ x 38 = $6.4x10^{-4}$. The overall frequency is calculated as follows:

1. Total frequency of a hole in the flanges = $6.4x10^{-4}$
2. Pipe usage factor = 1 month per year= = (1/12)
3. Total frequency = (1/12) x $(6.4x10^{-4})$ = $5.33x10^{-5}$

9.15 Scenarios 18: Hole in connection on bottom of header tank (A1551)

A hole (d=10mm) develops in one of the connections (flange or valve) on the bottom of the header tank resulting in the steady continuous release of the contents of the header tank (maximum 660 kg). There are 3 flanges and 1 valve, giving the frequency of a hole developing as 4 x ($5x10^{-6}$ [1]) = $2x10^{-5}$.

1. Total frequency of a hole in a connection = $2x10^{-5}$
2. Header tank usage factor = 1 month per year = (1/12)
3. Total frequency = (1/12) x $(2x10^{-5})$ = $1.67x10^{-6}$ /yr

9.16 Scenarios 19: Hole in connection on top of header tank (A1551)

A hole (d=10mm) develops in one of the connections on top of the header tank whilst full of bromine, resulting in the rapid release of 1 kg of bromine vapour. There are a total of 6 flanges on the top of the vessel.

1. Total frequency of a hole in a connection = 6 x ($5x10^{-6}$ [1]) = $3x10^{-5}$
2. Header tank usage factor = 1 month per year= = (1/12)
3. Total frequency = (1/12) x $(3x10^{-5})$ = $2.5x10^{-6}$ /yr

9.17 Scenario 20: Hole in man-way cover on top of the bromine bulk storage tank

A hole (25mm) in the man-way cover on the top of the bromine bulk storage tank develops, resulting in the fast release of 5kg of bromine vapour to the atmosphere. There is assumed to be no intervention to stop the flow of bromine vapour during the model run time. The bromine vapours disperse downwind of the bulk tank. The equivalent hole size is calculated as the area formed by the distance between 2 bolts and the gasket thickness:

1. Frequency of a 25mm hole = $5x10^{-6}$ /yr [1]

10.0 APPENDIX 3 - SCENARIO RESULTS

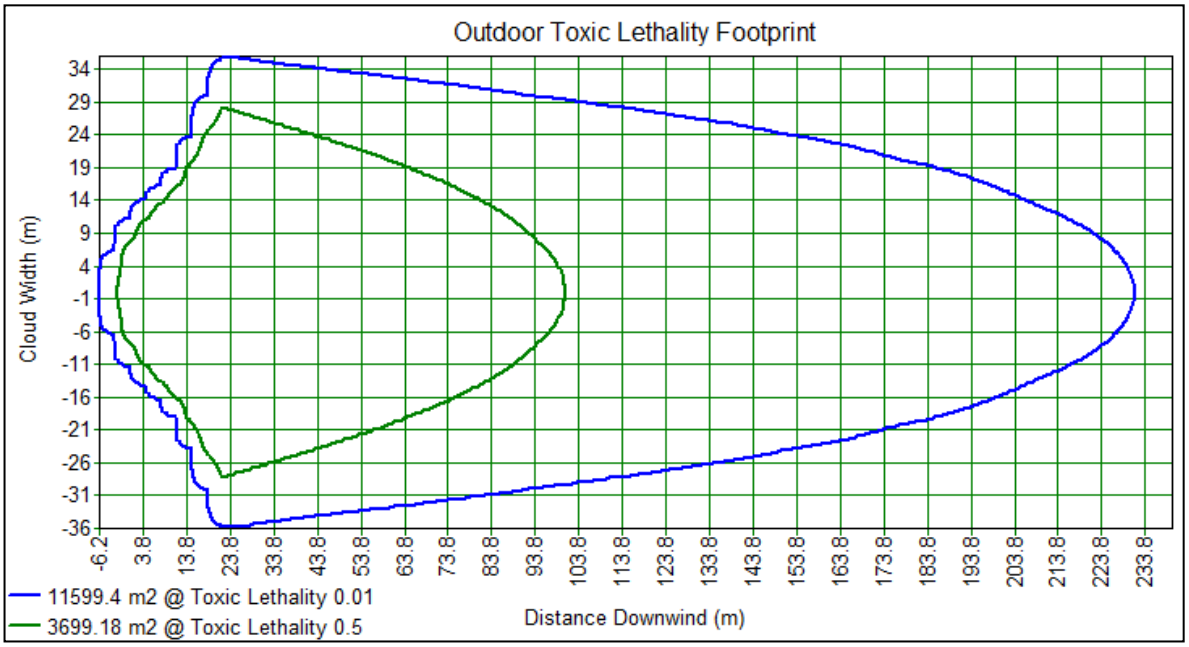
PHAST Risk assumes a flat surface for dispersion with a uniform roughness. It uses risk based criteria for halting the dispersion model. This means that once the probability of death with an exposure duration of one hour is less than the minimum specified, the dispersion will terminate. In the following section, the word 'site' refers to Shasun Pharma Solutions Ltd, Dudley.

The results are presented showing the wind blowing in the most likely direction, which is towards the north east corner of the site. A wind speed of 2 m/s and Pasquill stability class E (Moderately stable) was used to represent the worst case scenario for dispersion, except for cases 7-11, which occur during working hours when the weather is less stable and so have a Pasquill stability class D (Neutral – little sun and high wind or overcast/windy night).

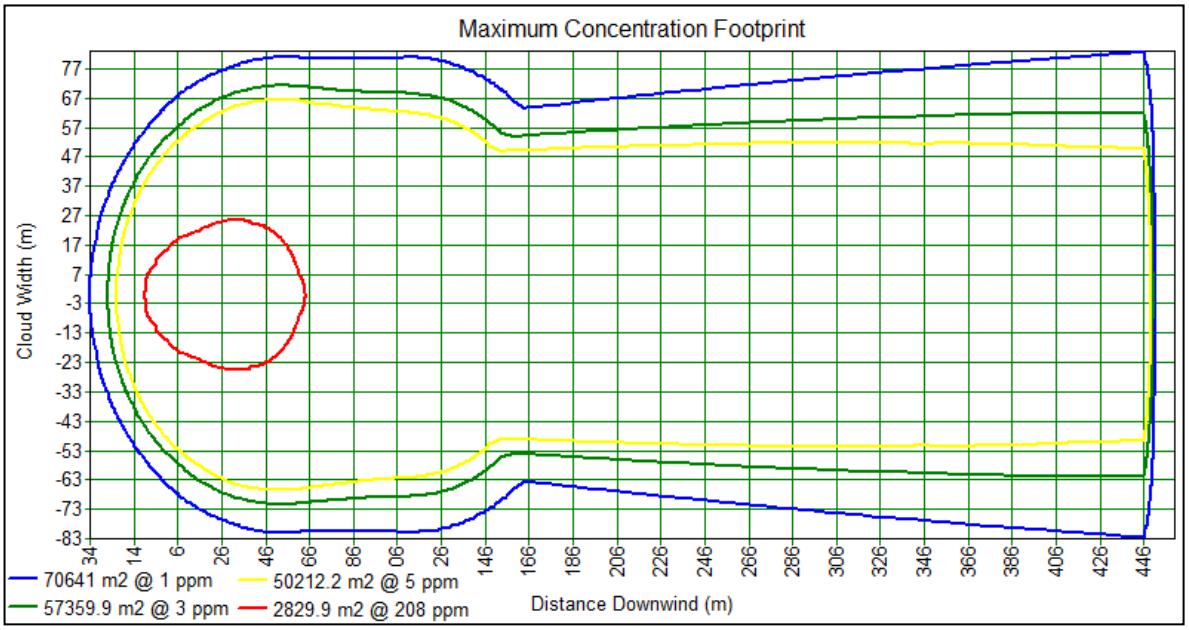
10.1 Scenario 1 Description: Catastrophic rupture of bromine bulk storage tank

Time after Release (mins)	**Consequence**
1	Cloud has expanded to largest diameter, centred on the non-flammable drum park which is encompassed by concentrations in excess of 100ppm
3	Cloud disperses downwind and concentration decreases. It reaches the centre of D1 building at 50ppm and the cloud is wide enough to reach the east side of the warehouse and the QC labs at a concentration of 5ppm
3.5	Cloud front reaches main office at 30 ppm and extends from security to the flammable tank farm at 1ppm
4	Cloud front reach site boundary to the east
4.5	Cloud front reaches housing opposite the site which experience concentrations no greater than 20ppm
5	The cloud front passes the rows of houses and reaches the large fields behind. The cloud is 180 m wide at a concentration of 1ppm

Outdoor lethal toxic 2E Weather; Scenario 1



Maximum concentration footprint 2E Weather; Scenario 1



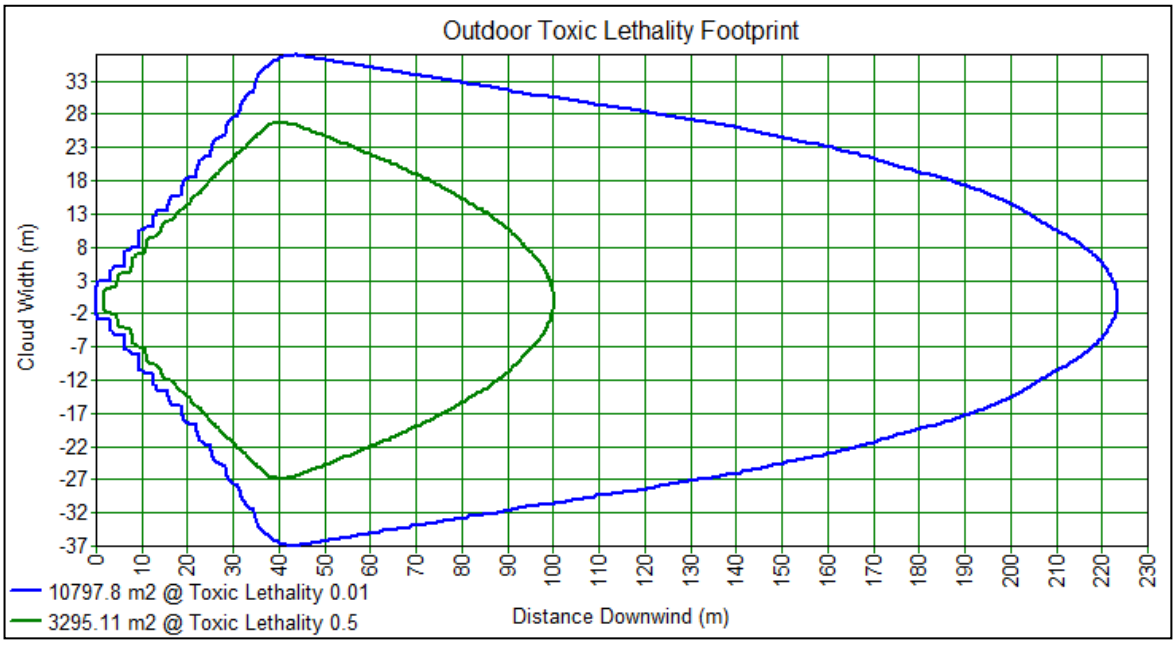
Map view of Scenario 1 (after 5 mins)

10.2 Scenario 2 Description: Small hole in base of bromine bulk storage tank

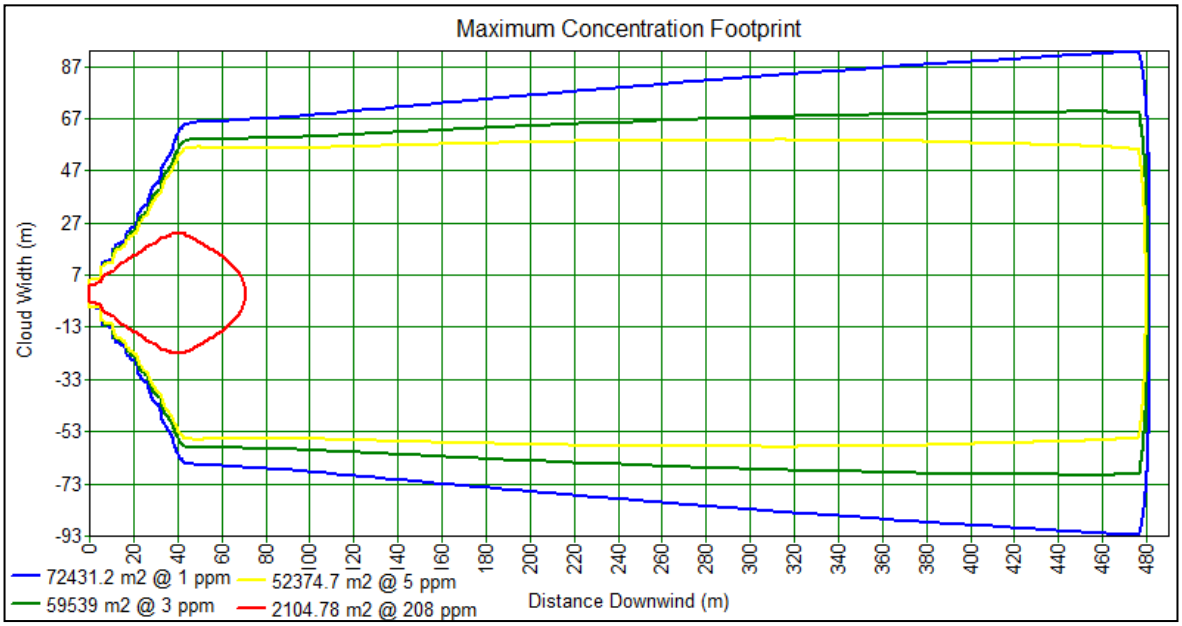
Time after release (mins)	Consequence
1	The release forms a cloud that covers most of the non-flammable drum park at a concentration of 75ppm or greater.
1.5	The cloud increases in size and approaches Dudley 1 at a centreline concentration of 40ppm. The cloud is wide enough at 1ppm to cover half of the warehouse and the north edge of Dudley 1.5.
2.5	The release is centred over D1 at a concentration of 20ppm and slowly increases in width as is moves downwind.
5.5	The cloud continues to increase in width and now covers most of D2 at concentrations ranging from 1-30ppm. The cloud also covers the main office at 20ppm extending to the site's north entrance and main entrance at 1ppm

6	The cloud has left the site boundary and has reached the first housing across the road at a concentration of 15ppm or less.
9	The cloud increases in width and length. It covers all the houses opposite the road that are north of the main entrance to the site at concentrations ranging from 1-20ppm
11	The cloud front extends into the fields behind the housing by approximately 100m

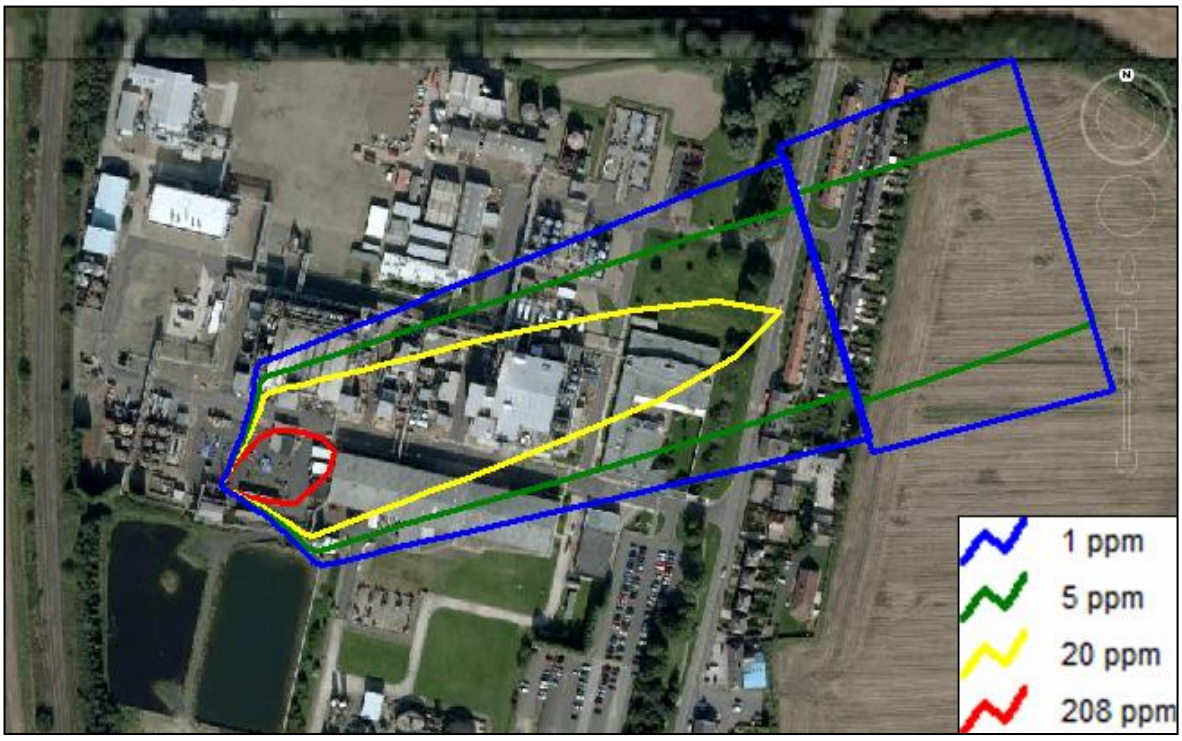
Outdoor lethal toxic 2E Weather; Scenario 2



Maximum concentration footprint 2E Weather; Scenario 2



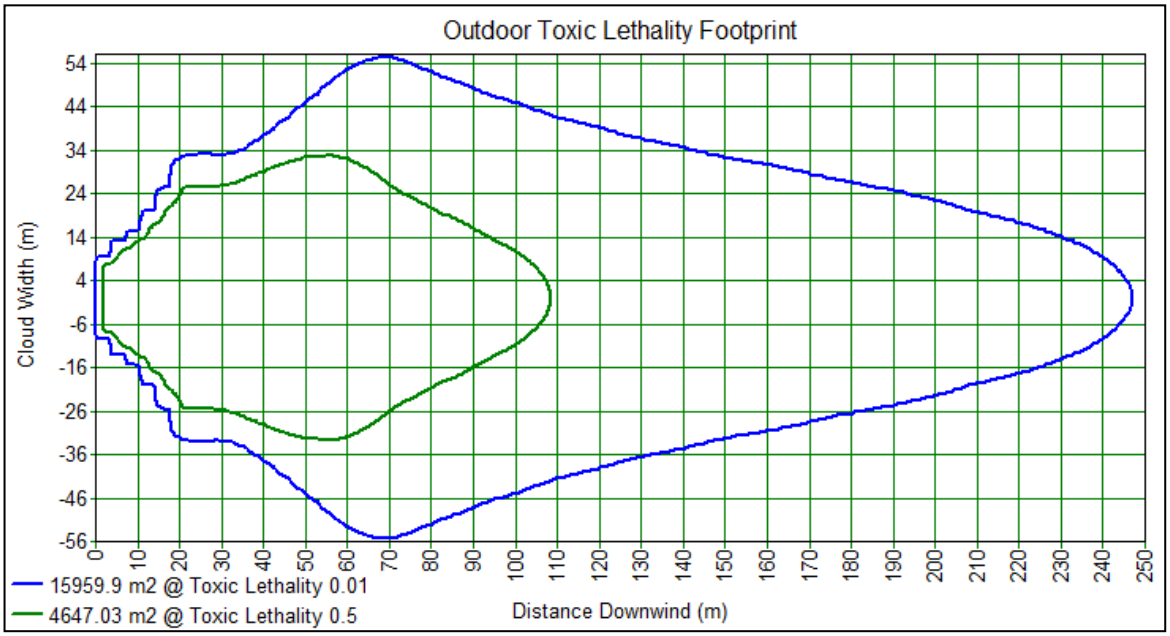
Map view of Scenario 2 (after 11 mins)



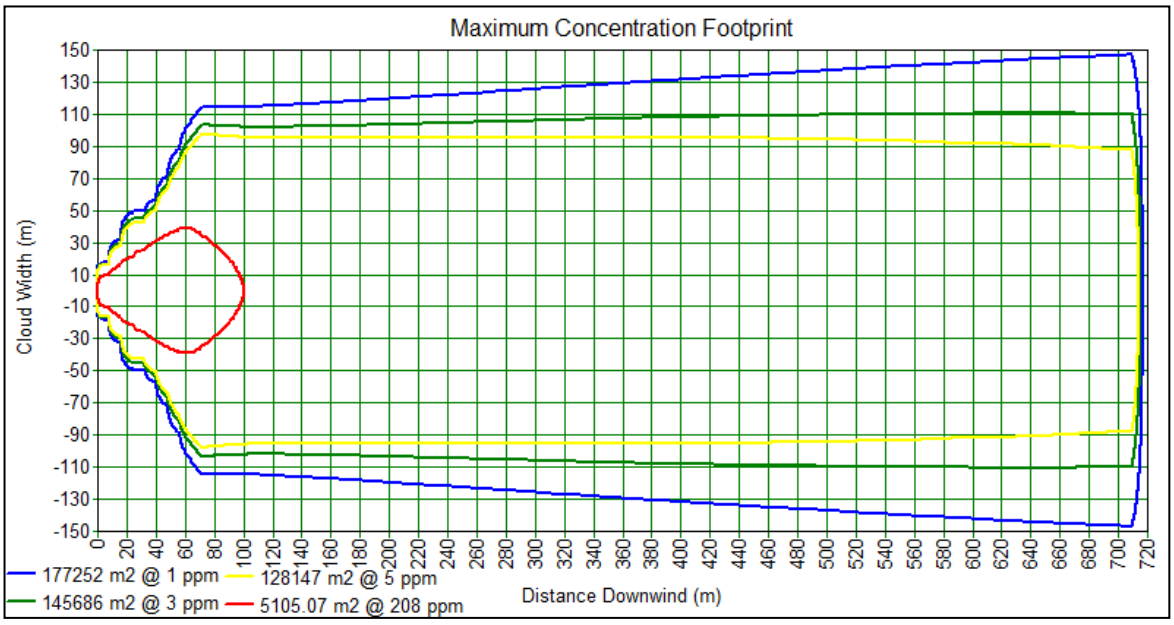
10.3 Scenario 3 Description: Large hole in base of bromine bulk storage tank

Time after release (mins)	Consequence
1	The release forms a wide cloud that covers the entire non-flammable drum park at a concentration of 75ppm or greater. The cloud extends from the edge of the development centre to the edge of the bioplant.
2	The cloud disperses downwind and reduces in concentration. The cloud front reaches Dudley 1, Dudley 1.5 is completely covered by bromine at a concentration of 50ppm or greater. It extends from the west edge of the car park to the QC labs at a concentration of 1 ppm.
3	The release is centred over the main office at a concentration of 40ppm. The south edge of the release has reached the road at a concentration of 1ppm.
4	The cloud front has left the site boundary and has reached the first housing across the road at a concentration of 42ppm or less.
5	The cloud continues to disperse downwind and covers the whole set of houses opposite the site and north of the main entrance at a concentration of 1-40ppm. The cloud continues to disperse downwind into the fields behind the housing
7.5	The cloud reaches the small roundabout behind the fields on Broad Law at a concentration of 1ppm

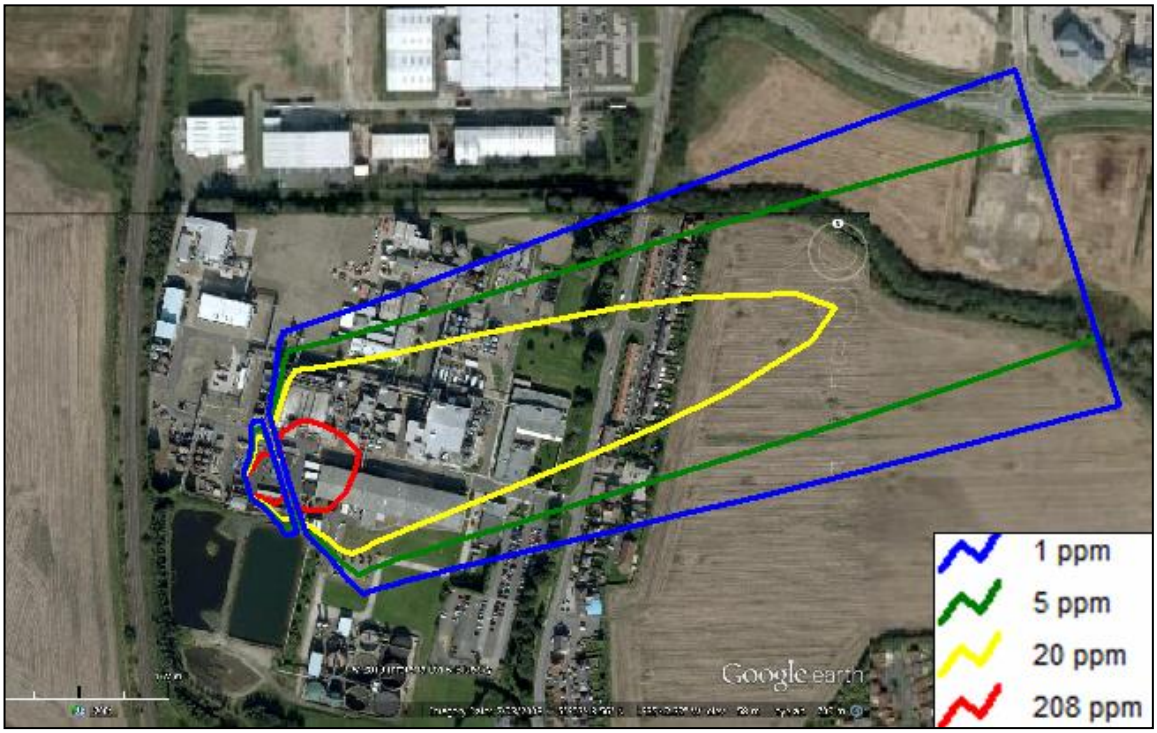
Outdoor lethal toxic 2E Weather; Scenario 3



Maximum concentration footprint 2E Weather; Scenario 3



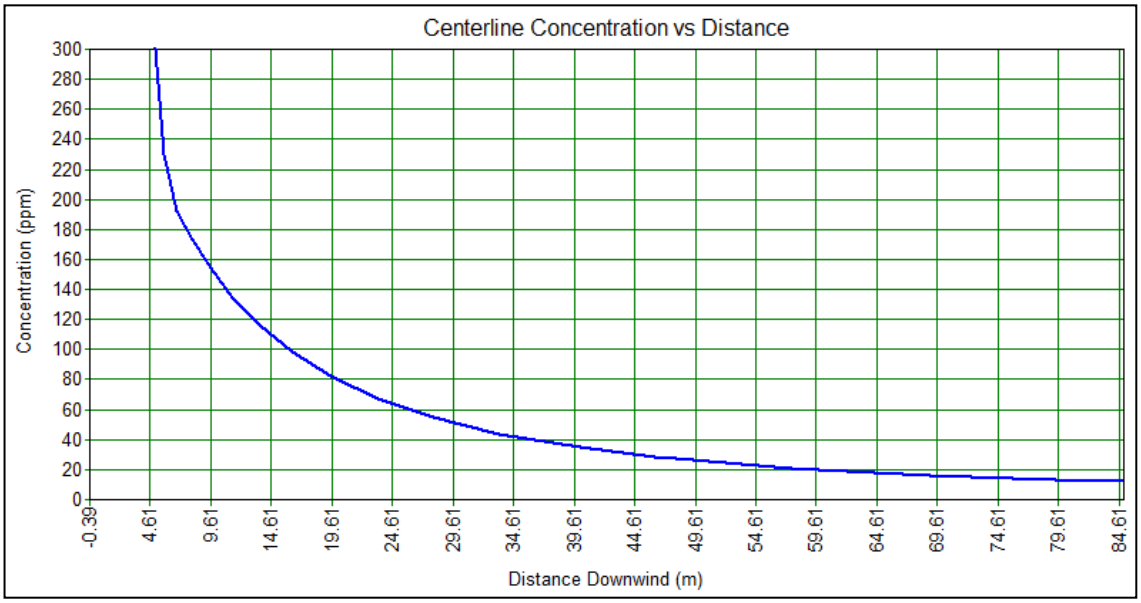
Map view of Scenario 3 (after 8.5 mins)



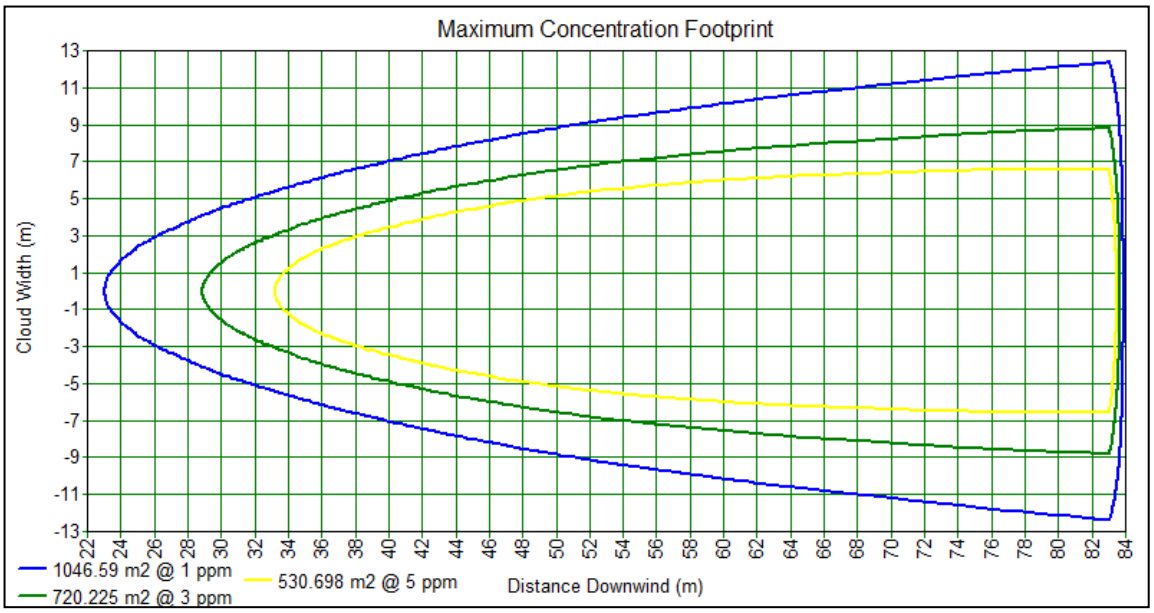
10.4 Scenario 4 Description: Hole in flange on top of the bromine bulk storage tank

This scenario was very small and short lived, and so the Phast Risk model provided no dispersion information.

Centreline Concentration vs. Distance 2E Weather; Scenario 4



Maximum concentration footprint 2E Weather; Scenario 4



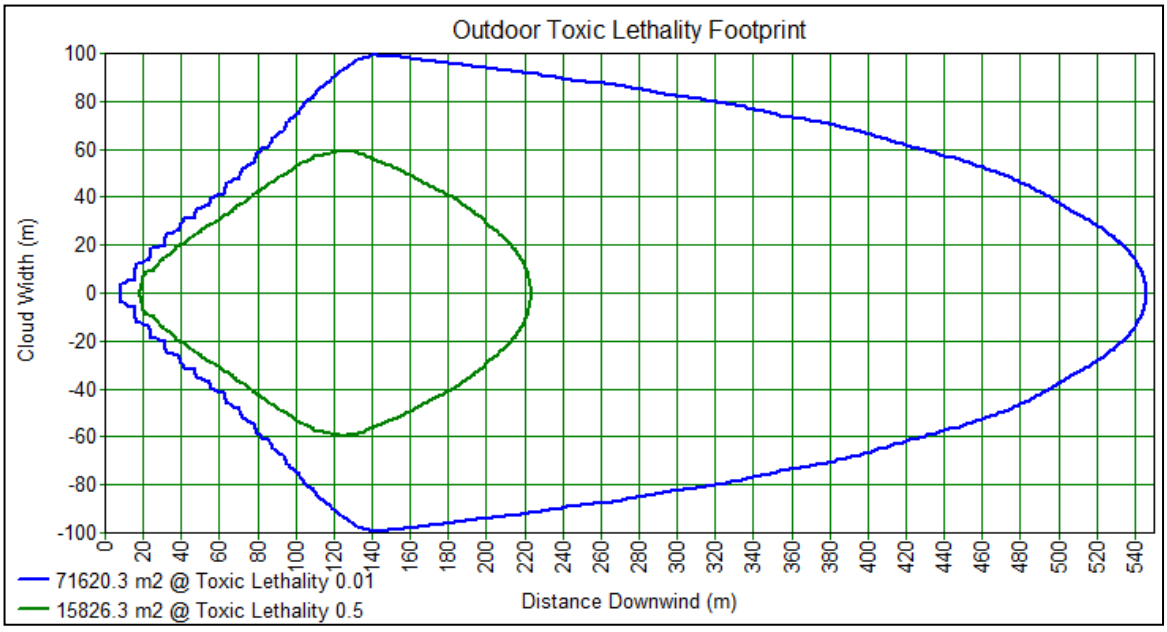
Map view of Scenario 4 (after 1 min)

10.5 Scenario 5 Description: Over pressurization of bulk tank (without lagging) due to external fire

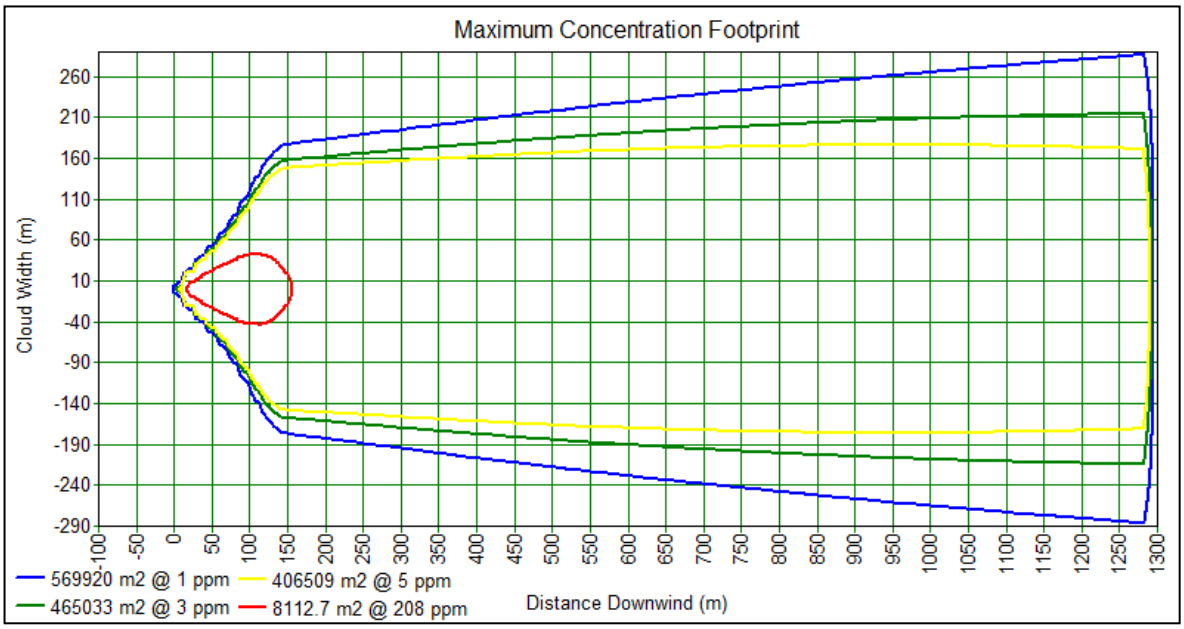
Time after release (mins)	Consequence
1.5	The release forms a wide cloud that rapidly expands sideways and covers all of the non-flammable drum park as well as Dudley 1.5 and most of the warehouse at a concentration of 75ppm or greater. The cloud extends from the south side of the car park to the north of the site, just west of the boiler house at a concentration of 1ppm or greater.
2	The cloud then disperses downwind and reduces in concentration. The cloud front reaches the main office at 110ppm and extends from Sandy's letch to the south side of the car park at 1ppm.
3	The cloud front has left the site boundary and has reached the first housing across the road at a concentration of 75ppm or less. The cloud crosses the site boundary to the north and enters the business park, reaching the first building.
4	The cloud continues to disperse downwind and covers the whole set of houses opposite the site and north of the site car park at a concentration of

	1-75ppm. The cloud continues to disperse downwind into the fields behind the housing.
7.5	The cloud continues to disperse downwind into the fields to the east of the site. It extends all the way to the main roundabout on the A19 and covers the business park and several residential houses at a concentration of between 1 and 10ppm.

Outdoor lethal toxic 2D Weather; Scenario 5



Maximum concentration footprint 2D Weather; Scenario 5

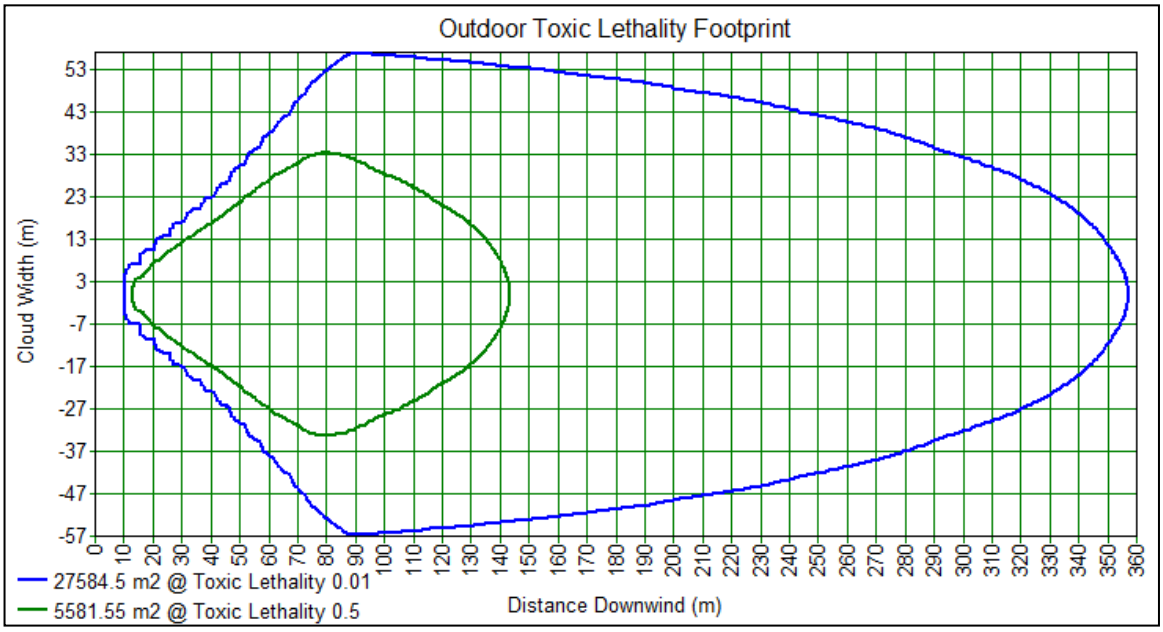


Map view of Scenario 5 (after 10 mins)

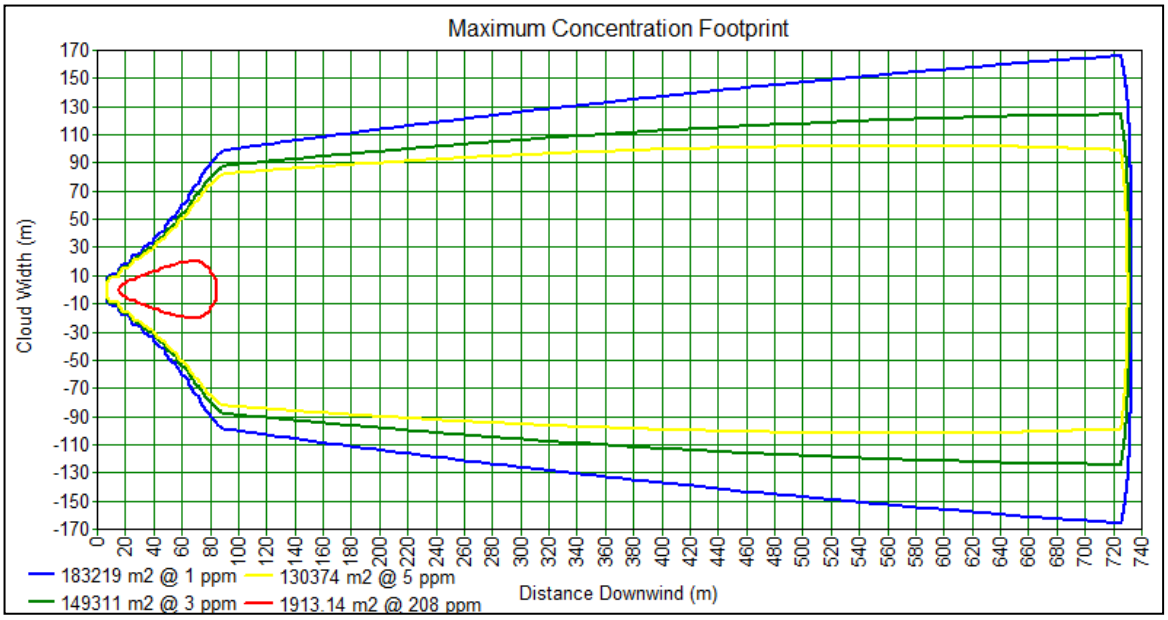
10.6 Scenario 6 Description: Over pressurization of bulk tank (with lagging) due to external fire

Time after release (mins)	Consequence
1	The release forms a wide cloud that covers most of the entire non-flammable drum park at a concentration of 75ppm or greater. The cloud extends from the edge of Dudley 2 to the north edge of flammable drum park 3.
1.5	The cloud disperses downwind and reduces in concentration. The cloud front reaches the centre of Dudley 1 at a concentration of 80ppm. Dudley 1.5 and the west half of the warehouse is covered by bromine at a concentration of 50ppm or greater. The cloud extends from the north edge of the QC Labs to the north-west corner of the car park at a concentration of 1 ppm.
2	The release is centred over the main office at a concentration of 48ppm. The south edge of the release has reached the road 20 metres south of the site's main entrance at a concentration of 1ppm.
3	The cloud front has left the site boundary and has reached the first housing across the road at a concentration of 37ppm or less.
4	The cloud continues to disperse downwind and covers the whole set of houses opposite the site and north of the site's car park at a concentration of 1-37ppm. The cloud continues to disperse downwind into the fields behind the housing.
6	The north edge of the cloud reaches the small roundabout behind the fields on Broad Law at a concentration of 1ppm.

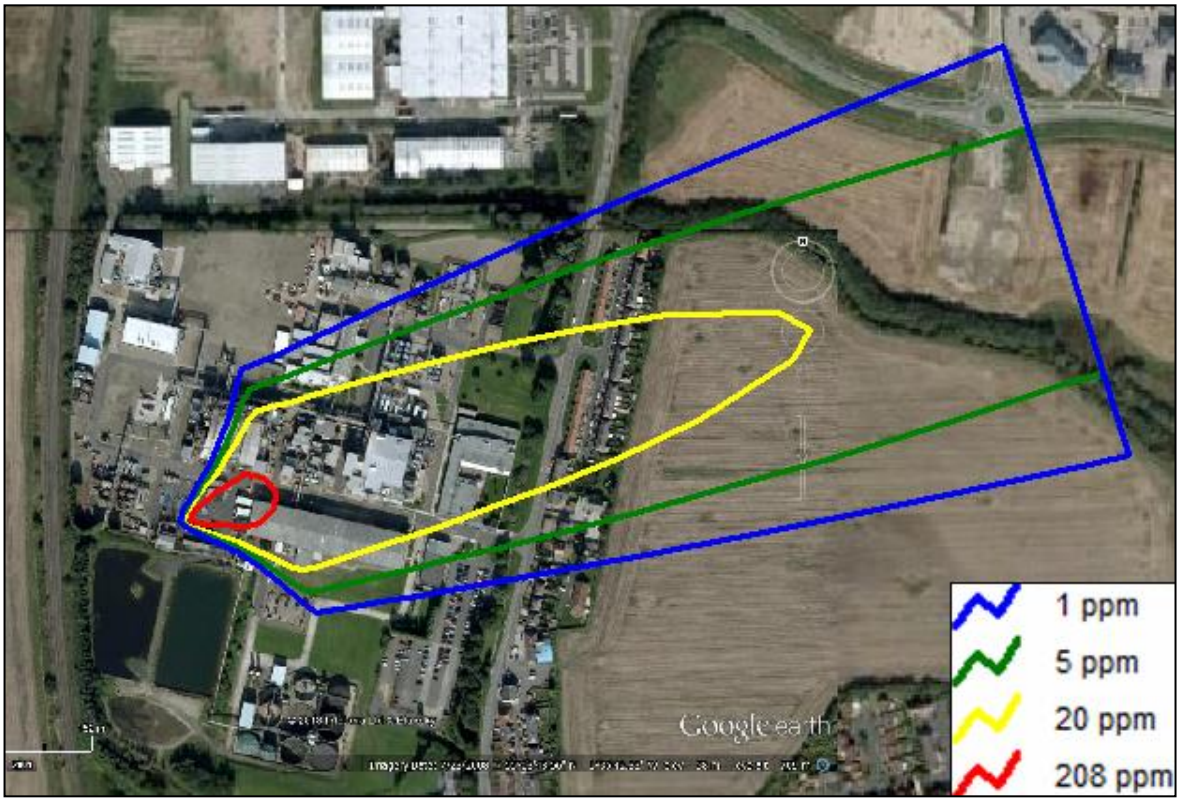
Outdoor lethal toxic 2D Weather; Scenario 6



Maximum concentration footprint 2D Weather; Scenario 6



Map view of Scenario 6 (after 6 mins)

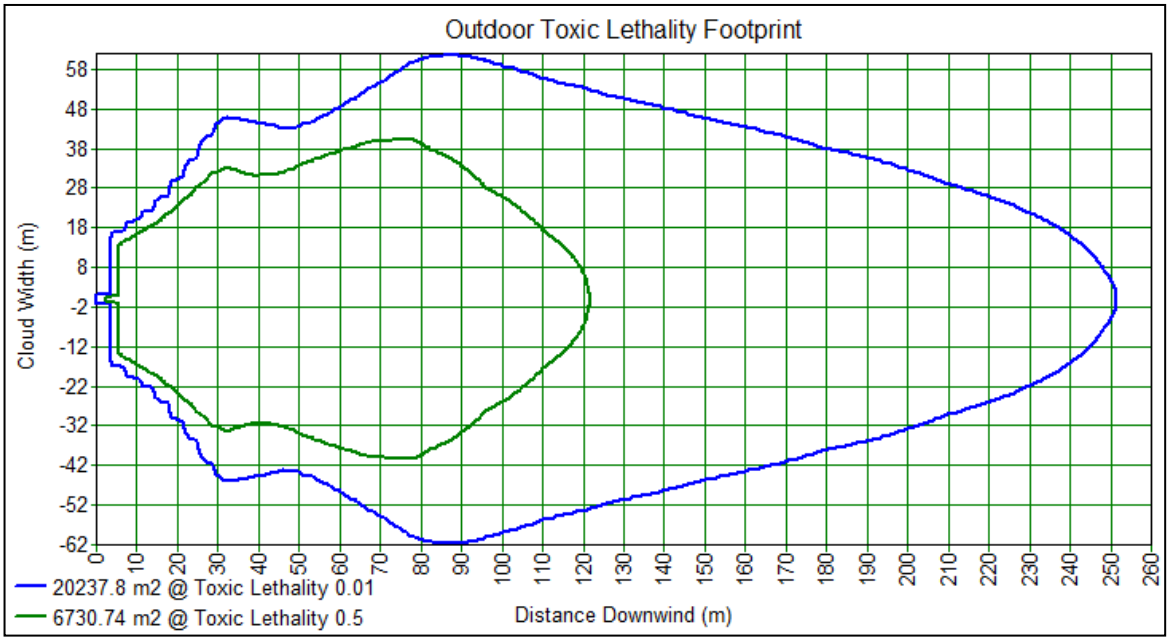


10.7 Scenario 7 Description: Leak from gaskets on Kynar/PFA lined mild steel pipe or Flexi during transfer

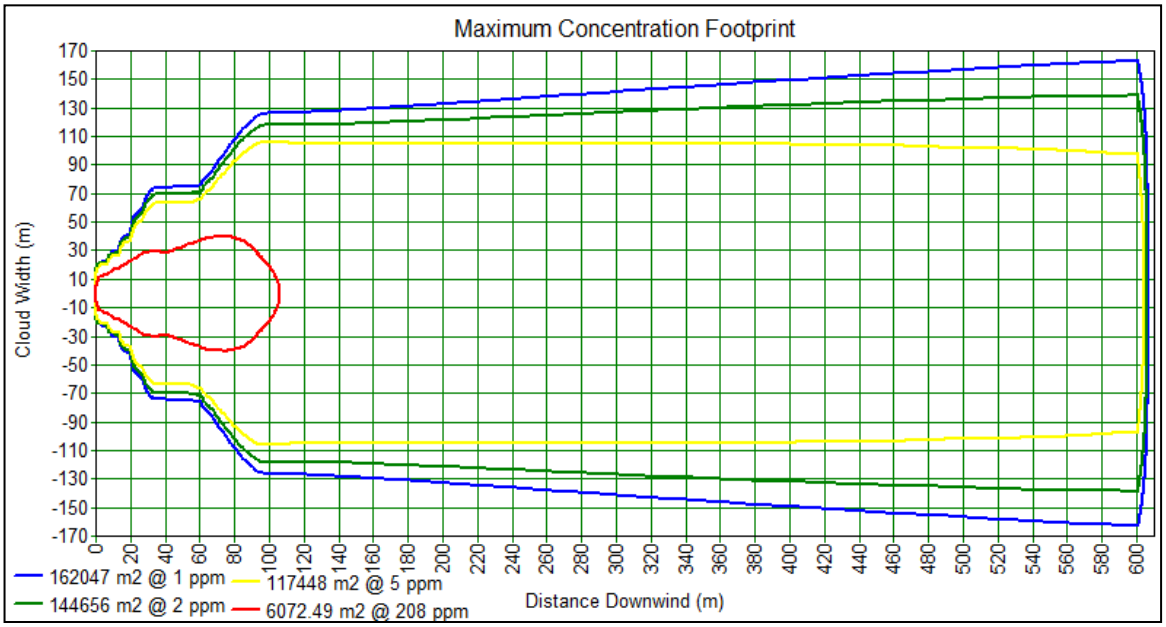
Time after release (mins)	Consequence
1	The release forms a cloud that covers the east half of the non-flammable drum park as well as the western third of the warehouse and half of Dudley2 at a concentration in the range of 1-100ppm.
2	The cloud then disperses downwind. The cloud front reaches the centre of the main office at 20ppm and extends from the security office to the east edge of the flammable tank farm at a concentration 1ppm.
3	The cloud front has left the site boundary and has reached the first housing across the road at a concentration of 75ppm or less. The cloud crosses the site boundary to the north and enters the business park, reaching the first building.

3.5	The cloud continues to disperse downwind and reaches the housing opposite the site at a concentration of 8ppm, the cloud slowly increases in size over time.
15	After 890 seconds the cloud has increased width and length. The concentration of bromine reaches in the houses opposite the site has a maximum of 20ppm and extends to all of the houses opposite the site north of the main entrance and also enters the fields behind the housing at a concentration of 1ppm.
37	The cloud continues to increase in width and length until 37 minutes after the initial release. Most of Dudley 1, 1.5 and 2 and the warehouse is encompasses by Bromine at a concentration of 75ppm or greater and the maximum concentration reaching the residential housing opposite the site is 30ppm. The north edge of the cloud approaches Broad Law but most of the cloud can be found in the fields behind the housing.

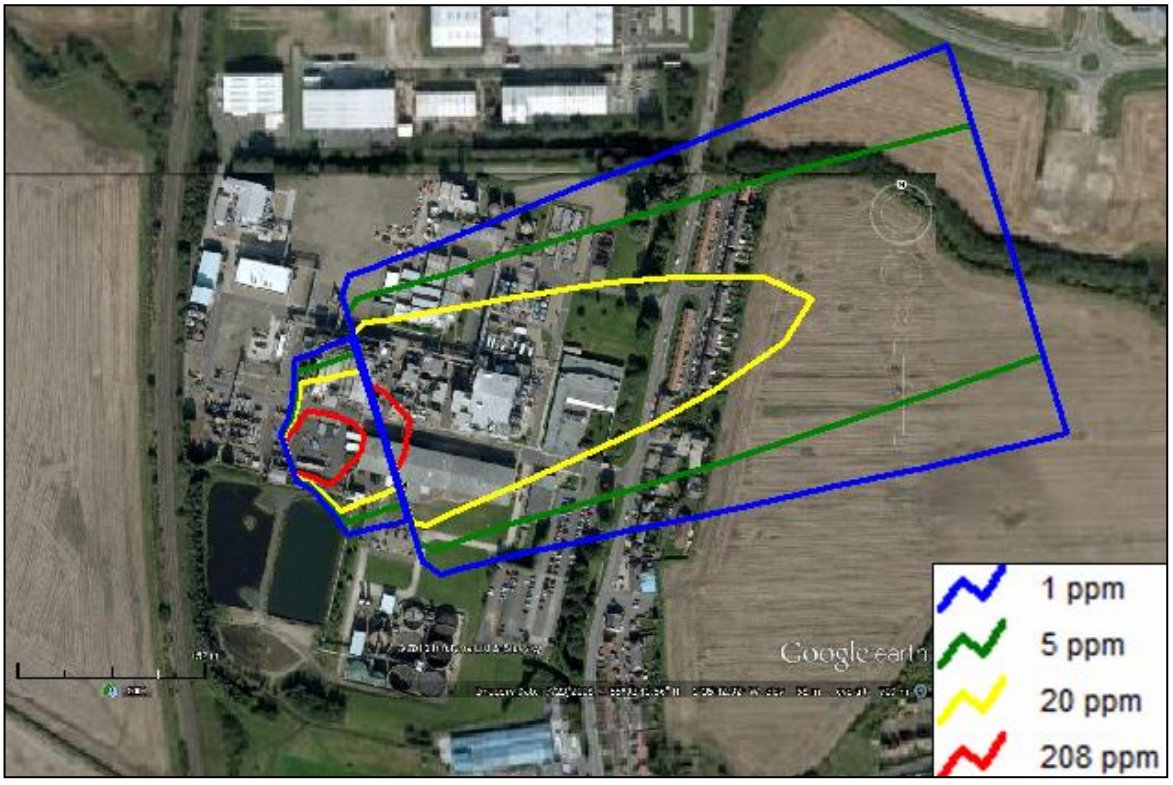
Outdoor lethal toxic 2D Weather; Scenario 7



Maximum concentration footprint 2D Weather; Scenario 7



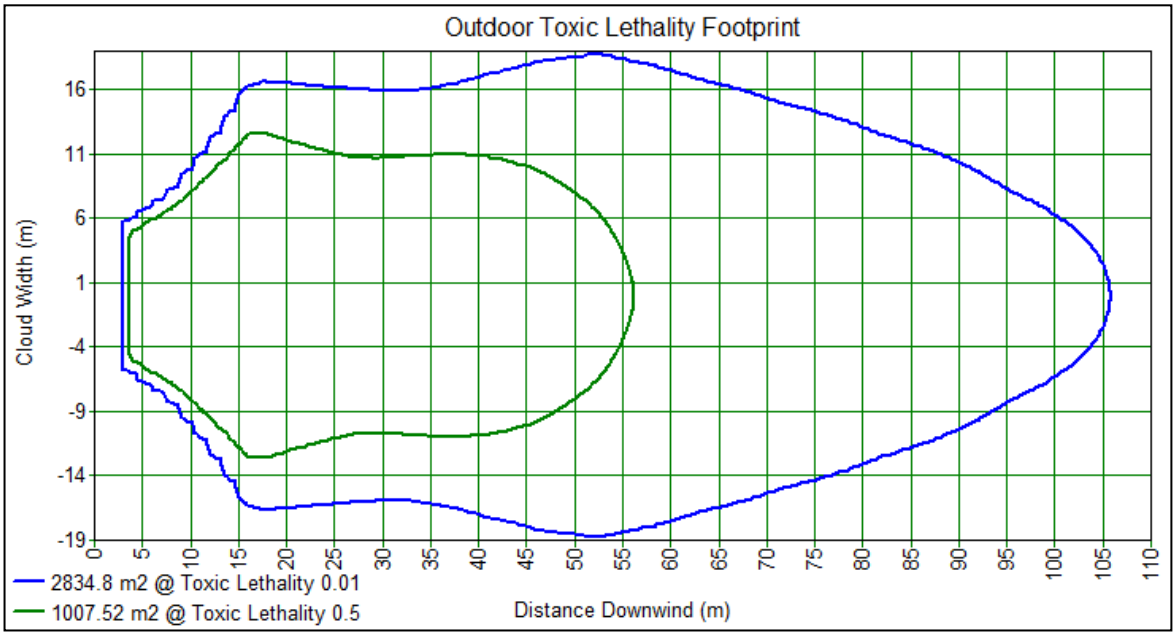
Map view of Scenario 7 (after 37 mins)



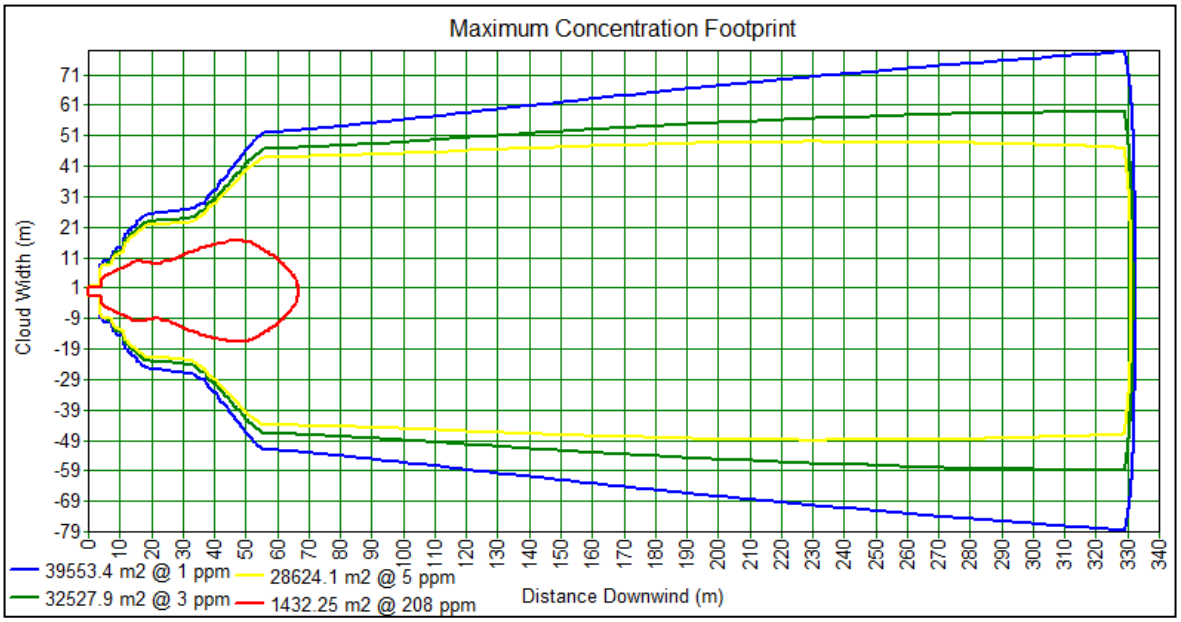
10.8 Scenario 8 Description: Leak from gaskets on Kynar/PFA lined mild steel pipe or Flexi during transfer

Time after release (mins)	Consequence
1	The release forms a cloud that covers the east third of the non-flammable drum park and just reaches the edges of the warehouse and Dudley2 at a concentration in the range of 1-100ppm.
1.5	The cloud then disperses downwind. The cloud front reaches Dudley 1 at 25ppm and extends from the road outside the QC labs to the road between D2 and the warehouse at a concentration 1ppm. The cloud covers most of the warehouse and all of Dudley 1.5.
4.5	The cloud slowly expands and disperses further downwind, reaching the main office at a concentration of 15ppm. The cloud covers the area from the security office to the flammable tank farm at a concentration of 1-15ppm.
7	The cloud has slowly expanded to its maximum size and has just about reached the housing opposite the site at a concentration of 10ppm. The cloud covers the first row of houses (approx 15 houses), north of the site's main entrance. The cloud begins to reduce in size as the release is stopped.

Outdoor lethal toxic 2D Weather; Scenario 8



Maximum concentration footprint 2D Weather; Scenario 8



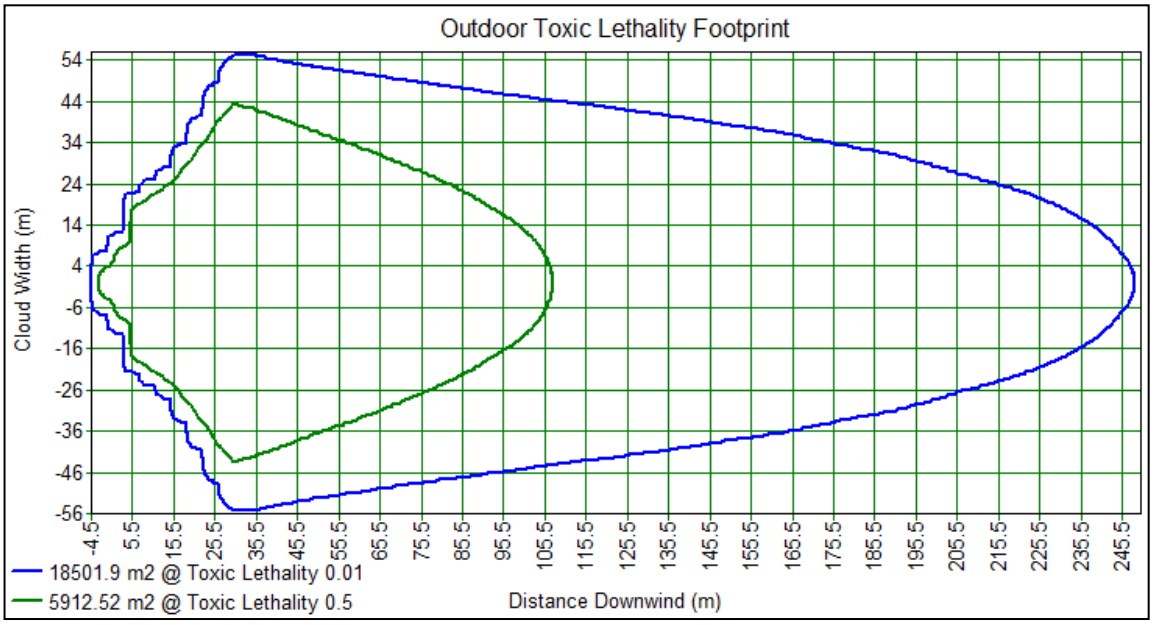
Map view of Scenario 8 (after 6 mins)

10.9 Scenario 9 Description: Catastrophic rupture of a Goslar

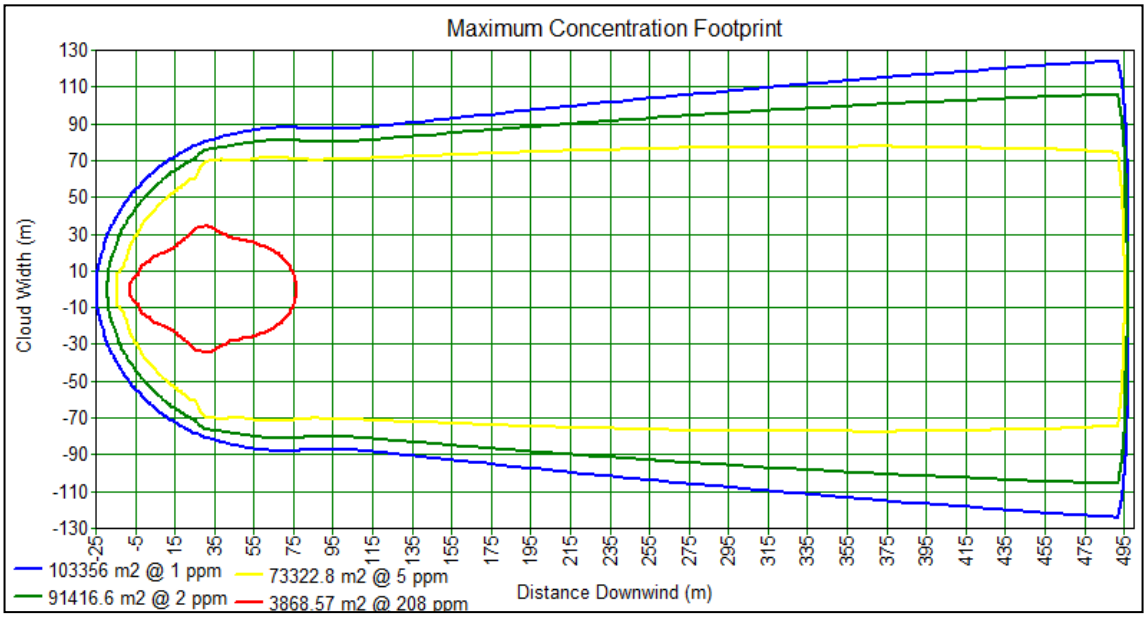
Time after release (mins)	Consequence
1	The rupture causes a sudden release of bromine that forms a circular cloud, centred over the west edge of the warehouse. The cloud contains Dudley 2, Dudley 1.5, the entire non-flammable drum park and half of the warehouse at a concentration ranging from 1ppm to around 200ppm at the centre.
2	The large circular cloud disperses downwind and reaches the centre of Dudley 1 at a concentration of 55ppm. The cloud extends from the fire department building to the QC labs at a concentration of 1ppm or greater.
3	The cloud reaches the main office at 35ppm and has reached the site's main entrance at 1ppm.
3.5	The cloud front has reached the housing opposite the site at a concentration of 23ppm.

4.5	The cloud has reached its maximum size and covers all of the housing opposite the site on Dudley lane, north of the site's main entrance and also extends into the field behind the housing. The concentration of bromine is between 1 and 23ppm.

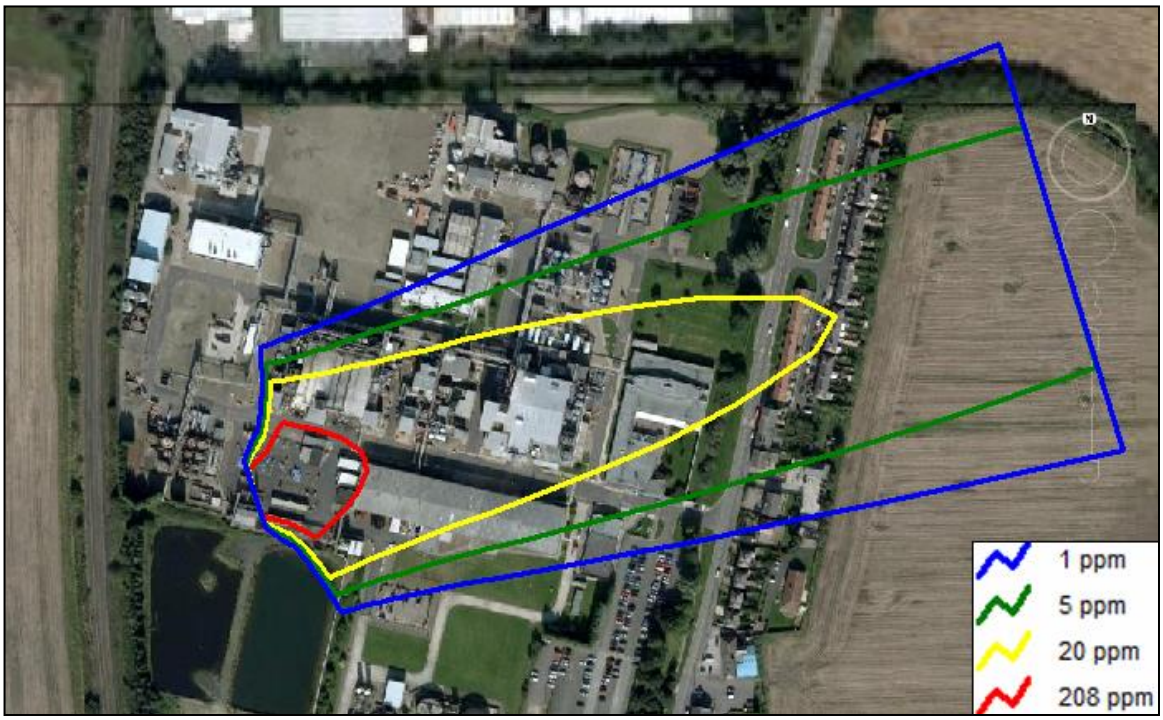
Outdoor lethal toxic 2E Weather; Scenario 9



Maximum concentration footprint 2D Weather; Scenario 9



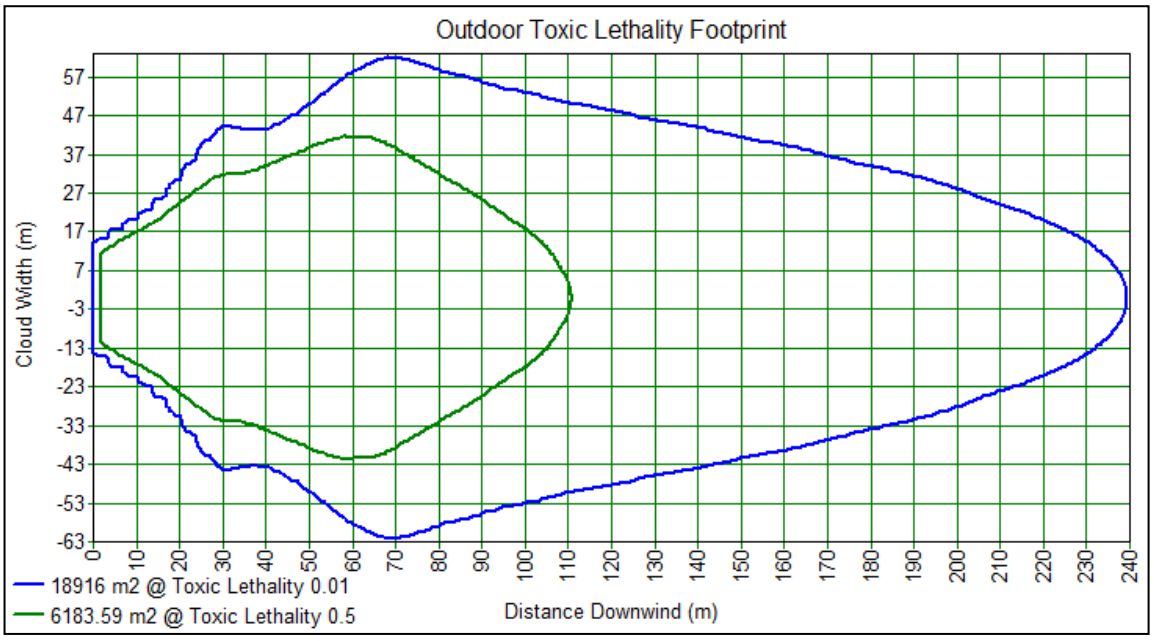
Map view of Scenario 9 (after 4.5 mins)



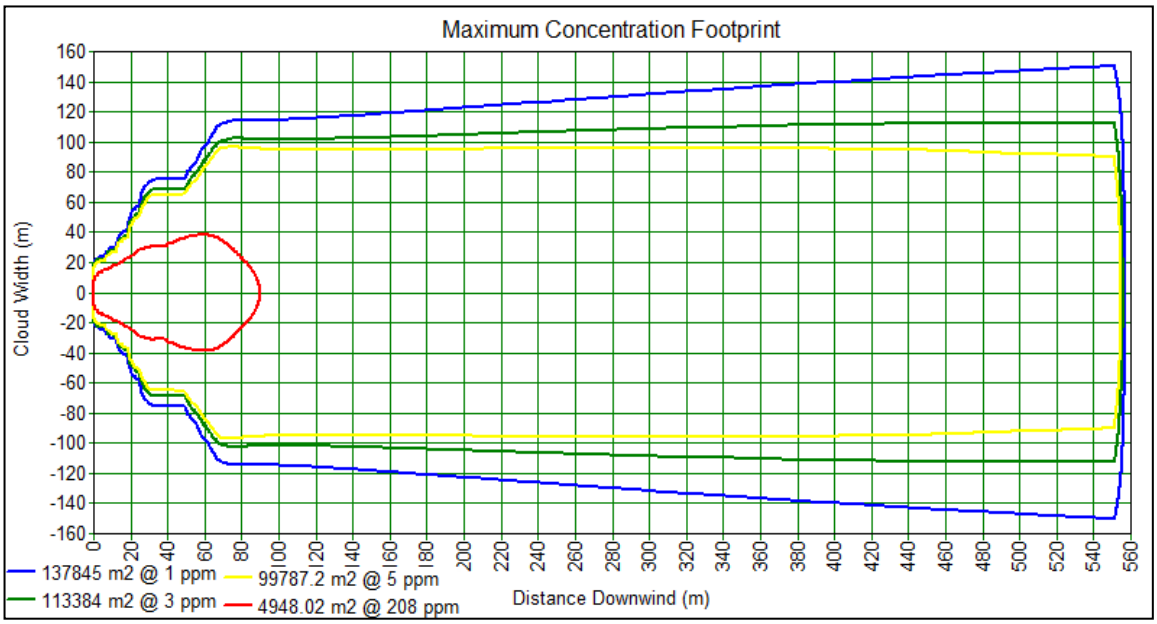
10.10 Scenario 10 Description: Small hole in the base of a Goslar

Time after release (mins)	Consequence
0.5	The release expands and forms a cloud that covers most of the non-flammable drum park at a concentration of 75ppm or greater. The edges of the cloud reach Dudley 2 and the old lime plant at 1ppm.
2	The cloud expands and disperses downwind, encompassing Dudley 1 with bromine at a concentration of 25 ppm or greater. The cloud is now wider and reaches from the QC labs to the fire department at concentrations of 1ppm.
3	The cloud moves quickly and reaches the main office at 15ppm before reaching the site boundary at 12ppm.
3.5	The cloud front has reached the housing opposite the site at a concentration of 23ppm. The slowly increases in size over time.
17	The cloud has now reached the housing opposite the site on Dudley lane at a maximum concentration of 10ppm. The cloud extends from the housing opposite the site's main entrance to the housing at the top of Dudley lane, before the roundabout. The concentration at the edges of the cloud is 1ppm.
37	The cloud continues to increase in width and length until 37 minutes after the initial release. The majority of the site east of the bromine tank is encompassed by bromine at a concentration of 15ppm or greater. The cloud has extended beyond the housing and far into the fields behind them. The maximum concentration experienced by the housing is 25ppm.

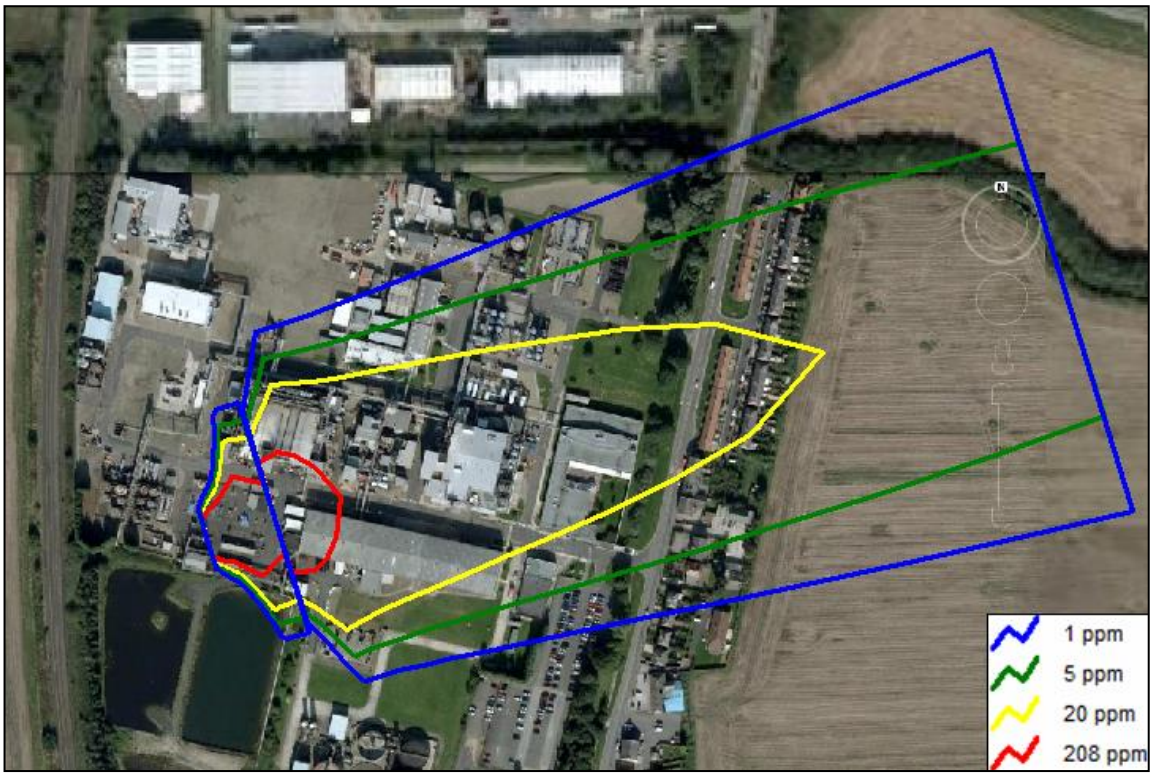
Outdoor lethal toxic 2D Weather; Scenario 10



Maximum concentration footprint 2D Weather; Scenario 10



Map view of Scenario 10 (after 46 mins)

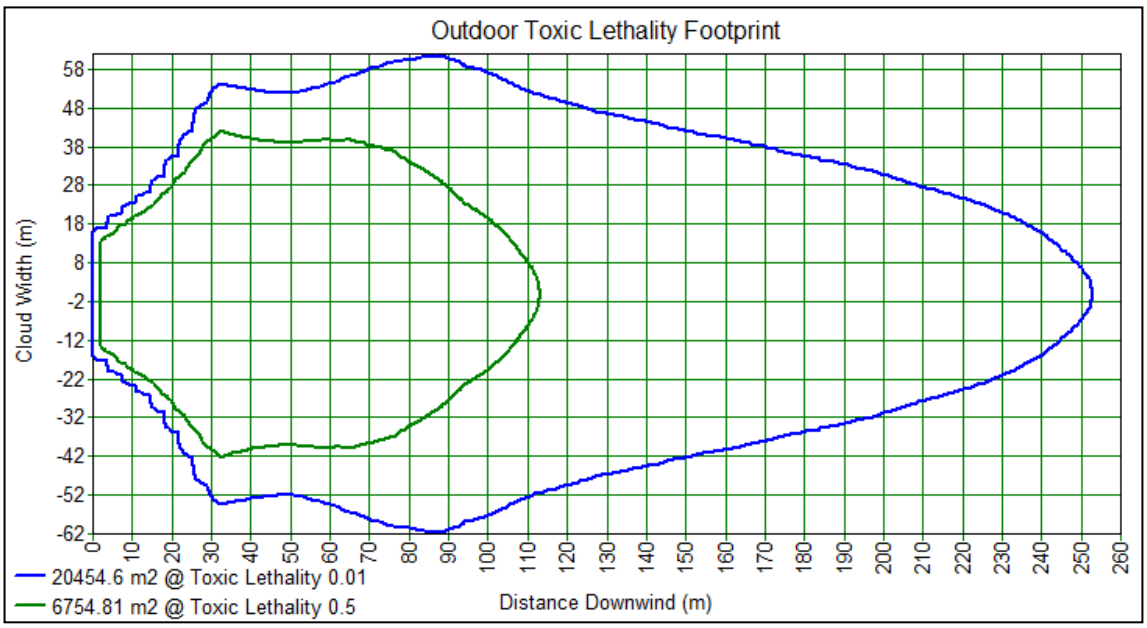


10.11 Scenario 11 Description: Large hole in the base of a Goslar

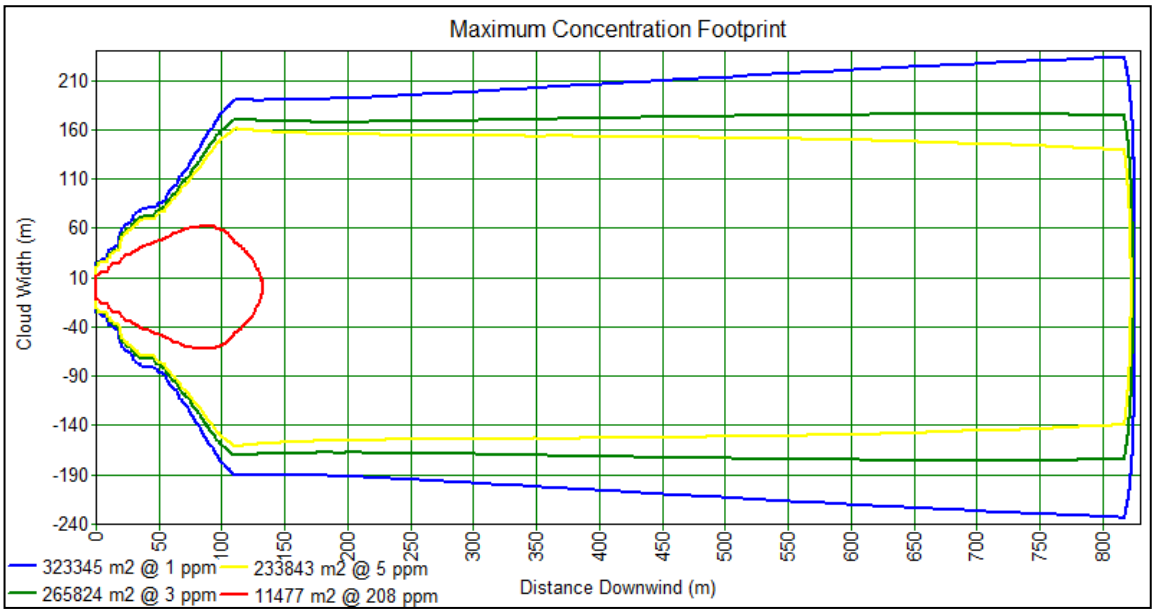
Time after release (mins)	Consequence
1	The release expands and forms a cloud that covers most of the non-flammable drum park at a concentration of 75ppm or greater. The edges of the cloud reaches 20m north of Dudley 2 and down to flammable drum park 3 at a concentration of 1ppm.
2	The cloud continues to expand and disperse downwind, it encompasses Dudley 1 with bromine at a concentration of around 70 ppm. The cloud is now wider and reaches from the engineering workshops to the fire safety department at concentrations of 1ppm.
3.5	The cloud moves quickly and reaches the main office after 3 minutes at 50ppm before reaching the site boundary and then the first houses across Dudley lane at a concentration of 25ppm.

5	The cloud has reached its maximum width, spanning from Sandy's letch to the south edge of the site's car park. The rows of houses north of the site's car park until the business park north of the site are completely covered by the cloud at concentrations ranging from 1 to 30ppm.
8.5	The cloud is dispersed downwind and reduces in size. The buildings half way along Broad Law experience concentrations of Bromine in the region of 1-5ppm.

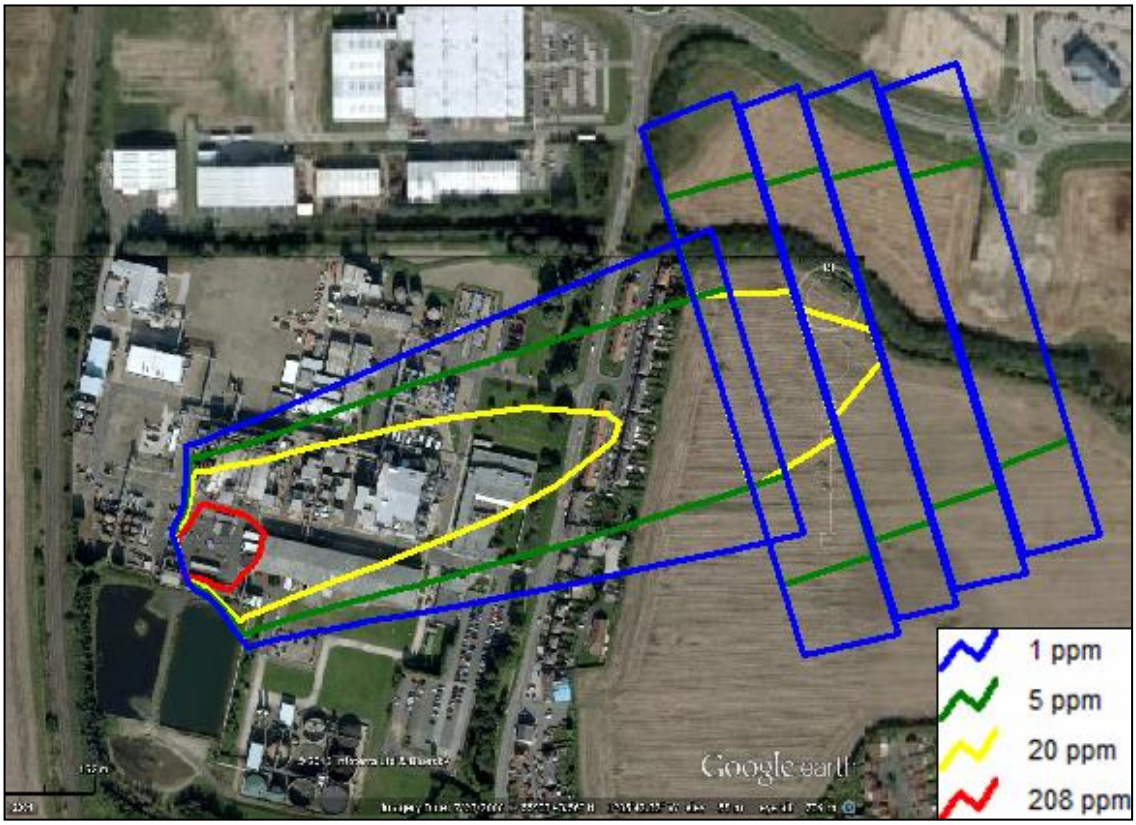
Outdoor lethal toxic 2D Weather; Scenario 11



Maximum concentration footprint 2D Weather; Scenario 11



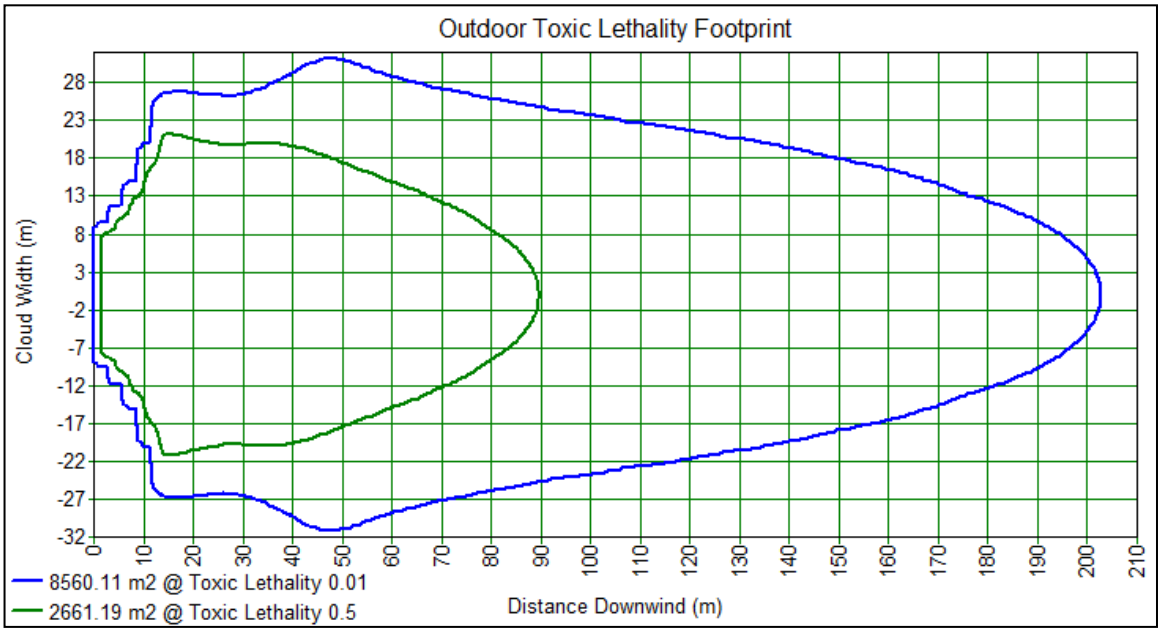
Map view of Scenario 11 (after 7 mins)



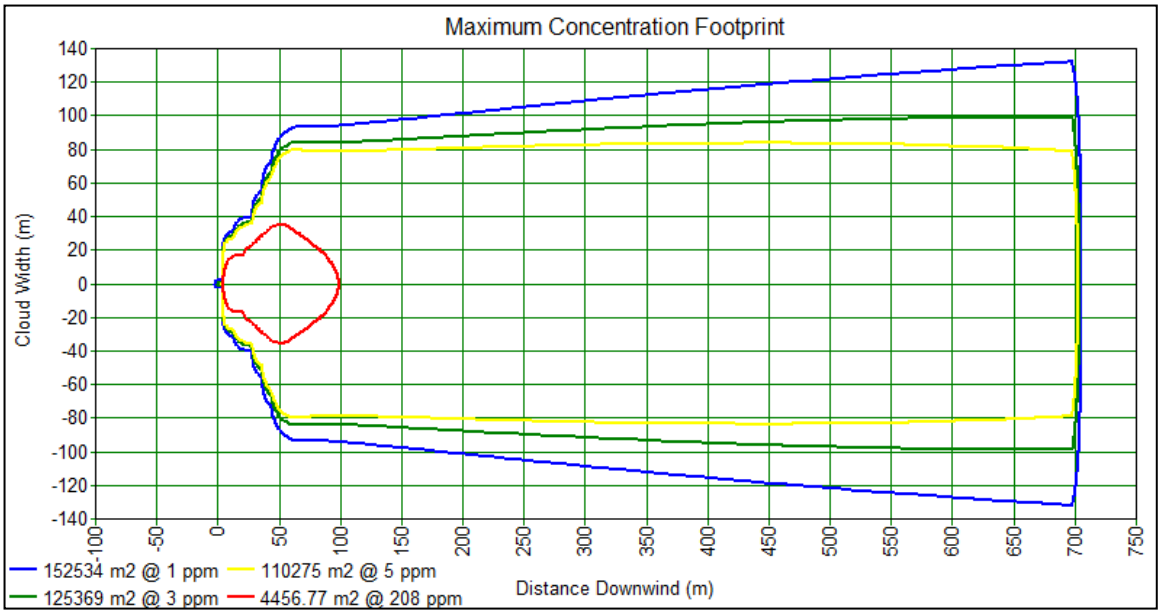
10.12 Scenario 12 Description: Failure of transfer line between bulk tank (B2-D5) and header (A1551) on Dudley 1.5 during transfer

Time after release (mins)	Consequence
1	The release expands and forms a cloud that covers half of the west side of the warehouse to the north side of Dudley 1.5, the concentration ranges from 1-200ppm.
2.5	The cloud continues to expand and disperse downwind, it encompasses Dudley 1 with bromine at a concentration of 75 ppm or greater. The cloud is now wider and reaches from the QC labs to the fire safety department at concentrations of 1ppm. The cloud front has just reached the main office at 65ppm.
3	The edge of the cloud has reached the site boundary, near the main gate at a concentration of 1ppm.
3.5	The cloud front has reached the first houses opposite the main office on Dudley lane. The concentration of bromine at the centre of the cloud is 35ppm.
4.5	The cloud moves over both rows of houses opposite the site and north of the main entrance. The concentration of Bromine is in the range of 1-45 ppm.
6	The cloud disperses into the fields behind the rows of houses and reduces in both size and concentration.

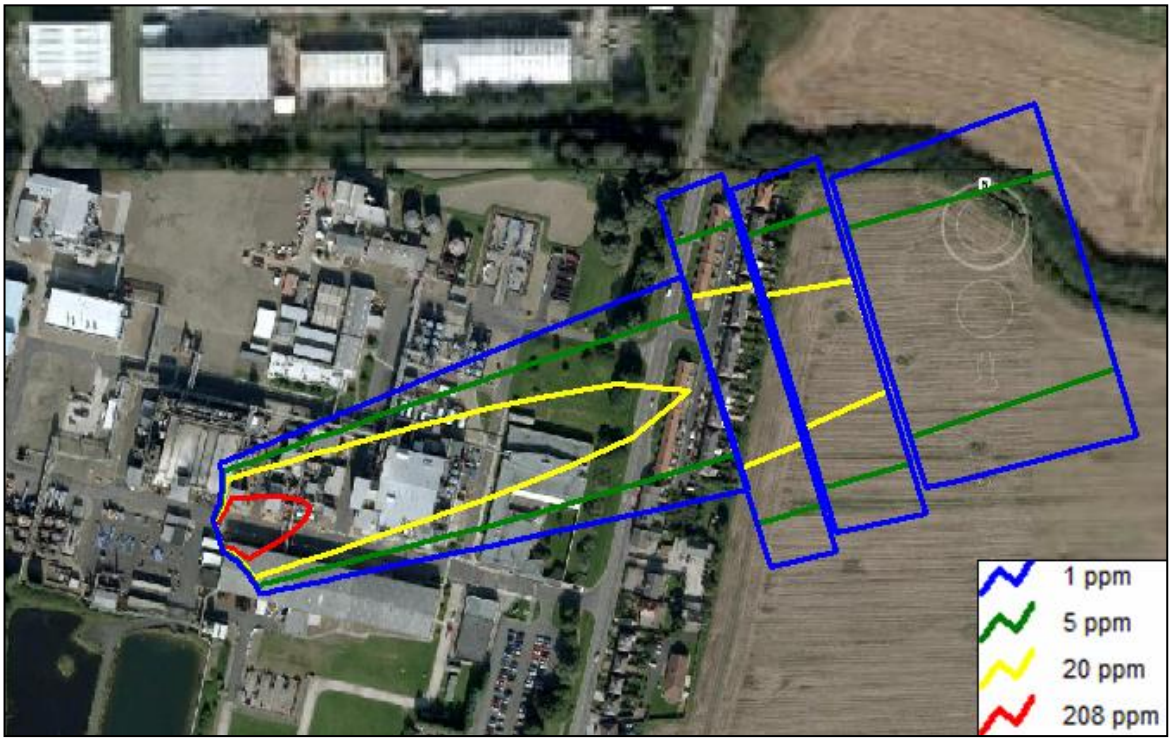
Outdoor lethal toxic 2E Weather; Scenario 12



Maximum concentration footprint 2E Weather; Scenario 12



Map view of Scenario 12 (after 5.5 mins)

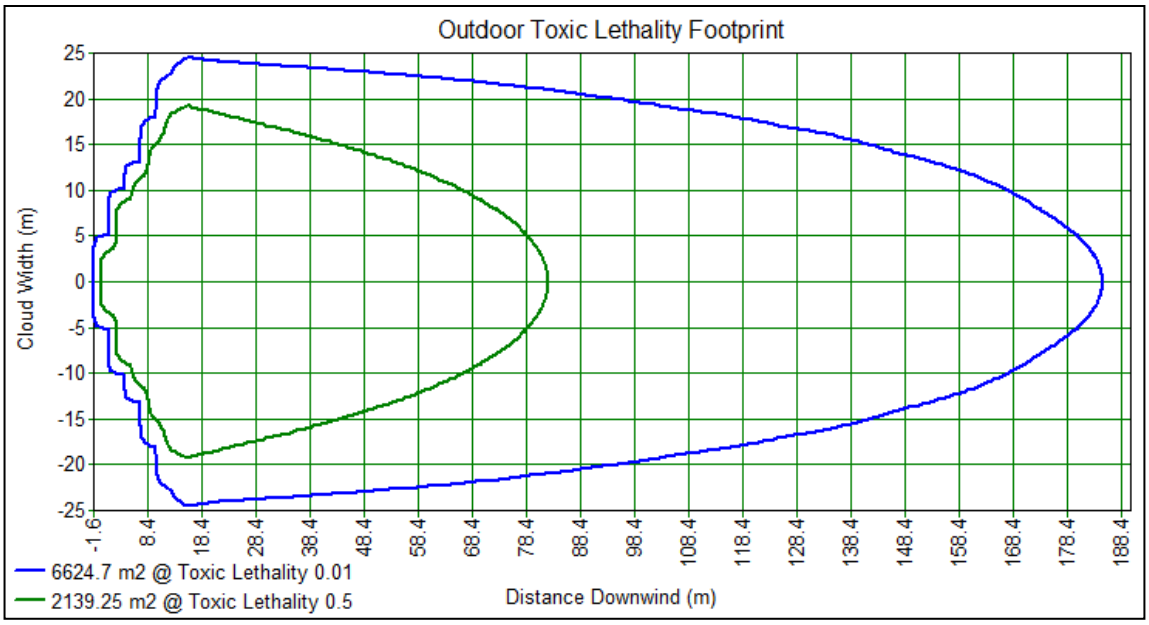


10.13 Scenario 13 Description: Catastrophic failure of header (A1551) while full of Bromine

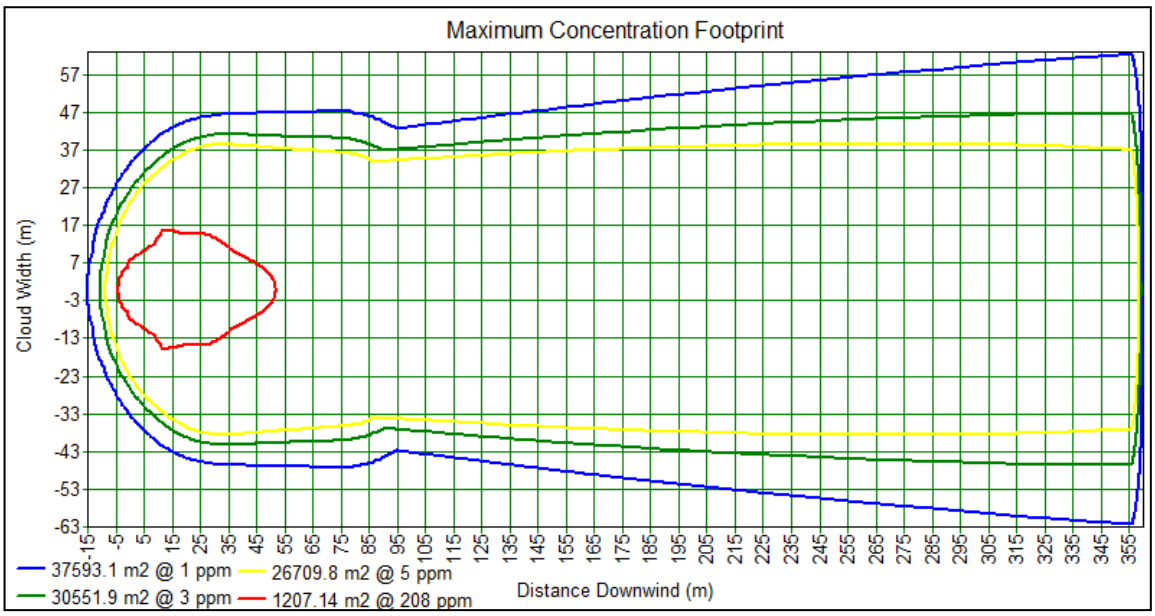
Time after release (mins)	Consequence
0.5	The release forms a circular cloud that covers the whole of Dudley 1.5 and half of Dudley 1. The roads to the north and south of Dudley 1.5 are also covered. The concentration of Bromine in this cloud ranges from 1ppm at the edges to around 200ppm near the centre.
2	The cloud is blown downwind and the edges of the cloud reach the main office at a concentration of 25ppm. The whole of Dudley 1 is covered at concentrations in the range of 1-100ppm, whilst the north edge of the cloud is over the tank farm.
3	The edge of the cloud has reached the site boundary, just below the site's north gate at a concentration of 30ppm.
4	The cloud front has reached the houses north of the main office on Dudley lane and begins to disperse into the fields behind. The

	concentration of bromine at the centre of the cloud is 25ppm. The cloud is 100 metres wide and has a concentration of 1ppm at the edges.

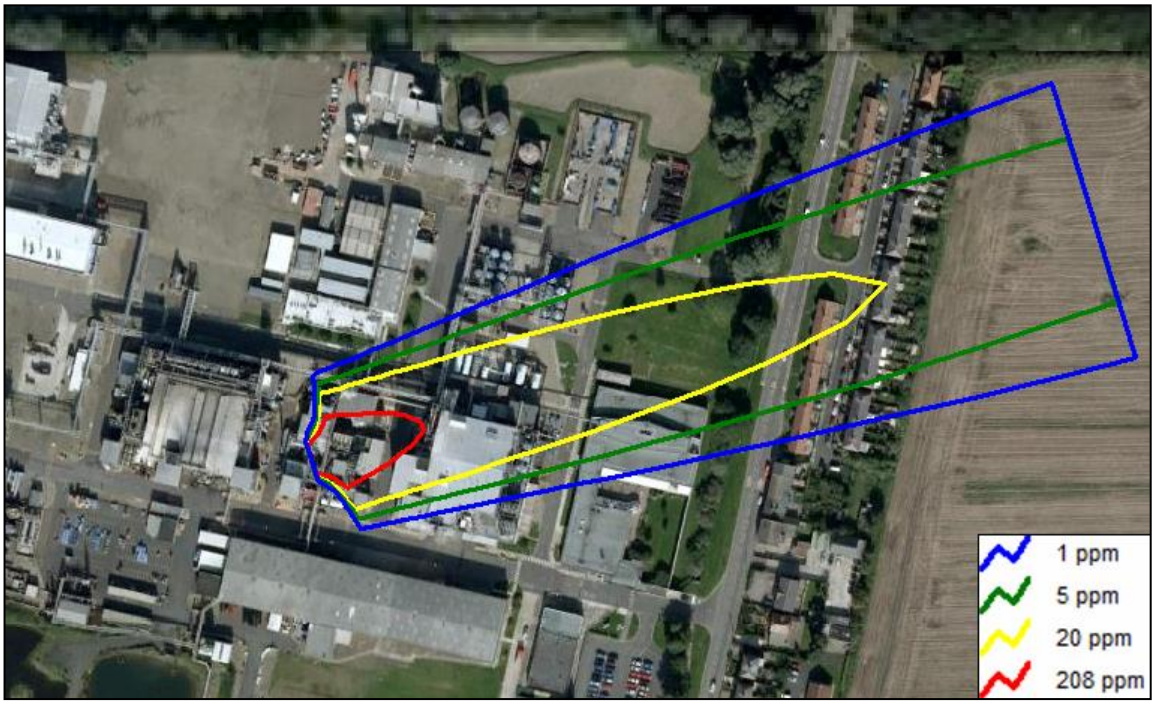
Outdoor lethal toxic 2E Weather; Scenario 13



Maximum concentration footprint 2E Weather; Scenario 13



Map view of Scenario 13 (after 4.5 mins)

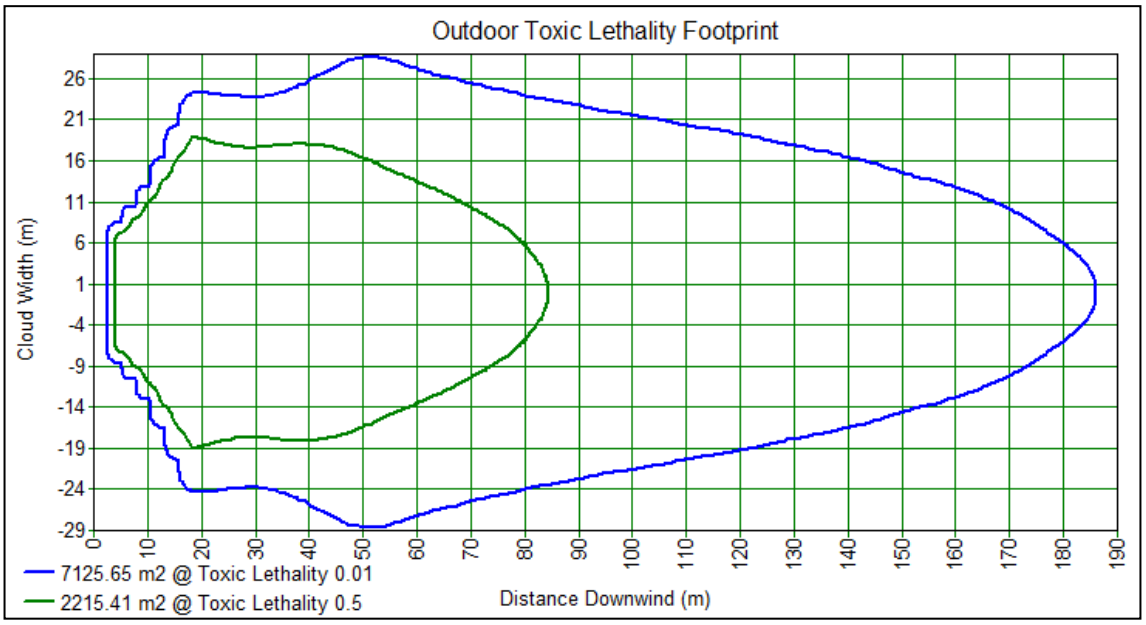


10.14 Scenario 14 Description: Small hole in header (A1551) while full of Bromine

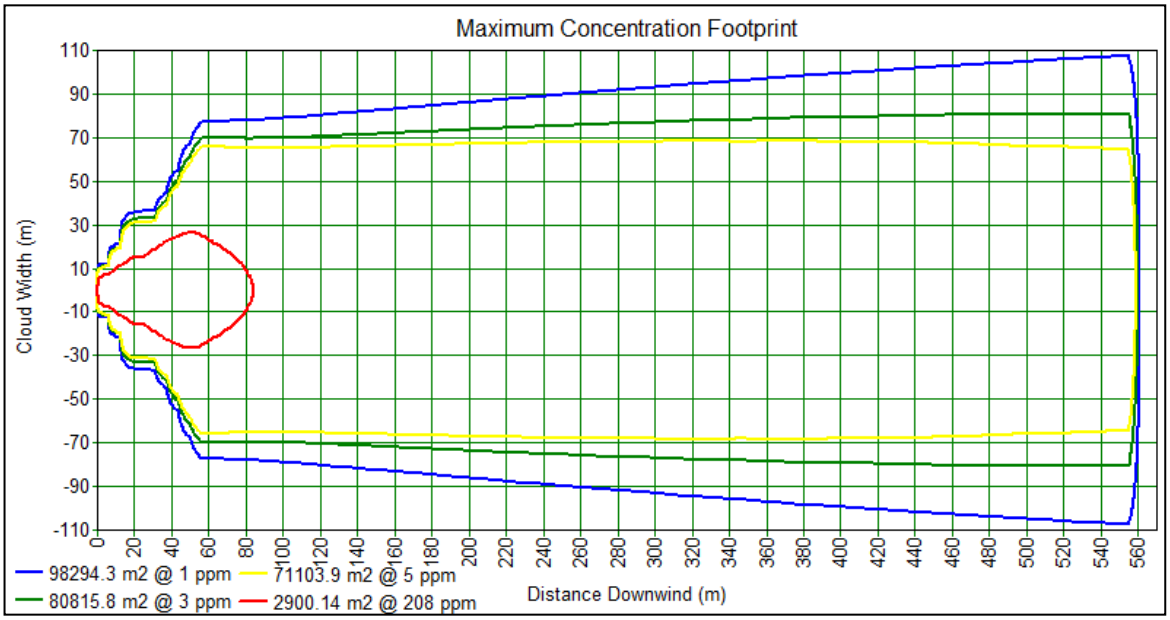
Time after release (mins)	Consequence
1	The release forms a cloud that spans from the engineering workshops to the south corner of Dudley 1 where the concentration of Bromine is 1ppm. The centre of the cloud is over the north-east edge of Dudley 1.5 and has a concentration of around 200ppm.
2	The cloud is blown downwind and the edges of the cloud reach the main office at a concentration between 1 and 25ppm. The whole of Dudley 1 is covered at concentrations in the range of 1-100ppm, whilst the north edge of the cloud is over the tank farm.
2.5	The edge of the cloud has reached the site boundary, just below the site's north gate at a concentration of 25ppm.
3	The cloud front has reached the houses north of the main office on Dudley lane. The concentration of bromine at the centre of the cloud is

	20ppm. The cloud is 120 metres wide and has a concentration of 1ppm at the edges.
7	The cloud continues to increase in both size and concentration downwind. The cloud has increased in width to 180m, covering from the solvent tank farm to the fire safety department on site, and all of the houses on Dudley lane north of the main entrance. The concentration at the edges of the cloud is 1ppm and at the centre, 40ppm.
10	The cloud reduces in size and disperses into the fields behind the row of houses.

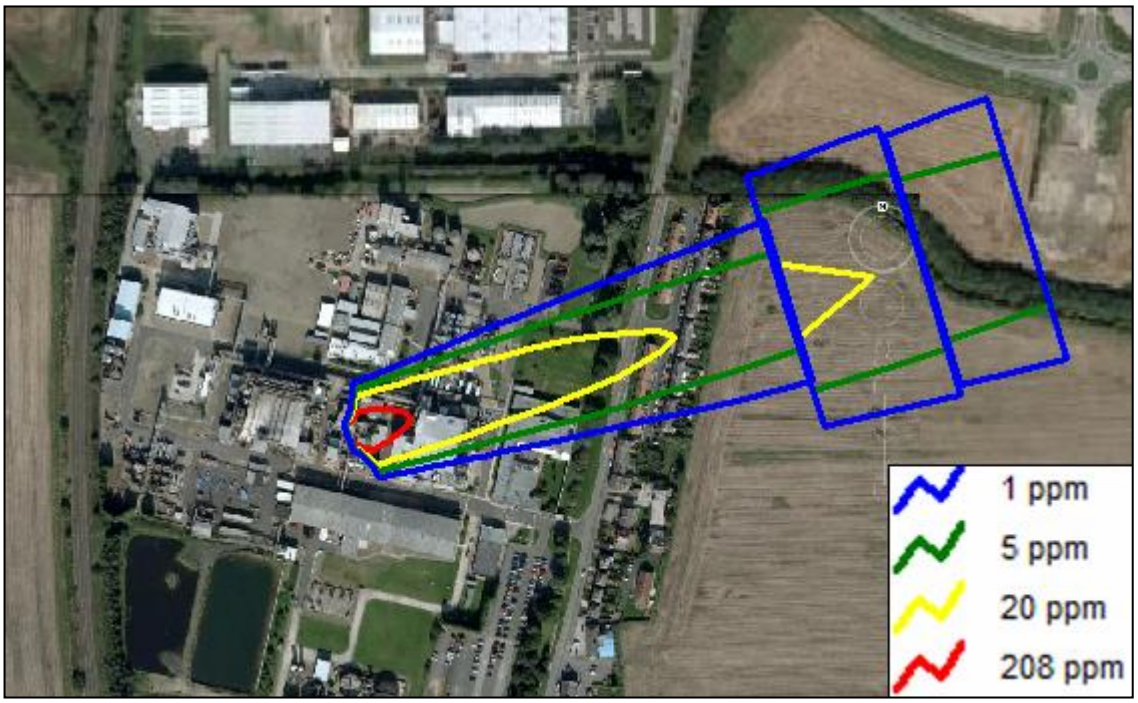
Outdoor lethal toxic 2E Weather; Scenario 14



Maximum concentration footprint 2E Weather; Scenario 14



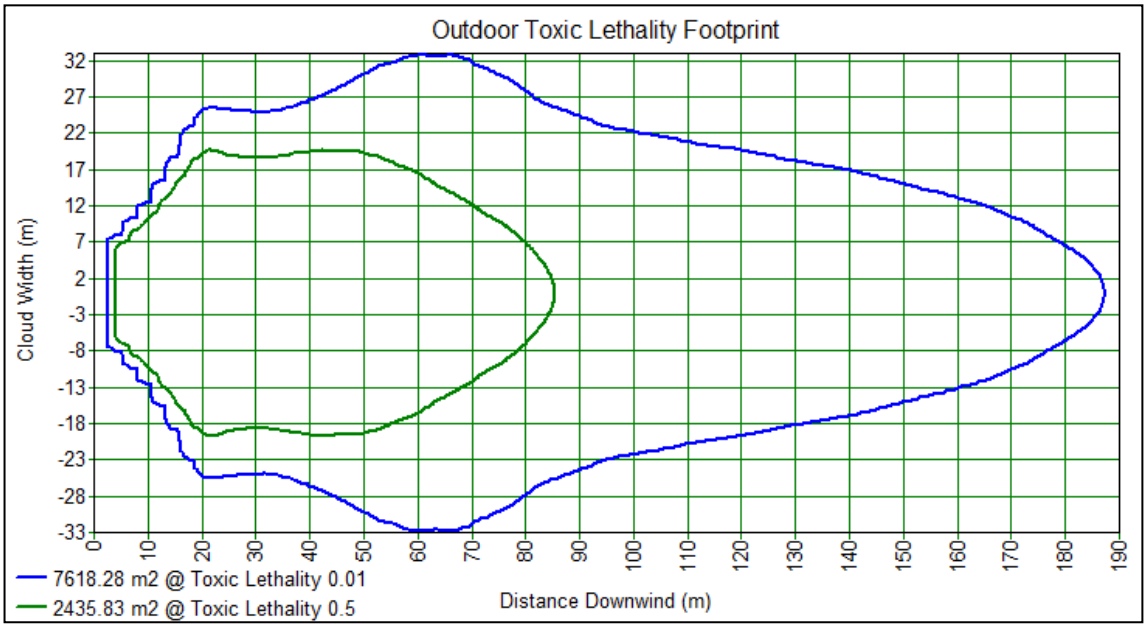
Map view of Scenario 14 (after 9 mins)



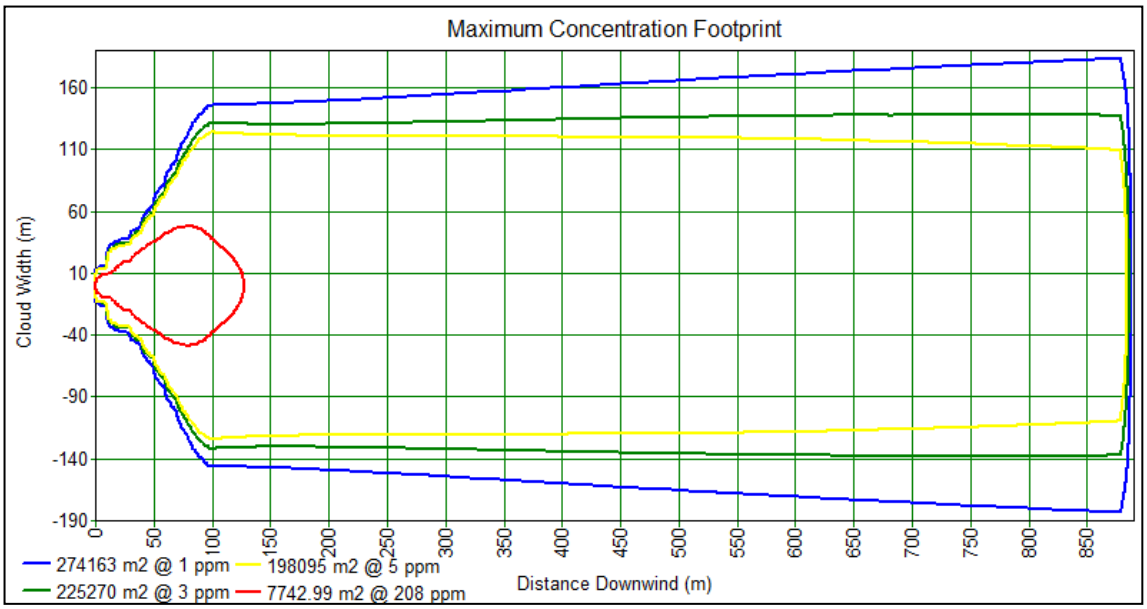
10.15 Scenario 15 Description: Large hole in header (A1551) while full of Bromine

Time after release (mins)	Consequence
1.5	The release forms a large initial cloud that expands and the edges reach the boiler house at the north of the site and all the way to the car park where the concentration of Bromine is 1ppm. The centre of the cloud is over the north-east edge of Dudley 1 and has a concentration of around 200ppm.
2	The large initial cloud is blown downwind and the edges of the cloud reach the site's main entrance at a concentration of 5ppm. The whole of Dudley 1 and Dudley 1.5 is covered at concentrations in the range of 1-150ppm, whilst the north edge of the cloud is over Drum park no. 1 to the north of the site. The cloud trailing the initial large release is much narrower.
3	The large initial cloud has reached the houses north of the site's main entrance on Dudley lane. The concentration of bromine at the centre of the cloud around150ppm. The large initial cloud is 320 metres wide and has a concentration of 1ppm at the edges. Whereas the training cloud is 120 metres wide and has reduced concentrations at the centre.
5	The large initial cloud disperses into the field and reduces in concentration to below 1ppm. The trailing cloud covers the houses north of the main office on Dudley lane at concentrations in the range of 1 to 25 ppm.

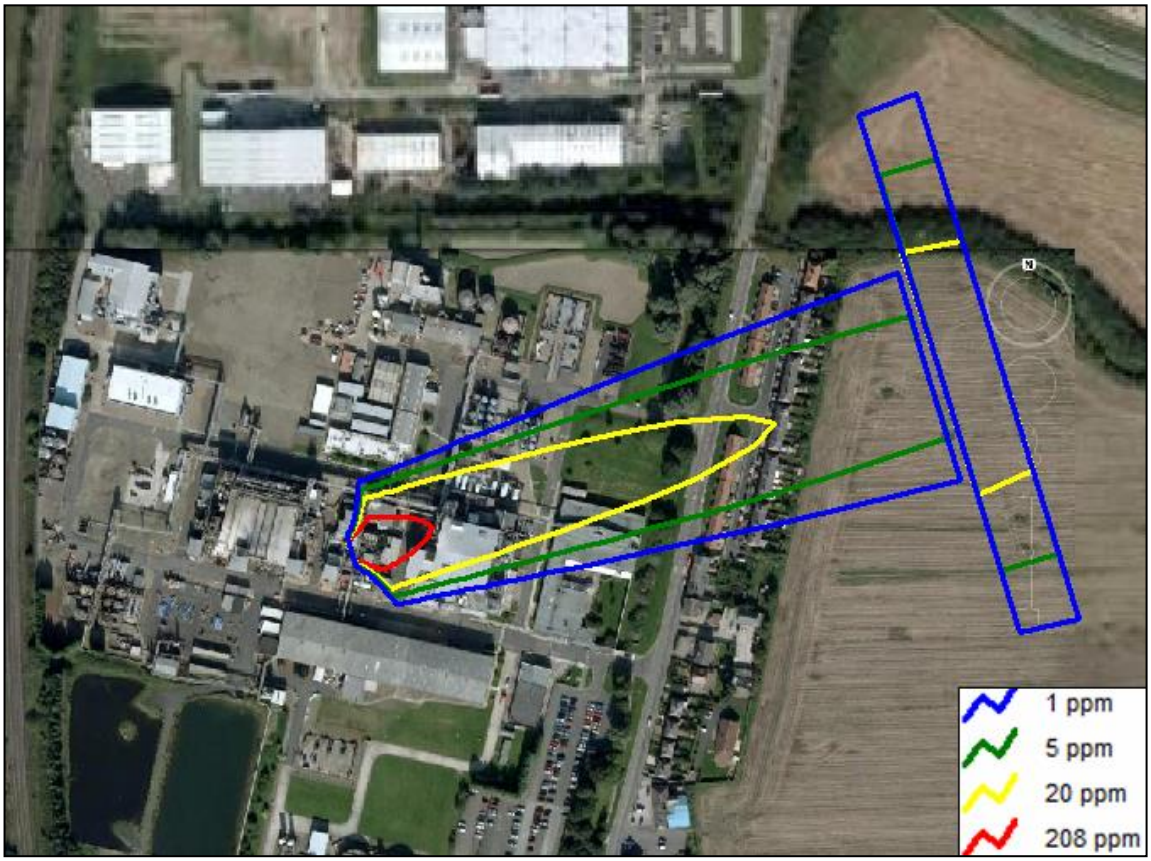
Outdoor lethal toxic 2E Weather; Scenario 15



Maximum concentration footprint 2E Weather; Scenario 15



Map view of Scenario 15 (after 4.5 mins)

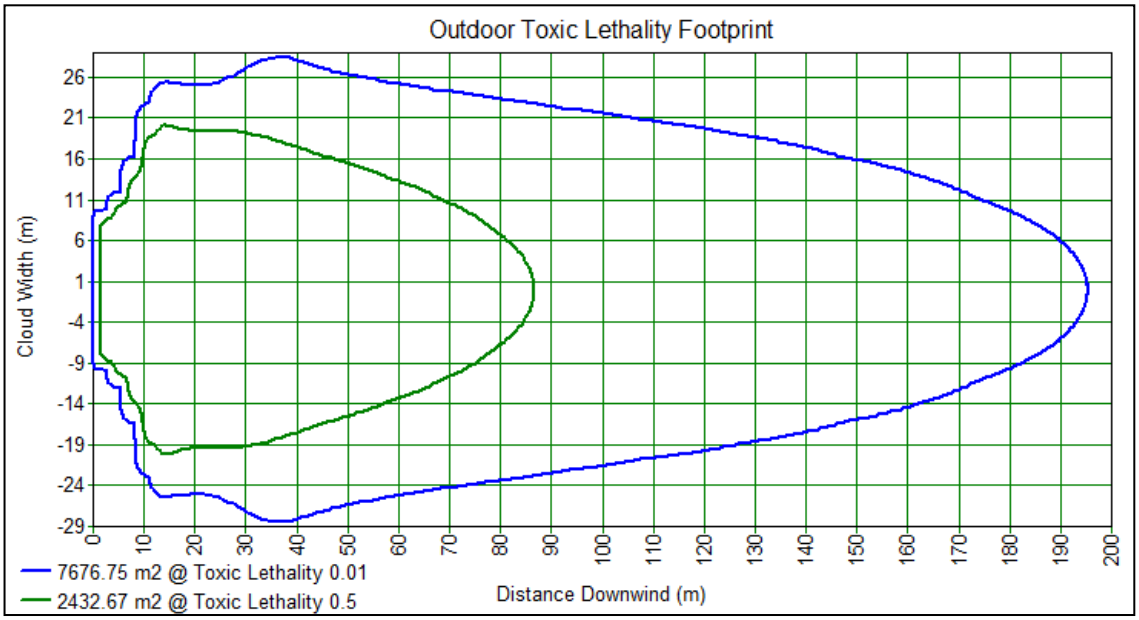


10.16 Scenario 16 Description: Rupture of the pump used to transfer liquid Bromine from the bulk storage tank to the header (A1551)

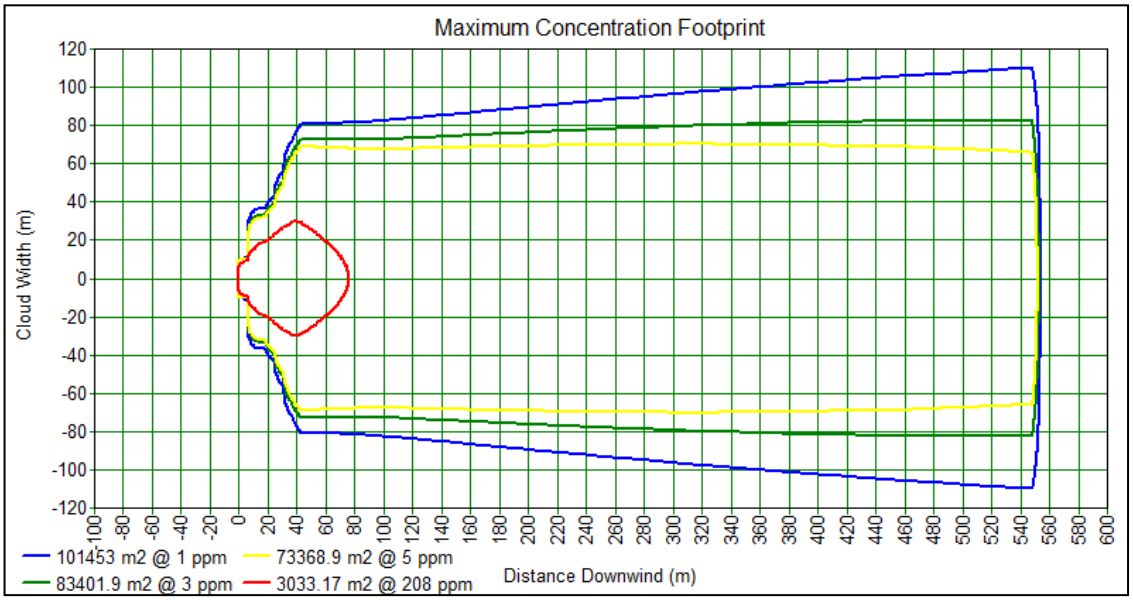
Time after release (mins)	Consequence
1	The release forms a cloud that spans from Dudley 2 to old lime plant where the concentration of Bromine is 1ppm. The centre of the cloud covers the eastern half of the non-flammable drum park and has a concentration of Bromine that is greater than 75ppm.
2	The cloud is blown downwind and the edges of the cloud reach from the east corner of the warehouse to the QC labs where the concentration is 1ppm. The cloud is centred over Dudley 1 at a concentration of 50ppm.
3	The edge of the cloud on the south side has reached the site boundary, just above the site's main entrance at a concentration of 1ppm. The cloud is centred over the main office at a concentration of 30ppm.

4	The cloud front has reached the houses north of the site's main entrance on Dudley lane. The concentration of bromine at the centre of the cloud is 15ppm. The cloud is 180 metres wide and has a concentration of 1ppm at the edges.
7	The cloud begins to reduce in size and concentration and disperses downwind into the fields behind the rows of houses to a concentration below 1ppm.

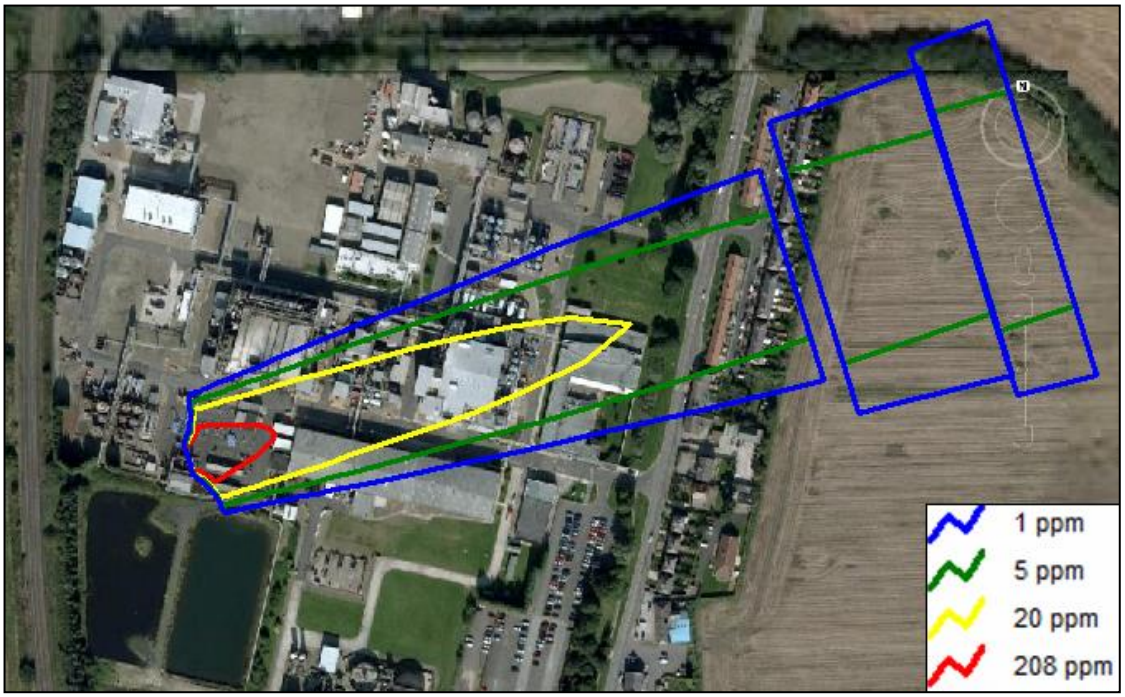
Outdoor lethal toxic 2E Weather; Scenario 16



Maximum concentration footprint 2E Weather; Scenario 16



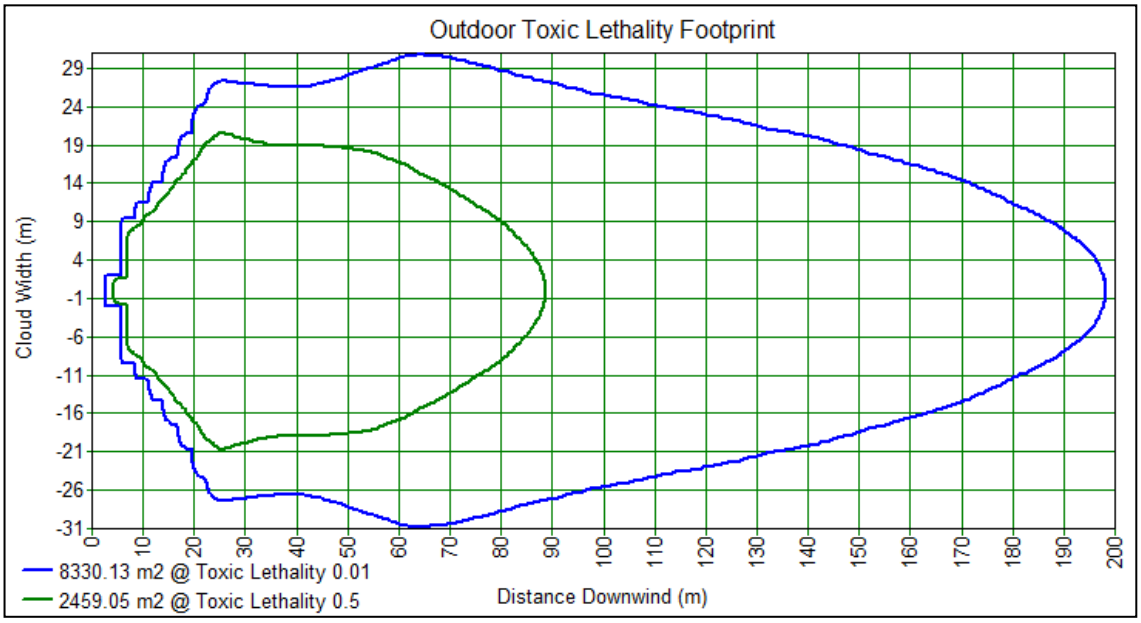
Map view of Scenario 16 (after 7 mins)



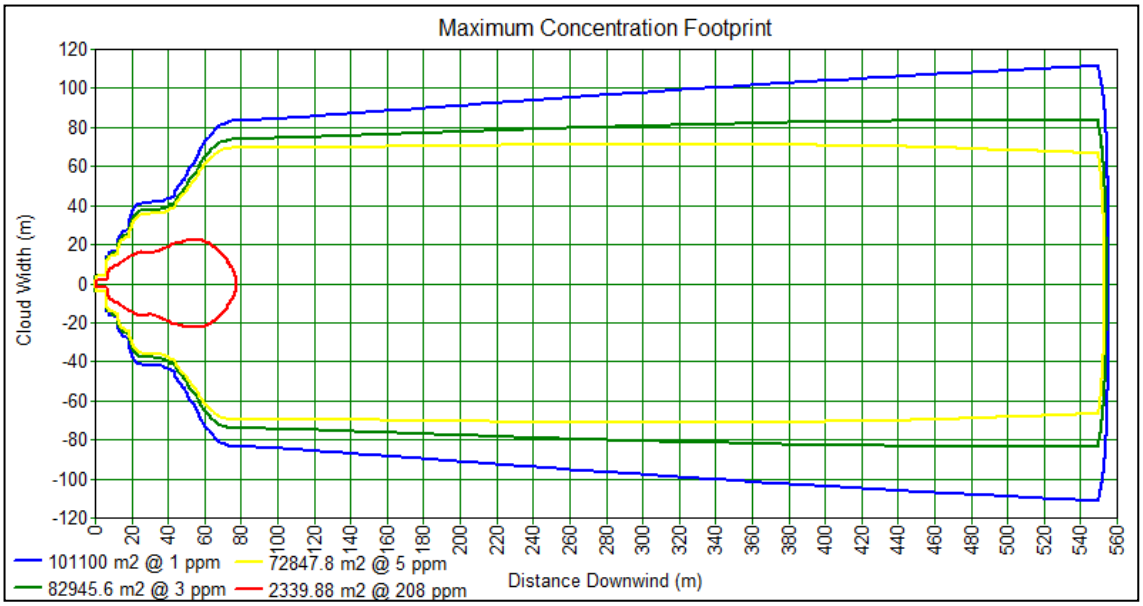
10.17 Scenario 17 Description: Hole in unseen flanges in line between bromine bulk storage tank and header during transfer

Time after release (mins)	Consequence
1	The release forms a cloud that is initially centred over Dudley 1.5 at a concentration greater than 75ppm. The cloud spans from the QC labs to the road between Dudley 1 and the warehouse, where the concentration of bromine is 1ppm.
2	The cloud front disperses downwind and reaches the main office at a concentration of 25ppm. The edge of the cloud to the south has reached the main entrance to the site at a concentration of 1ppm.
4	The cloud front has now reached the first row of houses on Dudley lane, opposite the main office. The maximum concentration at the cloud front is 12ppm.
8	The cloud has slowly increased in size and concentration. The cloud now spans from the site's main entrance, to the north east corner of the site. The concentration at the edges is 1 ppm and a third of the cloud is at concentrations greater than 75ppm.
12	The cloud now begins to reduce in size and concentrations. The majority of houses north of the main entrance on Dudley lane are experiencing concentrations greater than 75ppm as does the area enclosed by Dudley 1.5, Dudley 1 and the main office.

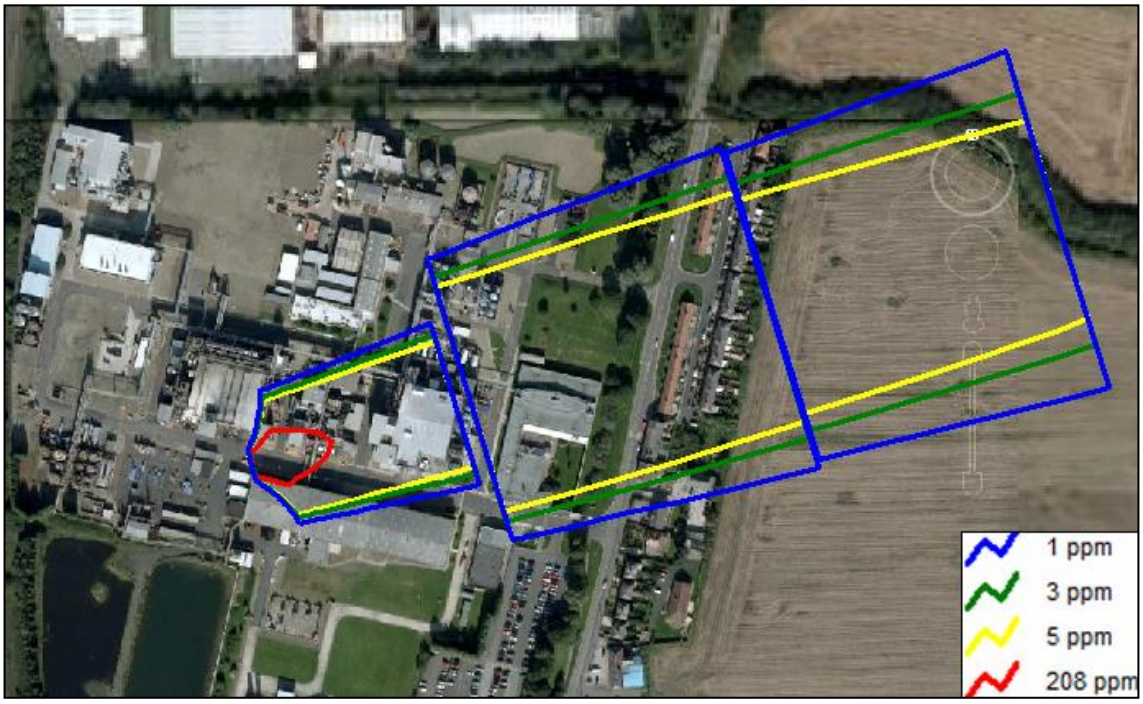
Outdoor lethal toxic 2E Weather; Scenario 17



Maximum concentration footprint 2E Weather; Scenario 17



Map view of Scenario 17 (after 12 mins)

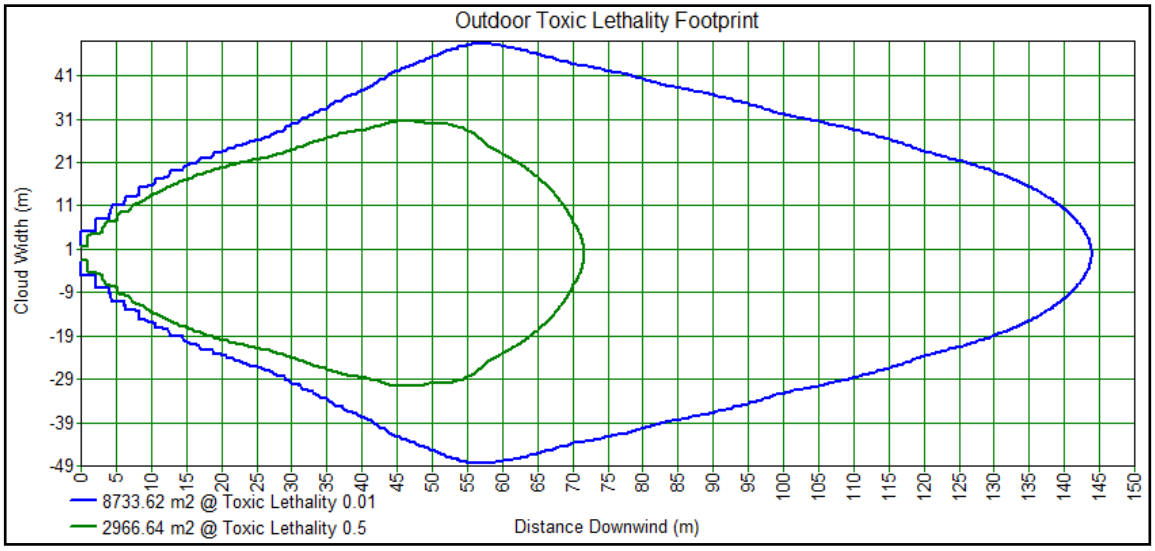


10.18 Scenario 18 Description: Hole in connection on bottom of header tank (A1551)

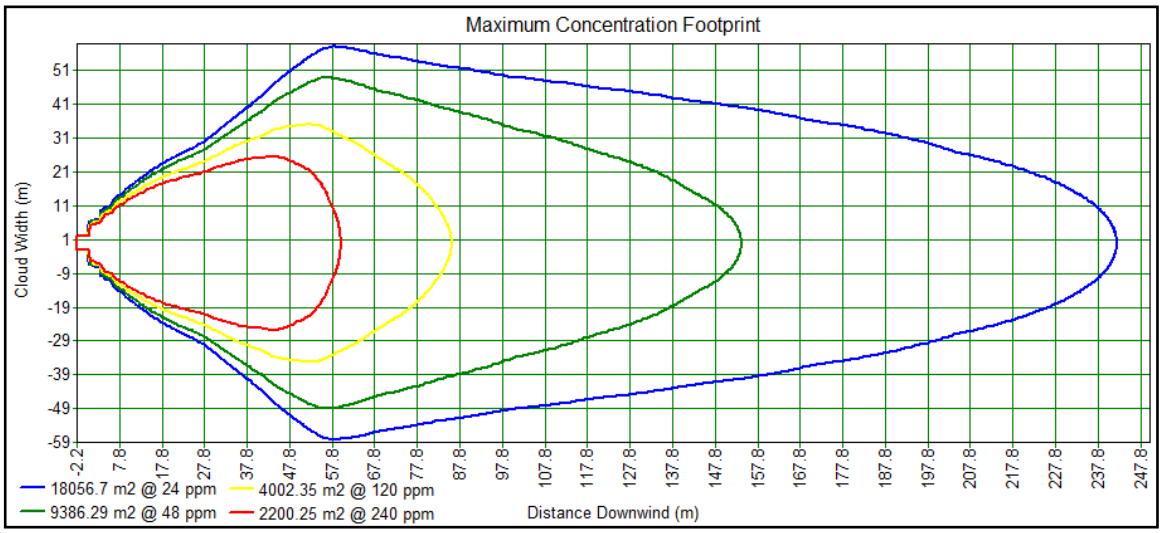
Time after release (mins)	Consequence
1	The release forms a cloud that is initially centred over Dudley 1.5 at a concentration greater than 240ppm. The cloud spans from the engineering workshop to the south-east corner of Dudley 1, where the concentration of bromine is 20ppm.
2	The cloud front disperses downwind and reaches the sites north entrance at a concentration of 25ppm. The edge of the cloud to the south has reached the main entrance to the site at a concentration of 1ppm, and the main office is encompassed by the cloud at a concentration of between 20 and 50ppm.
3	The cloud front has now reached the first row of houses on Dudley lane, opposite the site's north entrance and ceases to grow in size. The maximum concentration at the cloud front is 10ppm. Dudley 1.5 is encompassed by bromine at a concentration of 240 ppm or greater whilst

	Dudley 1 is surrounded by bromine at concentrations between 120 and 240ppm.

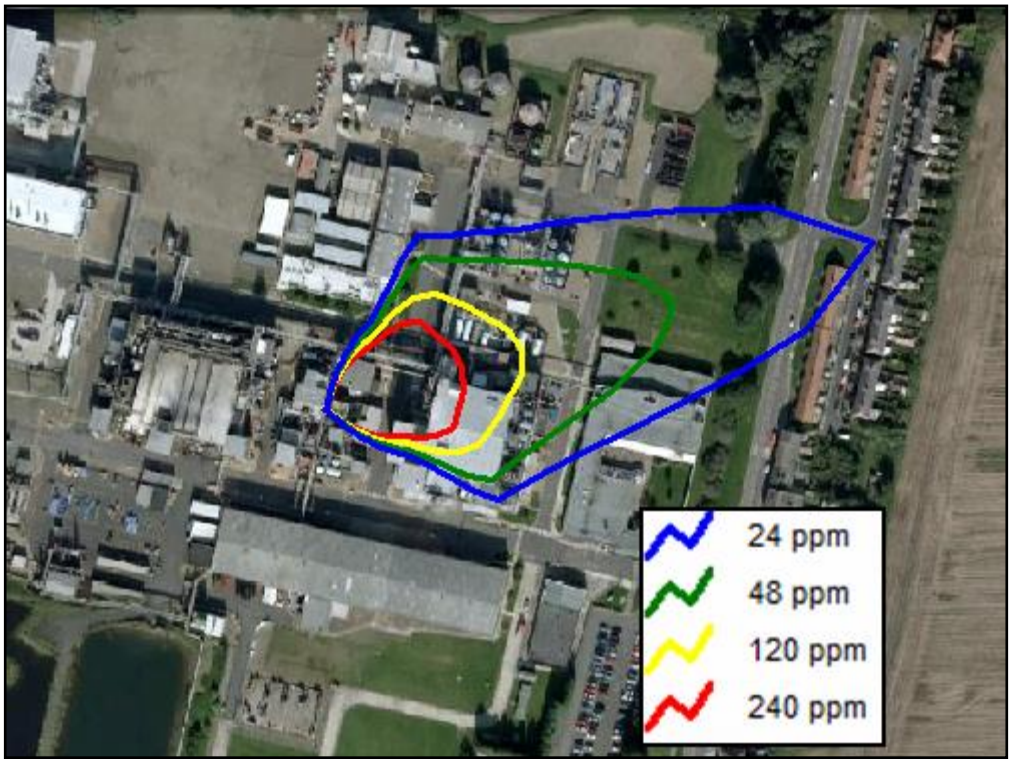
Outdoor lethal toxic 2E Weather; Scenario 18



Maximum concentration footprint 2E Weather; Scenario 18



Map view of Scenario 18 (after 3 mins)



10.19 Scenarios 19 (Hole in connection on top of header tank (A1551)) and 20 (Hole in man-way cover on top of the bromine bulk storage tank)

These scenarios were very small and short lived, and so the Phast Risk model provided no dispersion information.

11.0 REFERENCES

[1] Health and Safety Executive, *Failure Rate and Event Data for use within Risk Assessments*, (2012)

[2] Cox, Lees and Ang, *Classification of Hazardous Locations*, (1990)

[3] DNV, *Process Equipment Leak Frequency Data for use in QRA*, (2013)

[4] Public Health England, Toxicology Department CRCE, *Bromine Toxicological Overview*, (2009)

[5] Health and Safety Executive, *Reducing risks, protecting people – R2P2*, (2001)

[6] Health and Safety Executive, *Guidance on 'as low as reasonably practicable' (ALARP) Decision in Control Of Major Accident Hazards (COMAH),* SPC/Permissioning/12, Issue: Jul 2002, Review Jul 2004

12.0 DOCUMENT REVISION HISTORY

DATE	SEQUENTIAL CODE	ALTERATIONS, ADDITIONS, OMISSIONS
	PH001 Rev 0 – Dudley PHAST	

APPENDIX 2 – List of WasteModel Variables

Variable Name	Sub Name	Description
sub1flowdrum1	amp	Substance 1 Drum 1 inlet flow characteristics
	period	
	pulse	
sub2flowdrum1	amp	Substance 2 Drum 1 inlet flow characteristics
	period	
	pulse	
sub3flowdrum1	amp	Substance 3 Drum 1 inlet flow characteristics
	period	
	pulse	
sub4flowdrum1	amp	Substance 4 Drum 1 inlet flow characteristics
	period	
	pulse	
sub5flowdrum1	amp	Substance 5 Drum 1 inlet flow characteristics
	period	
	pulse	
	sub1coddrum1	Substance 1 Drum 1 inlet COD concentration
	sub2coddrum1	Substance 2 Drum 1 inlet COD concentration
	sub3coddrum1	Substance 3 Drum 1 inlet COD concentration
	sub4coddrum1	Substance 4 Drum 1 inlet COD concentration
	sub5coddrum1	Substance 5 Drum 1 inlet COD concentration
	sub1concdrum1	Substance 1 Drum 1 inlet Specific concentration
	sub2concdrum1	Substance 2 Drum 1 inlet Specific concentration
	sub3concdrum1	Substance 3 Drum 1 inlet Specific concentration
	sub4concdrum1	Substance 4 Drum 1 inlet Specific concentration
	sub5concdrum1	Substance 5 Drum 1 inlet Specific concentration
sub1flowdrum2	amp	Substance 1 Drum 2 inlet flow characteristics
	period	
	pulse	
sub2flowdrum2	amp	Substance 2 Drum 2 inlet flow characteristics
	period	
	pulse	
sub3flowdrum2	amp	Substance 3 Drum 2 inlet flow characteristics
	period	
	pulse	
sub4flowdrum2	amp	Substance 4 Drum 2 inlet flow characteristics
	period	
	pulse	
sub5flowdrum2	amp	Substance 5 Drum 2 inlet flow characteristics
	period	
	pulse	
	sub1coddrum2	Substance 1 Drum 1 inlet COD concentration
	sub2coddrum2	Substance 2 Drum 1 inlet COD concentration

	sub3coddrum2	Substance 3 Drum 1 inlet COD concentration
	sub4coddrum2	Substance 4 Drum 1 inlet COD concentration
	sub5coddrum2	Substance 5 Drum 1 inlet COD concentration
	sub1concdrum2	Substance 1 Drum 1 inlet Specific concentration
	sub2concdrum2	Substance 2 Drum 1 inlet Specific concentration
	sub3concdrum2	Substance 3 Drum 1 inlet Specific concentration
	sub4concdrum2	Substance 4 Drum 1 inlet Specific concentration
	sub5concdrum2	Substance 5 Drum 1 inlet Specific concentration
	b3065area	Tank B3065 Cross sectional area
	b3066area	Tank B3066 Cross sectional area
	d1pitarea	D1 Pit Cross sectional area
	d2pitarea	D2 Pit Cross sectional area
	pcarea	Primary Clarifier Cross sectional area
	scarea	Secondary Clarifier Cross sectional area
	biorarea	Bioreactor Cross sectional area
	minlevd1pit	Minimum D1 Pit Level for Pump Level Control
	minlevd2pit	Minimum D2 Pit Level for Pump Level Control
	pumpspeedd1	D1 Outlet Pump Flowrate
	pumpspeedd2	D2 Outlet Pump Flowrate
	b3065initvol	Initial Volume of Tank B3065
	b3066initvol	Initial Volume of Tank B3066
	pcinitvol	Initial Volume of Primary Clarifier
	bioinitvol	Initial Volume of Bioreactor
	scinitvol	Initial Volume of Secondary Clarifier
	b3065initcod	Tank B3065 Initial COD Concentration
	b3066initcod	Tank B3066 Initial COD Concentration
	pcinitcod	Primary Clarifier Initial COD Concentration
	bioinitcod	Bioreactor Initial COD Concentration
	scinitcod	Secondary Clarifier Initial COD Concentration
	b3065initconcsub1	Initial Concetration of Substance 1 in B3065
	b3065initconcsub2	Initial Concetration of Substance 2 in B3065
	b3065initconcsub3	Initial Concetration of Substance 3 in B3065
	b3065initconcsub4	Initial Concetration of Substance 4 in B3065
	b3065initconcsub5	Initial Concetration of Substance 5 in B3065
	b3066initconcsub1	Initial Concetration of Substance 1 in B3066
	b3066initconcsub2	Initial Concetration of Substance 2 in B3066
	b3066initconcsub3	Initial Concetration of Substance 3 in B3066
	b3066initconcsub4	Initial Concetration of Substance 4 in B3066
	b3066initconcsub5	Initial Concetration of Substance 5 in B3066
	pcinitconcsub1	Initial Concetration of Substance 1 in Primary Clarifier
	pcinitconcsub2	Initial Concetration of Substance 2 in Primary Clarifier
	pcinitconcsub3	Initial Concetration of Substance 3 in Primary Clarifier
	pcinitconcsub4	Initial Concetration of Substance 4 in Primary Clarifier

	pcinitconcsub5	Initial Concetration of Substance 5 in Primary Clarifier
	scinitconcsub1	Initial Concetration of Substance 1 Secondary Clarifier
	scinitconcsub2	Initial Concetration of Substance 2 Secondary Clarifier
	scinitconcsub3	Initial Concetration of Substance 3 Secondary Clarifier
	scinitconcsub4	Initial Concetration of Substance 4 Secondary Clarifier
	scinitconcsub5	Initial Concetration of Substance 5 Secondary Clarifier
	bioinitconcsub1	Initial Concetration of Substance 1 in Bioreactor
	bioinitconcsub2	Initial Concetration of Substance 2 in Bioreactor
	bioinitconcsub3	Initial Concetration of Substance 3 in Bioreactor
	bioinitconcsub4	Initial Concetration of Substance 4 in Bioreactor
	bioinitconcsub5	Initial Concetration of Substance 5 in Bioreactor
	d1valve	D1 Pit Valve Position
	d2valve	D2 Pit Valve Position
	tankervalve	Tanker Filling Valve Position
	drum1valvesub1	Drum 1 Filling Valve Position for Substance 1
	pcbypassvalve	Primary Clarifier Bypass Valve Position
	drum1valvesub2	Drum 1 Filling Valve Position for Substance 2
	drum1valvesub3	Drum 1 Filling Valve Position for Substance 3
	drum1valvesub4	Drum 1 Filling Valve Position for Substance 4
	drum1valvesub5	Drum 1 Filling Valve Position for Substance 5
tankerflow	amp	Tanker Flowrate Characteristics
	period	
	pulse	
	tankercod	
	d1flow	
	d1cod	
sub1flowd1	amp	Dudley 1 Pit Flow Characteristics for Substance 1 Flowrate Characteristics
	period	
	pulse	
sub2flowd1	amp	Dudley 1 Pit Flow Characteristics for Substance 2 Flowrate Characteristics
	period	
	pulse	
sub3flowd1	amp	Dudley 1 Pit Flow Characteristics for Substance 3 Flowrate Characteristics
	period	
	pulse	
sub4flowd1	amp	Dudley 1 Pit Flow Characteristics for Substance 4 Flowrate Characteristics
	period	
	pulse	

sub5flowd1	amp	Dudley 1 Pit Flow Characteristics for Substance 5 Flowrate Characteristics
	period	
	pulse	
	sub1codd1	Substance 1 Flow COD Concentration entering D1 Pit
	sub2codd1	Substance 2 Flow COD Concentration entering D1 Pit
	sub3codd1	Substance 3 Flow COD Concentration entering D1 Pit
	sub4codd1	Substance 4 Flow COD Concentration entering D1 Pit
	sub5codd1	Substance 5 Flow COD Concentration entering D1 Pit
	sub1concd1	Substance 1 Flow Concentration entering D1 Pit
	sub2concd1	Substance 2 Flow Concentration entering D1 Pit
	sub3concd1	Substance 3 Flow Concentration entering D1 Pit
	sub4concd1	Substance 4 Flow Concentration entering D1 Pit
	sub5concd1	Substance 5 Flow Concentration entering D1 Pit
	d1initvol	D1 Pit Initial Volume
	d1initcod	D1 Pit Initial COD Concentration
	d1initsub1	D1 Pit Initial Mass of Substance 1
	d1initsub2	D1 Pit Initial Mass of Substance 1
	d1initsub3	D1 Pit Initial Mass of Substance 1
	d1initsub4	D1 Pit Initial Mass of Substance 1
	d1initsub5	D1 Pit Initial Mass of Substance 1
	d2flow	D2 Pit Initial Flowrate
	d2cod	D2 Pit Initial COD Concentration
sub1flowd2	amp	Dudley 2 Pit Flow Characteristics for Substance 1 Flowrate Characteristics
	period	
	pulse	
sub2flowd2	amp	Dudley 2 Pit Flow Characteristics for Substance 2 Flowrate Characteristics
	period	
	pulse	
sub3flowd2	amp	Dudley 2 Pit Flow Characteristics for Substance 3 Flowrate Characteristics
	period	
	pulse	
sub4flowd2	amp	Dudley 2 Pit Flow Characteristics for Substance 4 Flowrate Characteristics
	period	
	pulse	
sub5flowd2	amp	Dudley 2 Pit Flow Characteristics for Substance 5 Flowrate Characteristics
	period	
	pulse	
	sub1codd2	Substance 1 Flow COD Concentration entering D2 Pit

	sub2codd2	Substance 2 Flow COD Concentration entering D2 Pit
	sub3codd2	Substance 3 Flow COD Concentration entering D2 Pit
	sub4codd2	Substance 4 Flow COD Concentration entering D2 Pit
	sub5codd2	Substance 5 Flow COD Concentration entering D2 Pit
	sub1concd2	Substance 1 Flow Concentration entering D2 Pit
	sub2concd2	Substance 2 Flow Concentration entering D2 Pit
	sub3concd2	Substance 3 Flow Concentration entering D2 Pit
	sub4concd2	Substance 4 Flow Concentration entering D2 Pit
	sub5concd2	Substance 5 Flow Concentration entering D2 Pit
	d2initvol	D2 Pit Initial Volume
	d2initcod	D2 Pit Initial COD Concentration
	d2initsub1	D2 Pit Initial Mass of Substance 1
	d2initsub2	D2 Pit Initial Mass of Substance 1
	d2initsub3	D2 Pit Initial Mass of Substance 1
	d2initsub4	D2 Pit Initial Mass of Substance 1
	d2initsub5	D2 Pit Initial Mass of Substance 1
	d1pitgain	D1 Pit Gain
	d1relayswitchon	D1 Pit Level Switch High Activate
	d1relayswitchoff	D1 Pit Level Switch Low Activate
	d2pitgain	D2 Pit Gain
	d2relayswitchon	D2 Pit Level Switch High Activate
	d2relayswitchoff	D2 Pit Level Switch Low Activate
	b3065gain	B3065 Gain
	b3066gain	B3066 Gain
	pcgain	Primary Clarifier Gain
	biorgain	Bioreactor Gain
	scgain	Secondary Clarifier Gain
	biofactorcod	Biological Treatment Efficiency of COD
	biofactorsub1	Biological Treatment Efficiency of Substance 1
	biofactorsub2	Biological Treatment Efficiency of Substance 2
	biofactorsub3	Biological Treatment Efficiency of Substance 3
	biofactorsub4	Biological Treatment Efficiency of Substance 4
	biofactorsub5	Biological Treatment Efficiency of Substance 5
	howden	Dilution Factor in Howden Treatment Works
	tyne	Dilution Factor from Howden to Tyne River
Drum1	flowstartsub1	Start Time for Substance 1 Flow in Drum 1 Inlet
	flowstartsub2	Start Time for Substance 2 Flow in Drum 1 Inlet
	flowstartsub3	Start Time for Substance 3 Flow in Drum 1 Inlet
	flowstartsub4	Start Time for Substance 4 Flow in Drum 1 Inlet
	flowstartsub5	Start Time for Substance 5 Flow in Drum 1 Inlet
	flowstopsub1	Stop Time for Substance 1 Flow in Drum 1 Inlet
	flowstopsub2	Stop Time for Substance 2 Flow in Drum 1 Inlet
	flowstopsub3	Stop Time for Substance 3 Flow in Drum 1 Inlet
	flowstopsub4	Stop Time for Substance 4 Flow in Drum 1 Inlet

	flowstopsub5	Stop Time for Substance 5 Flow in Drum 1 Inlet
Drum2	flowstartsub1	Start Time for Substance 1 Flow in Drum 2 Inlet
	flowstartsub2	Start Time for Substance 2 Flow in Drum 2 Inlet
	flowstartsub3	Start Time for Substance 3 Flow in Drum 2 Inlet
	flowstartsub4	Start Time for Substance 4 Flow in Drum 2 Inlet
	flowstartsub5	Start Time for Substance 5 Flow in Drum 2 Inlet
	flowstopsub1	Stop Time for Substance 1 Flow in Drum 2 Inlet
	flowstopsub2	Stop Time for Substance 2 Flow in Drum 2 Inlet
	flowstopsub3	Stop Time for Substance 3 Flow in Drum 2 Inlet
	flowstopsub4	Stop Time for Substance 4 Flow in Drum 2 Inlet
	flowstopsub5	Stop Time for Substance 5 Flow in Drum 2 Inlet
D1pit	flowstartsub1	Start Time for Substance 1 Flow in D1 Pit Inlet
	flowstartsub2	Start Time for Substance 2 Flow in D1 Pit Inlet
	flowstartsub3	Start Time for Substance 3 Flow in D1 Pit Inlet
	flowstartsub4	Start Time for Substance 4 Flow in D1 Pit Inlet
	flowstartsub5	Start Time for Substance 5 Flow in D1 Pit Inlet
	flowstopsub1	Stop Time for Substance 1 Flow in D1 Pit Inlet
	flowstopsub2	Stop Time for Substance 2 Flow in D1 Pit Inlet
	flowstopsub3	Stop Time for Substance 3 Flow in D1 Pit Inlet
	flowstopsub4	Stop Time for Substance 4 Flow in D1 Pit Inlet
	flowstopsub5	Stop Time for Substance 5 Flow in D1 Pit Inlet
D2pit	flowstartsub1	Start Time for Substance 1 Flow in D2 Pit Inlet
	flowstartsub2	Start Time for Substance 2 Flow in D2 Pit Inlet
	flowstartsub3	Start Time for Substance 3 Flow in D2 Pit Inlet
	flowstartsub4	Start Time for Substance 4 Flow in D2 Pit Inlet
	flowstartsub5	Start Time for Substance 5 Flow in D2 Pit Inlet
	flowstopsub1	Stop Time for Substance 1 Flow in D2 Pit Inlet
	flowstopsub2	Stop Time for Substance 2 Flow in D2 Pit Inlet
	flowstopsub3	Stop Time for Substance 3 Flow in D2 Pit Inlet
	flowstopsub4	Stop Time for Substance 4 Flow in D2 Pit Inlet
	flowstopsub5	Stop Time for Substance 5 Flow in D2 Pit Inlet