Off-gas Nitrous Oxide monitoring for nitrification aeration control

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Publication Date:
2009

DOI:
https://doi.org/10.26190/unsworks/20284

OFF-GAS NITROUS OXIDE MONITORING FOR NITRIFICATION AERATION CONTROL

By

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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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July 2009

Abstract

Effective control of nitrification processes employed at municipal wastewater treatment plants is essential for maintaining process reliability and minimizing environmental impacts and operating costs. While a range of process control strategies are available, they share a dependence on invasive liquid phase monitoring and are based on a periphery understanding of the metabolic status of the processes being controlled. Utilization of off-gas nitrous oxide (N_2O) monitoring as a real-time indicator of the process metabolic status is a novel process control concept with the potential to address these concerns.

This thesis details the development and evaluation of an off-gas N_2O stress response based control technique. Examination of the stress response relationship demonstrated that it met the majority of the criteria of interest for process control. A simple feedback aeration control strategy was developed and evaluated through process simulation to determine the feasibility of implementation, cost effectiveness and associated environmental benefits.

The off-gas N_2O based control strategy provided better matching between aeration supply and metabolic demand, allowing the process to be maintained at the desired operating setpoints and avert nitrification failure. Performance was demonstrated to be similar to dissolved oxygen based feedback aeration control, although slightly more efficient at reduced dissolved oxygen concentrations. A technical, economic and environmental evaluation indicated that aeration control based on non-invasive off-gas N_2O monitoring is technically feasible and has the potential to offer significant environmental and economic benefits including reductions in operating costs and process capital investment, as well as improved effluent compliance and reductions in emissions of gaseous pollutants including greenhouse gases.

Overall, while off-gas N_2O monitoring based aeration control techniques have the potential to provide significant economic and environmental benefits, a number of research questions remain to be answered. Future work in the form of long-term field trials is required to address these issues and allow quantification of economic and environmental benefits.

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Acknowledgements

Over the course of my candidature, I have had the privilege of meeting and working with many fantastic people. I would like to express my gratitude to all of them for their part in making this time an interesting and enjoyable experience.

I would particularly like to take this opportunity to thank my supervisor Professor Richard Stuetz. In addition to providing the opportunity and freedom to conduct an interesting research progam, his support, guidance and opinions were highly valued. Furthermore, I would like to thank him for his patience during this adventure (which is probably the appropriate term for a PhD involving a lab scale activated sludge processes).

Many thanks to my co-supervisor Dr. William Peirson for his guidance and supervision during the process modelling component of this work. Thanks are extended to the many staff members of the School of Civil and Environmental Engineering for their assistance during my candidature. I would also like to express my gratitude to Dr. Gautam Chattopadhyay, Paul Gwynne, and Kelvin Ong for their invaluable advice and assistance with technical matters, as well as for the many enjoyable conversations.

I would like to acknowledge the organizations that have provided funding support for this work, namely the Australian Research Council (DP0558029) "Removal of Potential Impact of Pharmaceutical Active Compounds during Wastewater Treatment", the Australian Government Department of Education, Science and Training, the University of New South Wales, and the Faculty of Engineering Dean's Awards.

Finally, though definitely far from least, a special thanks to friends and family who, despite the great distances, have been with me throughout this journey. I would like thank my mom and my grandparents for their support, love and faith in me, and for making me the person I am today.

In memory of James Stanton Vibert

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Nomenclature

General Abbreviations

Anammox	anaerobic ammonium oxidation
ANN	artificial neural network
AOB	ammonia oxidizing bacteria
ASM	activated sludge model
AUD	Australian dollars
BNR	biological nitrogen removal
BOD	biochemical oxygen demand
CANON	completely autotrophic removal over nitrite
COD	chemical oxygen demand
CSTR	continuous stirred tank reactor
FA	free ammonia
FB	feedback
FF	feedforward
FNA	free nitrous acid
HRT	hydraulic retention time
IR	infrared
ISE	ion selective electrode
MPC	model predictive control
NDIR	non-dispersive infrared
NOB	nitrite oxidizing bacteria
OLAND	oxygen limited nitrification and denitrification
pe	population equivalent
PBN	particulate biodegradable organic nitrogen
PI	proportional integral
RBCOD	readily biodegradable organic carbon
SBCOD	slowly biodegradable organic carbon
SBN	soluble biodegradable organic nitrogen
SBR	sequencing batch reactor
SHARON	single reactor system for high rate ammonia removal over nitrite
SND	simultaneous nitrification and denitrification
SRT	sludge retention time

TOC	total organic carbon
TSS	total suspended solids
UV	ultraviolet

Liquid Phase Models (ASM1, ASM1-Nowak, ASM3, ASMN, Reduced Model)

b_A	autotrophic biomass decay coefficient (d^{-1})
$b_{A,NO}$	autotrophic biomass anoxic endogenous respiration rate (d^{-1})
$b_{A,O}$	autotrophic biomass aerobic endogenous respiration rate (d^{-1})
b_H	heterotrophic biomass decay coefficient (d^{-1})
$b_{H,NO}$	heterotrophic biomass anoxic endogenous respiration rate (d^{-1})
$b_{H,O}$	heterotrophic biomass aerobic endogenous respiration rate (d^{-1})
$b_{L,A1}$	AOB decay coefficient (d^{-1})
$b_{L,A2}$	NOB decay coefficient (d^{-1})
$b_{L,H}$	heterotrophic biomass decay coefficient (d^{-1})
$b_{STO,NO}$	storage product anoxic endogenous respiration rate (d^{-1})
$b_{STO,O}$	storage product aerobic endogenous respiration rate (d^{-1})
COD_I	influent total COD (mg COD•L^{-1})
f_p	fraction biomass degrading to particulate products
f'_D	fraction biomass degrading to debris
f_I	fraction biomass degrading to intert products
$i_{N/XB}$	active biomass nitrogen content (mg N•mg COD_{XB}^{-1})
$i_{N/XD}$	biomass debris nitrogen content (mg N•mg COD_{XD}^{-1})
i_{XB}	biomass nitrogen content (g N/g COD_{XBM})
i_{XP}	particulate product nitrogen content (g N•g COD_{XP}^{-1})
K_1	aeration calibration parameter (d^{-1})
K_2	autotrophic oxygen consumption (mg DO•L^{-1}•d^{-1})
K_3	autotrophic ammonium consumption (mg NH_4^+-N•L^{-1}•d^{-1})
K_4	ammonification parameter (mg NH_4^+-N•mg COD^{-1}•d^{-1})
k_a	ammonification rate constant (m^3•g X_H^{-1}•d^{-1})
$K_{A,NH}$	autotrophic bacteria ammonium half-saturation constant (mg N•L^{-1})
$K_{A,NO}$	autotrophic bacteria nitrate half-saturation constant (mg N•L^{-1})
$K_{A,O}$	autotroph oxygen half-saturation constant (mg DO•L^{-1})
K_{FA}	FA half-saturation constant (mg N•L^{-1})
K_{FNA}	FNA half-saturation constant (mg N•L^{-1})

k_H	hydrolysis rate constant (g X_S•g X_H^{-1}•d^{-1})
K_{I9FA}	AOB growth FA inhibition coefficient (mg N•L^{-1})
K_{I9FNA}	AOB growth FNA inhibition coefficient (mg N•L^{-1})
K_{I10FA}	NOB growth FA inhibition coefficient (mg N•L^{-1})
K_{I10FNA}	NOB growth FNA inhibition coefficient (mg N•L^{-1})
kLa	aeration mass transfer coefficient (d^{-1})
K_{NH}	autotrophic biomass ammonium half-saturation coefficient (mg NH_4^+-L^{-1})
$K_{NH,M}$	AOB ammonium half-saturation constant (mg N•L^{-1})
K_{NO}	nitrate half-saturation constant (mg N•L^{-1})
K_O	heterotroph oxygen half-saturation constant (mg DO•L^{-1})
$K_{NO2,N}$	NOB nitrite half-saturation constant (mg N•L^{-1})
K_{NO3}	heterotroph nitrate half-saturation constant (mg N•L^{-1})
$K_{O,A}$	autotrophic biomass oxygen half-saturation coefficient (mg DO•L^{-1})
$K_{O,A1}$	AOB oxygen half-saturation constant (mg DO•L^{-1})
$K_{O,A2}$	NOB oxygen half-saturation constant (mg DO•L^{-1})
$K_{O,H}$	heterotrophic biomass oxygen half-saturation coefficient (mg DO•L^{-1})
$K_{O,H1}$	heterotroph oxygen half-saturation constant (mg DO•L^{-1})
$K_{O,M}$	AOB oxygen half-saturation constant (mg N•L^{-1})
$K_{O,N}$	NOB oxygen half-saturation constant (mg N•L^{-1})
K_S	substrate half-saturation constant (mg COD•L^{-1})
$K_{S,1}$	substrate half-saturation constant (mg COD•L^{-1})
k_{STO}	storage rate constant (g SS•g XH^{-1}•d^{-1})
K_{STO}	storage product half-saturation constant (g X_{STO}•gX_S^{-1})
K_X	hydrolysis half-saturation constant (g X_S•g X_H^{-1})
η_g	heterotrophic growth rate correction factor for anoxic conditions
η_h	hydrolysis correction factor for anoxic conditions
η_{NO}	anoxic reduction factor
Q_{inf}	influent flow (L•h^{-1})
S_{ALK}	alkalinity (mole HCO_3^-•L^{-1})
S_{FNA}	FNA concentration (mg N•L^{-1})
S_I	inert soluble COD concentration (mg COD•L^{-1})

S_{N2}	dinitrogen concentration (mg N•L^{-1})
S_{ND}	soluble biodegradable organic nitrogen concentration (mg N•L^{-1})
S_{NH}	ammonia concentration (mg NH_4^+-N•L^{-1})
$S_{NH,I}$	influent ammonia (mg NH_3-N•L^{-1})
S_{NS}	soluble biodegradable organic nitrogen concentration (mg N•L^{-1})
S_{NO}	nitrate + nitrite concentration (mg N•L^{-1})
S_{NO2}	nitrite concentration (mg NO_2^-•L^{-1})
S_{NO3}	nitrate concentration (mg NO_3^-•L^{-1})
S_O	dissolved oxygen concentration (mg DO•L^{-1})
$S_{O,S}$	dissolved oxygen saturation concentration (mg DO•L^{-1})
S_S	readily biodegradable COD concentration (mg COD•L^{-1})
$S_{S,I}$	influent readily biodegradable COD (mg COD•L^{-1})
∑NOx	nitrate + nitrite concentration (mg N•L^{-1})
t	ASM3 stoichiometric factor
μ_A	autotrophic biomass maximum specific growth rate (d^{-1})
μ_{A1}	AOB maximum growth rate (d^{-1})
μ_{A2}	NOB maximum growth rate (d^{-1})
μ_H	heterotrophic biomass maximum specific growth rate (d^{-1})
μ_M	AOB maximum growth rate (d^{-1})
μ_N	NOB maximum growth rate (d^{-1})
x	ASM3 stoichiometric factor
X_A	autotrophic biomass concentration (mg COD•L^{-1})
$X_{B,A1}$	AOB concentration (mg COD•L^{-1})
$X_{B,A2}$	NOB concentration (mg COD•L^{-1})
$X_{B,H}$	heterotrophic biomass concentration (mg COD•L^{-1})
X_H	heterotrophic biomass concentration (mg COD•L^{-1})
X_I	inert particulate COD concentration (mg COD•L^{-1})
X_M	AOB biomass concentration (mg COD•L^{-1})
X_N	NOB biomass concentration (mg COD•L^{-1})
X_{ND}	particulate biodegradable organic nitrogen concentration (mg N•L^{-1})
X_{NS}	particulate biodegradable organic nitrogen concentration (mg N•L^{-1})
X_P	particulate produce concentration (mg COD•L^{-1})

X_S	slowly biodegradable COD concentration (mg COD•L^{-1})
$X_{S,I}$	influent slowly biodegradable COD (mg COD•L^{-1})
X_{STO}	internal storage product concentration (mg COD•L^{-1})
X_{TS}	total suspended solids (mg TSS•L^{-1})
y	ASM3 stoichiometric factor
Y_A	autotrophic biomass yield (mg COD•mg COD^{-1})
Y_{A1}	AOB yield (mg COD_{XA1}•mg N^{-1})
Y_{A2}	NOB yield (mg COD_{XA2}•mg N^{-1})
Y_H	heterotrophic biomass yield (mg COD•mg COD^{-1})
$Y_{H,NO}$	heterotrophic yield, anoxic conditions (g X_H•gX_{STO}^{-1})
$Y_{H,O}$	heterotrophic yield, aerobic conditions (g X_H•gX_{STO}^{-1})
Y_M	AOB yield (g COD_{XM}•g N_{SNH}^{-1})
Y_N	NOB yield (g COD_{XN}•g N_{SNO2}^{-1})
$Y_{STO,NO}$	storage product yield, anoxic conditions (g X_{STO}•gS_S^{-1})
$Y_{STO,O}$	storage product yield, aerobic conditions (g X_{STO}•gS_S^{-1})
z	ASM3 stoichiometric factor

Off-gas N2O Models

C_{N2O}	off-gas N_2O concentration (ppm N_2O)
$K_{DO,1}$	off-gas N_2O model #2 DO proportionality parameter (ppm N_2O)
$K_{DO,2}$	off-gas N_2O model #2 switching parameter (mg DO•L^{-1})
$K_{FNA,1}$	off-gas N_2O model #2 FNA proportionality parameter (ppm N_2O•L•mg N^{-1})
$K_{N2O,1}$	off-gas N_2O model #1 proportionality parameter (ppm N_2O)
$K_{N2O,2}$	off-gas N_2O model #1 switching parameter (mg DO•L^{-1})
$K_{N2O,3}$	off-gas N_2O model #1 off-set parameter (dimensionless)
SFNA	liquid phase free nitrous acid concentration (mg N•L^{-1})
SO	liquid phase dissolved oxygen concentration (mg DO•L^{-1})

Sensitivity analsyis

$S_{i,j}$	normalized sensitivity coefficient
X_i	manipulated process parameter
Y_j	state variable

Chapter 1 Introduction

The effective control of nitrification processes employed at municipal wastewater treatment plants is essential for maintaining process reliability, as well as minimizing the associated environmental impacts and operating costs. A range of process control strategies are available and have been implemented for nitrification processes. However, these strategies share a dependence on invasive liquid phase monitoring (with the associated instrumentation limitations), and are based on a periphery understanding of the metabolic status of the processes being controlled.

Utilization of off-gas nitrous oxide (N_2O) monitoring as a real-time indicator of the process metabolic status is a novel process control concept for activated sludge nitrification processes that has the potential to deliver non-invasive control and improve aeration efficiency. This thesis focuses on the development of a control system utilizing this concept, and assesses the technological and economical feasibility as well as the environmental benefits associated with its implementation.

A discussion of the rationale for this research project, a brief overview of the historical development of the concepts utilized, an overview of the research objectives, and the thesis structure are presented in the following sections.

1.1 Project Rationale

While current process control methodologies for activated sludge nitrification processes (discussed in **Section 2.4**) are in general sufficient to maintain stable operation, regulation in response to environmental and health/safety concerns is a key external force that is driving the water industry to innovate and improve. In addition to this external force, internal pressures to reduce operational costs are also driving innovation. The rationale for this project is firmly based on these driving forces and their impact upon research and development in this field. At the heart of the majority of the issues generating the regulatory driving forces is the emission of nutrients to the environment, in particular the nutrient enrichment of water bodies (eutrophication).

1.1.1 Eutrophication

Eutrophication of water bodies has been the subject of increasing research and regulation in recent years as the adverse effects of eutrophication on the environment and humans have become increasingly apparent. Aquatic microorganisms such as algae and bacteria grow under nutrient limited conditions (Cloern 2001), with the specific limiting nutrient depending on the conditions at the specific location being studied. As noted by Anderson et al. (2002), two of the key limiting nutrients in many aquatic environments are phosphorus (predominately in freshwater environments) and nitrogen (predominately marine and estuarine environments). These two nutrients are thus of particular interest since their emission from anthropogenic sources to the environment has increased rapidly in recent times and is expected to continue to increase (Bennett et al. 2001; Galloway et al. 2004; Smith et al. 1999).

The presence of elevated nutrient levels in water bodies can upset the natural balance of the ecosystem and promote the rapid growth and reproduction of algae and cyanobacteria. If eutrophication occurs in the presence of other contributing factors such as sunlight, warm temperatures, and low or stable flow conditions, the rapid growth can result in a substantial shift in the aquatic biodiversity and result in a cyanobacterial bloom (NHMRC and NRMMC 2004).

Cyanobacterial blooms effect aquatic ecosystems and degrade drinking and recreational water quality. One of the direct adverse effects of cyanobacterial blooms on aquatic ecosystems is a reduction in species biodiversity due to their competitive advantages over other microorganisms sharing similar niches (de Figueiredo et al. 2004). Another adverse effect which can be quite drastic in nature is related to the blooms effect on dissolved oxygen (DO) concentration. During a bloom, the photosynthetic cyanobacteria produce oxygen during the daytime which assists in maintaining the DO content in the water body. When the bloom reaches the point where it can no longer be supported by conditions in the water body, the rate of organism death increases and the bloom begins to be decomposed by heterotrophic bacteria which exerts and added oxygen demand on the water body, resulting in an oxygen deficit that can kill other aquatic species (Smith et al. 1999).

The second area of concern (and becoming increasingly so as the results of more research are becoming available), degradation of drinking and recreational water quality, is primarily a result of toxins that can be produced and emitted by certain species of cyanobacteria. Cyanobacteria are ubiquitous on the planet, occurring primarily in aqueous environments, but also being found in soils, rocks fissures and ice (Svrcek and Smith 2004), however the unnatural presence of cyanobacteria (and hence the associated toxins if toxin producing species are present) in high concentrations during blooms can result in toxic effects on other life forms. While not all species of cyanobacteria are capable of producing toxins (de Figueiredo et al. 2004), many species are capable of producing toxins that are typically either liver toxins (hepatotoxins) such as microcystins and nodularins (Karner et al. 2001) or neurotoxins such as anatoxin-a and saxitoxins (Svrcek and Smith 2004).

Cyanobacterial blooms have been reported on all inhabited continents (de Figueiredo et al. 2004; Svrcek and Smith 2004) and many cases of the toxic effects of cyanobacterial blooms on animals and human populations are documented in literature, with several reviews being available (de Figueiredo et al. 2004; Falconer 2005; Svrcek and Smith 2004). In general the hepatotoxic effects of the cyanobacterial toxins have been the main area of scrutiny in these studies. Recent years have seen a rise in concerns about the potential carcinogenicity of cyanobacterial toxins, although despite several studies this has not yet been conclusively proven (Falconer 2005).

In addition to toxins, the presence of cyanobacteria or algae can result in the emission of off-flavours, or tastes and odours (NHMRC and NRMMC 2004) to the source waters which may not be completely removed during conventional drinking water treatment. While these issues are primarily of aesthetic concern, they can result in elevated levels of customer complaints during bloom episodes, reduce consumer confidence in the water supply (Jardine et al. 1999; Svrcek and Smith 2004), and potentially increase health risks if the consumers switch to a less safe water source due to the perceived lower quality of the treated water (World Health Organization 2004).

1.1.2 Regulatory Pressures

Considering the trend of increasing bloom frequency corresponding to the global trend of increasing eutrophication of water bodies observed by de Figueirdo et al. (2004), it can be concluded that the environmental impacts associated with eutrophication will become an even greater concern in the future. Furthermore, with the contributing conditions for blooms (sunlight and low or stable flow conditions) being commonly found in some rivers and most large reservoirs used to supply water to large towns and urban areas, the potential for cyanobacterial blooms to impact water supplies will continue to increase in the future. Thus, it is expected that the control of these blooms and the contaminants generated by them will become increasingly emphasized by regulatory agencies.

Globally, anthropogenic nitrogen emissions to aquatic environments are dominated by non-point sources such as fertilizer, energy generation using fossil fuels, and agriculture (Seitzinger et al. 2005). However, in more densely populated (urbanized) environments, nitrogen emissions from wastewater disposal can also have a significant influence on nitrogen loadings to water bodies (Smith et al. 1999). With a trend of increasing global urbanization and human population (United Nations 2002; United Nations 2005), nitrogen emissions from wastewater disposal will increase in importance and will correspondingly experience greater levels of scrutiny and increasingly stringent regulation.

A good example of the evolution and spread of water policy is that of the European Union (EU). Prior to 2000, the EU water pollution regulations were based upon management of specific emissions using two directives; the Urban Waste Water Directive for sewage and biodegradable industrial wastewater, and the Nitrates Directive for nitrates emissions from agriculture (Bloch 2001). These directives specified minimum standards of waste water collection and biological treatment for communities (greater than 2000 population equivalents) and nutrient removal where receiving waters were subject to eutrophication (Bloch 2001).

In 2000, with the introduction of EU Water Framework Directive (WFD), the EU expanded its focus from specific regulation and minimum treatment standards to the overall management of all water bodies (including both surface and groundwater). The WFD places the onus for specific regulation on member states to manage their inputs to water bodies based upon achieving water quality objectives (Andersen et al. 2006). This approach has lead to a greater focus being placed on the control and reduction of anthropogenic sources of nutrient emissions in member states as they seek to identify the most cost effective means of meeting these objectives.

Sweden's introduction of national environmental quality objectives in 1999 provides an interesting example of the impact that changing environmental policy and regulation can have on the wastewater treatment industry. The introduction of the environmental objective of zero eutrophication with an interim target of a 30% reduction (from 1995 levels) in anthropogenic nitrogen emissions to coastal zones (Swedish Environmental Protection Agency 2005) has led to the development of more stringent emission standards for wastewater treatment plants. These increasingly stringent standards have resulted in a corresponding increase in process efficiency on the order of 15% from 1998 – 2000 (Swedish Environmental Protection Agency 2004), and an increase in the amount of households being serviced by nitrogen removal systems from approximately 10% in 1998 to 50% in 2000 (Swedish Environmental Protection Agency 2002).

As seen in the above example, regulations and policy based on environmental and heath/safety concerns can indeed be a strong driver for increases in the levels of process performance and the uptake of nutrient removal technology. As the uptake

of nitrogen removal treatment systems increases in response to changing regulations, eventually the focus for new treatment applications will shift from larger sources such as municipal wastewater treatment plants servicing large urban populations to plants serving progressively smaller populations. This will have a number of implications with respect to the evolution of these treatment processes since the cost (capital and operating), process complexity, and process reliability are commonly seen as barriers to the uptake of this treatment technology in small plants (Boller 1997). The introduction of advanced process monitoring and control will be an integral part overcoming these barriers and achieving compliance with evolving environmental regulations.

1.1.3 Economic Drivers

The costs associated with the construction, operation and maintenance of wastewater treatment plants are an ever present concern for wastewater operators. Improved process monitoring and control provides an opportunity for the wastewater industry to reduce costs and improve process reliability.

Nitrogen removal processes (which will be discussed in greater depth in **Section 1.2.1**) are strongly dependent on the aeration supply. Indeed up to 50% of a wastewater treatment facility's electricity consumption is associated with the supply of aeration air (Ferrer et al. 1998). Furthermore, due to diurnal variations in wastewater loadings to treatment plants, if plants are operated at constant air flow rates or the air supply is poorly matched to the oxygen demands of the wastewater, periods of oxygen over supply (wasted energy) and periods of oxygen deficiencies (reduced nitrification efficiency) will occur. The application of improved aeration process control in several recent studies (Galluzzo et al. 2001; Ingildsen et al. 2002; Sahlmann et al. 2004), has resulted in aeration cost savings on the order of 5% to 15%. These savings represent a substantial economic benefit which could be achieved through improved process monitoring and control.

In addition to the cost perspective, aeration has a strong influence on process efficiency and sludge settling characteristics. DO limited conditions not only reduce nitrogen removal (by limiting one of the substrates), but they can also provide

competitive advantage for filamentous bacteria which can have a negative impact on sludge settling properties (Jenkins et al. 2004). Furthermore, excessive aeration rates can shear existing sludge flocs which will impair sludge settling properties. Poor sludge settling is a key contributor to deterioration in effluent quality and process upset/failure.

Improved process control allows for increased reliability (in terms of nitrogen removal and reduced frequency of process upset/failure) and this in turn reduces the costs and liabilities associated with poor process performance and upset/failure episodes. Process reliability becomes increasingly important for small-scale or remote plants where it is not economical to maintain full time supervision and support. By improving process monitoring and control, the level of automation can be increased, reducing the financial burden on wastewater treatment operators. With increasing nutrient removal technology uptake and requirements to serve smaller communities, it is expected that the economics associated with the operation of smaller or onsite treatment systems will become a greater concern for wastewater operators.

1.2 Historical Development

1.2.1 Nitrogen Removal Processes

Conventional wastewater treatment has evolved over time to match our understanding of wastewater contaminants and their impact on the environment and human health. Primary (physical) wastewater treatment was initially applied to separate easily visible solids from wastewater via physical separation (settling). As the importance of organic matter and its effect on aquatic environments became apparent, secondary biological wastewater treatment was developed. Activated sludge processes have become the most common secondary biological wastewater treatment process worldwide (Sorour and Bahgat 2004), being applied in over 9000 plants in the USA, 500 in the UK, and 600 in France (Nuhoglu et al. 2005). With increasing understanding and regulation of wastewater nutrient emissions, tertiary biological treatment (primarily biological nutrient removal processes) has emerged. The most common nitrogen removal processes mirror the natural nitrogen transformations observed in estuarine environments and in soils, a two step process referred to as nitrification/denitrification.

A simplified version of the nitrification/denitrification process commonly applied for nitrogen removal at wastewater treatment plants is depicted in **Figure 1-1**. The presented mechanism neglects many of the possible side reactions and alternative nitrification/denitrification pathways. The first stage in the process is called nitrification which is performed by aerobic (oxygen consuming) bacteria. This process consists of converting dissolved ammonium (NH_4^+) into nitrite (NO_2^-) and then converting to nitrate (NO_3^-). The exact mechanisms of intermediate and side reactions are quite complex and can be dependent on the system operating conditions (Colliver and Stephenson 2000). These mechanisms will be discussed further in **Section 2.1**. Denitrification is an anoxic process (where in the absence of elemental oxygen nitrate acts as the oxygen source) whereby the nitrate (NO_3^-) is reduced to a gas (a mixture of nitrogen (N_2), nitric oxide (NO), and nitrous oxide (N_2O) that is dependent on operating conditions), which eventually diffuses from the treated wastewater to the atmosphere (Metcalf and Eddy 2003). As this thesis is

focused on the nitrification (aerobic) component of this process, the anoxic denitrification aspects of nitrogen removal processes will not be discussed further.

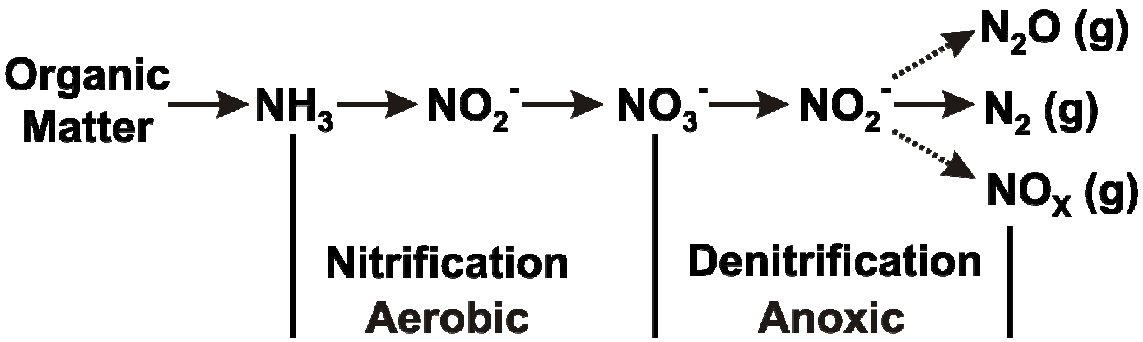


Figure 1-1 Simplified biological nutrient removal process.

While there are many possible configurations of biological nutrient removal (BNR) processes which can provide various advantages from an operational perspective, it is common to combine these processes with biochemical oxygen demand removal in an activated sludge process (Metcalf and Eddy 2003), which requires only operational changes to existing equipment to allow nutrient removal. The principles and operation of activated sludge nitrification processes will be discussed in greater depth in **Section 3.1**.

While the above is currently the most commonly applied nitrogen removal process, a number of advanced nitrogen removal processes utilizing alternative metabolic pathways and bacteria are emerging and gaining acceptance. These processes include SHARON (ammonium conversion to nitrite over nitrate), Anammox (anaerobic ammonium oxidation), and combined processes such as CANON (Ahn 2006), and will be discussed further in **Section 2.1**. A common aspect to all of these advanced processes is a dependence on improved process instrumentation and control to maintain very specific operating conditions.

1.2.2 Process Control and Instrumentation

Process control has been applied in the wastewater industry for over 30 years (Olsson 2006). Historically it has not been as well developed as in other process industries (Lynggaard-Jensen 1999), and only recently has the application of process

control at wastewater treatment plants started to evolve from specific parameter control to process/plant wide control applications (Olsson 2006). While there are many parameters which can be monitored and controlled at wastewater treatment plants (including flow rates, sludge/hydraulic retention times, and mixed liquor suspended solids concentrations), this discussion will be restricted to the control of aeration supply to bioreactors, the focus of this thesis.

The most basic form of aeration control consists of setting a constant air flow, with the setting primarily chosen based on operator experience and observation of the resulting effluent conditions. While its is possible to achieve reasonably stable operation via manual control, the impact of typical diurnal variations on the process (**Figure 1-2**) will result in a number of inefficiencies.

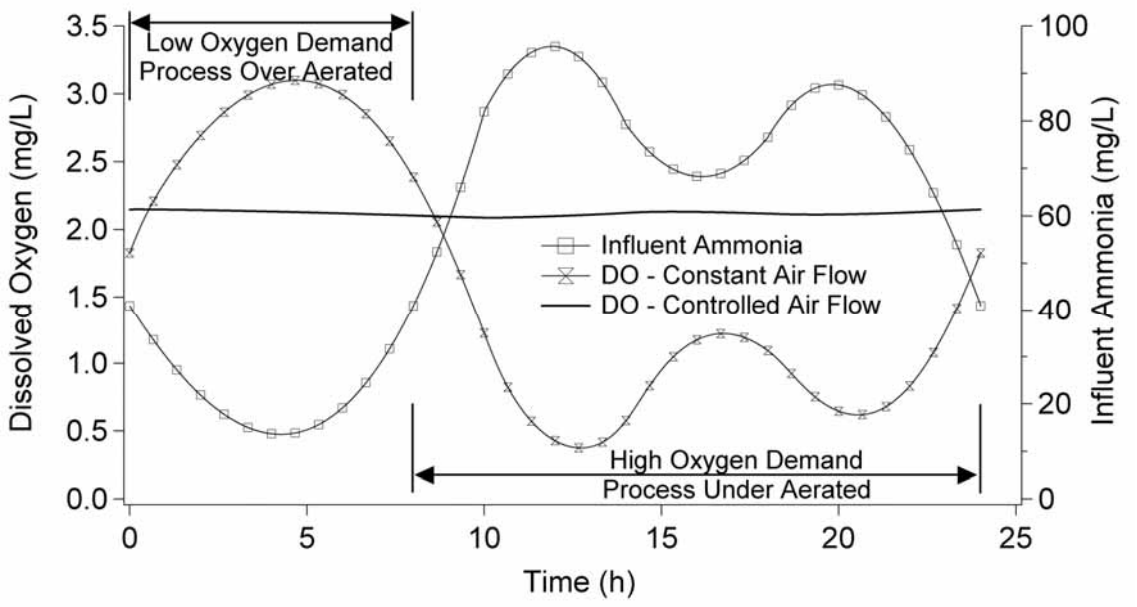


Figure 1-2 Simulation of the effect of diurnal loading variations on process DO concentrations.

As seen in **Figure 1-2**, a constant air flow does not match the air supply and demand, resulting in periods of over supply (wasted air and energy costs) and periods of under supply (reduced process efficiency). The application of process instrumentation and control is directed at minimizing these inefficiencies, thereby reducing operating costs and increasing process efficiency/reliability.

Traditional DO control for activated sludge bioreactors consists of a simple feedback loop using a DO sensor to measure the controlled variable and the aeration air supply as a master control variable. The DO setpoint is typically fixed at a value based upon operational experience and theoretical considerations. A number of more advanced process control strategies have been investigated to improve bioreactor control and reduce aeration requirements, and will be discussed in depth in **Section 2.4**.

A common concept in all of the existing and proposed aeration control strategies is the use of aqueous phase parameters for process control purposes. These methods are thus dependent on aqueous phase monitoring. With wastewater being a hostile environment for instrumentation, in particular due to fouling and its effects on sensor drift and instrument sensitivity (Bourgeois et al. 2003c), the effectiveness of these process control methods my be impaired by instrumentation limitations.

Indeed, a review of the application of instrumentation and process control in the wastewater treatment industry has indicated a need for robust and reliable online sensors to enable more sophisticated methods of process control (Hill et al. 2002). Non-invasive wastewater process monitoring techniques have the potential to provide sensors which meet these criteria by removing the sensor from contact with the hostile wastewater environment. A number of non-invasive monitoring techniques have been proposed, including optical sensing methods (Thomas and Constant 2004) and off-gas nitrous oxide (N_2O) monitoring (Burgess et al. 2002a; Burgess et al. 2002b). A review of the research and evaluation conducted to date with regards to the application of these monitoring techniques is presented in **Section 2.3**.

1.2.3 Off-Gas N_2O

One of the emerging non-invasive wastewater monitoring techniques is off-gas N_2O monitoring. The feasibility of the use of off-gas N_2O analysis as an indicator of the operation of nitrification systems has been investigated by a research group at Cranfield University in the United Kingdom. This research, which will be reviewed in **Section 2.1.4** of this thesis, demonstrated that gaseous N_2O emissions from

aerobic nitrification processes could be used as a real-time indicator of the operation of these systems (Burgess et al. 2002a).

Off-gas N_2O monitoring utilizes a stress response relationship to determine the biological status of autotrophic nitrifying bacteria (Burgess et al. 2002b), specifically, the generation of N_2O (the response) as a result of metabolic inhibition due to conditions like low DO and/or the application of inhibitory chemicals (the stresses). The concept of microbial stress indictors and a review of nitrification process stress responses will be presented in **Section 2.1.4** of this thesis. N_2O is stripped from the liquid phase by the aeration air and the concentration in the off-gas is monitored by a conventional continuous emissions monitor (such as a non-dispersive infrared detector). Utilizing a gas phase control parameter provides the advantages of using well established gas monitoring technologies and conducting the required process monitoring in a less hostile environment. The monitoring equipment utilized and principles of operation will be discussed in **Section 3.2**.

Previous research (Burgess et al. 2002a; Burgess et al. 2002b; Butler et al. 2005; Butler et al. 2009; Stuetz et al. 2003) has focused on applying this monitoring technique as a means of upset early warning to detect conditions which could result in process failure. While off-gas N_2O monitoring does indeed have upset early warning potential, the integration of the real-time process monitoring aspects of this technique into an aeration process control system has not been investigated.

In this thesis, an alternative process control methodology is investigated which utilizes off-gas N_2O as a measured variable and aeration air supply as the master control variable. This thesis will build upon previous research conducted in this area (Burgess et al. 2002a; Burgess et al. 2002b; Butler et al. 2005; Butler et al. 2009; Stuetz et al. 2003) by increasing the understanding of the response of nitrification systems to stresses (in terms of nitrous oxide production) and evolves the preliminary monitoring/control concept into an operational control system. The primary focus of the developed system will be on improving process reliability and reducing aeration costs. This thesis will also present a feasibility assessment of the developed control system, considering the technical, environmental and economic aspects of its application. The specific research objectives that must be achieved to accomplish these goals are presented in the following section.

1.3 Research Objectives

As discussed previously, the overall aim of the project is to develop a control system for nitrification processes using gas phase N_2O monitoring to reduce aeration requirements and mitigate process upset. In achieving this aim, a number of objectives must be achieved which will result in the generation of additional knowledge with respect to nitrification processes and their control. These objectives include:

- investigating the operation of activated sludge nitrification processes to evaluate gaseous N_2O emissions from the process under normal operating conditions and during process upset scenarios;
- developing a model of gaseous N_2O emissions from the process to correlate these emissions to liquid phase process parameters;
- designing a nitrification process control concept; and
- evaluating the developed control concept to determine feasibility of implementation, cost effectiveness, and environmental costs/benefits.

1.4 Thesis Structure

This thesis is presented in 7 sections. A review of relevant literature that provides the background material used in the development of this research is presented in **Chapter 2**, while a description of the experimental apparatus and methodologies used in this research is provided in **Chapter 3**. The stress response relationship for off-gas N_2O emissions from nitrifying bacteria is explored in **Chapter 4**, which forms the basis for the process control concept development and process modelling, both of which are presented in **Chapter 5**. An evaluation of the developed process control concept is provided in **Chapter 6**. Finally, conclusions and recommendations for further research are presented in **Chapter 7** of this thesis.

Chapter 2 Literature Review

Prior to conducting the experimental portion of the project, a literature review was conducted to gather the background information required to provide context for this project, identify knowledge gaps to support the development of project concept, and assist in methodology development.

This review concentrated on four key areas of interest. A review of the current understanding of the biological processes involved in nitrification, as well as the potential pathways for the production of gaseous N_2O emissions is presented in **Section 2.1**. The conceptual basis of activated sludge process modelling is reviewed in **Section 2.2**, along with calibration methodologies and current applications. Existing and emerging non-invasive wastewater monitoring technologies are reviewed in **Section 2.3**, and the feasibility of their incorporation into process control strategies is discussed. Finally, existing aeration control strategies for biological nitrogen removal processes are reviewed in **Section 2.4**.

2.1 Biological Nitrogen Removal – Processes and Gaseous Emissions

The emission of nitrogen to the natural environment from wastewater is undesirable from an environmental perspective, and mounting regulatory and economic pressures are driving uptake of nitrogen removal technologies. Biological nitrogen removal is seen as the most efficient and cost effective means of nitrogen removal, and as such is the dominant nitrogen removal process employed in wastewater treatment (Ahn 2006).

Biological nitrogen removal (BNR) processes utilize the microbiological component of the global nitrogen cycle to achieve nitrogen removal from the liquid phase (wastewater). Removal of ammonia, which is produced via ammonification of nitrogen-containing organic substances such as amino acids and urea (Siripong 2005), by conversion dinitrogen gas (N_2) occurs in nature in a wide range of environments from water (salt/fresh waters and sewage) to rocks and masonry, to extreme habitats such as Antarctic soils, acid environments and soda lakes (Abeliovich 1992; Schmidt 2008). Much of the knowledge of biological mechanisms in wastewater treatment processes has originated and evolved from research conducted to identify nitrogen transformation mechanisms involved in the soil component of the global nitrogen cycle.

Historically, nitrogen removal was only thought to occur via two processes: nitrification (a two step process) and denitrification, which were believed to be strictly aerobic and anoxic, respectively. Recent research has challenged this paradigm and it has been demonstrated that the metabolism and types of bacteria involved in the nitrogen cycle are indeed quite diverse, with many new removal pathways and types of bacteria being identified. Current recognized nitrogen removal pathways are summarized briefly in **Table 2-1**.

Table 2-1 Summary of nitrogen removal pathways.

Process	Environment		Inputs		Products*
	Aerobic	Anoxic	Electron Donor	Electron Acceptor	
Nitrition	✓		NH_3	O_2 (or HNO_2)	NO_2^-
Nitration	✓		NO_2^-	O_2 (or HNO_2)	NO_3^-
Heterotrophic Nitrification	✓		NH_3	O_2	NO_2^-
Aerobic Denitrification (Autotrophic)	✓		No consensus	NO_2^- (or HNO_2)	N_2O (NO/N_2)
Aerobic Denitrification (Heterotrophic)	✓		Organic Carbon	Successive steps: NO_3, NO_2^-, NO, N_2O	N_2/N_2O/ NO
Anammox		✓	NH_4^+	NO_2^-	N_2 (NO_3^-)
Heterotrophic Denitrification		✓	Organic Carbon	Successive steps: NO_3^-, NO_2^-, NO, N_2O	N_2 (N_2O/NO)

*Minor products are presented in parentheses.

While some of these processes (in particular nitrification and denitrification) are well understood from both biological and mechanistic perspectives, knowledge of many of the more recently identified processes continues to evolve and many knowledge gaps and areas of contradiction remain. These pathways will be discussed in further depth in **Sections 2.1.1** and **2.1.2** for nitrification and denitrification pathways, respectively.

The discovery and investigation of alternative nitrogen removal pathways has spurred the development of many novel BNR processes. Due to the nature of these pathways, many of the emerging processes are directed at very specific wastewater types, for example the SHARON and CANON processes are best suited to high ammonia/low carbon wastewaters (Khin and Annachhatre 2004) which often originate from industrial sources or internal process flows like sludge digestion liquors (Jetten et al. 2005). A full review of the development and current status of these emerging nitrogen removal processes is beyond the scope of this study, and the reader is directed to several recent reviews for further information (Ahn 2006; Khin and Annachhatre 2004; Schmidt et al. 2003). An overview of the biological

mechanisms involved in these processes (which will be discussed in the following sections) is provided as **Table 2-2**.

Table 2-2 Nitrogen removal processes.

Treatment Process	Biological Process						Process Selector
	Aerobic				Anoxic		
	Nitration (Autotrophic)	Nitrition (Autotrophic)	Denitrification (Autotrophic)	Denitrification (Heterotrophic)	Denitrification (Anammox)	Denitrification (Heterotrophic)	
Nitrification/ Denitrification	✓	✓				✓	N/A
Shortcut Nitrification/ Denitrification	✓					✓	DO, temperature, pH
SND	✓			✓			DO, floc size
Anammox					✓		SRT
Sharon + Anammox	✓				✓		Temperature, SRT
SHARON	✓					✓	Temperature, SRT
CANON	✓				✓		DO
OLAND	✓		✓				DO

Legend
SND - Simultaneous Nitrification and Denitrification
SHARON – Single Reactor System for High Rate Ammonia Removal Over Nitrite
CANON – Completely Autotrophic Removal Over Nitrite
OLAND – Oxygen Limited Nitrification and Denitrification

Much of the research presented in the literature is directed towards process development, which is dependent on the application of long term selective pressures on microbiological communities to achieve the desired dominant processes. This thesis however, is focused on aeration process control and as such requires much shorter time scales. Thus, this review will focus on metabolic pathways and short term stress responses, particularly with regards to changes in substrate concentrations and inhibitory substances.

2.1.1 Nitrification Processes

A wide range of microorganisms have the capability to degrade ammonia to nitrate/nitrite, including autotrophic bacteria, heterotrophic bacteria, and fungi, although only autotrophic bacteria obtain energy from the process (Udert et al.

2005). While autotrophic bacteria and heterotrophic bacteria are of interest and relevant to wastewater treatment processes, fungi are not generally a significant population under normal process conditions and will not be discussed further.

2.1.1.1 Autotrophic Nitrification

No species of autotrophic bacteria are known to directly produce nitrate (NO_3^-) from ammonia (Hooper et al. 1997). Instead two types of bacteria coexist and interact to achieve the conversion via two sequential steps. In the first stage (nitrition), ammonia is converted to nitrite (NO_2^-) by ammonia oxidizing bacteria (AOB). The second stage (nitration) consists of the conversion of NO_2^- to NO_3^- by nitrite oxidizing bacteria (NOB).

Nitrition

The most commonly recognized autotrophic nitrifiers are *Nitrosomonas* genera (Ahn 2006), in particular *Nitrosomonas europea* has been extensively studied (Hagopian and Riley 1998), although *Nitrosospira* were recently recognized as being important (Siripong and Rittmann 2007). It is interesting to note that, as discussed by de Beer et al (1999), only a small segment of microbial populations are cultivatable by traditional identification techniques. These techniques favour the growth and domination of species which are adapted to high concentrations of the specific substrates utilized. Less competitive bacteria would be outcompeted and as a result not identified, leading to underestimation of bacterial populations and diversity. More recent microbial identification techniques such as fluorescent *in situ* hybridization (FISH) has revealed much greater diversity in populations, and recognized AOBs now include bacteria of the genera *Nitrosococcus*, *Nitrosolobus* and *Nitrosovibrio* (Hagopian and Riley 1998).

It is generally accepted that ammonia (NH_3) and not ammonium (NH_4^+) is the substrate for nitrition (Jianlong and Ning 2004; Stein and Arp 1998). pH is thus an important parameter since it controls the equilibrium between NH_3 and NH_4^+ in liquid phase, in addition to playing a role in other sources of AOB inhibition (Udert et al. 2005). Nitrition is conventionally represented as a two step process in which ammonia is first oxidized to hydroxylamine, which is in turn oxidized to nitrite with oxygen acting as the terminal electron acceptor (Colliver and Stephenson 2000). It

should be noted that the first step of the reaction (ammonia oxidation to hydroxylamine) does not generate energy, which is instead generated in the second step (Abeliovich 1992). Each step is catalysed by a specific enzyme; ammonia monooxygenase (a membrane bound enzyme) and hydroxylamine oxidoreductase (a soluble enzyme) catalyse the first and second step, respectively (Abeliovich 1992; Stein and Arp 1998). The conventional nitrition mechanism is summarized below (Colliver and Stephenson 2000).

$$NH_3 + O_2 + 2e^- \rightarrow NH_2OH + H_2O$$
$$NH_2OH + H_2O \rightarrow HNO_2 + 4H^+ + 4e^-$$
$$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

More recent research has suggested that DO is not utilized directly to oxidize ammonia in the first step, instead dimeric nitrite (N_2O_4) is used (Schmidt 2008). While this represents a departure from the conventional model, the oxygen in hydroxylamine originates from DO, therefore DO is still involved, albeit in an indirect manner (Schmidt 2008). This reaction adds an additional layer is to the nitrition mechanism in which NO_2^-/N_2O_4 is used to oxidize ammonia and produces nitric oxide (NO), which is then oxidized back to NO_2^-/N_2O_4 (regenerated) by DO.

Nitration

Bacteria of the genus *Nitrobacter* are generally considered the most important NO_2^- oxidizer, however *Nitrospira* is now also recognized as a dominant NOB (Siripong and Rittmann 2007). Bacteria of genera *Nitrospina*, *Nitrococcus*, *Nitrocystis* are also known to oxidize NO_2^- (Ahn 2006). Like nitrition, there is some ambiguity in the mechanism, in this case with regards to the specific substrate utilized in the single step reaction. NO_2^- has been the historically recognized substrate, however the possibility has been raised that nitrous acid (HNO_2) is instead the substrate, although this has not yet been verified (Shiskowski 2004).

Nitration is catalysed by nitrite oxidoreductase (also called nitrite dehydrogenase), a membrane bound enzyme (Hagopian and Riley 1998):

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$
$$2H^+ + 2e^- + 0.5O_2 \rightarrow H_2O$$

Under ideal conditions, nitration is a relatively fast reaction and nitrition is rate limiting, thus NO_2^- does not typically build up and the overall process is often modelled as a single step conversion of NH_3 to NO_3^- (Ficara et al. 2000). However, NOB are more sensitive than AOB to many environmental parameters such as ammonia, free nitrous acid (Beline et al. 1999), and DO concentrations (Zheng et al. 1994). During suboptimal growth conditions nitrition will no longer be rate limiting. NO_2^- will accumulate, resulting in stress to the AOB and an associated response. These stresses and responses will be discussed further in **Sections 2.1.2.2** and **2.1.4** for for autotrophic bacteria and the off-gas N_2O responses, respectively.

2.1.1.2 Heterotrophic Nitrification

Heterotrophic nitrification is performed by a range of microorganisms including algae, fungi and bacteria (Kuenen and Robertson 1994; Schmidt et al. 2003), although it is most common in fungi which nitrify in low pH soils (Wrage et al. 2001). Common heterotrophic nitrifiers include species of *Anthrobacter*, *Pseudomonas*, as well as *Alcaligenes faecalis* and *Thiosphaera pantotropha* (Kuenen and Robertson 1994).

Heterotrophic nitrifiers convert NH_3 to NO_2^- (and less commonly to NO_3^-), but unlike autotrophic nitrifiers they do not obtain energy directly from the process (Hooper et al. 1997; Kuenen and Robertson 1994), and instead use organic carbon as their energy source (Wrage et al. 2001). Furthermore, heterotrophic nitrifiers can metabolize a range of nitrogen compounds and are not restricted to NH_3 like autotrophic nitrifiers (Kuenen and Robertson 1994; Papen et al. 1989).

While heterotrophic and autotrophic nitrifiers share the same substrates, intermediates and products, they utilize different enzymes (Wrage et al. 2001).

Heterotrophic nitrification rates are generally lower than autotrophic nitrification rates except in specific environments (such as acidic ones) that are unfavourable for autotrophic nitrification (Schmidt et al. 2003). Even though they have lower nitrogen conversion rates per unit of biomass, heterotrophic nitrifiers generally exist at much higher concentrations and as such in favourable conditions can easily match and surpass autotrophic nitrification (Kuenen and Robertson 1994). Heterotrophic nitrification is believed to be negligible in conventional wastewater treatment processes except at very high COD/N ratios (van Loosdrecht and Jetten 1998).

While knowledge of heterotrophic nitrification processes is increasing, there remains a need to further identify the process mechanisms, as well as investigate the conditions/environmental parameters which promote this process. Development of new knowledge in this field is further complicated by the diversity of heterotrophic nitrifiers, which can also denitrify in anoxic environments (Papen et al. 1989) as well as perform aerobic denitrification (Kuenen and Robertson 1994). These two processes will be discussed in **Sections 2.1.2.1** and **2.1.2.2** for anoxic and aerobic denitrification, respectively.

2.1.2 Denitrification Processes

Historically denitrification was considered to be an anoxic process conducted by heterotrophic bacteria. However, recent research has demonstrated that the process is much more widespread and diverse, including aerobic denitrification processes as well as autotrophic bacteria.

2.1.2.1 Anoxic Denitrification

Conventional denitrification is conducted in anoxic environments by a wide range of heterotrophic bacteria including members of the genera *Achromobacter*, *Acinetobacer*, *Agrobacterium*, *Alcaligenes*, *Arthrobacter*, *Bacillus*, *Chromobacterium*, *Corynebacterium*, *Flavobacterium*, *Hypomicrobium*, *Moraxella*, *Neisseria*, *Paracoccus*, *Propionibacterium*, *Pseudomonas*, *Rhizobium*, *Rhodopseudomonas*, *Spirillium*, *Thiobacillus*, and *Vibrio* (Ahn 2006; Metcalf and Eddy 2003). Denitrification occurs in a series of sequential steps in which NO_3^- is

successively reduced to N_2, with each reduction stage being mediated by specific enzymes (Shrestha et al. 2002):

- NO_3^- → NO_2^- (nitrate reductase)
- NO_2^- → NO (nitrite reductase)
- NO → N_2O (nitric oxide reductase)
- N_2O → N_2 (nitrous oxide reductase)

Each of the enzymes have different inhibition characteristics with respect to chemicals and environmental conditions, and these differences are particularly important with regards to the accumulation of undesirable intermediates due to incomplete denitrification (in particular N_2O and NO). For example, the nitrous oxide reductase is the most sensitive denitrification enzyme with regards to DO, thus intrusion of DO into the anoxic zone can result in N_2O accumulation (Tallec et al. 2008).

Organic carbon (from a wide variety of sources) is used as the electron donor and carbon source for all of the above reactions (Ahn 2006), and is required in significant quantities (Khin and Annachhatre 2004). Limitation of the organic carbon supply is another common cause of incomplete denitrification and accumulation of denitrification intermediates (Hwang et al. 2006).

For an in-depth review of the biological mechanisms and specific enzymes involved in anoxic heterotrophic denitrification the reader is directed to Zumft (1997). While anoxic denitrification is fairly well understood, knowledge of denitrification processes by other types of microorganisms as well as in aerobic environments contains many gaps and contradictions and remains an active area of research and consensus building.

2.1.2.2 Aerobic Denitrification

While denitrification had been historically observed in aerobic environments, limitations in DO monitoring and inhomogeneous cultures used in classic experimental work (which could produce anoxic microzones) led to the concept of

aerobic denitrification being dismissed as conventional denitrification until the late 1970s (Robertson and Kuenen 1984b). Even though most of the identified aerobic denitrifiers are heterotrophic bacteria (Bernat and Wojnowska-Baryla 2007), autotrophic bacteria also have the potential for aerobic denitrification, although via different processes and mechanisms.

Aerobic Heterotrophic Denitrification

Despite many examples of aerobic heterotrophic denitrification being provided in literature, the specific mechanisms of heterotrophic denitrification remain unclear. Two main mechanisms are currently being investigated; one a physical mechanism, the other a biological one (Itokawa et al. 1996; Oh and Silverstein 1999; Pochana et al. 1999).

The physical aerobic denitrification mechanism is based on the formation of anoxic microzones inside of activated sludge flocs due to limitations in oxygen diffusion from the bulk liquid. Heterotrophic bacteria perform conventional denitrification inside these anoxic zones, and as such it is not true aerobic denitrification (i.e. denitrification in the presence of oxygen), instead it is anoxic denitrification in an aerobic bulk medium. This phenomena has been demonstrated using sequencing batch reactors (Pochana and Keller 1999; Pochana et al. 1999), wherein changes in floc size had no effect on the rates of NH_3 or NO_2^- oxidation, but strongly influenced denitrification rates. Reductions in floc size increase oxygen penetration into the flocs, thereby producing a corresponding reduction in the size and availability of the anoxic microzones for anoxic heterotrophic denitrification.

True aerobic denitrification is a biological mechanism in which heterotrophic bacteria continue to denitrify in the presence of oxygen (Holman and Wareham 2005). This is often referred to as co-respiration, and there are many examples of these types of processes in nature (Ahn 2006; Bernat and Wojnowska-Baryla 2007). It has been proposed that aerobic denitrification is related to the impact of DO on the synthesis and activity of denitrification enzymes, in particular repression of enzyme synthesis and inhibition of enzyme activity (von Schulthess et al. 1994). Robertson and Kuenen (1984b) demonstrated that some denitrification enzymes can function in the presence of oxygen, and it is likely that while DO has a strong inhibitory effect, it is not a pure "on-off" switch (Oh and Silverstein 1999). Holman and

Wareham (2005) postulated that denitrification enzyme synthesis is deactivated in the presence of oxygen but the enzymes themselves are slow to disappear (i.e. a lag effect), but this mechanism would only allow for temporary denitrification instead of a sustainable process.

While support exists for both denitrification mechanisms, the physical one is most likely the mechanism being employed in the majority of the proposed simultaneous nitrification and denitrification (SND) treatment processes. Since it is entirely possible for both phenomena to occur simultaneously, it can be difficult to differentiate between them (von Schulthess et al. 1994). Despite recent investigations of aerobic heterotrophic denitrification, there remains a lack of agreement on the specific mechanisms involved (Holman and Wareham 2005) and the pathways have yet to be studied in depth (Ahn 2006). Additional research is required to solidify understanding of the mechanisms and processes involved before SND can overcome its perception of being unpredictable (Bernat and Wojnowska-Baryla 2007), and start to gain acceptance as a wastewater treatment process.

Aerobic Autotrophic Denitrification (Nitrifier Denitrification)

A range of autotrophic bacteria have been shown to be capable of denitrification using various inorganic electron acceptors including sulphur, hydrogen and nitrite (Ahn 2006). In the application of aerobic autotrophic nitrification as a treatment process, this alternative metabolic pathway, often referred to as nitrifier denitrification, is of particular interest. The potential for AOB to denitrify was demonstrated in the 1980s (Poth 1986; Poth and Focht 1985) and much of the research in this area has focused on pure cultures (Bock et al. 1995; Kester et al. 1997; Poth 1986; Poth and Focht 1985; Shrestha et al. 2002), primarily *Nitrosomonas* sp., and in particular *Nitrosomonas europaea* and *Nitrosomonas eutropha*. However, nitrifier denitrification has also been observed in full scale biological wastewater treatment process containing mixed populations of nitrifiers (Helmer and Kunst 1997; Tallec et al. 2006a) and is likely to be more widespread than previously believed.

Unlike aerobic heterotrophic denitrification, nitrifier denitrification is primarily attributed to a biological mechanism and not a physical one (Helmer and Kunst

1997). It is seen as a metabolic response by AOB to external stress, in particular to reduced DO concentrations (Philips et al. 2002), NH_3 shock loads, increases in NO_2^- concentrations (Burgess et al. 2002a; Burgess et al. 2002b) and the presence of nitrification inhibitors (Burgess et al. 2002b). Aerobic denitrification is thought to provide enough energy for survival but not growth (Jetten et al. 1998).

Poth and Focht (1985) postulated several mechanisms in which a switch to an aerobic denitrification pathway could improve survivability:

- conservation of DO for NH_3 oxidation;
- consumption of NO_2^- to prevent accumulation which could be toxic to AOB; and
- consumption of NO_2^- to reduce available NOB substrate and thus the associated competition with AOB for remaining DO.

Much of the nitrifier denitrification mechanism research has been conducted on pure cultures of *Nitrosomonas europaea*. Poth and Focht (1985) demonstrated via N^{15} tracer experiments that NO_2^- serves as a terminal electron acceptor for AOB during periods of oxygen stress and is reduced to N_2O while NH_4^+ is oxidized. These findings were supported by work conducted by Bock et al. (1995) which showed that both *Nitrosomonas europaea* and *eutropha* utilize NH_4^+ as the electron donor for nitrifier denitrification. The products of nitrifier denitrification include N_2O, NO, and N_2 (Hooper et al. 1997), although complete denitrification to N_2 is less common and NO/N_2O are the primary products (Colliver and Stephenson 2000).

There has been some discussion of alternative electron donors such as hydroxylamine (an intermediate of ammonia oxidation) and hydrogen (Ahn 2006; Jetten et al. 1998), although primarily in the context of anoxic autotrophic denitrification. While working with nitrite reductase deficient *Nitrosomonas europaea* cells, Beaumont et al. (2002) observed that the bacteria could still produce N_2O (a primary produce of nitrifier denitrification), suggesting that there may be other mechanisms involved and the role of hydroxylamine should be further investigated.

There appears to be consensus on the role of NO_2^- as electron acceptor (Bock et al. 1995; Poth 1986; Poth and Focht 1985; Tallec et al. 2006a), although more recent work conducted by Shiskowski and Mavinic (2006) investigating the effects of pH on nitrifier denitrification indicated that nitrous acid (HNO_2) and not NO_2^- may be the electron acceptor. The role of NO_2^- in nitrifier denitrification my be more than just that of an electron acceptor, and may act as a regulatory signal to induce denitrification (Schmidt et al. 2003), possibly due to inhibition of respirometric enzymes to permit alternative pathways to proceed (Iranpour et al. 1999).

Nitrifier denitrification has been investigated as a wastewater treatment process called OLAND (oxygen limited autotrophic nitrification and denitrification), which utilizes oxygen limitation to force simultaneous nitrification and denitrification by autotrophic bacteria, with a portion of the AOB using the available DO for ammonia oxidation while the remaining AOB switch to an aerobic denitrification survival mechanism (Philips et al. 2002). While this treatment process has been demonstrated at a laboratory scale to achieve nitrogen removal without a need for organic carbon, the specific mechanisms involved are not yet well understood (Ahn 2006; Schmidt et al. 2003), and the process currently has low loadings and conversions (Ahn 2006).

Even though a clear biological rationale for nitrifier denitrification has been identified, the process mechanism remains unclear. Without bacterial studies to identify specific mechanisms, much of the current knowledge of aerobic denitrification has been generated by inference using time series profiles of specific parameters (Holman and Wareham 2005). As noted by Wrage et al. (2001), there exists a lack of clear and consistent terminology to refer to the various forms of aerobic denitrification, which when combined with inference based knowledge, has generated confusion in the research area. While there is some research effort being put into gaining insight into the specific process mechanism, there appears to be more interest in related off-gas N_2O emissions, which will be discussed in **Section 2.1.4**.

2.1.3 Anammox

The Anammox process, in which ammonium is oxidized with NO_2^- to form N_2 (Ahn 2006), was discovered in the early 1990s (Schmidt et al. 2002) and is conducted by a diverse population of Planctomycete bacteria (Schmidt et al. 2003). This reaction is conceptually similar to autotrophic denitrification. However, unlike autotrophic bacteria which denitrify as a survival mechanism in times of oxygen stress or inhibition, Anammox bacteria are able to obtain sufficient energy to allow growth (Jetten et al. 1998).

Anammox bacteria oxidize NH_4^+ with NO_2^- as the electron acceptor while fixing carbon dioxide (Ahn 2006), with hydrazine and hydroxylamine as intermediates (Kuenen 2008). The overall metabolic stoichiometry has been identified (Khin and Annachhatre 2004; Kuenen 2008):

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 0.066CH_2O_{0.5}N_{0.15} + 1.02N_2 + 0.26NO_3^- + 2.03H_2O$$

NO_2^- is the preferred electron acceptor, thus the process requires a nitrite source in addition to ammonia (NH_4^+ and NO_2^- are consumed in a ratio of 1:1.3), so some initial partial nitrification is required (Schmidt et al. 2003).

While the stoichiometry has been identified, the specific steps and enzymatic processes remain an area of active research. Anammox bacteria are highly sensitive to DO and are inhibited completely in its presence (Jetten et al. 1998; Khin and Annachhatre 2004). In the natural environment, these bacteria are believed to be responsible for over half of the total nitrogen turnover and can be found at oxic/anaerobic interfaces near clusters of AOB which produce NO_2^- and consume inhibitory oxygen (Kuenen 2008). In wastewater treatment processes, Anammox is preceded by a partial nitrification process such as SHARON, or applied simultaneously to nitrification in an oxygen limited environment (CANON). The primary benefits of Anammox as a wastewater treatment process are reduced aeration and organic carbon demand compared to conventional nitrification/denitrification. Slow growth (which results in a long start-up time) and

the lack of a pure culture are seen as challenges to its application (Schmidt et al. 2003).

2.1.4 Off-gas N_2O Generation

The emission of off-gas N_2O from nitrogen removal processes is an emerging issue which has generated interest in recent years due to the increasing emphasis being placed on greenhouse gas emissions. Off-gas N_2O emissions from nitrogen removal processes have been historically attributed to incomplete denitrification by heterotrophic bacteria in anoxic conditions. With the emergence of the many alternative nitrogen removal pathways discussed in this review, the number of N_2O generation mechanisms to be considered has increased. However, the dominant source of N_2O emissions likely remains linked to incomplete denitrification, in particular aerobic denitrification (autotrophic and heterotrophic).

Relative Contribution of AOB and Heterotrophic Bacteria to N_2O Emissions

At low DO concentrations both AOB and heterotrophic bacteria have the potential to reduce NO_2^- and produce N_2O simultaneously (Shiskowski et al. 2004), producing a mixed signal containing both processes. The identification of specific off-gas N_2O sources has necessarily received a greater level of attention in dealing with nitrifier denitrification. In pure culture work using a representative of each of the three bacteria types of interest; an AOB (*Nitrosomonas europaea*), a NOB (*Nitrobacter winogradskyi*), and a heterotrophic nitrifier (*Alcaligenes faecalis*), Inamori et al. (1997) observed that the AOB had highest N_2O production capacity, on the order of 18 to 53 times that of the heterotrophic nitrifier, while the NOB generated negligible N_2O emissions. While these results are considered representative of typical bacteria of their type, it should be noted that variability in N_2O generation has been noted among bacterial species (Wrage et al. 2004) and among experimental conditions (Mao et al. 2006). Furthermore, mixed bacterial populations can have interactions that can change overall behaviour, in particular mixed populations of AOB and NOB have been observed to have lower N_2O emissions than pure cultures of AOB (Inamori et al. 1997; Kester et al. 1997), possibly due to the NOB reducing NO_2^- build up.

Heterotrophic denitrification is accepted as the dominant source of N_2O in fully anoxic conditions, particularly at low COD/N ratios (Liu et al. 2008; Tallec et al. 2008). As DO is introduced into the reactor and conditions change to aerobic, the dominant source begins to shift from heterotrophic denitrification to nitrifier denitrification. Tallec et al. (2006a) conducted a batch analysis of N_2O emissions from wastewater and biomass obtained from a full scale municipal wastewater treatment plant in Paris to identify specific emissions sources. The results of their work indicated that nitrifier denitrification was the dominant source of N_2O at all DO concentrations investigated, with the percentage contribution to the total emissions increasing steadily from 59% at 0.1 mg/L DO to 83% at 2 mg/L DO. Conversely the contribution for autotrophic denitrification decreased from 41 to 17% over the same range of DO contributions but it should be noted that the emissions associated with denitrification were not negligible (Tallec et al. 2006a). Similar magnitude of results were obtained in a later study by the same researchers (Tallec et al. 2008) in which the DO was varied between 0.4 and 1.1 mg/L. However, the contributions to the N_2O emissions from the two processes of interest were much more consistent across the investigated DO range, with 56.7% to 63.8% of total N_2O originating from nitrifier denitrification (conversely 36.2% to 43.3% originating from heterotrophic denitrification), with no apparent direct correlation to oxygen concentration.

While these results are interesting and provide insight into the relative importance of specific processes for N_2O generation, caution should be used in interpreting these results (as well as extending them to full scale) due to the strong dependence on a number of parameters which may vary between laboratory (in particular pure culture) setups, as well as from laboratory to full scale treatment processes. The biokinetics of bacteria have been shown to be strongly dependent on conditions in which they are cultured (Sliekers et al. 2005), and processes like heterotrophic denitrification would be strongly influenced by floc size and mixing which may vary highly among lab scale setups (Robertson and Kuenen 1984a) as well as from lab scale to full scale. Furthermore, the relative populations of autotrophic and heterotrophic bacteria could strongly influence the observed contributions to N_2O emissions as seen in Inamori et al. (1997).

N_2O Generation by Heterotrophic Bacteria

Generation of N_2O by heterotrophic denitrifying bacteria is reasonably well understood in conventional denitrification processes. Under optimal conditions, none of the intermediate denitrification steps are rate limiting and NO_2^- is reduced sequentially to N_2. The nitrous oxide reductase is the most oxygen sensitive denitrification enzyme (von Schulthess et al. 1994). Therefore, in the presence of oxygen, N_2O reduction will be the most severely inhibited step in the denitrification process and the reduction chain will end at N_2O, allowing it to build up in the liquid phase. A similar inhibition mechanism has been suggested for elevated concentrations of NO and NO_2^- (von Schulthess et al. 1995). Furthermore, low pH, short sludge retention times (SRT) and low COD/N ratios have been shown to promote the generation of N_2O (Itokawa et al. 2001), possibly via producing increased NO_2^- concentration, (von Schulthess and Gujer 1996).

These mechanistic studies have focused on liquid phase N_2O concentrations and not off-gas emissions. The nature of anoxic processes (i.e. not being sparged by aeration air) can provide challenges in identifying the dominant sources of off-gas N_2O emissions since the N_2O generated during the anoxic period will accumulate in the liquid phase and then be stripped during aeration along with any N_2O generated by aerobic processes (nitrification or denitrification), providing a mixed signal. A more recent approach utilized by Tallec et al. (2006b) consisted of sparging the reactor with a mix of air and nitrogen at a constant flow and adjusting the gas composition to obtain desired DO concentrations. Such a method serves to remove the potential bias associated with changing N_2O stripping efficiency due to variations in aeration flow, as well as allowing N_2O to be stripped during anoxic conditions, thereby improving the differentiation between anoxic and aerobic sources of N_2O generation.

N_2O Generation by Autotrophic Bacteria

As noted by Shiskowski and Mavinic (2006) and Poth and Focht (1985), AOB possess a nitrite reductase enzyme that is induceable at low DO concentrations and appears to be a survival mechanism, i.e. a response to stresses which result in metabolic inhibition. While there many studies have focused on DO, which has been termed the single most influential parameter for N_2O generation (Colliver and Stephenson 2000), a range of process parameters that can stress autotrophic bacteria (both

directly and indirectly) have also been shown to influence N_2O generation. In particular low pH, short SRT, and elevated ammonia concentrations are of importance (Colliver and Stephenson 2000; Kampschreur et al. 2008a; Ruiz et al. 2003).

While not a typical process operating parameter, NO_2^- has been shown to play a central role in the generation of N_2O. In particular N_2O production is dependent on NO_2^- concentration and is not directly related to NO_2^- or ammonia oxidation (Gejlsbjerg et al. 1998), suggesting that inhibition by NO_2^- is responsible for N_2O generation. Indeed, it has been demonstrated that NO_2^- debilitates ammonia monooxygenase, one of the primary AOB metabolic enzymes which, as noted by Iranpour et al. (1999), can in effect render aerobic environments anoxic and force bacteria to utilize alternative metabolic pathways. Free nitrous acid can also act as an inhibitor (Beline et al. 1999) and is likely the electron acceptor utilized in aerobic denitrification (Shiskowski and Mavinic 2006). It is possible that the other process parameters of interest, DO, pH, SRT and ammonia initiate N_2O generation via specific inhibitory effects (or a chain of these effects) that result in free nitrous acid accumulation.

N_2O generation is seen to be unavoidable from nitrification processes (Zheng et al. 1994), indeed N_2O has been shown to be generated over a wide range of DO concentrations (Dundee and Hopkins 2001) and responds strongly to aeration rate/cycle (Kampschreur et al. 2008b). A trend exists in the literature of increasing N_2O generation with decreasing DO concentrations below 2 mg/L, however there is a maximum point after which generation decreases as DO approaches zero (Tallec et al. 2006a).

Some variation exists in the reported observed DO concentration that corresponds to maximum N_2O generation, ranging from 0.4 mg/L to 1 mg/L (Tallec et al. 2006a; Tallec et al. 2008; Zheng et al. 1994). It is possible that this range in values is the result of the reported variability in N_2O yield amongst autotrophic bacteria species (Colliver and Stephenson 2000), or is related to the applied measurement techniques (in particular instrument sensitivity and N_2O stripping efficiency/dilution). Low DO concentrations can inhibit AOB (providing the necessary stress for nitrifier denitrification), as well as inhibiting NOB (Jianlong and

Ning 2004), which would result in NO_2^- accumulation that provides the electron acceptor and AOB metabolic stress required for nitrifier denitrification.

The role of pH in N_2O generation has only recently been systematically assessed. During sequencing batch reactor (SBR) tests, Shiskowski et al. (2006) observed that while changing the reactor pH had a negligible effect on DO, ammonia and NO_2^- concentrations, it had a strong influence on nitrous acid and off-gas N_2O concentrations. Decreasing the pH from 8.2 to 7.2 resulted in subtle changes in nitrous acid and N_2O concentrations, while increasing pH from 7 to 7.9 resulted in a substantial decrease in both nitrous acid and N_2O concentrations. These results support the theory of nitrous acid as the electron acceptor instead of NO_2^-, although further research into this possibility is needed. While pH can have a significant direct influence on bacterial metabolism, it is possible that it influences N_2O generation and emission via controlling the equilibrium between NO_2^- and nitrous acid, which could effect two important aspects of nitrifier denitrification; the electron donor supply, and the concentration of inhibitory substances (although a comparison of relative toxicity of NO_2^- and nitrous acid as not been found in literature).

Reactor SRT has a strong influence on the bacterial population balance in wastewater treatment processes and has been utilized as a population control mechanism in several alternative treatment processes such as SHARON and shortcut removal via NO_2^-. The effect of SRT on N_2O generation has received little focus to date, possibly since SRT is a fundamental process parameter which has a long term effect determining the nature of the microbiological community and is not a short term parameter suitable for routine process control. Noda et al. (2003) observed that SRT less than 10 days resulted in increased N_2O generation. Similar results were obtained by Zheng et al. (1994), where N_2O generation was significantly increased for SRT less than 5 days. Decreases in SRT result in decreased AOB and NOB population (although AOB are less sensitive) and corresponding increases in ammonia and NO_2^- concentrations (Zheng et al. 1994), both of which are important factors in N_2O generation.

Ammonia has been demonstrated to have a strong influence on N_2O generation, with its presence deemed an absolute requirement (Kampschreur et al. 2008a; Liu et

al. 2008) In laboratory scale work with a nitrifying activated sludge, Burgess et al. (2002a) observed a strong correlation between ammonia shock loadings and N_2O off-gas concentrations, although there appeared to be a maximum ammonia concentration above which there was a saturation effect and off-gas N_2O emissions were no longer proportional. The observed N_2O generation response to rapid increases in ammonia concentration is highly dynamic, with a nearly immediate response and peak N_2O concentrations being reached within 10 minutes (Burgess et al. 2002a; Kampschreur et al. 2008a). It is likely that ammonia triggers N_2O generation via the resulting depletion in DO concentrations as it is metabolized, which in turn promotes N_2O generation as discussed previously.

As seen in the preceding discussions, while some of the specific mechanisms remain unclear and require further investigation (in particular for nitrifier denitrification), off-gas N_2O emissions are strongly linked to suboptimal metabolic conditions. Many of the emerging alternative treatment processes (such as OLAND, CANON, SHARON, and Anammox) require operation at suboptimal conditions, which could result in significant off-gas N_2O emissions. Gaining knowledge of these production mechanisms is a priority since the possibility exists to convert a water pollution issue into an air pollution one, potentially offseting some of the benefits of these alternative processes.

A number of challenges exist with regards to improving knowledge of N_2O generation processes. Mao et al. (2006) noted that N_2O generation rates reported in literature vary widely. In addition to variability in N_2O generation potential amongst bacterial species (Colliver and Stephenson 2000), the variation in measured N_2O emissions could also be due to the lack of a standardized monitoring protocol. As discussed previously, a range of parameters can influence both nitrifier and heterotrophic denitrification, and as a result N_2O generation. Thus, variations in experimental apparatus, reactor operation and sampling techniques can have a strong influence on the measured emissions. As a result there is a need to standardize monitoring to allow greater reproducibility and better comparison of results from different processes and research groups.

Limited data exists for N_2O emissions from full scale wastewater treatment processes (Kampschreur et al. 2008a), and while it can be useful to extend laboratory

scale data to full scale applications for emissions estimation purposes, care must be taken in doing so. Differences in the microbiological communities as well as the environmental and operational parameters can limit the applicability of pure culture and laboratory scale data to full scale wastewater treatment processes (Kampschreur et al. 2008a), and furthermore N_2O stripping from the liquid phase in laboratory scale reactors can be substantially greater than that in full scale processes, resulting in overestimation of emissions (van Loosdrecht and Jetten 1998).

2.1.5 Summary

While the biological aspects of conventional ammonia removal processes are well understood, substantial gaps exist in our knowledge of alternative nitrogen removal processes and pathways. In particular gaps exist with regards to the specific reaction mechanisms involved in aerobic denitrification processes, as well as the identification of specific substrates and electron donors/acceptors. The role of nitrous acid as an electron acceptor for nitrifier denitrification in particular warrants additional investigation.

Another existing knowledge gap concerns N_2O emissions from emerging alternative nitrogen removal processes such as SHARON, CANON, OLAND and Anammox. A need exists to better define emissions from these processes and determine if the potential impacts of these emissions counterbalance their benefits. Finally, there is a lack of *in situ* data to assess the importance of nitrifier denitrification in off-gas N_2O emissions from full scale wastewater treatment plants, as well as the influence of specific operational parameters on these emissions.

A number challenges exist in this research area which, if overcame, could improve the rate and quality of knowledge generation. Ambiguity and confusion has been generated by inconsistent use of terminology in literature to refer to the various nitrification and denitrification processes. Aerobic denitrification and N_2O generation are highly dependent on process conditions and microbial populations. The utilization of a wide range of monitoring techniques and protocols impedes the comparison and interpretation of data from multiple sources. Development of standardized methodologies or agreement on best practices would enhance the quality and comparability of collected data, which is particularly important with regards to data collection from full scale processes.

While this thesis does not place any particular focus on the biological aspects of alternative nitrogen removal processes and off gas generation, the stress response data obtained as part of model development (**Chapter 4**) provides some insights into the influence of specific process parameters and contributes to overall process understanding.

2.2 Activated Sludge Process Modelling

As with any chemical or biological process, it is desirable to be able to predict process performance for a wide range of applications including process design, optimization, control, and the evaluation of impacts of process changes or changes in operating conditions. These predictions are made using a process model. For activated sludge processes, the process model is in fact a combination of three submodels: a reactor hydraulic model, a settler model, and a biological process model. For the scenario being studied, hydraulic modelling and settler modelling can be approached in a relatively simplified manner (see **Section 5.1.2** for a discussion of the rationale for this approach). As such, the biological process model will be the primary focus of this review.

Models of the biological processes which occur in activated sludge bioreactors have evolved steadily in recent years. While Monod kinetics (which form the basis of most activated sludge models) were proposed in the 1940s, and some simplified process models were developed between 1950s and 1970s, it was indeed in the late 1970s where increases in computing power allowed increases in model complexity (Jeppsson 1996). This increase in model complexity resulted in a shift from a focus on steady state modelling to dynamic process modelling, culminating in the release of the general kinetic model developed by Dold research group at the University of Cape Town (UCT) in 1980 (Dold et al. 1980). The UCT model became the basis for the development of the current generation of activated sludge models such as the International Water Association's (IWA) Activated Sludge Model (ASM) series (Gernaey et al. 2004; Hu et al. 2003; Jeppsson 1996).

The first IWA ASM (referred to as ASM1) was introduced in 1987, and was intended to provide a framework for the development of future activated sludge models (Henze et al. 2000). This model provided the capability to simulate both organic carbon removal and nitrogen removal. With the increased uptake in biological phosphorus removal processes in the late 1980s and early 1990s (Henze et al. 2000), the existing models were expanded with additional biological concepts. Three of the primary biological phosphorus removal models are the UCT model, the IWA ASM models (ASM2 and ASM2d), and the Delft University of Technology

phosphorus (TUDP) removal model (Gernaey et al. 2004; Hu et al. 2003). While the UCT biological phosphorus removal model is an extension of the original UCT activated sludge process model, both the IWA and the Delft University of Technology models use a common basis of the ASM1 model to represent autotrophic and heterotrophic biological reactions. However, the IWA and Delft University of Technology models utilize differing approaches to simulate the phosphorus removal process. As the focus of the research presented in this thesis is on nitrogen removal processes, further discussion of the workings of the biological phosphorus removal models is beyond the scope of this work. For additional information on biological phosphorus removal models, the reader is directed to two reviews of activated sludge process modelling: Gernaey et al. (2004), which provides a good overview of the current status of the IWA ASM and the Delft University of Technology models, and Hu et al. (2003), which provides an excellent in-depth discussion of the fundamental differences between the available biological nutrient removal models.

The most recent addition to the IWA ASM family, ASM3, represents a change in the conceptualization of the heterotrophic biological reactions occurring in activated sludge processes. These modifications include the addition of a structured heterotrophic biomass, the addition of several state variables to the process model, and changes to the microbial decay pathways. Key differences between the models will be discussed further in **Section 2.2.1**.

Several other biological process model formulations exist, such as a biochemical oxygen demand (BOD) based model (Argaman and Papkov 1995), as well as more unified models which incorporate a number of aspects traditionally modelled with separate models (biological growth, settling/clarification and gas-liquid transfer) into a single model (Seco et al. 2004). A number of alternative nitrogen removal models, in particular multiple step models (Chandran and Smets 2000; Chandran and Smets 2005; Hiatt and Grady 2008a; Hiatt and Grady 2008b; Iacopozzi et al. 2007; Nowak et al. 1994; Ossenbruggen et al. 1996) have also been proposed. Despite the alternatives, the IWA ASM family of models (and modelling software based upon them) have become industry standard for most applications (Gujer et al. 1999; Seco et al. 2004).

As they are the industry standard and applicable to the system being studied, this review will concentrate on the IWA ASM family of models, particularly exploring the differences between ASM1 and ASM3 since we are not concerned with phosphorus removal models (the focus of ASM2 and ASM2d). Also, with the focus of this work being on the aerobic segment of the nutrient removal process, anoxic processes will not be considered in this review. Three key areas of interest with regards to these models will be reviewed:

- the conceptual bases of the models;
- protocols and methodologies for model calibration; and
- model uptake and application, including enhancements for prediction of additional pollutants and off-gases.

Other aspects of activated sludge process modelling, such as model formulation and selection rationale will be discussed in **Chapter 5**.

2.2.1 Model Conceptual Basis

ASM1 and ASM3 are both process models that have been derived to approximate the underlying processes responsible for biomass production, along with the transformation of oxygen, carbon, and nitrogen in activated sludge wastewater treatment processes. It is important to note that the models reflect the current understanding of these processes and are continually subject to scrutiny and change as that understanding evolves.

As mentioned in the previous section, ASM3 was introduced to enhance the representation of specific processes occurring within activated sludge processes. The default model formulations are presented on the following pages as **Table 2-3** and **Table 2-4**, for ASM1 and ASM3, respectively.

Table 2-3 ASM1 formulation matrix.

Category	Process	Process State Variables													Rate
		S_I	S_S	X_I	X_S	X_H	X_A	X_P	S_O	S_{NO}	S_{NH}	S_{ND}	X_{ND}	S_{ALK}	
Het. Processes	Aerobic growth		$-\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{Y_H}$		$-i_{XB}$			$-\frac{i_{XB}}{14}$	$\mu_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{O,H}+S_O}\right)X_H$
	Anoxic growth		$-\frac{1}{Y_H}$			1				$-\frac{1-Y_H}{2.86Y_H}$	$-i_{XB}$			$\frac{1-Y_H}{14\bullet 2.86Y_H}-\frac{i_{XB}}{14}$	$\mu_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{O,H}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\eta_g X_H$
Auto. Processes	Aerobic growth						1		$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{XB}-\frac{1}{Y_A}$			$-\frac{i_{XB}}{14}-\frac{1}{7Y_A}$	$\mu_A\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_O}{K_{O,A}+S_O}\right)X_A$
Biomass Decay	Decay (heterotrophic)				$1-f_P$	-1		f_P					$i_{XB}-f_P i_{XP}$		$b_H X_H$
	Decay (autotrophic)				$1-f_P$		-1	f_P					$i_{XB}-f_P i_{XP}$		$b_A X_A$
	Ammonification										1	-1			$k_a S_{ND} X_H$
	Hydrolysis – organics		1		-1										$k_h\left(\frac{\frac{X_S}{X_H}}{K_X+\frac{X_S}{X_H}}\right)\left[\left(\frac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\right]X_H$
	Hydrolysis – organic nitrogen											1	-1		$k_h\left(\frac{\frac{X_S}{X_H}}{K_X+\frac{X_S}{X_H}}\right)\left[\left(\frac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\right]\frac{X_H X_{ND}}{X_S}$

Table 2-4 ASM3 formulation matrix.

Category	Process	Process State Variable													Rate
		S_I	S_S	X_I	X_S	X_H	X_A	X_{STO}	X_{SS}	S_O	S_{NO}	S_{NH}	S_{N2}	S_{ALK}	
Het. Processes	Aerobic Storage		-1					$Y_{STO,O}$	t_2	x_2		y_2		z_2	$k_{STO}\left(\frac{S_O}{K_O+S_O}\right)\left(\frac{S_S}{K_S+S_S}\right)X_H$
	Anoxic Storage		-1					$Y_{STO,NO}$	t_3		x_3	y_3	$-x_3$	z_3	$k_{STO}\eta_{NO}\left(\frac{K_O}{K_O+S_O}\right)\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)X_H$
	Aerobic Growth					1		$-\frac{1}{Y_{H,O}}$	t_4	x_4		y_4		z_4	$\mu_H\left(\frac{S_O}{K_O+S_O}\right)\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_{ALK}}{K_{ALK}+S_{ALK}}\right)\left(\frac{\frac{X_{STO}}{X_H}}{K_{STO}+\frac{X_{STO}}{X_H}}\right)X_H$
	Anoxic Growth					1		$-\frac{1}{Y_{H,NO}}$	t_5		x_5	y_5	$-x_5$	z_5	$\mu_H\eta_{NO}\left(\frac{K_O}{K_O+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_O}\right)\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_{ALK}}{K_{ALK}+S_{ALK}}\right)\left(\frac{\frac{X_{STO}}{X_H}}{K_{STO}+\frac{X_{STO}}{X_H}}\right)X_H$
Auto. Processes	Aerobic Growth						1		t_{10}	x_{10}	$\frac{1}{Y_A}$	y_{10}		z_{10}	$\mu_A\left(\frac{S_O}{K_{A,O}+S_O}\right)\left(\frac{S_{NH}}{K_{A,NH}+S_{NH}}\right)\left(\frac{S_{ALK}}{K_{A,ALK}+S_{ALK}}\right)X_A$
Biomass Decay	Hydrolysis	f_{S_I}	x_1		-1				$-i_{XS}$			y_1		z_1	$k_H\left(\frac{\frac{X_S}{X_H}}{K_X+\frac{X_S}{X_H}}\right)X_H$
	Aerobic Endogenous Respiration (Heterotrophic)			f_I		-1			t_6	x_6		y_6		z_6	$b_{H,O}\left(\frac{S_O}{K_O+S_O}\right)X_H$
	Anoxic Endogenous Respiration (Heterotrophic)			f_I		-1			t_7		x_7	y_7	$-x_7$	z_7	$b_{H,NO}\left(\frac{K_O}{K_O+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)X_H$
	Aerobic Respiration (Storage Compounds)							-1	t_8	x_8					$b_{STO,O}\left(\frac{S_O}{K_O+S_O}\right)X_{STO}$
	Anoxic Respiration (Storage Compounds)							-1	t_9		x_9		$-x_9$	z_9	$b_{STO,NO}\left(\frac{K_O}{K_O+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)X_{STO}$
	Aerobic Endogenous Respiration (Autotrophic)			f_I			-1		t_{11}	x_{11}		y_{11}		z_{11}	$b_{A,O}\left(\frac{S_O}{K_{A,O}+S_O}\right)X_A$
	Anoxic Endogenous Respiration (Autotrophic)			f_I			-1		t_{12}		x_{12}	y_{12}	$-x_{12}$	z_{12}	$b_{A,NO}\left(\frac{K_{A,O}}{K_{A,O}+S_O}\right)\left(\frac{S_{NO}}{K_{A,NO}+S_{NO}}\right)X_A$

The specific stoichiometric factors (t, x, y, and z) are obtained by solving conservation equations for theoretical oxygen demand, nitrogen, and atomic charge for each specific process. The conservation matrix and solution methodology is presented in Henze et al. (2000).

ASM3 is fundamentally similar to ASM1, particularly with respect to the kinetic form and representation of nitrification processes. Monod kinetics are used extensively in activated sludge models, and form the basis for the switching functions utilized in the ASM family of models (Gujer et al. 1999; Henze et al. 2000). These switching functions are applied more for mathematical convenience than out of process understanding (Gujer et al. 1999). Typical switching functions found in the ASM family have one of the two following forms:

$$\frac{S_X}{K_X + S_X}$$

$$\frac{K_X}{K_X + S_X}$$

Where S_X is the concentration of a generic substrate and K_X is a generic half saturation constant.

The first equation represents the most commonly used type of switching function, in which the process rate is reduced as the substrate concentration decreases. This form is primarily used to represent the effect of primary substrate availability on biokinetic reaction rates, such as organic carbon for heterotrophic bacteria or ammonium for autotrophic bacteria. The second form, as shown in the second equation, is a less commonly used switching function which generally represents the inhibition of reactions by the presence of a substance, i.e. the process rate is reduced as the concentration of the substance is increased. An example of this process-substrate relationship would be anoxic denitrification processes in which the reaction rates are inhibited by the presence of dissolved oxygen.

ASM1 and ASM3 are also identical in their representation of nitrification processes. Both models represent nitrification as a single step process, where NH_4^+ is oxidized to NO_3^-, and it is assumed that nitrite is short lived within the reactor (Gernaey et al. 2004). Recently, a number of studies (Chandran and Smets 2000; Iacopozzi et al. 2007) have investigated the validity of the single step nitrification models. The single step nitrification model used in both ASM1 and ASM3 is unable to provide the

resolution to achieve a proper simulation of advanced nitrogen removal processes (such as the SHARON process) where elevated levels of nitrite form (Gernaey et al. 2004), as well as during process upset scenarios or for plants with specific nitrite limits (Iacopozzi et al. 2007). Current research into alternative nitrification models will be reviewed in **Section 2.2.3**.

Despite the overall similarities of the models, there are a number of key areas in which ASM3 has been modified. Key differences in the aerobic phase reactions utilized in the two models have been identified in **Table 2-5**, and are discussed in greater depth in the following paragraphs. Model identifiability will be discussed in **Section 2.2.2**.

Table 2-5 Differences between ASM1 and ASM3 (aerobic phase).

Model Aspect	ASM1	ASM3
Heterotrophic Growth	Direct growth on soluble substrate.	Soluble substrate storage followed by growth on storage compounds.
Biomass Decay	Primary degradation via death-regeneration concept. Secondary degradation using multistep model (hydrolysis and ammonification).	Primary degradation via endogenous respiration model. Secondary degradation using a single step hydrolysis model.
Model Identifiably	Multiple linked parameters.	Enhanced identifiably via process decoupling.
Model Complexity	11 state variables. 7 processes.	13 state variables. 7 processes. Simplified degradation of primary decay products.

Heterotrophic Growth

The heterotrophic growth model is one of the defining differences between ASM1 and ASM3. These differences are based on the assumed pathways in which organic carbon is assimilated by the bacteria. These assimilation processes are primarily concerned with readily biodegradable organic carbon (RBCOD), which is the fraction of the total organic carbon (typically small molecules like volatile fatty acids) that can be absorbed by the biomass and utilized directly (Henze et al. 2000). This fraction is generally modelled as soluble organic carbon.

Neither of the models allow for direct growth on slowly biodegradable organic carbon (SBCOD). The SBCOD fraction is modelled as a particulate and consists of complex molecules (including colloids) that must first be degraded extracellularly before they can be absorbed (Henze et al. 2000). These extracellular degradation processes (such as hydrolysis) are discussed as part of the biomass decay discussion in the following section. It should be noted that the ASM models do not treat soluble and particulate phase components differently, thus the presence of insoluble RBCOD or soluble SBCOD is of little consequence to the model results.

ASM1 utilizes a simple and straightforward growth process concept in which the RBCOD is absorbed into the cells along with dissolved oxygen and ammonium and is broken down to produce the energy required for cell growth and maintenance. While this process concept generally provides an adequate simulation for typical activated sludge processes (Koch et al. 2000), including pre-denitrification processes where storage compounds are not significant (Koch et al. 2000), and in plants where aerobic and anoxic processes occur in separate reaction vessels (Wang et al. 2007), the concept does not provide an adequate simulation of process scenarios where the presence of storage compounds is significant such as elevated concentrations of readily biodegradable organic substrates (Gujer et al. 1999), and in activated sludge processes with sequential aerobic and anoxic zones in a single reaction vessel (Balku and Berber 2006).

During the development of ASM3 there was a move to a structured heterotrophic microorganism model (influenced by ASM2). In this model, RBCOD is first absorbed into the cell and converted into storage products such as poly-hydroxy-alkanoates and glycogen (Henze et al. 2000). The heterotrophic microorganisms then consume the storage products to produce the energy required for cell growth and maintenance. This provides a slight increase in complexity through the addition of an additional state variable, the concentration of storage compounds (XSTO), as well as multiple decay processes (aerobic and anoxic) for these compounds. This increase in complexity is somewhat offset by the simplifications made in the secondary degradation processes.

It was recognized during ASM3 model development that this sequential storage/growth mechanism was chosen as a simplification (Krishna and Van

Loosdrecht 1999; Sin et al. 2005a). However, despite this conscious choice, the mechanism has remained an area of interest and criticism (Guisasola et al. 2005), with research aimed at improving the representation of heterotrophic storage/growth processes, in particular with respect to sequencing batch reactors (SBRs) operating under feast/famine regimes. For these operational regimes, it has been observed that fitting the data using ASM3's default sequential growth/storage model required the use of two different growth rates (Krishna and Van Loosdrecht 1999). This growth rate discontinuity, which has been subsequently reported in other studies (Avcioglu et al. 2003; Karahan-Gul et al. 2003), called into question the validity of the default ASM3 sequential storage/growth model.

As a result of the above observations, a number of modifications to this process have been proposed recently (Guisasola et al. 2005; Ni and Yu 2008; Sin et al. 2005a), primarily consisting of a simultaneous storage and growth concept, with the two processes occurring in competition and growth on storage products being dominate as substrate depletes. The ASM3 storage/growth mechanism remains an area of active research and consensus building (Sin et al. 2005a), and no official modifications to the model framework have been made at the time of this work.

Biomass Decay

In addition to alterations in the heterotrophic growth model, the representation of decay processes was significantly changed in ASM3 from that used in ASM1. This discussion will consider two processes typically presented separately in the ASM model family. The first process, which will be referred to as "primary decay", is related to the breakdown of biomass. While this process is referred to as biomass decay in the ASM models, it includes many subprocesses since its is a lumped parameter that accounts for all oxygen demand during starvation conditions (when decay rates are typically measured). Thus, biomass decay includes both those processes which result in a decrease in the bacterial population (cell death, predation, and lysis) and those which have a respirometric oxygen demand during starvation conditions, namely endogenous decay (Henze et al. 2000). Processes related to the further breakdown of the microbial decay products (primarily hydrolysis, and in the case of ASM1 ammonification) are generally considered as a separate process in the ASM model family. However, it is important to consider them in conjunction with the primary decay processes since they complete the

nutrient cycle. The processes which act upon the products of the primary decay processes to decay them to their final state will be referred to as "secondary decay processes".

To gain insight into the differences in the decay process concepts utilized in the two models, it is useful to look at the flow of nutrients (carbon and nitrogen). These flows are presented in a graphical manner as **Figure 2-1** and **Figure 2-2** for carbon and nitrogen, respectively. Thes figures were developed based upon the processes in the model formulations presented in Henze et al. (2000), and only consider the aerobic components of the models.

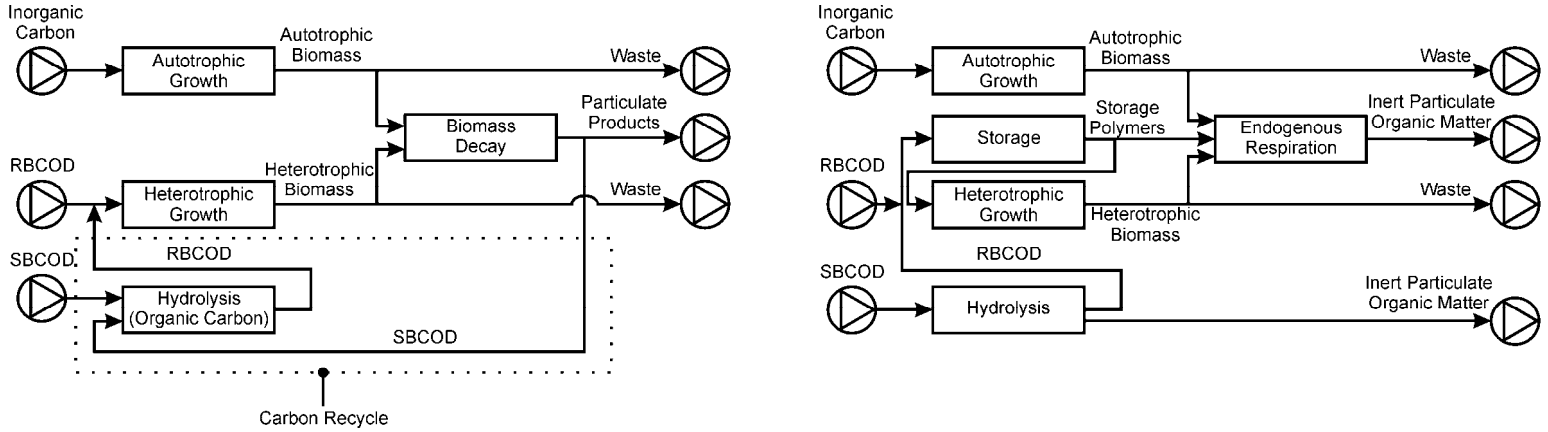


Figure 2-1 Comparison of carbon flow paths in ASM1 (left) and ASM3 (right).

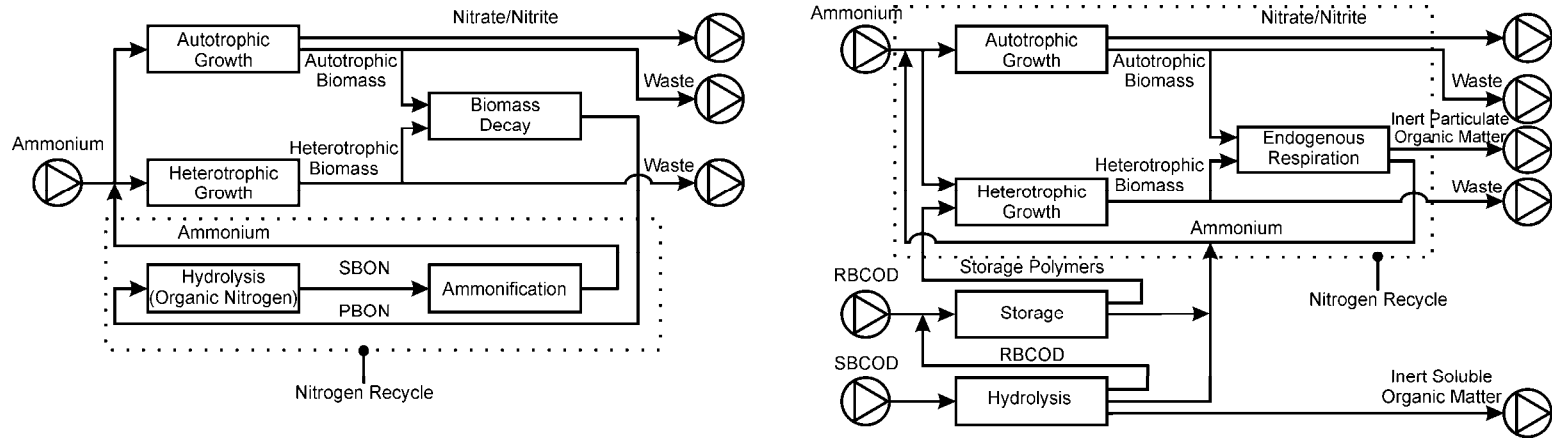


Figure 2-2 Comparison of nitrogen flow paths in ASM1 (left) and ASM3 (right).

An improvement in ASM3 over ASM1 is the provision for nitrogen balances in the model. As a result, the ASM3 model contains nitrogen fractions associated with all of the influent carbon streams (RBCOD and SBCOD). The completion of the mass balance results in a more complex nitrogen pathway in ASM3 over ASM1, which used a simplified flow pathway in which influent nitrogen was not associated with the influent carbon but instead assumed to be all in the form of influent ammonium.

In ASM1 (seen on the left sides of **Figure 2-1** and **Figure 2-2**), the decay process is referred to as a "death-regeneration" concept. In this concept, the decay products from the primary decay process are consumed by secondary decay processes to produce substrate which can then be metabolized to produce additional biomass. Effectively ASM1 allows for cannibalization. The death-regeneration concept produces strong connections between the heterotrophic and autotrophic bacterial metabolic processes. These interconnections can generate identifiability issues (Gernaey et al. 2004) that can complicate model calibration (which will be discussed further in **Section 2.2.2**).

In general, literature discussing the ASM1 decay mechanisms (Gujer et al. 1999; Henze et al. 2000; Mussati et al. 2002) focues on the connections in the carbon pathway which allows heterotrophic bacteria to utilize decaying autotrophic bacteria as a food source. However, connections in the nitrogen pathways also exist in the model, allowing for the autotrophic bacteria to utilize the decaying autotrophic and heterotrophic bacteria as a food source. While often overlooked, these connections would have an influence on nutrient removal processes, particularly with respect to model calibration.

As seen in the representation of ASM3 in the right sides of **Figure 2-1** and **Figure 2-2**, the carbon decay process been changed to a "once-through" concept. In the once-through decay process, only feed substrate is available for consumption by biomass. Following growth, all metabolic and primary decay products are emitted from the process via waste or process effluent. This effectively decouples the autotrophic and heterotrophic metabolic processes, improving model identifiability (Gernaey et al. 2004) and subsequently easing model calibration. However, as seen in **Figure 2-2**, a nitrogen recycle pathway remains that allows autotrophic bacteria to utilize

decaying autotrophic and heterotrophic bacteria as a food source. Thus the nitrogen decay process in ASM3 remains a death regeneration concept.

Contrary to existing process understanding, there is no oxygen demand associated with biomass decay in ASM1 via the cell lysis process (Henze et al. 2000). Instead, biomass decay results in an indirect oxygen demand via biomass growth using substrates produced by secondary decay processes. In ASM3 there has been a shift in the primary decay process from cell lysis to endogenous respiration. As a result all biomass loss and non-growth energy requirements are characterized via respiration processes and exert a direct oxygen demand (Henze et al. 2000). This endogenous respiration concept provides a better analogy to the respirometric methods commonly applied to measure activated sludge biokinetic parameters.

In addition to changes in the overall decay process, the handling of process to produce substrate (i.e. hydrolysis and ammonification) has changed in ASM3. ASM1 contains three secondary decay processes; two distinct hydrolysis processes, and ammonification. Ammonification in particular was not easily quantified and was often eliminated from most practical ASM1 model formulations (Henze et al. 2000). In ASM3, all of these processes have been lumped into a single hydrolysis process which utilizes non-readily biodegradable substances in the feed wastewater to produce both ammonium and readily biodegradable organic carbon substrates for biomass growth.

While both ASM1 and ASM3 are conceptually quite different (particularly with respect to heterotrophic growth and biomass decay), both models are seen as being capable of providing an acceptable simulation of most municipal wastewater treatment processes (Koch et al. 2000). This is primarily due to the calibration methodologies employed which can compensate for the conceptual differences.

2.2.2 Model Calibration

While many process model parameters can be measured directly or indirectly using respirometry and a range of physical and chemical analytical techniques, it is generally the case where some parameters are not practical and/or economical to

measure. Due to this, some form of model calibration is employed by modellers to compensate for parameter assumptions and fit the model to the available process data.

In general, calibration methodologies are as varied as the users of the models, and are highly dependent on personal experience and modelling objectives. The calibration techniques used in these methodologies can be broken down into the following general categories:

- manual calibration techniques;
- mathematical calibration techniques; and
- sensitivity analysis.

Manual calibration techniques, sometimes referred to as the process engineering approach (Gernaey et al. 2004), are the most basic and common calibration methods employed. These techniques consist of adjusting parameters until a good visual agreement is reached between the model outputs and the reference data sets used for calibration. This is indeed a very subjective approach, with the choice in parameters (as well as the range in which to vary them) being based on the modeller's experience and process understanding. The use of process knowledge generally constrains parameters within typical ranges, preserving some of the mechanistic aspects of the process model.

Mathematical calibration techniques typically consist of statistical methods employed to objectively determine optimal parameter combinations. Objective determination requires a quality criterion for comparison, such as minimizing sum of square errors (Ni and Yu 2008; Stricker et al. 2003). These methods are generally used in the place of manual calibration techniques.

An important consideration when employing mathematical techniques is that the parameters being adjusted lose their mechanistic significance and become best fit variables (Amano et al. 2002). This will impose significant limitations on extending the model to situations beyond those which it was mathematically calibrated for.

Sensitivity analysis itself is not a calibration technique, but more of a tool to support manual or mathematical calibration techniques. Sensitivity analysis enables the modeller to gain an understanding of the impact of changes in specific model parameters on the model outputs. These results can be used to streamline the model calibration process by reducing the parameters considered to those which have the greatest influence on the model output being calibrated. This form of analysis can also serve to reduce the subjectivity in parameter selection in manual calibration techniques.

While quite useful, the results of sensitivity analyses must be interpreted and utilized while considering limitations imposed on the results by the parameter analysis methodology and the range of the parameters investigated. With the exception of two papers which did not contain sufficient detail with regards to the sensitivity analysis methodology employed (Ferrer et al. 2004; Stricker et al. 2003), all of the sensitivity analyses reported in the reviewed literature were conducted on a single parameter basis utilizing the methodology presented in van Veldhuizen et al. (1999). Single parameter sensitivity analysis consists of varying one parameter and determining the effect on model outputs (often reported as a ratio), then the parameter is returned to its original value and another parameter is varied. This sort of analysis does not allow for synergistic or antagonistic interactions which may occur when multiple parameters are varied simultaneously.

In addition to the specific limitations identified for each of the above techniques/tools, there are a number of **common limitations**. While models are generally calibrated around a specific set of data, they are often used to test potential operational scenarios which can be at markedly different conditions. This is particularly important with regards to the type of data utilized in calibration. Care must be taken to ensure a model calibrated purely on steady state data is not employed for dynamic predictions since the model would not have been calibrated to incorporate internal dynamics (Gernaey et al. 2004). Sensitivity analyses in particular are bound to the operating point at which they were conducted since the results are entirely based on deviations from the starting operating point and should not be applied to substantially different operating points or processes.

Parameter identifiability and interactions can further complicate both manual and mathematical calibration techniques. It is quite possible to achieve similar quality model fits using different combinations of adjusted model parameters (Gernaey et al. 2004), with potentially quite different levels of model performance for scenarios outside the calibration range.

The variation in calibration methodologies and the specific tools employed is readily apparent from the reviewed literature (summarized in **Table 2-6** and presented on the following page). Literature summarized in **Table 2-6** was limited to ASM model formulations applied to real systems (laboratory-scale, pilot-scale, or full-scale). Literature which proposed calibration methodologies or contained purely theoretical model applications was not included.

Table 2-6 Calibration techniques employed for ASM-based modelling studies.

Study	Model	Scale	Behaviour	Technique			Comments
				Man.	Math.	Sens.	
Krishna and Van Loosdrecht (1999)	ASM3	Lab	Dyn/SS	✓			SBR on acetate
Ni and Yu (2008)	ASM3	Lab	Dyn/SS		✓	✓	SBR, minimising SSQ error
Ferrer et al. (2004)	ASM2d	Full	SS	✓		✓	
Koch et al. (2000)	ASM3	Full	Dyn/SS	✓			
Koch et al. (2001a)	ASM3/BioP	Full	SS	✓		✓	
Koch et al. (2001b)	ASM3	Full/Pilot	SS	✓		✓	
Amano et al. (2002)	ASM2	Pilot	SS		✓		Optimal regulator method.
Weijers and Vanrolleghem (1997)	ASM1	Full	Dyn/SS		✓	✓	Mathematical and sensitivity analysis used to select calibration parameters.
Kristensen et al. (1998)	ASM1	Pilot	Dyn/SS		✓		Primarily curve fitting
Makinia et al. (2005)	ASM3/BioP	Pilot	Dyn/SS	✓		✓	
Nuhoglu et al. (2005)	ASM1	Full	Dyn/SS	✓			
Wichern et al. (2001)	ASM3	Full/Pilot	Dyn/SS	✓			
Stricker et al. (2003)	ASM1	Full	Dyn/SS	✓	✓	✓	Manual calibration followed by minimizing SSQ error for fine tuning.
Makinia et al. (2006)	ASM3	Lab	Dyn/SS	✓			
Sin et al. (2008)	ASM2d	Full	Dyn/SS		✓		Automated calibration method.

Behaviour
Dyn – Dynamic behaviour
SS – Steady state behaviour

Techniques
Man. – Manual calibration
Math. – Mathematical calibration
Sens. – Sensitivity analysis

Comments
SBR – Sequencing batch reactor
SSQ – Sum of Squares

As seen in **Table 2-6**, the dominant calibration technique utilized in the reviewed model applications was the manual process engineering approach. This reflects the simplicity and comfort of the approach. Mathematical calibration methods were much less common in the reviewed literature, likely reflecting the increased level of complexity involved in their use. Sensitivity analyses were quite commonly applied to support both calibration techniques by limiting the range of calibration parameters considered. Less common was the integration of all three techniques into one unified calibration method to draw on the strengths of the individual techniques. This is considered to be the optimal combination of calibration techniques (Gernaey et al. 2004) and is seen in the majority of the proposed modelling protocols (which will be discussed further in the following subsection).

It is interesting to note that the discussion of model calibration in much of the reviewed literature was rather cursory in nature, with many simply stating the method used without commenting on specific techniques employed. This can be reagarded as a weakness considering the strong influence of model calibration on final modelling results, and as such a thorough description of model calibration methodology and model assumptions should be a key part of every practical modelling paper.

Table 2-6 demonstrates that there remains a wide range of calibration options as well as individual techniques within options that can be applied to any given process. These approaches each have specific strengths and weaknesses, and an understanding of these is important in developing an appropriate and robust process model. However, the sheer volume of possible approaches (many of which can produce an equivalent "fit") can serve to confuse users, particularly those applying process modelling to solve specific problems in consulting and industry. Indeed, model calibration is seen as the key factor limiting the spread of models to full scale activated sludge processes (Sin and Vanrolleghem 2007). As a result, there has been a drive in recent years towards a more systematic and unified calibration approach, which could serve to enhance both uptake and confidence in activated sludge process modelling.

Calibration Protocols

In recent years a number of calibration protocols have been proposed. It should be noted that the scope of these protocols are not limited to the adjustment of parameters to fit a model to experimental data, they also encompass model development tasks including feed speciation, the collection of specific parameter data, development of subcomponent models (hydraulic and settling), and data reconciliation.

An excellent review of recently proposed calibration protocols was published in 2005 (Sin et al. 2005b). This review discussed the specific strengths and weaknesses of four recently proposed model calibration protocols:

- BIOMATH (Vanrolleghem et al. 1999a);
- STOWA (Hulsbeek et al. 2002);
- HSG (Langergraber et al. 2004); and
- WERF (Melcer 1999).

Sin et al. (2005b) noted that all of the protocols have common aspects in terms of assessing calibration needs based on study goals, emphasising data collection and reconciliation, and validation of developed process models. While they do share these aspects at conceptual level, the implementation is highly variable and represents the frame of reference of each of the protocol proponents (Vanrolleghem et al. 2006). These protocols provide a broad spectrum of approaches, ranging from the scientifically focused BIOMATH protocol, to the more generic HSG protocol, to the pragmatically focused STOWA and WERF protocols (Vanrolleghem et al. 2006). Each protocol places different emphasis on specific aspects of the model calibration process (including experimental methods, design of data collection campaigns, selection of calibration parameters, and specific calibration methods).

While these protocols attempt to standardize the model calibration process, they each leave fundamental components open to user interpretation and subjectivity. In particular, the BIOMATH protocol lacks detailed parameter calibration and data quality verification procedures, the STOWA protocol does not provide any detailed

guidance on hydraulic characterisation, sensitivity analysis or measurement campaign design, and the HSG protocol lacks specific guidance on influent/parameter characterisation as well as sensitivity analysis and calibration parameter selection (Sin et al. 2005b). The WERF protocol provides minimal guidance on settler model selection and determination of non-nitrification modelling parameters (Sin et al. 2005b; Vanrolleghem et al. 2006).

There is indeed a need to standardize the abovementioned components of the modelling process. *Ad hoc* experimental design can be quite problematic for activated sludge process modelling. A range of experimental methodologies exist to measure similar process model parameters (Vanrolleghem et al. 1999b), each requiring specific testing conditions and analytical techniques. In addition, there remains a lack of consensus and firm guidance with regards to the influence of many experimental parameters on these methods, including:

- suppression of heterotrophic bacteria by allylthiourea (a common nitrification inhibitor used in experimental methodologies), which would have an impact on the results of respirometric analyses (Benes et al. 2002);
- selection of substrate to biomass ratios for respirometric methods (Spanjers and Vanrolleghem 1995; Vanrolleghem et al. 1999b), which can influence test duration and at high ratios can result in growth and divergent evolution of the microbial population; and
- the use of alternative measurement techniques, such as the sequencing batch reactor based methods proposed by the WERF protocol (Melcer 1999), which can provide a different environment for microorganism growth that can result in divergent evolution and variability in kinetic parameter estimates (Grady et al. 1996; Sin et al. 2005b; Vanrolleghem et al. 2006).

In addition to a need to standardize the specific methods applied (both for ease of use and data quality purposes), a need also exists to improve the design of the overall sampling campaign to optimize the quality and quantity of data collected while minimizing the associated cost and time required. This need is based both on methodological/data quality concerns such as information density and capturing

appropriate dynamics, as well as more pragmatic concerns such as cost and time demands. While many researchers have proposed and assessed improvements to existing analytical techniques to increase information density, other research groups have looked at instead improving the design of the experimental sampling campaigns as a means of addressing both technical and pragmatic concerns. The BIOMATH protocol adopts the latter approach, focusing on the application of optimal experimental design techniques in the development of sampling campaigns. While this methodology has demonstrated the ability to optimize the balance between information content and pragmatic concerns in developing sampling campaigns, as noted by Sin et al. (2005b), being a model based process it requires specialist knowledge and appropriate software to implement, which could indeed limit the uptake of this technique.

While the calibration protocols place an emphasis on the bioprocess models, settling and hydraulic models can have a strong influence on model results. In particular, activated sludge process model outputs have been found to be highly sensitive to hydraulic parameters, in some cases more sensitive than to kinetic model parameters (Meijer et al. 2001). Errors in the simulation of reactor hydraulics are often the cause of large deviations in model parameters being required to achieve acceptable fits (Gernaey et al. 2004). Despite this, hydraulic models are only given cursory discussion in the majority of the modelling protocols, with the notable exception being the HSG protocol. The HSG protocol details development, calibration and validation of hydraulic models, and includes the use of tracer studies and computational fluid dynamic (CFD) modelling (Langergraber et al. 2004). While the more comprehensive approach to hydraulic modelling presented in the HSG protocol is a substantial improvement, the application of CFD may negatively impact the uptake and feasibility of model development due to the expertise required to conduct CFD modelling, and it has been noted that development of a CFD model for an activated sludge process is a time consuming task on par with the development of the biological model (Vanrolleghem et al. 2006).

The selection of calibration parameters is an area of potentially enormous variability and can strongly limit calibration reproducibility. Application of sensitivity analysis (which has emerged as a common method of parameter selection) is included in the BIOMATH protocol. However, while the methods to determine sensitivity are

generally fairly consistent with those presented by van Veldhuizen et al. (1999), the interpretation of the results remains quite subjective with regards to what level of sensitivity requires consideration and what can be left as default (insensitive). Furthermore, there are limitations with regards to the range of applicability since the sensitivity analysis is conducted around a specific operating point and only considers the influence of changing a single parameter at a time. Conventional sensitivity analysis ignores simultaneous changes in multiple parameters which could have synergistic or antagonistic effects.

Calibration incorporating sensitivity analysis results remains a manual technique, leaving much of the choice (selection of parameters, order of calibration, actual adjustment magnitudes, and fit quality criteria) in the hands of the modeller. With the existing variability amongst modellers with regards to process knowledge, technical backgrounds, and modelling experience, it is only natural that this manual process would result in the incorporation of substantial subjectivity and variability in the calibrated model.

An area of more recent research is the application of automated calibration procedures (primarily the adjustment of specific model parameters for fitting purposes). In addition to resulting in substantial time savings, these automated calibration procedures could impose much needed reproducibility and standardization. However, as noted by Sin et al. (Sin et al. 2005b), previous attempts at applying automated calibration procedures have not been successful due to complex interactions between model subcomponents. Thus automated model calibration remains an area of continued research.

Recently, Monte Carlo simulation has been applied to replace manual parameter adjustment, with good results during model validation (Sin et al. 2008). However, the authors note that this method could encounter limitations in model applicability and extrapolation if parameters are set to unrealistic values by the automatic calibration process, and this method requires further research and development. Being based on Monte Carlo simulation, the possibility exists to extend the automated procedures to provide information on other important aspects of the process model such as parameter (Smets et al. 2003) and prediction uncertainty (Koch et al. 2001b).

The presence of a range of calibration protocols (each with different focuses and methodologies) continues to provide confusion in the modelling community, limits the evaluation and comparison of results, and perpetuates the resistance noted by Sin et al. (2007) to the uptake of activated sludge process modelling. Furthermore, Sin et al. (2005b) identified model calibration as the weakest link in the activated sludge modelling process. While the need for a unified model calibration approach has been identified (Sin et al. 2005b), and the development of the recent protocols represent a drive towards standardization (and an improvement on the previous method of *ad hoc* calibration approach based on personal experience), unification remains to be achieved.

In developing a unified protocol, applicability is an area of concern. Sin et al. (2005b), for example, pushes for a more widely applicable protocol that could be extended to calibration of municipal wastewater treatment plants to non-conventional processes (attached growth processes, emerging processes such as alternative nitrogen removal processes like SHARON and CANON, and industrial wastewater), but at the same time acknowledges that this would require multiple specific protocols to achieve that objective. Therein lies one of the key dilemmas facing unification of calibration protocols, the trade-off that is required between applicability and standardization.

By producing a widely applicable protocol (such as the HSG protocol), the protocol becomes more of a high level guidance document in terms of specifying how the overall project should be conducted and which aspects considered, instead of the specific guidance to modellers with regards to tasks and methodologies. While such a protocol can ensure a common overarching approach, it allows for a high level of variability in the implementation of the actual calibration techniques, and as such does not address the problem of reproducibility and comparability amongst model calibration results.

More specific protocols allow for a much higher level of reproducibility and comparability by restricting the modeller's freedom via standardized methods. However, in doing so they restrict their range of applicability, for instance the use of respirometry and the experimental methods in BIOMATH restricts it to ASM models applied to specific wastewater process configurations. While this may not be an

issue for very common processes, it can be a problem in the future as models and processes evolve, since changes to processes or model structure can mandate the use of substantially different calibration techniques.

Indeed, both specific and generalized calibration protocols possess strengths and weaknesses, and none of the current proposed approaches are satisfactory to achieve the overall goal of comparable results which can be shared amongst model users. While a unified protocol is required, a novel approach is needed, which will likely be in the form of a hybridised protocol that combines the strengths of the individual protocols to overcome their individual weakness.

The hybridised model calibration protocol could be modular in form, with a common overarching model calibration philosophy (overall calibration process outline, experimental design technique, verification methodology, and quality/reporting requirements) which is then applied to key wastewater processes to develop highly specific calibration methodologies. This form of protocol would allow for a common approach to be applied, while at the same time providing guidance at a sufficient level of detail to allow meaningful comparison of modelling results within similar process types. Utilization of a modular framework would also allow for ease of horizontal protocol expansion (to incorporate new models and processes) without requiring established protocol modules to be reworked.

A lack of unified vision of the important components of calibration methodology, as well as the lack of consensus on specific calibration techniques and minimal guidance on model selection for specific processes and operational scenarios continues to limit the uptake and comparison/evaluation of activated sludge process modelling results. Achieving consensus amongst the activated sludge modelling community with respect to model calibration methodologies and the development of a unified model calibration protocol that is useable for both experienced and new modellers remains a challenge and an area of further research and development.

Model Identifiability

In addition to the development of model calibration methodologies there has been a recent research focus on model parameter analysis methods, primarily related to

model identifiability. In modelling, identifiability relates to the ability to determine a unique set of model parameters (i.e. a unique solution) to fit the model to a set of operational conditions (Brouwer et al. 1998). As seen in the previous discussion of activated sludge model calibration, reproducibility is a desired outcome. However, poor model identifiability introduces undesired subjectivity and variability into the model calibration process.

Two forms of model identifiability are discussed in the available literature; structural identifiability, and practical identifiability. Structural identifiability is based upon the model formulation, i.e. structure, and assumes the availability of perfect data in terms of both the quantity of state variables and data quality (Petersen et al. 2003). Structural identifiability is thus an inherent property of the model being used and is a fundamental model characteristic. Practical identifiability, on the other hand, is based upon the types and quality of the available data (Brouwer et al. 1998), and is more relevant to model development and calibration using experimental data. Furthermore, it is entirely possible for parameters that are identifiable from a structural perspective to not be identifiable from a practical perspective (Petersen et al. 2003), thus a thorough understanding of model identifiability is key to the development of meaningful experimental techniques for model calibration.

Structural identifiability of the ASM model family has been an active research area since the 1980s (Checchi and Marsili-Libelli 2005). Monod based (ASM type) process models are nonlinear in nature, and as such their structural identifiability are not as well understood and are complex to assess (Petersen et al. 2003). Activated sludge biological process models are considered to be overparameterised (Cox 2004) and, particularly in the case of ASM1, contain linkages between various processes such that the alteration of a single parameter can effect multiple state variables simultaneously (Gernaey et al. 2004). As such, many challenges exist to determine unique solutions for model parameter values.

The introduction of ASM3 as an intended successor to ASM1 was not only for the improved process mechanisms, but also for enhanced structural identifiability (Checchi and Marsili-Libelli 2005). It has been recognized that ASM3 has improved structural identifiability via the decoupling of many processes (Gernaey et al. 2004; Iacopozzi et al. 2007), in particular changing the decay process from a death-

regeneration concept to a once-through endogenous respiration concept, and alterating the hydrolysis processes. However, while the model has improved identifiability, ASM3 continues to have structural identifiability issues (Guisasola et al. 2005).

While all model parameters are structurally identifiable when both substrate and biomass parameters are available, when one moves to experimental applications with a reduced number of parameters being measured, not all parameters are uniquely identifiable and instead only specific combinations can be structurally identified, although they may not be practically identifiable (Petersen et al. 2003). Thus, practical model identifiability generally has a greater influence on model application (particularly on the development of experimental methodologies for parameter determination) and has been the focus of recent research efforts.

As noted by Brouwer et al. (1998), practical identifiability can be improved via optimising experimental design to maximize information content or reducing the number of unknown process parameters by fixing insensitive parameters or isolating specific processes. Indeed, much of the existing body of respirometric model parameter analysis methods (Kappeler and Gujer 1992; Spanjers and Vanrolleghem 1995; Vanrolleghem et al. 1999b) were developed based upon these techniques utilizing specific sequences/types of feed, as well as employing inhibitors to manipulate the biological processes to produce situations where specific components of the overall process were observable and the desired biological parameters were uniquely identifiable. Respirometric methods are fundamental methodologies commonly used in characterisation studies for ASM model calibration.

While these respirometric methods are quite well established, there has been a more recent interest in developing rapid or in some case online sampling methods to determine model parameters (Langergraber et al. 2003; Spanjers et al. 2002), as well as in the development of parameter measurement methodologies for more complex model formulations such as two-step nitrification models (Chandran and Smets 2000; Chandran and Smets 2005; Sin and Vanrolleghem 2007). These applications are complicated by the information density required to overcome practical identifiability issues.

A more recent approach in the literature is combining traditional respirometric analysis with additional monitoring to increase the available process information to enhance practical identifiability. These approaches have included augmenting respirometric analysis with titrimetric analysis (Sin and Vanrolleghem 2007) and titrimetric analysis combined with off-gas analysis (TOGA) for both oxygen and carbon dioxide uptake rates (Blackburne et al. 2007). These studies have demonstrated that enhanced identifiability can indeed be obtained via novel combinations of existing monitoring techniques. The analysis and application of these techniques (particularly with regards to parameter analysis for model calibration purposes) is an active research area, and further development/validation is required before they become accepted techniques for model calibration.

2.2.3 Model Uptake and Application

Activated sludge process models have been applied to wastewater treatment processes for a wide range of purposes, ranging from planning (process conceptual design and exploration of potential operating scenarios) to process and control system design, to operational implementation in model based control systems, to support tasks such as training (Langergraber et al. 2004). While activated sludge process models were developed to simulate biological reactions for activated sludge processes treating municipal wastewater, the versatility of the model base has allowed it to be extended and adapted for use in a range of applications including:

- modelling alternative suspended growth processes such as membrane bioreactors (Ng and Kim 2007);
- application for industrial wastewater treatment such as pulp mill effluent (Baranao and Hall 2004), cheese industry effluent, and pharmaceutical wastewater (Gernaey et al. 2004);
- investigation of biological processes in floc microenvironments (Li and Bishop 2003a; Li and Bishop 2003b); and
- integrated with expert systems as a tool to assist plant operators (Sorour and Bahgat 2004).

ASM3 has generally been accepted as containing many mechanistic improvements over ASM1 while being of a similar level of complexity (Gujer et al. 1999). However, being a newer model it is naturally less established and has a smaller pool of experience and evaluation of its predictive ability. This, coupled with ASM1 being able to sufficiently simulate most common wastewater processes (Koch et al. 2000) has slowed its uptake. Furthermore, there remains some doubt as to whether the improved fits obtained using this model are more a result of having additional parameters/processes to calibration than being a better mechanistic representation of the actual processes (Guisasola et al. 2005).

Thus, ASM1 remains the dominant activated sludge biological process model (Gernaey et al. 2004; Langergraber et al. 2004; Nuhoglu et al. 2005), used extensively in industrial applications as well as forming the core of most commercial activated sludge process modelling software packages (Mussati et al. 2002; Sorour and Bahgat 2004) and remains a continued source of novel research and development (Gernaey et al. 2004). Application of ASM3 has generally been restricted to specific situations where the improved mechanisms are of particular influence/importance, although the exact types of scenarios in which each model is the most appropriate choice remains to be defined, particularly as a part of the existing model calibration protocols.

At present, while ASM3 remains far from being the clear successor to ASM1 it was intended to be, the use and acceptance of ASM3 has been increasing. However, as discussed in **Section 2.2.1**, the internal storage processes (particularly related to feed/famine conditions) remains an area of current research and consensus (along with official model modification) has not yet been reached.

This discussion, like the majority of the literature reviewed, has focused on biological process models. However, bioprocess modelling is only one component (albeit an extremely important one) of wastewater process modelling. In general there has been a lesser focus in the literature on the other modelling aspects such as reactor hydraulics and settling and their impact on modelling results, although their importance has been recognized to varying extents in the recently proposed model calibration protocols (Hulsbeek et al. 2002; Langergraber et al. 2004; Melcer 1999; Vanrolleghem et al. 1999a).

With regards to model application there is a trend in the literature to discuss the biological process model components in depth, but provide much less detail for the other model components. There has been an attempt to develop a "whole package" model which incorporate the many submodels (including reactor hydraulics, settling, temperature, dissolved oxygen profiles, and biological processes) into one comprehensive model (Makinia and Wells 2000a; Makinia and Wells 2000b), however while more common in commercial modelling software, this type of model is in the minority in published literature.

As discussed previously, there has been some focus on the nonbiological components activated sludge process models in calibration protocols, however the level of focus is variable with respect to the protocols as well as the techniques employed to develop the individual submodels. The lack of a recognized "whole package" or standardized submodel development approach poses a challenge to the evaluation of model application, particularly with regards to drawing conclusions about specific submodels (such as biological models) when the results upon which the conclusions are based will contain influences from the other submodels (which are often accounted for in the "calibration" of the biological model).

In most literature, there has been a focus on short term studies, with some slightly longer term data (on the order of 1.5 - 2 months) being used for model validation in some studies (Makinia et al. 2005; Nuhoglu et al. 2005; Sin and Vanrolleghem 2007), however even these "long-term studies" are insufficient in duration to address issues related to long-term model application. Indeed, there has been little discussion of the long-term variability in model parameters and calibration lifespan remains an unexplored research area in the reviewed literature. This is particularly important for longer term applications such as model based control, model based expert systems, and assessment of long-term operational scenarios (seasonal basis). In long-term applications, variability in influent and environmental conditions will result in variable selective pressures on the microbiological communities employed in the wastewater treatment processes, allowing for population change over time and potential changes in biokinetic and stoichiometric parameter values. These changes (and the associated prediction errors/model uncertainty over time) could

limit the lifespan of the model calibration, which would have a strong influence on both the technical and economic feasibility of long-term model applications.

While the ASM model family has been quite successful in its base forms and has seen substantial uptake, many emerging model applications require the improvement of existing model mechanisms or the extension of the model package to incorporate additional parameters and processes. The evaluation of emerging nitrogen removal processes (such as SHARON and CANON) has led to development in ASM nitrification models since these process depend on "shortcut pathways" which involve emphasising one part of the nitrification process to achieve aeration savings. The ASM model family, however, utilizes a simplified one-step nitrification model. While this model is suitable for common processes operating under stable conditions (Iacopozzi et al. 2007), it cannot deal with scenarios where elevated nitrite concentrations occur (Gernaey et al. 2004) such as process upset conditions, low nitrification capacity processes, or the previously mentioned alternative nitrogen removal processes (Iacopozzi et al. 2007). With increasing focus on these processes, there is an emerging need for a better mechanistic understanding (and models) of the nitrification process.

As a step towards a improved mechanistic modelling of nitrification processes, a basic two-step nitrification model was proposed by Nowak et al. (1994). This model did not make any substantial changes to the remaining components of the ASM1 model base, and consisted of separating the lumped nitrification processes (autotrophic growth and decay) and state variables (autotrophic biomass and NO_2^-/NO_3^- concentration) into their individual components.

Chandran and Smets (2000) reviewed several of the proposed two-step nitrification models, and noted that all of the proposed models to date contained mechanistic limitations. Particularly notable was a failure by some of the models to account for ammonium uptake as part of the growth of ammonium oxidizing bacteria. Ossenbruggen et al. (1996) utilized a different approach, employing empirical fitting methodologies, however the model was directed more towards obtaining insight into mechanistic aspects, and as the authors noted, further work is needed to investigate if the mechanisms are indeed justified.

A more recent development is ASMN, proposed by Hiatt and Grady (Hiatt and Grady 2008a; Hiatt and Grady 2008b). Like many of the other two step nitrification models, this model was based on ASM1 and separated the lumped nitrification processes into AOB and NOB processes. In addition, several modifications have been made to the ASM1 model base to incorporate several new processes (mixotrophic growth of NOB, and assimilative NO_3^- reduction to NH_4^+) and adjustments to the reaction mechanisms for AOB and NOB growth. In ASMN, AOB and NOB growth utilize free ammonia and free nitrous acid as growth substrates, respectively. This introduces pH dependence into the nitrification process rates. While the model reflects the current understanding of nitrogen removal processes, there remains a need for further validation and the development of experimental techniques to evaluate specific model parameters.

There has been a focus in recent work (Chandran and Smets 2000; Chandran and Smets 2005; Sin and Vanrolleghem 2007) on the development of experimental methodologies to determine specific model calibration parameters for Monod based two-step nitrification models. The primary concern in these studies was identifiability of the individual process parameters, specifically obtaining a sufficient level of kinetic information from experiments to be able to uniquely characterise the two simultaneous components of the nitrification process (Chandran and Smets 2005). Identifiability issues have been approached in two ways, by the application of optimal experimental design techniques to optimize the quantity of kinetic information obtained from single respirogram assessment (Chandran and Smets 2005), and by using combined monitoring techniques (titrimetric and respirometric data) to increase information content (Sin and Vanrolleghem 2007). Despite advances in the development of two-step nitrification models, there remains a need for additional development and validation before they will become accepted enhancements to the ASM model family.

While there has been some research effort with regards to liquid phase nitrification enhancements to the ASM model family, the development of linkages between liquid phase models and the off-gas emissions for aerobic activated sludge processes remains a research gap. More specifically, a gap exists in published literature with regards to the modelling of off-gas nitrous oxide emissions from nitrification processes.

Even though this gap exists with regards to nitrification processes, research has been conducted to model the production of nitrous oxide by denitrification processes. These model studies (von Schulthess and Gujer 1996; Wicht 1996; Wild et al. 1995) focused primarily on liquid phase nitrous oxide concentrations (measured via gas stripping and subsequent gas analysis), although Wild et al. (1995) utilized an enzymatic approach to predict stripped gas concentrations directly. These modelling studies demonstrated that Monod processes were applicable to nitrous oxide generation, although as noted by Wild et al. (1995) these models contain a large number of unknown parameters which require the development of methodologies to determine them if proper mechanistic calibration is desired. Furthermore, it has been acknowledged that these models also include nitrous oxide generated in the aerobic nitrification part of the process, which would be significant, but not dominating (von Schulthess and Gujer 1996).

Understanding off-gas emissions is important not only for emerging non-invasive monitoring/control techniques, but for understanding emissions of greenhouse gases and other potential pollutants which are becoming of greater interest in a global climate of ever increasing emission regulation. The development of a nitrous oxide off-gas model for aerobic activated sludge nitrification processes will be presented in **Chapter 5**.

2.2.4 Summary

The ASM family of activated sludge biological process models remain the dominant model for domestic wastewater treatment, with the ASM1 model continuing to remain the industry standard despite the introduction of ASM3 (which contains mechanistic improvements) due to the existing pool of ASM1 knowledge and experience, as well as continued debate with regards to the implementation of some of the ASM3 mechanistic improvements.

While the ASM model family is well established and has been the subject of much investigation and evaluation, many knowledge gaps (and active research areas) remain, including:

- lack of consensus with regards to calibration goals and requirements;
- lack of a unified calibration protocol;
- poor understanding of long-term model calibration stability;
- requirement for continued development and refinement of model mechanisms such as storage phenomena and multistep nitrogen removal models; and
- lack of off-gas models for aerobic processes, specifically relating to nitrous oxide.

Of the abovementioned knowledge gaps, this thesis will focus on the development of liquid phase (ASM1) model extensions to allow the prediction of off-gas N_2O emissions from aerobic processes (**Chapter 5**). While the development and calibration of conceptually sound models is critical, it is important to note that modelling does not exist in a vacuum and model calibration/evaluation is highly dependent upon process monitoring, which will be the subject of the next component of this literature review (**Section 2.3**).

2.3 Non-invasive Activated Sludge Process Monitoring

Increasing cost pressures and effluent quality guidelines have lead to greater uptake of process monitoring technology at wastewater treatment plants (Hack and Wiese 2006). While process monitoring originated with off-site laboratory based techniques, there has been an evolution towards online instrumentation. The availability of online instrumentation provides a substantial increase in the quantity and quality of process information, enabling enhanced operation and control decisions.

Due to the inherent time variability in wastewater influent and treatment processes, online process monitoring has substantial benefits in terms of process tracking and ensuring compliance (Bourgeois et al. 2001), although it is the enhancement of process operation through improved control (Thomsen and Kisbye 1996) that provides the most significant benefits. In addition to providing improved compliance with effluent guidelines through more consistent operation, improved process control can have substantial economic benefits.

In a survey of UK wastewater treatment plants, Bogue et al. (1999) noted substantial operational costs savings associated with improved aeration control and avoided plant expansion due to increased process capacity associated with improved control. Indeed, improved control has been recognized as an efficient means of increasing facility throughput without increasing reactor size, i.e. capital cost investment (Vanrolleghem et al. 1994; Vanrolleghem and Lee 2003), in addition to improving process safety and allowing autonomous operation (Hack and Wiese 2006). Process control of activated sludge processes will be discussed in depth in **Section 2.4**.

Despite the apparent benefits, process monitoring is often infrequent in wastewater treatment plants (Bourgeois et al. 2003b), and along with process control/automation, has not experienced the same level of uptake as in other industries (Bourgeois et al. 2003b; Lynggaard-Jensen 1999). Indeed, many biological wastewater treatment processes rely on manual control, with the quality of the operation being a function of the operator expertise (Vanrolleghem et al. 1994). The

lack of uptake of process monitoring technology stems from a perception of poor reliability, reproducibility and data quality, as well as high cost/maintenance requirements (Bonastre et al. 2005; Love and Bott 2000). This perception is a result of the invasive nature of most sensors, which require continuous contact between the sensor and wastewater. Wastewater is a hostile environment for sensors and process monitoring equipment (Lynggaard-Jensen 1999; Yoo et al. 2008), causing instrument fouling, loss of sensitivity and reproducibility, and a need for frequent cleaning and calibration (Bourgeois et al. 2003b).

This poor perception has led to a widespread lack of confidence in online process monitoring (Bogue et al. 1999), with process monitoring being perceived as the weakest point in the control chain (Bonastre et al. 2005; Lynggaard-Jensen et al. 1996; Rieger et al. 2004b). With recent improvements to sensor/analyser performance and robustness (Bonastre et al. 2005; Bourgeois et al. 2001; Thomas and Constant 2004; Vanrolleghem and Lee 2003), this image may no longer be deserved. Vanrolleghem and Lee (2003) concluded that the most fundamental barrier to widespread acceptance of online process monitoring for process control is currently the wastewater treatment processes themselves, which have not been designed to accommodate real time process control, i.e. overdesigned and lacking flexible/controllable actuators.

Improved awareness of recent improvements and novel sensors amongst end users and practitioners is required to combat this negative perception. This task has been made more complex by the existence of a wide range of process monitoring techniques with variety of purposes, characteristics, states of development, as well as a lack of standardized instrument evaluation criteria. For the purposes of this literature review, monitoring techniques will be initially categorized based on their relationship with the medium being sampled. Two categories of monitoring techniques will thus be considered: invasive monitoring in which there is direct contact between the sensor and liquid wastewater medium, and non-invasive monitoring in which liquid phase conditions are indirectly determined by sensors that are not in contact with the wastewater.

As this work is focused on non-invasive process control, this review will concentrate on existing non-invasive monitoring techniques capable of delivering real time data

suitable for process control applications. Invasive process monitoring will be discussed briefly in **Section 2.3.1** to provide context and motivation for the emerging non-invasive techniques. These techniques will be grouped based upon response timescale. Non-invasive monitoring techniques will be classified based on their measurement objectives; specific parameter and process status monitoring techniques will be reviewed in **Sections 2.3.2** and **2.3.3**, respectively. Emphasis will be placed on the current status of techniques, as well as limitations, future research direction, and potential for incorporation into wastewater process control.

2.3.1 Invasive Process Monitoring

The majority of existing wastewater monitoring techniques are invasive in nature, including classic sensors such as pH, DO, conductivity and oxygen reduction potential, ion selective electrodes (ISEs), and more complex analytical systems such as respirometers, toxicity monitors, biosensors, automated wet chemistry analysers (colourimetric techniques), and titration off-gas analysers. These invasive techniques fall into one of two subcategories; *ex situ* monitors, in which a sample of wastewater is extracted from the process and sent to an analyser located outside of the process, and *in situ* monitors in which the sample analysis is conducted inside a probe immersed in the wastewater.

Ex situ systems are generally used for more complex analytical techniques (such as respirometers, toxicity monitors and automated wet chemistry analysers) that require controlled analytical environments, sample conditioning, and, for some analysers, chemical reactions. They thus require sample collection systems which include conveyance to the analyser and any necessary pre-treatment. While *ex situ* techniques allow for a wide range of process parameters to be analysed in a timelier manner than laboratory analysis, this comes at the cost of a number of significant disadvantages.

One of the main deterrents to the application of *ex situ* process monitoring is the requirement for sample transport and conditioning (Love and Bott 2000). Sample collection systems can block with rags and foul due to fats and biological growth (Russell et al. 2003), not to mention sample pumps are prone to clogging (Love and

Bott 2000). These issues, combined with reductions in pipe cross sections and sample cell size to reduce response time and chemical consumption (Schlegel and Baumann 1996), has led to sample filtration being required for all *ex situ* monitors. Membrane filtration processes (ultrafiltration) are most commonly used. Ultrafiltration units are high maintenance, with the maintenance frequency ranging from daily to every 6 weeks (Schlegel and Baumann 1996), depending on sampling location in the process train. A 2 to 3 week period between maintenance is seen as typical for systems sampling from aeration tanks (Lynggaard-Jensen 1999; Lynggaard-Jensen et al. 1996).

In addition to maintenance and reliability limitations associated with sampling and conditioning systems, concerns also exist with regards to the representativeness of the samples. Most invasive sampling systems collect small samples from a single point in the reactor. As such, the results are highly dependent on reactor hydraulics to ensure that the flow at the point in the reactor is representative of the bulk process.

The greatest limitation with regards to the application of *ex situ* process monitors for process control purposes is response timescale. *Ex situ* analysers have response times on the order of 10 to 25 minutes (Lynggaard-Jensen et al. 1996). With the addition of a sampling and conditioning system, a further time lag on the order of up to 20 minutes (Thomsen and Kisbye 1996) is introduced between the measurements and the actual process conditions. A 5 to 10 minutes measurement response has been identified as being ideal for online process control (Lynggaard-Jensen 1999; Lynggaard-Jensen et al. 1996; Thomsen and Kisbye 1996), thus *ex situ* process monitoring is incompatible with the majority of process control applications and there has been a movement in the industry towards *in situ* probes with much reduced response times.

In situ process monitoring focuses on specific process parameters of operational interest, and includes many classic process instruments such as temperature, pH, conductivity, oxygen reduction potential, and dissolved oxygen probes. With the increased interest in process monitoring utilizing *in situ* techniques, a number of new probes have emerged, extending *in situ* monitoring capabilities to include many parameters previously only possible via *ex situ* or offline analysis. These

emerging sensors include ISEs, biosensors, and invasive optical monitoring methods. *In situ* process monitoring has been the subject of many reviews in literature (Bonastre et al. 2005; Bourgeois et al. 2001; Hack and Wiese 2006; Lynggaard-Jensen 1999; Rodriguez-Mozaz et al. 2004; Thomas and Constant 2004; Vanrolleghem and Lee 2003; Winkler et al. 2004) and an in depth discussion is beyond the scope of this work. Instead a brief summary of the key benefits and limitations of *in situ* monitoring techniques is presented and the reader is directed to these reviews for greater detail.

Conventional Sensors

Classic *in situ* sensors (pH, DO, oxygen reduction, turbidity) are seen as having been refined to a point in which they are suitable for practical use (Lynggaard-Jensen 1999). This is supported by their prevalence in wastewater treatment plants. A survey of wastewater treatment plants in North America (Hill et al. 2002) demonstrated that DO, pH, and temperature sensors were by far the dominant process sensors employed to monitor reactor conditions in secondary wastewater treatment processes. DO probes in particular are considered to be reliable and accurate provided they are suitably located and properly maintained (Vanrolleghem and Lee 2003). There has been some recent emergence of optical DO sensors which have several advantages associated with the elimination of electrolyte, i.e. reduced maintenance and absence of sensor poisoning/electrolyte dilution (Hack and Wiese 2006), although conventional probes remain popular.

Ion Selective Electrodes (ISEs)

ISEs are a more recent sensor technology which has be gaining increasing acceptance and receiving a lot of research interest (Bonastre et al. 2005). In particular, the newer generation of ISEs are highly accurate at low concentrations and cope well with hostile environments (Kaelin et al. 2008), ideal for application in aeration tanks. ISEs are of particular interest for monitoring nutrients (nitrogen and phosphorus) in tertiary wastewater treatment (Vanrolleghem and Lee 2003), offering much reduced response time and reagent consumption over their colourimetric *ex situ* counterparts.

However, the application of ISEs to wastewater process monitoring is not without its limitations. ISEs utilize a membrane capable of binding the specific ions of interest.

Certain undesirable ionic species, referred to as disturbance ions, also bind to the membrane causing interferences. While the presence of these ions can be accounted for during calibration, issues can arise if the process is highly dynamic and disturbance ion concentrations vary temporally (Winkler et al. 2004). Effects of disturbance ions are particularly relevant when measuring at low concentrations (such as aeration tanks and process effluent), where the relative errors associated with the disturbance ions can become quite significant (Winkler et al. 2004). ISE maintenance requirements are generally moderate, with an average period 10 to 14 days between calibrations, membrane lifespans of up to 6 months (depending on water type), and electrolyte replacement required on a yearly basis (Winkler et al. 2004). Research and development of ISEs continues, with a focus on minimizing interferences as well as increasing the sensor lifespan and reliability (Bonastre et al. 2005).

Biosensors

Biosensors cover a wide range of sensors which consist of a biological component that is exposed to the wastewater medium on one side, and a sensing component on the other side that measures its response (Vaiopoulou et al. 2005). DO sensors are quite popular for response detection (Bourgeois et al. 2001), although other sensors (electrochemical, optical, mass or thermal) are used (Vaiopoulou et al. 2005). The selection of an appropriate biological component is key in sensor development. For biosensors applied in activated sludge wastewater treatment processes a trade-off exists between single species probes and probes utilizing broad microbiological communities. In general, pure culture probes are easier to manufacture (Vanrolleghem et al. 1994) and standardize (Vanrolleghem and Lee 2003), however this comes at the cost of a narrow substrate response range (Vaiopoulou et al. 2005; Vanrolleghem et al. 1994), which may cause inaccuracies and poor reproducibility in measurements.

A range of parameters are measured using biosensors, although the primary applications are BOD analysis and toxicity monitoring (Bonastre et al. 2005). There has been a lot of progress in the development of biosensors (Bonastre et al. 2005), and they are viewed as a promising technology although still needing more research and development (Thomas and Constant 2004). Particular areas of improvement include standardizing sensor maintenance and storage (temperature/pH control and

feeding), improving sensor lifespans (which are currently a matter of days to months), overcoming the substrate specificity while maintaining the manufacturing benefits of single culture probes, and reducing susceptibility to poisoning and deactivation (Bourgeois et al. 2001; Larsen et al. 2000; Rodriguez-Mozaz et al. 2004; Vaiopoulou et al. 2005; Vanrolleghem and Lee 2003).

Optical Monitoring

Optical methods have a long history in chemical analysis (Bourgeois et al. 2001) and form the basis for many analytical methods, particularly colourimetric analysis. The extension of optical methods to *in situ* sensors has focused on methods without reactions, including spectrophotometry (absorption and fluorimetry), light scattering techniques, and image analysis (Thomas and Constant 2004). Light scattering and image analysis techniques are primarily utilized for monitoring of solid material (suspended solids concentrations and activated sludge floc properties, respectively), and will not be discussed further in this review.

Spectral techniques allow for the analysis of a range of parameters primarily associated with organic matter (COD, BOD, TOC), as well as nutrients (NO_2^-/NO_3^-) and suspended solids (Rieger et al. 2004a; Thomas and Constant 2004). Spectral methods have several advantages including fast response speed, high versatility, low operation cost, no requirement for chemicals, and limited sample handling (Rieger et al. 2004a). *In situ* optical sensors have several challenges, primarily related to contact with the hostile wastewater medium. Optical sensors experience interferences by grease, oil, turbidity, organic matter, and inorganic ions such as chlorate and nitrate (Palmer et al. 2002). In addition to these interferences, optical sensors are subject to biofouling which can have negative impacts on calibration stability and instrument selectivity, and can experience significant signal noise associated with agitation and aeration (Rieger et al. 2004a). Optical analysis thus remains an active research area (Thomas and Constant 2004), and the development of non-invasive forms of optical analysis will be discussed in **Section 2.3.2.1**.

Overall, *in situ* process monitoring techniques have evolved to the point where they provide reasonably reliable process information in a timely manner suitable for process control applications. However, being invasive in nature, they do still suffer from the effects of fouling. In addition to losses in sensitivity and reproducibility

(Bonastre et al. 2005), fouling results in increased maintenance requirements (Schlegel and Baumann 1996) and associated costs.

While the majority of the reviewed research has been focused on improving invasive process monitoring techniques/technology, some research effort has been directed at the development of non-invasive means of extracting process information. Lacking the drawbacks of direct sensor contact with the hostile wastewater environment, the development of non-invasive monitoring techniques has the potential to result in highly reliable sensors with substantially reduced maintenance requirements. In general, the non-invasive techniques can be split into two broad categories based on their measurement objectives. The first family of non-invasive monitoring techniques (reviewed in **Section 2.3.2**) focus on the determination of specific liquid phase parameters of operational interest. An alternative approach is to monitor specific process parameters as surrogates for the metabolic status of biological reactions (**Section 2.3.3**).

2.3.2 Non-invasive Process Monitoring – Specific Parameters

Many of the developed non-invasive process monitoring techniques focus on the measurement of specific wastewater parameters, in particular lumped parameters to measure organic carbon (COD/BOD/TOC). These techniques include non-invasive optical methods and sensor arrays (electronic noses).

2.3.2.1 Optical Methods

As discussed previously, optical methods have a long history in wastewater analysis (Thomas et al. 2005) and are utilized for a wide range of parameters including various measures of organic carbon (BOD, COD, TOC), nutrients (total nitrogen, total phosphorus, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}), and solid material in the form of TSS and turbidity. Optical analysis methods cover a range of techniques including light scattering, UV/Vis/IR spectrophotometry, colourimetry, fluorimetry, and image analysis (Thomas and Constant 2004). With such versatility in techniques and parameters, it is only natural that these methods were adapted for online wastewater process monitoring.

While the focus of this review is on non-invasive optical monitoring techniques, these techniques have evolved from their invasive counterparts and share many technical aspects. As a much greater pool of experience and knowledge exists with regards to invasive optical monitoring, it is useful to draw upon this knowledge to provide a basis on which to assess the non-invasive techniques.

First generation optical online sensors were primarily *ex situ* in nature, owing to the negative impact/interference of suspended particulate matter which necessitated sample filtration. The dependence of traditional *ex situ* monitors on sample pre-treatment, in particular nutrient sensors based on colourimetry, limited the existing techniques' suitability for *in situ* process monitoring. As such, much effort is being placed in developing new optical monitoring techniques, with the upcoming generation of *in situ* optical sensors focusing on physical responses which include spectrophotometric techniques such as light absorption and fluorimetry for soluble substances, and light scattering techniques for particulate matter (Thomas and Constant 2004). These same techniques form the basis for non-invasive optical monitoring methods.

Technical aspects common to both invasive and non-invasive optical monitoring techniques development include data quantity and analysis techniques, wavelength ranges, and the combination of responses to different optical stimuli.

Data Quantity and Analysis

Historically, optical analysis of physical responses via absorbance or fluorimetry has been conducted utilizing single wavelength methodologies with linear regression, although sometimes two wavelengths have been used to compensate for interferences (Fogelman et al. 2006; Thomas et al. 2005; Thomas et al. 1996). A number of criteria are considered in wavelength selection, including the absorbance or fluorescence of the compound and interfering substances at the wavelength of interest, and response identifiability (Jeong et al. 2007). This has resulted in a wide range of potential wavelengths for specific parameters and a lack of standardized methods (Nyberg et al. 1996), although organic loadings are traditionally measured at a 254 nm wavelength (Russell et al. 2003).

There has been some recent research involving the application of more advanced data analysis techniques to single wavelength analysis to improve sensor robustness and component identification. Jeong et al. (2007) trained an artificial neural network (ANN) using UV data at a 300 nm wavelength to assess a number of wastewater properties of interest while at the same time eliminating the need for sample pre-treatment. While such a method requires longer term or intensive sampling to collect training data and is quite site specific, strong correlations and predictive capacity were obtained for TSS, total phosphorus and COD (Jeong et al. 2007). Detection of total nitrogen was limited due to the presence of solids which interfered with the detection of ammonia (Jeong et al. 2007), which would limit its application in dynamic environments where ammonia concentrations vary.

More recently, there has been a trend towards the utilization of full spectra analysis to assess both global wastewater parameters and the concentration of specific substances (Thomas et al. 2005; Thomas and Constant 2004). This transition has been enabled by increases in available computing power (Fogelman et al. 2006) as well as developments in advanced data analysis techniques. The absorbance/fluorescence response to any specific light wavelength is a mixture of the response of each of the individual components in the wastewater. Utilizing full spectra provides a much greater density of data and allows for the differentiation of the individual components of these mixed responses. In general, the application of multicomponent analysis techniques (including ANNs) is more pervasive in the analysis of multi-wavelength datasets (spectra) to determine concentrations of specific compounds (Fogelman et al. 2006), although multicomponent analysis has been applied for nonparametric analysis utilizing "fingerprint" techniques in other research areas such as chromatography and fluorescence (Thomas et al. 2005), and sensor arrays (discussed in **Section 2.3.2.2**).

Wavelength Range Considered

The far majority of optical monitoring techniques applied to wastewater analysis employ light at wavelengths greater than 200 nm. This is primarily due to the strong absorbance of UV light by water itself at wavelengths less than 200 nm (Fogelman et al. 2006; Lynggaard-Jensen 1999). Some organic compounds absorb only in this range (Thomas et al. 1996) and thus cannot be assessed by single wavelength optical methods. While this strong absorbance interferes with single wavelength

applications (Fogelman et al. 2006), the emergence of multiwavelength techniques allow the extraction of the useful data from this range via pattern recognition and chemometric analysis (Bro 2006; Fogelman et al. 2006), and sensors utilizing these techniques have emerged on the market (Lynggaard-Jensen 1999).

Response Combination

Another trend in optical monitoring techniques is the combination of responses (absorbance, fluorescence, and scattering) to multiple forms of light stimuli (UV, visible, and infra-red light). This combination of responses is seen as an emerging area of research (Bonastre et al. 2005; Thomas and Constant 2004) and serves to substantially increase the data density, improving the identifiability of individual response components and allowing for the application of more advanced data analysis techniques.

Reports of combined method techniques are quite limited in literature, particularly for non-industrial wastewater (Bonastre et al. 2005; Thomas and Constant 2004). Nataraja et al. (2006) combined fluorescence and UV absorption as a means of assessing wastewater BOD, however sensitivity was limited and interferences due to false positive influences by non-biodegradable organic matter were experienced. While this would not be significant for raw wastewater, which has a higher fraction of biodegradable organic matter, this interference would become increasingly significant as the biodegradable fraction decreases, such as inside an activated sludge process or in wastewater effluent. A second example of response combination is the combination of light scattering and fluorescence to non-invasively measure suspended solids and organic matter content (COD) of wastewater. This application, being non-invasive in nature, with be discussed further in the following paragraphs.

Application to Non-invasive Process Monitoring

With the transition to *in situ* methods, which require little to no sample pre-treatment, it is only natural that next step would be to remove the sensor from contact with the wastewater. Non-invasive optical monitoring for organic loading and suspended solids has been investigated as part of the Loadmon project (Russell et al. 2003). In this project, a prototype sensor based on a combination of light scattering and fluorescence was developed and trialled at wastewater treatment

plants. Two forms of the sensor were developed: one a short range sensor (10-20 cm) based on LED light sources which would be suitable for liquid flows in which the surface height does not change significantly, and the second a long range (up to 2 m) version utilizing diode lasers suitable for flows with highly variable surface heights such as those inside sewer systems.

Monitoring with the short range sensor corresponded well to actual COD and TSS concentrations (Russell et al. 2003). The long range sensor had good performance with regards to TSS (although large debris/solids were not detected and produced some variability), but performed quite poorly for COD, possibly due to interferences from ambient light on the long range sensor (Russell et al. 2003). This technique shares the benefits of *in situ* optical sensors, in particular a short response time, not requiring chemicals, and having a relatively low operational cost (Bourgeois et al. 2001; Stuetz et al. 2003; Vanrolleghem and Lee 2003), but without the probe tip fouling (and resulting sensitivity and reproducibility loss) associated with contact with the wastewater medium (Bonastre et al. 2005; Bourgeois et al. 2001). Furthermore, this type of sensor would be quite efficient for use in influent monitoring, where *in situ* optical sensors have been reported to have very poor reliability due to clogging and ragging (Nyberg et al. 1996).

While this non-invasive monitoring technique has been demonstrated at the laboratory scale and in some initial facility trials, the need remains for refinement including improvement of the ability of the long range system to track liquid levels (Russell et al. 2003). This monitoring technique has been mainly directed towards influent and effluent monitoring, and was not tested inside aeration tanks. Effluent monitoring results in dampening and a time shift of reactor dynamics (Ingildsen and Wendelboe 2003), thus monitoring in aeration tanks is generally more desirable from a process control standpoint. *In situ* optical sensors do experience noise due to aeration/agitation and interference by the presence of air bubbles (Bourgeois et al. 2001). It is likely that these effects, in addition to air/water interface disturbances associated with aeration, would introduce substantial signal noise, although this remains to be investigated.

This technique has potential to be incorporated into process control applications for activated sludge processes focusing on COD removal, but it would likely be of

more limited use for nitrogen removal processes. It remains to be seen if this monitoring concept could be extended to other optical techniques to allow for a wider range of parameter assessment and control concepts.

2.3.2.2 Sensor Arrays

Sensor arrays are non specific monitoring devices which attempt to mimic human sensory systems, in particular the sense of smell (electronic nose) and sense of taste (electronic tongue). While the electronic tongue is an invasive instrument used for liquid phase monitoring, the electronic nose samples gaseous emissions and is thus of interest for non-invasive process monitoring and will be the focus of this review.

From a technical standpoint, the application of sensor arrays differs from conventional monitoring techniques which focus on maximizing the sensor specivity to the analyte of interest. Sensor arrays attempt to mimic the human process of odour recognition though the use of a bank of sensors which are partially specific by design (i.e. they are designed to respond to a range of chemical compounds). The responses from these sensors are analysed using pattern recognition techniques to identify "fingerprints" for specific odours or compounds of interest.

Sensor Types

The two most common sensor types utilized in water quality monitoring are metal oxide sensors and conducting polymer sensors, although new sensor materials (such as composite polymers and nanocomposites) are constantly being developed (Ameer and Adeloju 2005). Metal oxide sensors are most useful in the detection of combustion gases (Gardner and Bartrlett 1999) and have the advantage of high sensitivity (low limits of detection), low production cost, and small size (Goschnick et al. 2005). Conducting polymer sensors offer greater versatility and allow for customization to a particular application through modification of the functional groups attached to the polymer chains. This versatility has led to conducting polymer sensors being the basis for the majority of the reported water monitoring applications.

Data Analysis

Sensor arrays can generate large quantities of data since multiple parameters are measured for each individual sensor in the array. Data reduction techniques (in particular multivariate data processing) are employed to reduce the dimensions of the data to a level that can be interpreted (Onkal-Engin et al. 2005). Both statistical approaches and ANNs have been evaluated for their effectiveness in analysing electronic nose data for environmental monitoring applications.

Principal component analysis techniques have been utilized in many studies (Bourgeois and Stuetz 2002; Canhoto and Magan 2005; Canhoto and Magan 2003; Dewettinck et al. 2001; Gardner et al. 2000; Nake et al. 2005; Stuetz 2004) to recognize patterns in electronic nose data by reducing the number dimensions while at the same time maximizing the variance of the data. The application of artificial neural networks for data analysis is widely used in many research fields for pattern recognition purposes (Gardner and Bartrlett 1999), and while ANNs have seen extensive use in the food and beverage industries to interpret electronic nose data, their application in environmental monitoring is more recent (Onkal-Engin et al. 2005).

An important difference between these two data analysis methods is the requirement for training. Principal component analysis is an untrained statistical approach, thus the data is examined for patterns without any outside influences. Artificial neural networks require training, which introduces an outside influence into the interpretation of the results, in addition to the cost and time associated with data collection. While no definitive data analysis methodology has been selected for electronic noses, both methods have been employed successfully to analyse electronic nose data, and good agreement was found when Onkal-Engin et al. (2005) analysed datasets using both statistical techniques and an ANN.

Applications

The development of odour monitoring devices based on non-specific sensors dates back to the 1960s, although the pace of development increased rapidly in the 1980s with advances in sensors, electronics and computing methods (Gardner and Bartrlett 1999). While there have been many successful applications of electronic noses for quality control purposes in the food and beverage industry (Gardner and

Bartrlett 1999), uptake of this technology for water quality monitoring has been slow, with research primarily related to the identification of microorganisms and monitoring sewage odours staring in the late 1990s (Dewettinck et al. 2001).

Applications of electronic nose monitoring techniques to water quality can be generally divided into two categories, potable water supply applications and wastewater treatment applications. Potable water supply applications have built on the use of electronic noses to identify bacteria and spoilage in the food industry, and have included detection of faecal contamination in water samples (Canhoto and Magan 2005; Canhoto and Magan 2003), detection/prediction of algal or cyanobacterial blooms (Gardner et al. 2000), and detection of chemical contamination by oil/fuel (Bourgeois et al. 2003a; Ogawa and Sugimoto 2002) and chlorinated organic solvents (Goschnick et al. 2005). While these applications have all demonstrated promising results, they remain emerging applications and the need exists for continued research and development, particularly with regards to operation of these systems on a long term basis to evaluate their stability.

Some of the applications of electronic noses for water quality monitoring are also applicable to the wastewater treatment industry. The detection of organic chemicals such as oil/fuel and chlorinated organic compounds is of use to the wastewater treatment industry as many of these compounds can interfere with treatment processes.

In a similar vein, electronic noses have been used for non-specific sensing to detect sudden changes in wastewater quality which could have impacts on facility operation (Bourgeois et al. 2003a; Stuetz 2004). These studies analysed data collected during field studies at a wastewater treatment facility for periods of 12 months and 6 months for Bourgeois et al. (2003a) and Stuetz (2004), respectively, and represent the most extensive field assessment of the application of electronic noses for online water quality assessment found in literature. Data mining algorithms were developed to efficiently interpret large datasets and reduce the influence of temperature, relative humidity and diurnal/seasonal variations on sensor response (Bourgeois et al. 2003a; Stuetz 2004). These algorithms enhanced the recognition of deviations from normal influent quality, and the monitoring system was able to

detect influent sewage quality changes due to unknown pollutants and spikes, providing early warning monitoring (Bourgeois et al. 2003a; Stuetz 2004).

While the detection of variability in influent quality is useful and can allow for control actions to be taken, these methods provide qualitative data and are not suitable for routine control of specific operational parameters in wastewater treatment processes. Knowledge of specific process parameters is highly desirable for process control purposes. Since odour monitoring is a global type parameter (an odour is really the combined sensor response to many odorants), excellent analogies can be drawn between this and many of the global wastewater parameters such as BOD that are used to characterize wastewater.

Stuetz et al. (1999b) utilized an electronic nose to evaluate wastewater BOD at various locations in three wastewater treatment plants. Using statistical data analysis methods, this study demonstrated the ability of electronic noses to differentiate between wastewater from different sources, and a linear correlation was developed between the sensor response patterns and the measured sewage BOD (Stuetz et al. 1999b). No general correlation could be made between the sensor responses and the measured BOD if data from all three plants were considered as one sample set (Stuetz et al. 1999b). This would be expected since the electronic nose responds to the individual substances making up the odour (analogous to the various types of organic matter contributing to the wastewater BOD) which would vary depending on the source of the sewage. Application of this form of monitoring would thus require the development of individual correlations for each facility. Onkal-Engin et al. (2005) followed up this work using a similar methodology, with the exception of artificial neural networks being used for pattern recognition. Similar conclusions were reached with respect to the applicability of electronic noses for online BOD monitoring.

Limitations and Suitability for Non-invasive Process Monitoring

While it has been demonstrated that electronic noses have potential for real time monitoring and process control applications for wastewater treatment, response variability (associated with environmental factors, particularly temperature and relative humidity) remains a challenge (Bourgeois et al. 2003b; Nake et al. 2005). Two approaches have been applied to deal with these effects: establishing a controlled

environment for the sensor to operate in, and software compensation (Bourgeois et al. 2003c).

The use of controlled sensing environments was fairly common in the reviewed literature. Ogawa and Sugi (2002) designed a system consisting of heating the water sample to vapourize the volatile organic compounds, passing the resulting gas sample though a humidity controller, and finally sending it to a temperature controlled cell containing the sensor array. A simpler design approach was evaluated by Bourgeois et al. (2003b; 2002), that consisted of bubbling inert nitrogen gas though the liquid sample to transfer the odorants to the gas phase, delivering them to a temperature controlled sensor array in the headspace.

While the effectiveness of environmental control for reducing the effects of temperature and relative humidity on sensory arrays has been demonstrated (Bourgeois et al. 2003b), these modifications increase the cost and technical complexity of the monitoring system. Furthermore, they result in the system being partially invasive since a liquid sample must be removed from the bulk process and sent to the analysis chamber. This introduces several of the limitations associated with invasive monitoring techniques, particularly sample representativeness, sample collection system fouling, and increased sensor response time.

An approach to compensate for the effects of these parameters in the sampling results (called parametric compensation) is required to evolve electronic nose monitoring to a fully non-invasive technique. Bourgeois et al. (Bourgeois et al. 2003a) utilized a moving window technique to mitigate the effects of temperature and relative humidity changes, as well as sensor drift. While this method was quite successful in identifying deviations from normal influent conditions, it is not suitable for the determination of specific component concentrations. The development of correlations between temperature, relative humidity and flow with sensor response has been problematic, although some success has been achieved by utilizing these parameters as inputs to ANNs (Bourgeois et al. 2003c).

Long term sensor response stability remains an area of ongoing investigation. Exposure to the high odorant concentrations found in wastewater over extended periods of time can contribute to sensor aging or poisoning, reducing instrument

sensitivity (Gardner and Bartrlett 1999). Furthermore, sewage odours are a reflection of the composition of the wastewater (Stuetz et al. 1999a) and experience corresponding time dependent variations (Stuetz et al. 1999b). In utilizing sensor arrays to predict wastewater BOD, poor correlation was observed over the long-term (due to temporal variations), although strong correlations could be obtained for short term periods of 4 weeks or less (Stuetz et al. 1999a; Stuetz et al. 1999b). This temporal dependence could impose the requirement for frequent recalibration or training which would have a negative impact on useability and acceptance at wastewater treatment plants.

Overall, the use of electronic noses for non-invasive wastewater process monitoring is a rapidly emerging application. Many of these applications are at varying stages of maturity, with non-specific monitoring techniques for wastewater influent being the most developed. While electronic noses themselves are commercially available and possess the advantages of being a relatively low cost and non-invasive means of process monitoring, a number of research and technical challenges remain before these applications become a commercially viable and accepted monitoring techniques. These challenges are primarily related to data analysis, in particular reducing the expertise requirement, development of a systematic method for selecting appropriate data analysis techniques, and advancement of data analysis techniques to enhance compensation for sensor drift, aging, temperature/relative humidity effects, and temporal variations in the wastewater matrix.

With further development, electronic noses have the potential to be incorporated into process control applications for activated sludge COD removal processes. To date, research with electronic noses in wastewater has focused on specific parameter monitoring (organic loadings). It remains to be seen if these sensing arrays could be utilized to detect specific off-gasses which are generated by the metabolic processes occurring in biological wastewater treatment processes, enabling real time monitoring of process status.

2.3.3 Non-invasive Monitoring of Process Status

While specific parameter monitoring has been used widely as part of process control applications at wastewater treatment plants, monitoring for process status is an emerging technique. Process status monitoring represents a shift in monitoring and control philosophy. In conventional applications, the monitored/controlled parameter is one believed to be of operational significance (typically reaction products or environmental parameters), and parameter setpoints are based upon process understanding. For process status monitoring, specific parameters (stress responses) are monitored as real time indicators of biological metabolic status, and control decisions are based upon that status. To date, non-invasive process status monitoring methods have been composed entirely of off-gas analysis techniques.

Many substantial advantages are associated with process monitoring techniques based on off-gas analysis. In particular, the parametric and IR based analysers used for measuring most gas phase compounds of interest are robust, accurate, have relatively low operational costs, and have similar acquisition cost as traditional liquid phase analysers (Hellinga et al. 1996). Off-gas analysers are low maintenance, and calibration is easily automated, allowing for stringent data quality control. Furthermore, off-gas analysis allows leveraging of existing technology and experience in industrial air emissions monitoring. Finally, since samples are taken from the reactor off-gas which is generally a well mixed flow, off-gas analysis techniques provide a good representation of overall reactor conditions and do not have the sample location selection issues inherent in liquid phase analysis (Hellinga et al. 1996; Weissenbacher et al. 2007).

Despite these advantages, off-gas process monitoring techniques have received rather limited attention (Hellinga et al. 1996). For activated sludge processes, two non-invasive process monitoring techniques have been proposed and evaluated to date. Off-gas CO_2 monitoring, which is an evolution of respirometry work, will be discussed in **Section 2.3.3.1**. The second non-invasive process monitoring technique, off-gas N_2O monitoring, utilizes metabolic stress responses to indicate process metabolic status and will be discussed in **Section 2.3.3.2**.

2.3.3.1 Off-gas CO_2 Monitoring

Process monitoring utilizing off-gas CO_2 analysis is an extension of respirometric techniques. Respirometry focuses on the determination of biological parameters (in particular process kinetics) through the measurement of oxygen consumption rates under specific conditions (Vanrolleghem et al. 1999b). These oxygen consumption rates can be measured directly in the liquid phase using DO probes, although many respirometers utilize sealed chambers and a non-invasive measurement approach consisting of headspace gas analysis, or CO_2 absorption and monitoring the resulting pressure or volume reduction in the apparatus headspace.

On-line respirometers are generally *ex situ* in nature. As discussed in **Section 2.3.1**, *ex situ* monitoring techniques do not provide data suitable for real time process control applications. Moving the off-gas analyser from the controlled environments contained in respirometers to the headspace of biological treatment processes allows for monitoring on a timescale more suitable for process control. Hellinga et al. (1996) investigated the potential for off-gas CO_2 and O_2 process monitoring to provide biological process information. This assessment was conducted from a theoretical perspective utilizing simulation techniques.

Hellinga et al. (1996) demonstrated that while it was possible to identify the substrate COD/TOC ratio and detect large changes in nitrification rate through off-gas analysis, the off-gas monitoring technique was unable to identify the ratio of carbon oxidation to nitrogen removal. Limitations in this monitoring technique were primarily attributed to interferences due to CO_2 production associated with bicarbonate chemistry, i.e. alkalinity consumption (Hellinga et al. 1996).

Building upon the theoretical work discussed above, Weissenbacher et al. (2007) conducted off-gas CO_2 monitoring on a pilot scale biological wastewater treatment process operating both as a batch and a continuous process. In order to overcome the limitations associated with bicarbonate chemistry influences and CO_2 mass transfer sensitivity to pH, a model was utilized to correct for both pH and alkalinity effects (Weissenbacher et al. 2007). The model provided good simulation of reactor bicarbonate concentrations and allowed for detection of changes to reactor biological activity using non-invasive off-gas CO_2 measurements (Weissenbacher et

al. 2007). While there was some dependence on liquid phase conditions for the corrective model (pH, temperature, flow and alkalinity), these parameters are generally readily available for most wastewater treatment processes. Furthermore, robust *in situ* sensors are available for pH, temperature and flow, while the required alkalinity measurements are periodic in nature and do not require online measurement.

Despite this monitoring technique being capable of providing real time process status information, its applicability for real time process control may be limited since it is a very broad technique, i.e. responds to a wide variety of process stresses/conditions, and would lack a specific control handle. This monitoring technique may be more suited as a process upset detection tool, although this suitability may change since it is an emerging technique and further research and development is required.

2.3.3.2 Off-gas N_2O Monitoring

The biological basis for off-gas N_2O emissions as a real time indicator of process stress was reviewed in **Section 2.1**. While there has been substantial research interest in off-gas N_2O emissions from nitrifying bacteria (both in soils and wastewater treatment processes), utilization of this response for process monitoring/control has received limited attention.

Off-gas N_2O emissions have been investigated as an upset early warning detection technique by a research group at Cranfield University in the UK (Burgess et al. 2002a; Burgess et al. 2002b; Butler et al. 2005; Butler et al. 2009; Stuetz et al. 2003). These studies were conducted on laboratory and pilot scale activated sludge wastewater treatment processes, and focused on analysing the off-gas N_2O response to various process stresses/upset conditions (influent ammonia spikes, substantial reductions in aeration supply, and the addition of nitrification inhibitors). N_2O was detected in the process off-gas for the full range of applied process stresses (Burgess et al. 2002a; Burgess et al. 2002b; Butler et al. 2005; Butler et al. 2009; Stuetz et al. 2003), indicating that the off-gas N_2O emissions are a generic

autotrophic metabolic stress response, and thus have strong potential for process upset monitoring.

Also of interest was the delay between the applied process stress and the appearance of unfavourable effluent conditions (i.e. NH_3 and NO_2^- in the effluent), which ranged from 0.43 up to 0.9 times the reactor HRT (Burgess et al. 2002b; Butler et al. 2009; Stuetz et al. 2003). Even though some of this lag would be biological in nature, it is likely that the far majority is due to reactor hydraulics. Off-gas N_2O concentrations were measured above the aeration tank, while liquid phase concentrations (NH_3 and NO_2^-) were measured in the process effluent from the settling tank. Effluent sampling introduces a hydraulic time lag in the measured liquid phase concentrations, and thus the observed early warning period would primarily be a function of the hydraulic properties of the aeration tank and settler (HRT and mixing). This dependence on hydraulics could be the source of the observed variability in the length of the early warning period.

Off-gas N_2O generation occurs simultaneously to process stress. Thus its detection indicates that a process is under stress and its performance is impaired, even though the effects of process failure (elevated effluent NH_3 and NO_2^- concentrations) will only be observed later due to reactor/settler hydraulics. While off-gas N_2O emissions do indeed provide early warning of deterioration in effluent quality, corrective action must be taken immediately since any deterioration in process performance will be ultimately seen in the effluent following the hydraulic time lag. As a warning technique, off-gas N_2O monitoring does not provide for advanced process control, and serves instead as a tool to assist process operators in decision making.

If proportional relationships can be identified between the level of process stress and the response (off-gas N_2O concentrations), the possibility exists to extend this method for routine process control. Burgess et al. (2002a) compared maximum off-gas N_2O concentrations to NH_3 shock loadings and identified a linear relationship, although there appeared to be a plateau at very high ammonia shock loadings. It is likely that as the spike loading increases, the increased metabolic stress forces more autotrophic bacteria to utilize the alternative metabolic pathway which generates N_2O. Eventually, a point is reached where the maximum possible amount of bacteria

are utilizing this pathway and the addition of extra stress (spike loading) has no effect in terms of increasing the rate of N_2O generation (and corresponding the off-gas concentration). The excess loading likely serves to extend the duration of the upset period. Analysis of net N_2O generation versus spike loading could provide a better correlation and warrants investigation.

For shock loaded processes, Stuetz et al. (2003) demonstrated that increasing the aeration rate when off-gas N_2O was detected allowed for mitigation of the process upset and a corresponding decrease in measured off-gas N_2O concentrations. This indicates that aeration has potential as a control handle for the process stress indicated by off-gas N_2O concentrations. It should be noted that there are some limitations to aeration as a process stress control handle. In particular, the presence of inhibitory chemicals such as ATU results in off-gas N_2O production without any net change in reactor DO (Burgess et al. 2002b; Butler et al. 2009). Thus aeration is unsuitable as a control handle during periods of process stress due to chemical inhibition. Further investigation is required into the suitability and limitations of aeration as a control handle.

The application of off-gas N_2O monitoring for nitrogen removal sequencing batch reactor (SBR) aeration control was investigated by Shishkowski (2004). Shiskowski (2004) utilized off-gas N_2O concentrations to identify changes in the oxygen consumption dynamics in the reactor and to signify important points in the operational cycle which could be used to initiate a control action (i.e. change in process aeration). The proposed control application was based on pattern recognition by an ANN which utilized off-gas N_2O and liquid phase DO and pH data as inputs, with the aeration flow adjusted based upon the recognized patterns (Shiskowski 2004). Such an application focuses on cycle optimization, which is quite different from real time aeration control in continuous wastewater treatment processes. While a control concept exists, it has yet to be applied to an operating wastewater treatment process and further research and development is required.

To date there has been no reported investigation of the potential for the application of off-gas N_2O monitoring for routine aeration control of continuous activated sludge nitrification processes. Evaluation of this potential requires the development of clear linkages between the monitored parameter (off-gas N_2O concentrations)

and the process stress (reactor loading/DO concentrations), as well as confirming the efficacy of the control handle (aeration supply) in adjusting the process. These aspects will be evaluated in **Chapters 4** to **6** of this thesis.

2.3.4 Summary

While many process monitoring techniques have made the move from *ex situ* to *in situ* analysers, non-invasive process monitoring remains an emerging area requiring further research and development. The potential benefits of non-invasive process monitoring are quite substantial; however the majority of these techniques have only been investigated in laboratory settings and have yet to be developed as full scale applications.

Many of the proposed non-invasive process monitoring techniques are dependent on the nature of wastewater and/or properties of the process' microbiological community, both of which can vary temporally. A need thus exists for the assessment of the long term stability and robustness of these techniques before they will gain acceptance and application in industrial settings. Furthermore, most of the non-invasive monitoring techniques are dependent on advanced data analysis techniques. While these applications will benefit from continued improvement of ANNs and statistical data analysis methods, this dependence may limit uptake due to the specialized expertise required for the establishment and operation of these systems.

The majority of the reviewed non-invasive techniques focused on process monitoring applications, and there has been limited assessment of the applicability of these techniques for wastewater process control. At their current state of development, process status monitoring techniques such as off-gas N_2O monitoring have demonstrated the greatest potential for future application in process control systems (aeration control in particular), but require further research and development. The current status of activated sludge aeration process control will be reviewed in **Section 2.4**, and the potential application off-gas N_2O monitoring for nitrifying activated sludge process control will be assessed in **Chapters 4** to **6**.

2.4 Aeration Control for Activated Sludge Nitrification Processes

Operation of BNR processes is complicated by diurnal and seasonal variations in influent, the adaptive nature of the microorganisms involved in the process, and random disturbances such as rain events (Islam et al. 1999) or intermittent/accidental industrial discharges. These operational concerns, along with increasing cost pressures and more stringent effluent quality guidelines have lead to a greater focus on enhanced process control for wastewater treatment plants.

The cost saving aspect of process control has been of particular interest for the wastewater treatment industry. A survey of wastewater treatment plants in North America (Hill et al. 2002) indicated that the primary rationale for the installation of process control and automation has been to realize energy, consumable and labour cost savings. Improved process control has been recognized as an efficient means of increasing facility throughput without increasing reactor size, i.e. capital cost investment (Olsson 2006; Vanrolleghem et al. 1994; Vanrolleghem and Lee 2003), as well as allowing autonomous operation (Hack and Wiese 2006).

Despite the economics advantages and being an accepted part of wastewater treatment processes, opportunities exist to expand the application of process control in wastewater treatment plants (Olsson 2006). The Australian wastewater treatment industry in particular has been seen as underutilizing process control in BNR processes (Islam et al. 1999).

As discussed previously in **Section 2.1**, biological nitrogen removal is performed by two distinct sub-processes which require different environments (aerobic and anoxic environments for nitrification and denitrification, respectively), each having their own performance objectives and manipulated variables. The purpose of nitrification is the conversion of NH_4^+ to NO_3^-. As such, the removal of NH_4^+ is the performance objective and dissolved oxygen concentration (via aeration supply) is the primary manipulated variable. Denitrification removes NO_3^- produced by nitrification, thus this removal is the performance objective. In practice, denitrification is commonly applied either as a predenitification process (upstream of the nitrification), or as alternating zones with nitrification. NO_3^- is supplied to the

denitrification zones through internal recycle flows from the nitrification zones. These recycle flows, along with external carbon addition rates, are commonly used as manipulated variables to control denitrification (Holenda et al. 2008). As this work focuses on the control of the nitrification component of BNR processes using aeration, denitrification control will not be included in this review, although denitrification control is included in many of the reviewed studies.

Dissolved oxygen is a key parameter with regards to the operation of nitrification processes. Furthermore, aeration is the single largest energy consuming component of most biological wastewater treatment processes, and has been reported to be on the order of 50% of the total facility energy consumption (Ferrer et al. 1998; Ingildsen et al. 2002). However, for some plants aeration can have an even higher relative energy demand, approaching 60% to 80% of total facility energy consumption (Chachuat et al. 2005a; Hamilton et al. 2006). Aeration control is thus seen as one of the most important factors for the safe and effective operation of nitrification processes, and has been widely accepted in wastewater treatment plants (Alex et al. 2002), although its application is not universal (Hill et al. 2002).

To provide a basis for the evaluation of the non-invasive aeration control concept developed in this work (**Chapter 6**), several aspects of importance to aeration control will be reviewed. A discussion of the various aeration strategies applied for BNR processes will be presented in **Section 2.4.1**. Existing techniques to evaluate process control strategies will be summarized in **Section 2.4.2**, while existing and emerging aeration control techniques will be reviewed in **Section 2.4.3**. Finally, the performance of the various aeration control strategies will be discussed in **Section 2.4.4**, and a review of existing barriers to the increased uptake of process control strategies in the wastewater industry will be presented in **Section 2.4.5**.

2.4.1 Aeration Strategies for Biological Nitrogen Removal Processes

The selection and development of control strategies for biological nitrogen removal processes are strongly influenced by the form of aeration utilized. Typically, most nitrogen removal processes utilize either continuous or intermittent aeration, with the difference between the two processes being the location of the anoxic

(denitrification) zones. For continuously aerated processes, the anoxic and aerobic process components are separated spatially based on which compartments receive aeration. In intermittent aeration processes, both aerobic and anoxic zones exist in the same reactor volume, but are instead separated temporally based upon the aeration schedule.

Intermittent aeration is commonly applied in small-scale nutrient removal processes (Chachuat et al. 2005b), and is well suited for batch type processes such as sequencing batch reactors. Generally, control of intermittent aeration processes can be seen as an optimization problem, and much of the focus is on the detection of the endpoints of the nitrification and denitrification steps to optimize the process cycle. The control of intermittently aerated nitrogen removal processes has been the subject of much research effort (Balku and Berber 2006; Balslev et al. 1996; Cecil 2003; Chachuat et al. 2005b; Fikar et al. 2005; Habermeyer and Sanchez 2005; Kaelin et al. 2008; Kalker et al. 1999; Lukasse et al. 1999). However, since the focus of this work is on larger scale continuously aerated processes, control of intermittent aeration processes will not be discussed further.

While much of the control research for continuously aerated nitrogen removal processes has focused on the adjustment of process DO concentrations to better satisfy the oxygen demands, the opportunity also exists to improve operation via control of process capacity (i.e. aerated volume). As noted by Vanrolleghem et al. (2003), historically, activated sludge processes were designed to guarantee a certain effluent quality without process control. Many of the processes were designed based on maximum capacity and are overdesigned for normal or low loading conditions. Thus, at low loadings the full capacity of the reactor is not being used and nitrification reaches completion before the end of the aerated component of the process, with the remaining aerated volume performing aerobic sludge stabilization, an inefficient use of aeration (Sahlmann et al. 2004).

Since most large treatment processes are constructed as a series of connected zones with independent aeration, the opportunity exists to reduce aeration demands by tailoring the active volume (facility capacity) to match the demand. Two distinct approaches exist in the literature; the first approach consists of simply shutting off the excess aeration volume and converting the zones into anoxic ones

(Brouwer et al. 1998; Ekman et al. 2006; Krause et al. 2002; Samuelsson and Carlsson 2002; Thomsen et al. 1998), reducing overall aeration requirements. Aeration to these zones is re-established when facility loading increases. A second approach, proposed by Sahlman et al. (2004), is to control the DO in the zones to reduce the nitrification rate so that the entire volume becomes active (i.e. nitrification reaches completion at the end of the final aerated zone). This makes use of the full reactor volume and aeration savings are realized through increased oxygen transfer efficiency at reduced operating DO concentrations.

With the on/off nature of both intermittent aeration control and aeration volume control, they are quite amenable to rule based control techniques. While the remainder of this review will focus on techniques for controlling nitrifying processes which are continually aerated, the control techniques discussed in **Section 2.4.3** are also of interest for intermittent aeration control and aeration volume control.

2.4.2 Control Strategy Evaluation

The development and evaluation of novel control strategies, along with their dissemination into the wastewater community is complicated by the variable nature of wastewater treatment processes. Differences in process layout and influent properties/variation patterns can influence control strategy performance. As a result, it is extremely difficult to compare the application of control strategies at different plants, and equally difficult to extend these applications to existing processes.

Benchmarking through process simulation offers the benefit of testing proposed control strategies without requiring investment in equipment or introducing variability associated with the performance of *in situ* process monitors (such as representativeness of monitoring locations, instrument fouling, and instrument reliability). The primary benchmark utilized for wastewater process control strategy development is the COST benchmark simulation model (Jeppsson and Pons 2004). This platform independent benchmark was developed to provide a consist basis on which to develop and evaluate control strategies, and consists of an ASM1 based

simulation model for a predenitrification process (consisting of 5 reactors in series with a settling tank and an influent profile representing different weather conditions and loading variations), and a testing protocol to compare control strategies (Vanrolleghem and Gillot 2002). While the COST benchmark was developed for a predenitrification process using an ASM1 model (to represent the most common application), this was intended to be a starting point, with the extension of the benchmark to incorporate additional processes and improved models being an ongoing process (Jeppsson and Pons 2004).

The far majority of recent simulation based literature utilized the process simulation component of the COST benchmark in its entirety (or with some minor modification), indicating substantial adoption of the protocol by the research community. Deviations from the benchmark (excluding site specific model studies), have primarily been to investigate alternative models such as distributed parameter models (Lee et al. 2006) and bilinear models (Ekman 2008).

Both the hydraulic modelling and controllability of the default predenitrification process contained in the COST benchmark have been questioned. Pons and Potier (2004) assessed the validity of the perfect mixing assumption utilized in the COST benchmark process model. They argued that based on the size of the benchmark process, the reactors would be large channels in which vertical recirculation cells could form, resulting in hydrodynamics that is between perfect mixing and plug flow and producing concentration gradients. However, when the process model was modified to incorporate these hydrodynamics, the observed effects were minor with regards to control performance, and simulation time was increased substantially (Pons and Potier 2004). Modification of the hydraulic model in the COST benchmark does not appear to be warranted since only a small gain in accuracy would be obtained at the cost of a large increase in simulation time (a decrease in usability).

Both Carlsson and Rehnstrom (2002) and Stare et al. (2007) reported limitations in control performance attributed to insufficient process capacity (i.e. the default process included in the COST benchmark is overloaded in some situations), concluding that additional aerated volume is required for the benchmark process. Insufficient capacity results in controller saturation which produces an excessively

high (and inefficient) operating DO concentration (Samuelsson and Carlsson 2002). Stare et al. (2007) converted one of the two anoxic compartments in the default process into an aerobic reactor to enhance nitrification capacity at the cost of denitrification. This modification reinforces the observation by Thomsen et al. (1998) that controlling aeration volume is more efficient then DO setpoint control for overloaded processes.

To assess control strategies, the COST benchmark utilizes a greyscale evaluation process in which the performance of a specific control strategy is represented by a colour, with the best performance being closer to white and worst performance being closer to black. For each of the 24 criteria considered in the evaluation process, the best and worst performing control strategies are used to set the range (the best performer is assigned 10% black, the worst performer 90% black), and the remaining control strategies are assigned colours based on a linear interpolation of their performance within that range (Vanrolleghem and Gillot 2002). Vanrolleghem and Gillot (2002) noted several limitations in this approach, namely that the results are highly dependent on the scenarios picked (relative analysis), and that the analysis lacks weighting to establish the relative importance of each of the evaluated criteria, which is necessary to properly assess the costs and benefits associated with control strategies.

In reviewing recent aeration control simulation literature utilizing the COST benchmark, it was interesting to note that while the facility layout, influent and process model components of the benchmark have been utilized, evaluations of the proposed control strategies have typically been limited to aeration savings and the effects on effluent quality (in particular average and peak effluent NH_4^+ concentrations), with the greyscale assessment procedure not being utilized. Thus, while progress has been made in providing a common basis for assessing control strategies, a need remains to standardize the assessment of the costs and benefits of implementing these strategies.

Several alternative process control evaluation strategies have been proposed. These strategies all focus on assigning cost values to the relevant process aspects (such as aeration supply, chemical addition and effluent discharges) to enable cost based comparisons.

Evaluation techniques proposed by Stare et al. (2007) and Vanrollegehem and Gillot (2002) utilize data generated from the COST benchmark model and operate as extensions to the existing benchmark. Stare et al. (2007) proposed a total cost approach which assigned costs to aeration, sludge disposal, external carbon addition, and effluent fines, but did not account for costs associated with the implementation and operation of sensors, actuators and other equipment associated with the process control strategy. A similar approach (TCI – Total Cost Index) was developed by Vanrolleghem and Gillot (2002), although this approach also considered the investment costs associated with control strategy implementation. Both of these strategies utilized sensitivity analysis to assess the robustness of the controller with respect to a range of process variations including fluctuations in temperature and influent flow, as well as performance during storm and rain events. Inclusion of sensitivity analysis greatly enhances the evaluation process, providing insight into potential limitations in the control strategies and assisting in the selection of applicable control strategies for existing full scale processes.

An important consideration with regards to cost based assessment of control strategies is the site specific nature of the cost weightings (Vanrolleghem and Gillot 2002), which result in the assessment being highly location dependent while the other aspects of the process used in the evaluation (process layout and influent) are generic in nature. The MAgIC (Matrix for Advanced Instrumentation and Control) methodology (Devisscher et al. 2006) represents a move towards a fully site specific assessment of control strategies. This methodology is based on the COST benchmark, but uses modified models that have been extended to include cost prediction for energy consumption (aeration, pumping and mixing), as well as for chemical addition and sludge treatment/disposal. The methodology does not account for costs associated with the implementation and operation of the control strategy. Furthermore, an influent data generator is provided that utilizes existing data to generate suitable model inputs for the simulation; filling data gaps as needed and generating an appropriate range of influent variations and discrete events such as first flush (Devisscher et al. 2006). The methodology specifies a baseline control scenario and control strategies are tested for a range of influent variation amplitudes and levels of facility loading, with cost functions being developed to estimate savings and allow comparison over a range of operation.

2.4.3 Nitrification Process Aeration Control

As discussed in **Section 2.4**, the application of aeration control offers many benefits in terms of cost savings and improved process performance. A wide range of aeration control strategies have been evaluated for application in biological nitrogen removal processes. In general, control strategies are categorized based on the location in the process where data is obtained for the control algorithm. This results in two broad categories of process control, feedback and feedforward control, whose basic forms are illustrated in **Figure 2-3**.

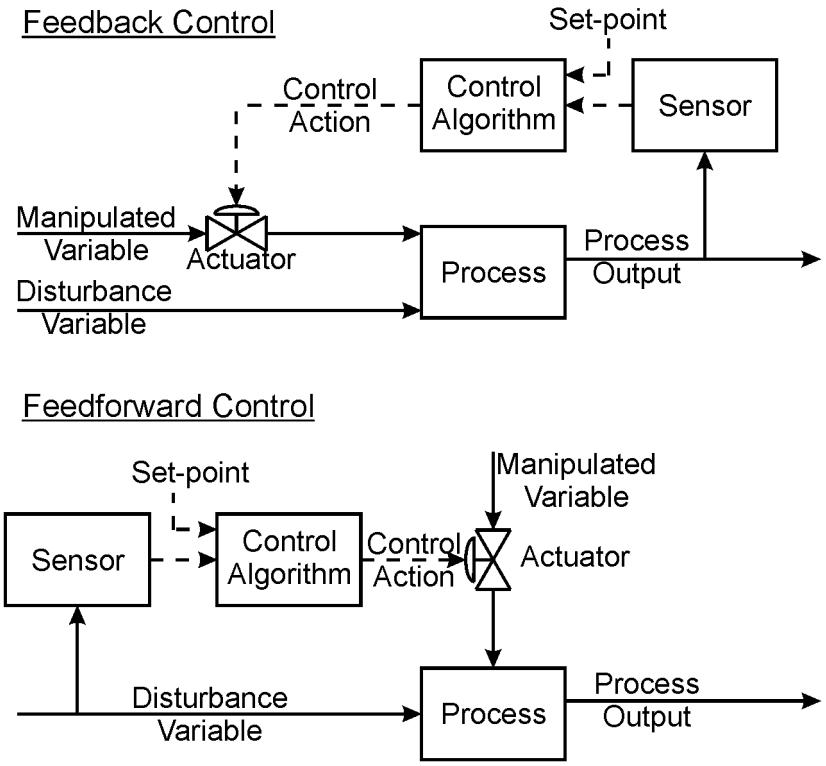


Figure 2-3 Feedback and feedforward control.

Feedback control (discussed in **Section 2.4.3.1**) is simpler in implementation than feedforward control since the control action is directly based on the process outputs. Sensor location is of particular importance for feedback control; in activated sludge nitrogen removal processes monitoring from the aerated chambers is preferred over monitoring effluent from the settler due to smoothing and latency effects (Ingildsen and Olsson 2002; Muñoz et al. 2009). While feedback control provides accurate control of effluent quality (Olsson 2006), the hydraulic delays in

wastewater treatment processes result in disturbances propagating through the reactor prior to being observed in the effluent and subsequently acted upon, limiting control authority.

Feedforward control is utilized as a means of increasing control authority and providing better disturbance rejection (Olsson 2006). In feedforward control, the process disturbances are measured and utilized to project the future state of the process, with a control action being implemented to control the process based upon these projections. Thus, action is taken to attenuate the disturbance before it propagates through the process (Ingildsen and Olsson 2002). With the long hydraulic delays inherent to activated sludge processes, feedforward control is seen as being an efficient means of process control (Vrecko et al. 2003). It is important to note that since the projection of the process state requires a process model, the quality of the control strategy is strongly dependent upon the model, which can introduce a level of complexity and uncertainty into the control strategy. Limitations associated with the incorporation of a process model into control strategies will be discussed in **Section 2.4.3.3**.

Fuzzy control and model predictive control (MPC) are the two primary forms of feedforward control that have been presented in the reviewed literature. Both forms typically operate in a hierarchical fashion (often called cascade control), acting as a supervisor which determines appropriate setpoints for the process. These setpoints are utilized by subordinate controllers (often simple feedback control loops for DO) to make the actual process adjustment. The primary difference between the two forms of hierarchical control lies in how the setpoints are determined. Fuzzy control (discussed in **Section 2.4.3.2**) utilizes a schedule of predetermined setpoints based on either simulation using process models of varying degrees of complexity and/or process experience. MPC (reviewed in **Section 2.4.3.3**) utilizes a range of influent (disturbance) parameters to simulate the process and selects the appropriate setpoint based on the results of this simulation.

It should be noted that the distinction between these forms of process control are not absolute, and examples exist of control strategies which combine different forms of control to achieve better performance in specific operating conditions.

These combined techniques will be categorized based on the most advanced technique employed (fuzzy or MPC).

In addition to aeration control, the control of the upstream aeration processes (compressors/blowers) has the potential to realize cost savings, and will be discussed briefly in **Section 2.4.3.4**. Finally, with increasing focus on process integration and process economics, a number of control strategies have emerged that incorporate process costs in an attempt to provide an optimal compromise between operational costs and process performance. These cost-based control strategies will be reviewed in **Section 2.4.3.5**.

2.4.3.1 Feedback Aeration Control

While much of the recent work discussed in the literature has focused on feedforward control strategies (**Sections 2.4.3.2** and **2.4.3.3**), feedback control is utilized extensively at the bottom level of control hierarchies to adjust aeration flows and maintain process DO concentrations at their setpoints, as well as for conventional DO control processes using manually determined setpoints. Several examples of feedback control that leverages improvements in nutrient sensor technology have been presented in the literature. In particular, effluent NH_4^+ concentrations have been utilized in a hierarchical manner to generate DO setpoints for implementation by a subordinate DO controller (Suescun et al. 2001; Vrecko et al. 2006), directly control the aeration supply (Ingildsen and Wendelboe 2003; Krause et al. 2002), or as a supplement to feedforward control to compensate for model approximations and improve controller performance (Ingildsen and Wendelboe 2003; Krause et al. 2002; Vrecko et al. 2003; Yamanaka et al. 2006).

Feedback NH_4^+ based control strategies have been demonstrated as being an effective means of controlling effluent NH_4^+ concentrations and achieving substantial reductions in aeration requirements (Ingildsen and Wendelboe 2003; Suescun et al. 2001). Furthermore, these controllers are relatively simple in nature and easy to implement in full scale processes. While feedback control strategies are often outperformed by the more advanced feedforward strategies (which will be discussed in the following sections), a number of concerns exist with regards to

feedforward control strategies including the complexity of implementation and long-term validity of process models. With these concerns and the existing comfort level with feedback control, feedback control strategies remain an important part of aeration process control.

2.4.3.2 Fuzzy Aeration Control

Fuzzy control is a rule-based control technique based on fuzzy logic which attempts to mimic the human decision making process. These controllers take input data and convert it into fuzzy data which is represented as a membership function; rules are then applied to this data to select the appropriate controller output, with the final step being the conversion of the process output from fuzzy data to a numerical action (Serralta et al. 2002).

Two primary advantages are associated with fuzzy control. These controllers are robust (accommodate a wide range of process conditions), and the rules used for the decision making process are written in a transparent, easy to understand manner (Reznik 1997). This transparency allows greater understanding by operators and facilitates modification, increasing acceptance (Meyer and Popel 2003; Yong et al. 2006). The rule-based nature of the fuzzy control makes it particularly suitable for on-off control and the uptake of fuzzy control for intermittently aerated and variable aeration volume processes is increasing (Chachuat et al. 2005a; Kalker et al. 1999).

While it is possible to control specific process parameters utilizing fuzzy controllers, fuzzy control strategies are more commonly applied in aeration control as a supervisor in a hierarchical control scheme. Both feedback and feedforward control strategies can be applied using fuzzy logic, and examples of both have been reported. Feedback fuzzy aeration control has been investigated via simulation (Galluzzo et al. 2001; Kalker et al. 1999; Serralta et al. 2002) and evaluated for a full scale process (Husmann et al. 1998). The control strategies utilized effluent NH_4^+ concentrations as the monitored variable, with the fuzzy controller increasing the DO setpoint for the subordinate controllers when the effluent NH_4^+ concentration

increases above a threshold, and decreasing the setpoint when it drops below the threshold.

A range of different fuzzy control strategies can be implemented using the same fundamental monitored variable (in this case effluent NH_4^+ concentration) through the imposition of constraints on the controller. For example, Serralta et al. (2002) restricted control to the final aerated chamber, maintaining a constant DO setpoint in the preceding chambers. This resulted in a form of process capacity control similar to that investigated by Salhlmann et al. (2004), and aeration savings on the order of 10% were projected. A more comprehensive fuzzy control strategy was applied by Husmann et al. (1998) which utilized a fuzzy supervisor to produce DO setpoints for subordinate controllers in each of the aerated compartments and adjusted the influent flow distribution to the process. This control strategy implemented DO setpoint changes in steps of 0.5 mg/L and was implemented on a full scale process for a period of one year, achieving a 16% reduction in aeration along with significant reduction in peak effluent NH_4^+ concentrations (Husmann et al. 1998).

Galluzzo et al. (2001) noted the possibility to improve fuzzy controller performance though the measurement of influent variations and implementation of feedforward control strategies. These potential performance improvements were confirmed in a comparative evaluation of NH_4^+ based fuzzy control strategies (Krause et al. 2002). In this study, a combined feedforward-feedback fuzzy control strategy (aeration volume determined by the feedforward component and individual compartment DO setpoints selected by the feedback component) was demonstrated to offer superior performance over its feedback counterpart, with reduced switching frequency (i.e. less wear and tear on process equipment) along with significant projected reductions in peak and average effluent NH_4^+ concentrations. Some increase in aeration requirements was observed (Krause et al. 2002), however given the significant projected increases in effluent quality, the possibility exists to reduce process performance and realize aeration savings.

Both Meyer and Popel (2003) and Yong et al. (2006) investigated the application of NH_4^+ based feedforward-feedback fuzzy controllers though process simulation and pilot scale application. Meyer and Popel (2003) predicted aeration reductions of up

to 25%, with energy savings during low loading periods and extended aeration volumes during peak periods to provide adequate process capacity. Slightly lower performance was observed during implementation at pilot scale, which would be expected moving from simulated perfect controllers/actuators to their real counterparts. Time delays had an impact on the feedback component of the control strategy, however substantial aeration reductions on the order of 23% were obtained, while the magnitude of effluent NH_4^+ peaks were reduced by 58% (Meyer and Popel 2003). A similar improvement in effluent quality (15.9% and 48% reduction in average and peak effluent NH_4^+ concentrations, respectively) was reported by Yong et al. (2006) though the application of combined external carbon and aeration feedforward-feedback fuzzy controllers, however a much lower aeration reduction of 10% was achieved (although this still represents a significant reduction).

Overall, fuzzy control strategies offer the potential to realize improved operation (tighter control of average and peak effluent NH_4^+ concentrations) and cost savings through more efficient aeration. Furthermore, their simplicity and transparency facilitates implementation and acceptance. The use of rules for setpoint selection does, however place some limitations on overall controller performance. In particular, the use of discrete sets of predetermined process setpoints limits the maximum possible controller efficiency. Fuzzy control strategies utilize a single setpoint to control a defined range of process conditions, unlike MPC (discussed in the following section) where the setpoint is optimized for the specific process conditions.

2.4.3.3 Feedforward Model Predictive Aeration Control

For the reasons discussed in **Section 2.4.3** (increasing control authority, disturbance rejection, and overall performance), the majority of literature focused on feedforward control strategies, in particular those based on MPC. Like fuzzy control, MPC is typically applied in a hierarchical fashion, determining setpoints for subordinate controllers. Unlike fuzzy control, MPC utilizes and explicit process model to predict future performance, which is used as a basis for determining the setpoints (Holenda et al. 2008). MPC control techniques originated in the power and petroleum industries, but have spread rapidly to other industries, and are of

particular interest for non-linear systems like wastewater treatment processes (Holenda et al. 2008).

The quality of control achieved by a MPC strategy is strongly dependent on the quality of the process model. Since the online application of the current generation of non-linear activated sludge process models (ASM family of models) is viewed as difficult if not impossible due to their complexity, the majority of MPC strategies utilize reduced models only describing important parameters (Stare et al. 2006). Several alternative model forms have been investigated ranging from linear models such as those developed using disturbance modelling principles (Zarrad et al. 2004), to bilinear (Ekman 2008) and nonlinear models (Stare et al. 2006).

Investigation of MPC strategy development using disturbance modelling principles (Zarrad et al. 2004) indicated that while a suitable model was developed, from a regulation point of view the proposed disturbance accommodating controller was difficult to tune and its performance was inferior to a conventional PI controller. The authors concluded that the process model developed using this technique was likely more suitable for diagnostic purposes than process control (Zarrad et al. 2004). Slightly more success was obtained using an MPC strategy based on a bilinear black-box model (Ekman 2008), although only small improvements were obtained versus a linear MPC strategy.

Stare et al. (2006) investigated the application of an ASM1 based nonlinear model and a linear black-box model in MPC strategies. The nonlinear controller provided the best performance in terms of effluent quality (mean and variance of effluent NH_4^+ concentrations), particularly during periods of low loading where the process nonlinearities become more significant (Stare et al. 2006). The authors conceded that since the development of nonlinear models is time consuming and costly, additional work is required at pilot scale to confirm the performance and determine if the benefit outweighs the increased implementation costs and complexity.

While demonstrating some promise, the utilization of more complex process models as a basis for MPC strategies represents a substantial increase in complexity, and further work is required (particularly at pilot and full scale) before they become accepted techniques and challenge the current generation of MPC strategies based

on reduced models. These studies also illustrated a trend within the MPC literature. The far majority of the reported work was based on simulation studies (which are a low cost, efficient means of developing and evaluating novel control concepts), and reports of MPC strategy application in pilot and full scale processes are quite limited (Ingildsen et al. 2002).

Ingildsen et al. (2002) provides an example of full scale implementation of a feedforward MPC strategy utilizing influent NH_4^+ concentrations. The control strategy focused primarily on optimizing the timing in which aeration was applied to the process (i.e. matching the supply with the demands). Influent NH_4^+ loadings were utilized as a tracer, with a relatively simple hydraulic model propagating the load through the reactor to determine its position with time. DO setpoints in the individual aeration compartments were adjusted according to the load position using a set of gain functions (Ingildsen et al. 2002). Despite constraints associated with limited compressor turndown, the control strategy achieved aeration savings on the order of 5-15% versus a reference lane operated using conventional DO control, while providing the same effluent quality.

While the majority of the MPC strategies encountered in the literature were feedforward in nature, a few exceptions did exist. Feedforward-feedback MPC strategies have been evaluated as a means of compensating for uncertainty associated with approximations used in process models. The potential for these strategies to improve controller performance in terms of both aeration requirements and effluent quality has been demonstrated (Ingildsen and Wendelboe 2003; Murphy et al. 2009; Vrecko et al. 2003), although only through testing on simulated processes.

Despite the potential benefits of MPC, a gap exists with regards to pilot and full scale implementation of MPC strategies, and a move from simulations to real processes must be made in order to obtain the firm assessments of benefits and implementation costs/issues required facilitate uptake into the wastewater treatment industry. Furthermore, questions remain with regards to the long term stability of these control concepts and requirements for retuning and recalibration. Biological wastewater treatment processes have time varying dynamics (in terms of the biological processes) which are not captured by the existing process models,

and the impacts of these variations can only be assessed through long term application of the control strategies on real processes.

2.4.3.4 Aeration Supply Control

The control strategies reviewed in **Sections 2.4.3.1** to **2.4.3.3** achieve aeration savings and improved process operation through the manipulation of aeration flows using control valves connected to a common header. The air in this header is pressurized by compressors which must replenish the air utilized to aerate the reactors. Opportunities exist to achieve further energy savings through improved compressor control and optimization (Alex et al. 2002).

Compressor operation is controlled to maintain a suitable pressure in the common header. Similar to DO control, it is possible to control the pressure to a constant value, or have variable pressure setpoints based on demand. In a simulation study, Alex et al. (2002) investigated the application of a "most open valve" control strategy in which the operating pressure is varied to maintain the air valves as open as possible. Simulations using this strategy indicated potential power savings of 11.4%, although it was noted that further optimization was possible (Alex et al. 2002). A similar reduction in compressor power costs (10%) was noted by Hewitt (1996) for a full scale activated sludge process by integrating the control of the entire aeration system (eliminating individual pressure control for each compartment) and applying a "most open valve" control strategy.

A hierarchical aeration controller was proposed in Piotrowski et al. (2008) to implement the DO setpoints generated by a supervisory controller. The proposed controller consists of two MPC layers, an upper layer which utilizes a dynamic model of process DO concentration to determine the airflow setpoints, and a lower layer utilizing an aeration system model to schedule blower operation and establish throttle valve setpoints. The authors report improved performance in simulation studies; however the benefits were not quantified.

While improved compressor control can result in significant cost savings, challenges exist in its implementation. In particular, tuning can be difficult and

interactions between control loops must be considered (Alex et al. 2002). Facility design also inhibits the application of improved compressor control. Compressors utilized to supply aeration systems in wastewater treatment plants are often oversized, limiting the controllability of the process, and in the case of insufficient turndown capacity, limit the potential aeration savings (Hill et al. 2002). Furthermore, if the compressors cannot be turned down below 50% capacity, a gap occurs in the output between one compressor operating at maximum flow and two compressors operating at minimum flow, impairing control and causing excessive compressor cycling (Hill et al. 2002).

2.4.3.5 Cost-based Aeration Control

While the feedforward and feedback control strategies discussed in **Sections 2.4.3.1** to **2.4.3.4** are capable of achieving improvements in effluent quality and reductions in aeration costs, the selection of specific operating points has a strong influence on the cost effectiveness of the process. In particular, improvements in effluent quality often come at the cost of increased aeration consumption, while reductions in aeration costs come at reduced effluent quality (Ingildsen and Wendelboe 2003). A further complication is the fact that the nitrification component of BNR processes does not exist in isolation, with several processes competing for DO and carbon (Olsson 2006).

The interconnections between processes can result in a single process input affecting several process outputs. This phenomenon, referred to as channel interaction, is common in wastewater treatment processes (Samuelsson et al. 2005). These interactions can result in cases of conflicting control objectives. For example, while increasing the DO concentration in the aerobic reactors can reduce effluent NH_4^+ concentrations, excess DO will be transported to the anoxic denitrification component of the process, impairing the overall nitrogen removal efficiency. These interactions are not considered when specific components of the process are controlled in isolation. A need thus exists to combine individual control systems (integration) and control the entire wastewater treatment facility as a cohesive unit (Olsson 2006), although it has been proposed to extend this integration to

encompass the entire process from sewer inputs to final effluent discharges (Schutze et al. 2004).

As processes are integrated, the number of manipulated variables and performance objectives increase. In addition to the fundamental objective of achieving stable operation and mitigating the effects of disturbances, control of the overall process also becomes an optimization problem. That is, determining which control handles are most efficient to mitigate a specific disturbance. This optimization needs to consider the costs associated with the potential control actions (such as chemical consumption through carbon addition or power consumption by blowers and pumps).

Process integration and cost-based control for BNR processes has received some attention in recent years (Cadet et al. 2004; Samuelsson et al. 2007; Yamanaka et al. 2006). While utilizing different approaches, a common goal exists of providing effluent which meets with the applicable discharge guidelines while minimizing operating costs.

In developing a multicriteria control strategy, Cadet et al. (2004) compared the performance of conventional DO control and a feedback aeration control strategy based on L/A control law using the COST benchmark process. They concluded that that conventional control was the most cost sensitive, while the L/A control law based strategy provided better effluent quality. These cost assessments were incorporated as part of a multicriteria control strategy using a fuzzy controller that determined the necessary compromise between cost and performance and selected the form of control to be applied accordingly (Cadet et al. 2004). While the multicriteria control strategy was successful at reducing operating costs and maintaining effluent quality, it is likely that improved performance could be obtained by replacing the L/A control law component with a feedforward control strategy (such as MPC).

Building on the economic evaluation procedure developed by Vanrolleghem and Gillot (2002), Yamanaka et al. (2006) developed and evaluated a total cost minimisation control strategy. This was a hierarchical control strategy which utilized a high level static optimizer based on a simplified process model and the Total Cost

Index evaluation procedure. The high level static optimizer operated in a feedforward manner to determine the most cost effective setpoints for the subordinate dynamic controllers. This optimizer represents a move towards more integrated process control, producing setpoints for the following manipulated variables:

- aerobic reactor NH_4^+ (controlled via a feedback loop using aeration flow);
- anoxic reactor NO_3^- (controlled via a feedback loop using external carbon addition);
- internal recycle flow rate ;
- return activate sludge flow rate; and
- waste sludge flow rate.

Subordinate feedforward controllers were investigated as part of the study, however compared to feedback alternatives they produced minimal performance improvement during low loading variation and substantially underperformed during high load variations (Yamanaka et al. 2006). On a cost basis, the control scheme was confirmed to be effective under relatively slow load variations, but less effective during large variations (Yamanaka et al. 2006). This increased cost is expected since more process resources (and hence cost) would be required to mitigate larger fluctuations. Comparison to a non-cost optimized process would be useful to provide a better indication of the potential benefits of the control strategy.

While the application of cost-based process control techniques has been limited in nature and restricted to simulation based studies, these techniques represent an important step towards integrated process control and could be a valuable tool in an environment of increasingly stringent effluent regulation and demands for cost reduction. Further research and development is required to apply these techniques to actual processes and evaluate their performance under a full range of operating conditions.

2.4.4 Evaluation of Aeration Control Strategies

A wide range of aeration control strategies have been reviewed in **Section 2.4.3**. While all of the reviewed studies evaluate the performance of the control strategies of interest, the evaluation was often conducted in a subjective manner, limiting comparison between studies. The lack of quantitative evaluation of control strategy performance is not unique to research, indeed in a survey of North American wastewater treatment plants (Hill et al. 2002) indicated that while the majority have installed automation to achieve cost reduction, less than 10% have followed up by conducting monitoring to demonstrate the cost savings in a quantitative manner. A summary of the quantitative performance evaluations presented in the literature is provided as **Table 2-7**, although it should be noted that this represents a small subset of the total volume of literature reviewed.

Similar to the observations by Ingildsen and Olsson (2002) and Hamilton et al. (2006), the majority of the implementations were based on simulated or pilot scale processes, and reports of full scale implementation were few in number. Based on the summary presented as **Table 2-7**, aeration reductions on the order of 6-28% are possible through the application of enhanced aeration control, while maintaining a similar or improved level of average effluent quality, and in many cases achieving substantial reductions in peak effluent NH_4^+ concentrations. However, due to the variability in the evaluation procedures and projected benefits, it is difficult to draw conclusions with regards to the relative merits of specific aeration control strategies.

Despite the COST benchmark being utilized as a basis for the majority of the simulation studies, the control strategy evaluation component of this benchmark has not been utilized. Instead, evaluation methodologies have been developed on a case by case basis, limiting comparability of the results. While some alternative evaluation methodologies have been proposed (and have been reviewed in **Section 2.4.2**), the lack of consensus persists.

Table 2-7 Comparison of aeration control strategies.

Controller Type	Monitored Parameter	Assessment Basis	Aeration Reduction*	Effluent Quality*		Source
				Average NH_4^+ Concentration Reduction	Peak NH_4^+ Concentration Reduction	
FB	Reactor NH_4^+	Full scale	12 - 28%	Up to 50%	NR	Ingildsen and Wendelboe (2003)
	DO	Simulation	11.1%	3.7%	NR	Stare et al. (2007)
FB supervisor	Effluent NH_4^+	Simulation	11%	Equivalent	Equivalent	Suescun et al. (2001)
			6.8%	8.1%	NR	Stare et al. (2007)
		Pilot scale	23%**	52.6%	52.5%	Vrecko et al. (2006)
FB rule-based	Effluent NH_4^+	Full scale	16%	33-50 %	NR	Husmann et al. (1998)
Fuzzy FB supervisor	Reactor NH_4^+	Simulation	10%	NR	NR	Serralta et al. (2002)
FF supervisor	Influent NH_4^+	Pilot scale	45%**	67.6%	71.8%	Vrecko et al. (2006)
FF MPC supervisor	All influent disturbances	Simulation	6.6%	20.4%	NR	Stare et al. (2007)
	Influent NH_4^+ Influent flow	Full scale	5-15%	Equivalent	Equivalent	Ingildsen et al. (2002)
FF-FB supervisor	Influent NH_4^+ Effluent NH_4^+ Influent flow	Simulation	6.1%	13.2%	NR	Stare et al. (2007)
Fuzzy FF-FB supervisor	Influent NH_4^+ Effluent NH_4^+	Simulation	7%	18%	11.9%	Yong et al. (2006)
		Pilot scale	10%	15.9%	48%	
		Simulation	25%	NR	NR	Meyer and Popel (2003)
		Pilot scale	23%	NR	58%	

* Relative to control using a constant DO setpoint
** on a per kg of ammonia removed basis

FB = Feedback
FF = Feedforward
FF-FB = Feedforward-feedback
NR = Not reported

Several challenges exist to developing a broadly applicable evaluation methodology; particularly the selection of a reference control strategy, and provision of standardized comparison criteria. Vanrolleghem and Gillot (2002) have proposed feedback DO based aeration control using a constant setpoint as the reference control strategy since it is a common and accepted control practice in wastewater treatment. Considering that this strategy is currently utilized as the reference in the majority of the reviewed studies, substantial changes to current practice would not be required, and this recommendation would likely find acceptance.

Two primary comparison criteria have been utilized in the reviewed literature; performance comparison to a reference strategy, and aeration efficiency. While cost based control evaluation techniques exist, their cost weightings are site specific in nature (Vanrolleghem and Gillot 2002), resulting in a highly site dependent analysis. Despite being a very useful tool for investigating the application of process control techniques for specific processes and sites, their site specific nature is a significant limitation from a knowledge transfer perspective, and they will not be discussed further.

While the comparison of aeration requirements and effluent quality to a reference strategy is relatively straightforward in nature and commonly applied, the current *ad hoc* approach is not compatible with cross study comparison. Operation of a wastewater treatment process represents a compromise between competing interests (cost and effluent quality), with emphasis on one aspect coming at the detriment of the other. Thus unless a consistent performance objective (level of effluent quality) is provided for the reference control strategy, the basis of the comparison (i.e. baseline aeration requirements and effluent quality) will vary, with these variations distorting the perceived benefits/costs of the control strategy being evaluated.

Furthermore, this performance objective needs to be extended to the control strategy being evaluated to ensure a fair comparison. As demonstrated by Ingildsen and Wendelboe (2003), variations in the performance objective can have a significant effect on the perceived strengths and weaknesses of a control strategy. For instance, by emphasizing cost savings a 28% aeration reduction and minimal change in effluent quality was obtained, whereas by emphasising effluent quality

using the same controller a 50% reduction in effluent NH_4^+ concentrations was obtained, although aeration savings were reduced to 12% (Ingildsen and Wendelboe 2003). While both scenarios were provided to illustrate possible range of performance, in most studies controller performance is only evaluated for one performance objective and its selection would strongly influence the perceived controller performance.

Only through the application of a consistent performance objective can this subjectivity be removed from the evaluation process. Selection of a common performance objective will be a difficult process. Being a localized criteron (generally established based on practical constraints, effluent quality regulations, and process costs), no single performance objective will be universally applicable. A compromise is required for the sake of providing a clear basis from which to evaluate and compare control strategies.

An efficiency based criterion was utilized by Vrecko et al. (2006) to evaluate several control strategies. This criterion consisted of a factor relating the amount of oxygen utilized in the process to the amount of ammonia removed and serves to tie together the two primary measures of process performance (aeration cost and effluent quality) into a single, easily interpreted performance index. Integrating aeration cost and effluent quality into a single index removes the dependence on performance objectives, producing a more robust evaluation criterion that can provide a consistent basis of comparison between studies without the requirement of a standardized performance objective.

Furthermore, an efficiency based evaluation criterion would be well suited for the evaluation of control strategies implemented in real processes (pilot and full scale). The application of a comparison approach based on a reference study is constrained by the requirement for the simultaneous operation of a reference process, and in the case of a standardized performance objective, it is possible that the specific objective may not be permissible at full scale in certain jurisdictions due to effluent quality regulations. Freed of these two constraints, the efficiency based evaluation criterion provides a simple and efficient means of evaluating control strategies implemented on pilot and full processes, as well as permitting direct comparison with simulation based evaluations. Care should be taken during the evaluation of

control strategies at full and pilot scale to ensure that a full range of operating conditions are investigated, otherwise the assessment of overall controller performance could be biased by a focus on specific operational scenarios where the controller excels or underperforms. This is not an issue in simulation based studies utilizing the COST benchmark since the included influent profile represents a full range of operational scenarios.

Of the two discussed evaluation methods, an efficiency based evaluation criterion appears to provide the greatest benefit in terms of improving cross comparability (including between simulation and pilot/full scale applications) while imposing fewer constraints on specific evaluation procedures. With the current lack of consensus in the literature, the need exists for a movement towards a robust, consistent and comparable evaluation technique to provide a clear representation of the benefits associated with the application of advanced control strategies. Such a representation is required to assist in removing the barriers that exist between advanced process control strategies and their acceptance/uptake into full scale processes (which will be discussed further in the following section).

2.4.5 Barriers

While many advanced aeration control strategies have been proposed and evaluated using process simulation studies, uptake into full scale processes remains fairly limited (Hamilton et al. 2006; Ingildsen and Olsson 2002). Indeed the development of plant/process wide control strategies is viewed as being in its infancy, although gaining momentum (Olsson 2006). Excluding perception issues (Huntington 1998; Kalker et al. 1999) and limitations in the evaluation and communication of control strategies and their benefits (discussed in **Sections 2.4.2** and **2.4.4**), two of the primary barriers to the uptake of advanced process control strategies in full scale processes are instrumentation and facility design.

Instrumentation has historically been seen as the weakest link in the control chain for wastewater treatment processes (Bonastre et al. 2005; Lynggaard-Jensen et al. 1996; Rieger et al. 2004b), limiting the development and implementation of advanced process control strategies. However, recent improvements in instrument

performance and robustness (Bonastre et al. 2005; Bourgeois et al. 2001; Thomas and Constant 2004; Vanrolleghem and Lee 2003) have addressed many of these weaknesses.

With substantial reductions in instrument related barriers, Vanrolleghem and Lee (2003) concluded that the most fundamental barrier to widespread acceptance of process control is the wastewater treatment processes themselves. Many existing wastewater treatment processes were not designed with the flexible and controllable actuators required for process control, instead being designed to guarantee effluent quality without control (Vanrolleghem and Lee 2003). As result, the controllability of wastewater treatment processes is perceived to be quite poor (Olsson 2006).

A common challenge to the successful implementation of improved aeration control is oversized equipment (airlines, control valves and compressors). The wastewater treatment facility survey conducted by Hill et al. (2002) indicated that air flow meters and control valves are often oversized to the point where they operate in the bottom 20% of their range (with poor accuracy and control authority, respectively), and oversized compressors limit the process controllability due to insufficient turndown capacity and can cycle excessively in some scenarios. Furthermore, the survey indicated that many of the process instruments and actuators were mounted in locations with poor access, reducing the frequency of maintenance and cleaning, further impairing control system performance (Hill et al. 2002). As newer processes are constructed and aging processes refitted, providing that process control and instrumentation are included as part of the design process (i.e. an integrated design approach similar to that used in other industries such as power and petroleum), this barrier will decrease in importance.

2.4.6 Summary

Historically, the implementation of instrumentation and advanced control techniques in wastewater treatment processes has lagged behind other industries. With the potential to increase treatment capacity, reduce operating costs, and allow operation closer to technical and regulatory boundaries, wastewater treatment

process control is receiving an increasing amount of focus and many new techniques are emerging.

Despite advances in terms of standardization through the development of a benchmark simulation environment (the COST benchmark), a high level of variability remains in the evaluation of control strategies which inhibits cross comparison and obscures the benefits associated with improved process control. As discussed in **Section 2.4.4**, a need exists for further standardization of the evaluation process and the development of easy to interpret performance criteria.

The majority of the control strategy evaluations presented in the literature were simulation based, with a small number of reported implementations at pilot scale, and even fewer at full scale. Further work is required to extend the proposed control strategies to full scale and fully investigate the benefits associated with improved control (in a quantitative manner) and address the perception issues limiting uptake.

A progression from very simple feedback based control strategies to more advanced feedforward ones (in particular fuzzy based control and MPC) is visible in the literature. While fuzzy based control strategies are gaining acceptance due to their transparent nature, the need exists to advance MPC strategies to realize further improved performance, as well as to meet the demands of increased process integration. The potential of cost based control concepts has been demonstrated through process simulation, but their effectiveness and benefits remain to be demonstrated at full scale. Finally, an integrated design approach (i.e. considering process control as a part of the wastewater treatment process instead of as an addition) is required to address common limitations associated with process equipment and instrumentation.

While a range of non-invasive process monitoring techniques were reviewed in **Section 2.3**, only off-gas N_2O process monitoring has been proposed (in concept only) as a basis for a process control strategy. In particular, as a means of controlling nitrifying/denitrifying sequencing batch reactors through pattern recognition (Shiskowski 2004). There is no evidence in the literature of any thorough investigation or application of non-invasive monitoring based process control strategies in wastewater treatment processes, either through simulation or at

pilot/full scale. Thus, non-invasive based nitrification process control remains a largely unexplored research area.

Chapter 3 Experimental Apparatus

In this chapter, the various experimental apparatus utilized to meet the research objectives will be discussed. The experimental phase of this research program had three primary objectives:

- characterize the wastewater process being studied;
- characterize the process response to applied stresses; and
- provide appropriate data to support process modelling and evaluation of the developed process control concept.

The experimental apparatus utilized in this study consisted of three key components; a lab-scale activated sludge plant, an off-gas monitoring system, and process instrumentation/control. Principles of operation, equipment specifications and operating conditions for each of these components will be discussed in the following sections. Specific experimental methodologies will be discussed in **Chapters 4** and **5**.

3.1 Activated Sludge Process

A pilot scale activated sludge process lies at the core of the experimental apparatus. This process is the home for the community of microorganisms that are being analysed/interacted with by the remaining components of the experimental apparatus (described in **Sections 3.2** and **3.3**).

3.1.1 Principles of Operation

Activated sludge wastewater treatment processes are biological processes that employ a community of microorganisms (predominately bacteria) to degrade wastes. These microorganisms utilize specific components of the wastewater as substrates for their metabolic processes to generate energy for cell maintenance, growth and reproduction.

As such, the effectiveness of the treatment process is highly dependent on the types of the microorganisms present in the reactor and their metabolic status. Due to the wide range of microorganisms present in sewage and their adaptability to various substrates, these processes are quite versatile. By varying a number of process parameters, such as the sludge retention time and the oxygen concentrations (providing oxygen rich, anoxic or even anaerobic zones), the process can provide for the selection of bacteria with desirable metabolic pathways which can allow for the removal of a range of undesirable substances including carbon, nitrogen, and phosphorus.

The activated sludge process is a suspended growth process in which the biomass (activated sludge) is mixed with the influent wastewater and held in suspension in an aeration tank. Since the biomass is suspended in the wastewater, it is free to flow out of the unit with the effluent, and must be separated from the treated waste water using a clarifier. A portion of the activated sludge is recirculated back into the aeration tank (recycled) to maintain the bacterial populations while the remainder is purged from the system (wasted). An image of the most basic form of an activated sludge process (consisting of an aerated tank and a clarifier) is presented as **Figure 3-1**.

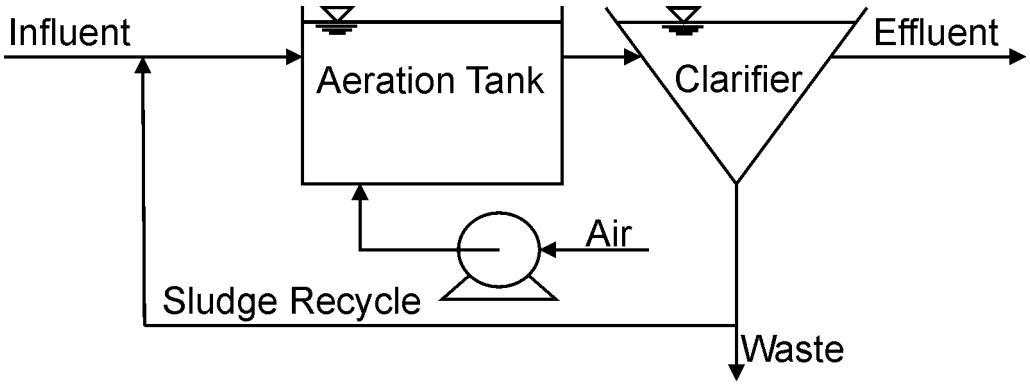


Figure 3-1 Activated sludge process.

As a suspended growth process, the retention of biomass is strongly dependent on an efficient liquid solid separation in the clarifier, thus the biomass settling properties are key parameters of interest. A wide range of process parameters including pH, temperature, dissolved oxygen concentrations and feed to microorganism ratios can influence the population dynamics in activated sludge bioreactors and as a result the biomass settling properties. The effects of these parameters on nitrification processes and N_2O production have been discussed in **Section 2.1**. For further information on the influence of specific process parameters on biomass settling properties, the reader is directed to two recent discussions of activated sludge bulking mechanisms and control (Eikelboom 2000; Martins et al. 2004).

The setup depicted in **Figure 3-1** is the most common form of AS process used for heterotrophic degradation of carbonaceous substances (COD removal). This process can be modified with the addition of anoxic or even anaerobic zones to facilitate the removal of other substances. It should be noted that in practice the process does not consist of individual tanks, instead it is performed in long channels called activated sludge lanes. A good overview of the wide range of potential reactor configurations is presented in Metcalf and Eddy (Metcalf and Eddy 2003).

In general, BNR processes consist of an anaerobic zone where NH_4^+ is oxidized to NO_2^- and then to NO_3^-, and an anoxic zone where NO_3^- is reduced to nitrogen gas (N_2). Denitrification in these systems is primarily conducted by heterotrophic bacteria using organic carbon as the carbon source (Metcalf and Eddy 2003). Often

the anoxic zone is placed at the front of the lane and a substantial portion of the effluent is returned to the influent where it is denitrified, which is referred to as predenitrification (Metcalf and Eddy 2003). Predenitrification has the advantage of allowing the influent COD to be utilized as a carbon source, eliminating the need and cost of separate carbon addition (typically methanol) to the reactor.

The activated sludge process employed in this research was designed and operated to limit the investigated biological processes to combined COD removal and nitrification, and thus was a fully aerobic system with no anoxic zone. Physical specifications of this experimental apparatus will be presented in the following section.

3.1.2 Equipment Specifications

The pilot scale activated sludge process (shown in **Figure 3-2**) consisted of four key components, a reaction vessel, an aeration system, a clarifier, and a feed delivery system.

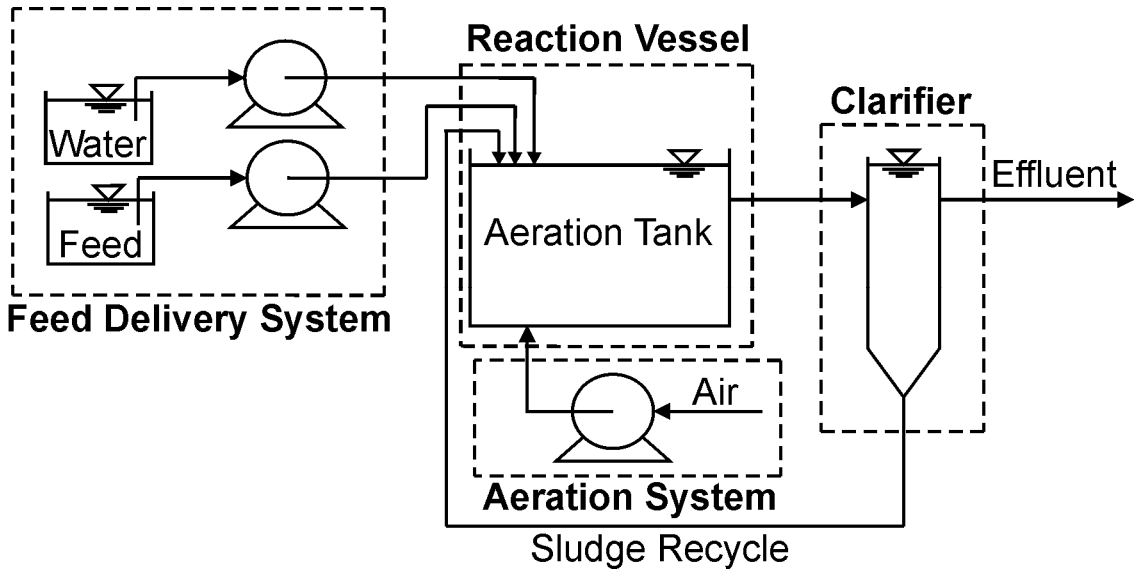


Figure 3-2 Lab scale activated sludge process.

A Perspex reaction vessel was the primary component of the system. This vessel had the following external dimensions: 43 cm high x 40 cm long x 27.5 cm wide, and was equipped with sloping edges at the base to reduce dead zones and minimize sludge

accumulation (along with the resulting anoxic zones). The overall aerated liquid volume at a normal operating liquid depth of 34 cm was 28.7 L. This vessel was hooded to allow the capture and venting of process off-gas, and equipped with ports to support influent, effluent, and aeration air lines.

Aeration air was supplied via the pilot hall compressed air system. A regulator was used to reduce the airflow to an operating pressure of 120 kPa. Rotameters and a needle valve were connected to the air line to the reactor to allow manual adjustment of the aeration air flow. Aeration air was delivered to the aerator located in the bottom of the activated sludge tank. This aerator consisted of two flexible airstones to provide fine bubbles with a higher oxygen transfer efficiency than a coarse bubble diffuser. The use of fine bubble diffusers was required to reduce the total volume of aeration air required, which reduced the dilution of the sparged N_2O into the off-gas and allowed for improved detection by the off-gas analysis system (**Section 3.2**).

Mixed liquor from the aeration tank was transferred to an external clarifier for solids separation and recycle. The clarifier (**Figure 3-2**) was cylindrical in shape (15.5 cm in diameter) with a conical base for sludge collection and an 8.25 L normal operating volume. A scraper was installed inside the clarifier to remove accumulated sludge from the vessel walls to enhance settling. Wastewater was fed into the bottom 30% of the clarifier, generally the sludge blanket was achieved in the bottom 50% of the reactor and the supernatant reached the top of the clarifier and was discharged. A peristaltic pump was connected to the underflow to control the return of the settled sludge to the reactor. No automatic sludge wastage was conducted (sludge wastage will be discussed further in **Section 3.1.3**).

The feed system in the pilot hall was shared between the activated sludge process utilized in this research and a membrane bioreactor. Feed was prepared in a concentrated form, typically in 4 to 5 L portions to last for a 72 hour period. This time frame was selected to minimize degradation of the feed during use. The feed was autoclaved prior to use and all feed components routinely cleaned and disinfected in a hypochlorite solution to further minimize degradation while in use. Concentrated feed was delivered via a peristaltic pump and dilution water was

simultaneously supplied from a reservoir tank to achieve the desired feed concentration. The concentrated feed was prepared as follows:

Table 3-1 Synthetic feed recipe.

Component	Amount in 4 L (g)
Glucose	126.4
Sodium acetate	101.6
Ammonium chloride (NH_4Cl)	61.12
Peptone	28.0
Meat extract	17.2
Magnesium sulphate ($MgSO_4$)	10.0
Dipotassium hydrogen orthophosphate (K_2HPO_4)	5.2
Calcium Chloride ($CaCl_2$)	5.2
Iron (II) Sulphate ($FeSO_4$)	1.04

When diluted to approximately 1:150, this proved a feed with a composition of 367 ± 22 mg/L COD and 27.5 ± 4.1 mg/L NH_4^+-N and along with all trace nutrients.

3.1.3 Operating Conditions

Sludge from the recycle line of a full scale sludge nutrient removal process was used to seed the pilot scale reactor. The reactor was operated on the synthetic seed described in the previous section for over a year. During this time, it was observed that the off-gas N_2O response decreased over time, likely due to loss of autotrophic bacteria from the system (a corresponding deterioration in the ammonia removal efficiency was observed). Eventually the remaining bacteria were washed from the reactor and it was dominated by fungi and had to be reseeded.

Since adaptation to the synthetic feed was reducing the desired response, it was necessary to operate on much shorter timescales to obtain data before the adaptation effects became significant. The reactor was seeded from a full scale activated sludge nutrient removal process and operated for a 2 to 3 week period. When the reactor began to show signs of instability the sludge was removed and the reactor was reseeded and operated for another short period, with this cycle being repeated until the end of the experimental campaign. Specific details with regards to these aspects, in particular experiments conducted and temporal effects related to adaptation, will be presented in **Chapter 4**.

The nitrification process was operated at a 16.6 to 17.6 hour hydraulic retention time. Activated sludge return from the clarifier to the reaction vessel was operated in a cycle of 3.5 hours of underflow from the clarifier followed by 0.5 hours of relaxation (no underflow). The target operating mixed liquor suspended solids (MLSS) concentration was approximately 3500 mg/L, with this concentration being maintained by wasting activated sludge from the aeration tank. Wasting was conducted from the aeration tank and not from the clarifier underflow to simplify the determination of the sludge retention time since the MLSS concentration would be the same as that measured routinely from the reactor. Due to deterioration in sludge settling properties during the spike testing, the MLSS did vary considerably and it was not possible to estimate the sludge retention time (SRT) due to losses in the effluent.

Routine maintenance was conducted on the aeration system, feed system and clarifier. Once per month the aerators were scrubbed while in the tank to reduce fouling and unblock aeration holes. The concentrated feed was changed every third day, with the feed lines being replaced and sterilized between uses. Daily checks were made on the settler to remove any floatable material from the tank and ensure the outlet was not being obstructed.

3.2 Off-Gas Monitoring

The off-gas N_2O monitoring system consisted of a non-dispersive infrared (NDIR) gas analyser and its supporting equipment; a sampling conditioning system and a data acquisition system. This system is depicted in **Figure 3-3** and photographs of the specific components are presented as **Figure 3-4** and **Figure 3-5**.

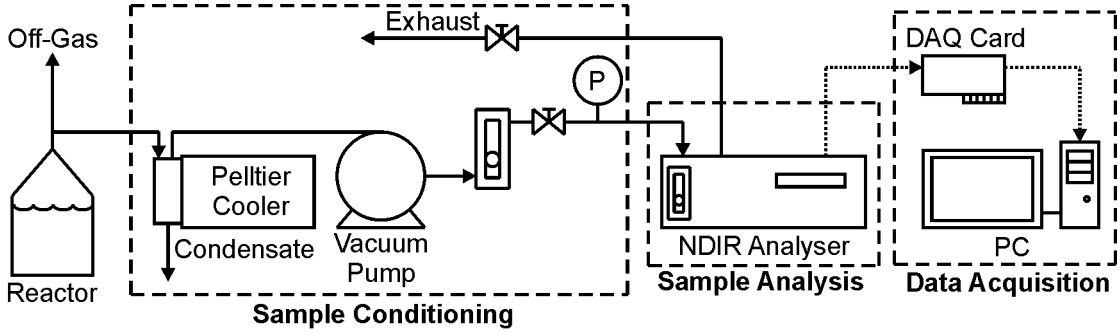


Figure 3-3 Off-gas analysis system.

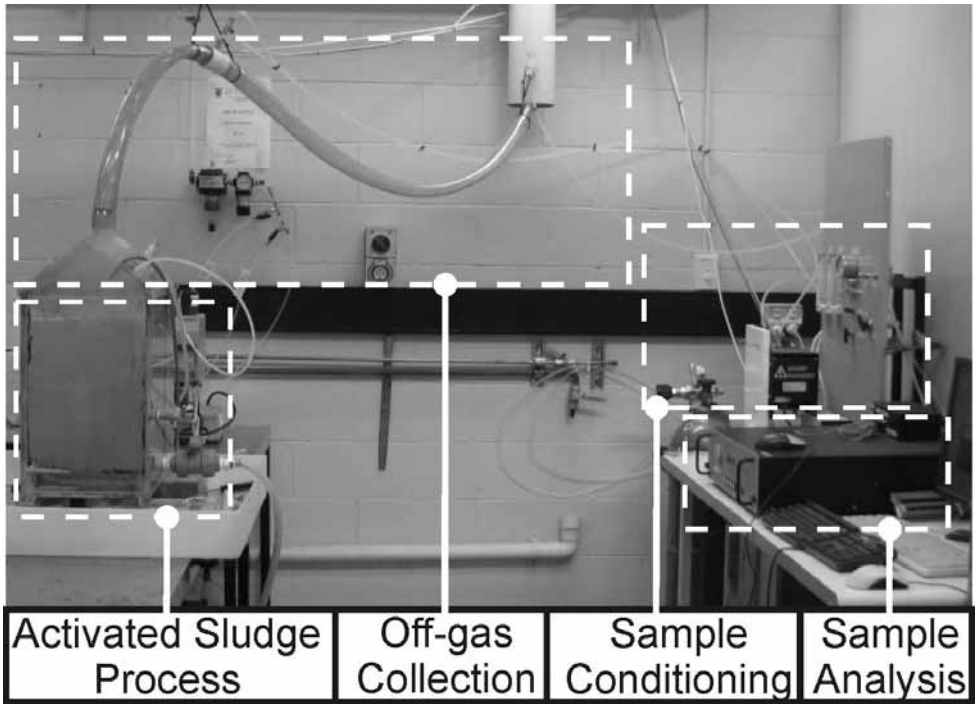


Figure 3-4 Photograph of sample collection, conditioning and analysis equipment.

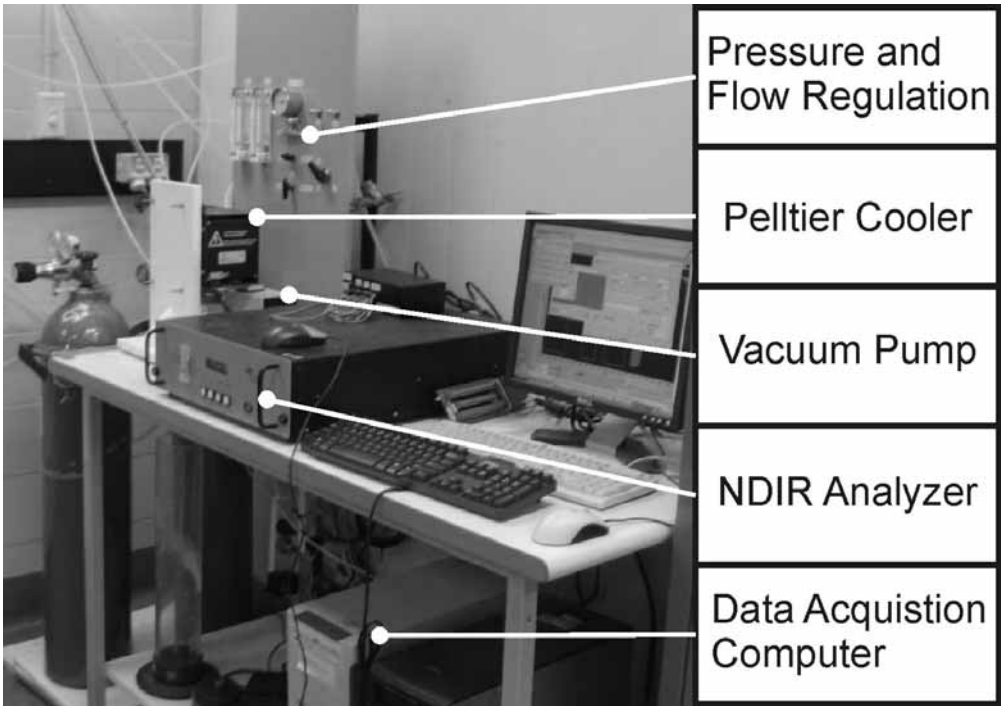


Figure 3-5 Photograph of sample conditioning, analysis and data acquisition equipment.

3.2.1 Principles of Operation

NDIR analysers determine gas concentrations by correlating the absorbance of infrared light at characteristic wavelengths to the gas concentration. The analyser utilized in this study was based on a dual chamber balanced detector, which does not rely on direct absorbance measurement. Instead, this detector is based on the differential absorbance of infrared light in the detector's sample chambers and measurements of the resulting mass flow.

While there are many other important components, the core of the analyser is the optical bench (**Figure 3-6**), which consists of an infrared light source, a sample cell, and a detector.

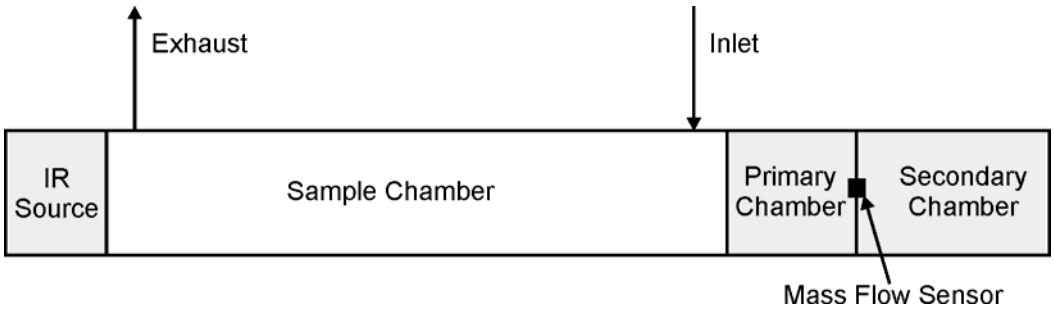


Figure 3-6 NDIR analyser optical bench.

The detector used in the analyser's optical bench consists of two gas chambers (of unequal volumes) filled with the gas of interest (in this case N_2O) that are connected in optical series through which the infrared light passes. In the first chamber (primary chamber, which is smaller in volume) infrared absorption occurs at the most strongly absorbed characteristic wavelengths for the gas in the infrared spectrum. The non-absorbed radiation passes through to the secondary chamber where, due to its longer length, infrared light is absorbed at the weakly absorbed characteristic wavelengths (less intense absorption). This difference in absorption causes the gas in the two chambers to heat differentially (more intense heating in the primary chamber), resulting in a pressure differential and hence a flow of gas between the two chambers. An orifice and mass flow sensor located between the two chambers measures the flows between them and generates a signal which is used to determine the gas concentration.

When a gas sample is delivered to the sample cell, infrared light is absorbed by the gas of interest and less energy is applied to the detector. The gas of interest in the sample cell will absorb the strongly absorbing wavelengths of the applied infrared light, thus there will be less energy available to be absorbed in the primary chamber. However, the weakly absorbing wavelengths are not absorbed as much in the sample cell and the reduction in energy gained by the secondary cell is not as intense. This change in energy effects the mass flows between the sample cells and produces an inversely related signal to the concentration of the gas of interest relative to a zero gas sample.

3.2.2 Equipment Specifications

The off-gas analysis system (**Figure 3-5**) consisted of three components; sample conditioning, sample analysis, and data acquisition. Specifications for the sampling conditioning system were dictated by the requirements of the sample analysis system. In particular, the sample conditioning system had to remove moisture to protect the analyser, and provide constant sample pressure, temperature, and flow to maintain similar analysis conditions as those used during calibration (to maintain a suitable level of measurement accuracy).

The primary components of the sample conditioning system were an M&C diaphragm pump (Series N N3KP18), and an M&C ECP 1000 electric gas cooler. A Peltier type gas cooler was used in this system. This type of gas cooler uses a voltage applied to dissimilar metals to generate an active heat pump that can cool below ambient temperatures. The cooling block surrounds a glass heat exchanger, and as the gas flows through the heat exchanger it cools and water vapour condenses on the sides and is trapped at the base of the heat exchanger. A Peltier type gas cooler minimizes gas-liquid contact and reduces the capture of soluble gas components in the liquid phase. The sample conditioning system included rotameters and a flow regulator needle valve to measure and adjust the gas sample flow through the analyser, as well as a pressure gauge and a needle valve on the analyser outlet to monitor and adjust system pressure.

Off-gas N_2O analysis was conducted using an Enviromax Model 2010 NDIR gas analyser. This analyser was connected to the outlet of the gas conditioning system and the exhaust was piped to the pilot hall gas exhaust system. N_2 and N_2O gas cylinders were connected to the analyser for calibration purposes. The analyser had three user selectable ranges (0-20 ppm, 0-100 ppm, and 0-200 ppm), and generated a 0-10 V signal in proportion to the N_2O concentration, with a 0.1 ppm resolution. This signal was acquired by a National Instruments based data acquisition system (NI PCI-6221 data acquisition card) and a PC running data acquisition software coded using LabVIEW.

3.2.3 Operating Conditions

In the interest of data quality, consistent operating conditions were maintained during calibration and operation. Specifically, a 0.7 L/min sample flow and an analyser operating pressure of 1.75 psig was used. The analyser was operated in the 0-20 ppm range and the calibration (analyser zero and span) was verified on a weekly basis using N_2 gas as a zero and 14.9 ppm N_2O in balance N_2 as a span gas, with the analyser being recalibrated where necessary. Condensate from the conditioning system was drained on a daily basis. The monitoring system was run continuously and N_2O concentration data was recorded by the data acquisition system as 30 second averages.

3.3 Liquid Phase Process Instrumentation

Liquid phase process instrumentation consistsed of a dissolved oxygen probe and associated datalogging equipment.

3.3.1 Principles of Operation

DO analysis was conducted using a polarographic DO probe. In general DO probes are liquid phase sensors consisting of a sensor body housing an electrolyte and two metal electrodes (an anode and a cathode) with an open end which is inserted into the sample matrix. The open end is covered with a polymer membrane which is permeable to oxygen molecules but impermeable to most other ions/species, thus preventing the electrolyte from escaping the probe and mixing with water. As the oxygen diffuses through the membranes it is reduced at the cathode and a current is generated. This current is proportional to the rate of oxygen diffusion into the probe, which is in turn proportional to the oxygen partial pressure in the liquid phase. The current generated by the probe is monitored and converted to concentration units that are reported by the instrument. Unlike galvanic probes which can reduce dissolved oxygen without any external influence, polarographic probes use two noble metal electrodes and thus require an external voltage (polarization) for oxygen reduction to occur. This is a particularly important consideration when operating these probes since they require a specific polarization time (on the order of 24 hours) before they can be put into service.

3.3.2 Equipment Specifications

DO concentrations were monitored using a Mettler Toledo InPro 6800 polarographic probe. The probe had a stainless steel body with a 12 cm immersion length and was equipped with a thermocouple to provide temperature data. Dissolved oxygen was measured by the probe as % saturation, and both the % saturation and temperature data were collected by a Mettler Toledo M300 signal transmitter and sent to the LabVIEW based data acquisition system (discussed previously in **Section 3.2**). The data acquisition system converted this data to DO

concentrations in mg/L which was logged along with the temperature as 30 second averages.

3.3.3 Operating Conditions

The DO probe was operated on a continuous basis. Being a polarographic probe, in the event of a power interruption the probe was allowed a 24 hour repolarization period prior to being put back into service. Calibration and maintenance were performed on a biweekly basis, consisting of removing the probe from the reactor, rinsing the membrane with deionized water and verifying the zero and span by inserting the probe in water sparged with N_2 gas and air, respectively.

Chapter 4 Stress Response Analysis

The first step in assessing the feasibility of utilizing off-gas N_2O emissions as a basis for aeration process control consisted of investigating the nature of these emissions. As discussed previously in **Section 2.1**, the dominant source of off-gas N_2O emissions in the aerobic component of activated sludge nitrogen removal processes is believed to be aerobic autotrophic denitrification (Tallec et al. 2006a; Tallec et al. 2008), which is an alternative metabolic pathway possessed by autotrophic bacteria that is initiated by metabolic stress.

Off-gas N_2O emissions from nitrifying processes are thus a response to metabolic stress experienced by autotrophic nitrifying bacteria. The concept of stress-response relationships and their role in activated sludge process upset was analysed by Love and Bott (2002). They concluded that gaining understanding of these relationships would allow for the development of new monitoring techniques and operational strategies.

In utilizing a stress response as the basis for a process control concept, several criteria must be satisfied. Specifically, the response being utilized must:

1. occur when a stress is present and disappear when the stress has been removed;
2. occur in a time scale suitable for process control;
3. have a stable relationship with the stress, i.e. be a reproducible response;
4. be proportional to the applied stress; and
5. be sufficiently sensitive to allow for control in an appropriate operating range.

To assess the potential of this stress response for process control, discrete experiments were designed and conducted to evaluate the stress response against each of these criteria. Furthermore, the data presented in this chapter forms the basis for process modelling and the development of a novel off-gas N_2O emission correlation, the results of which are presented in **Chapter 5** of this thesis.

4.1 Methodology

Two types of experiments were conducted to assess the stress response against the criteria identified in the previous section. These experiments consisted of shock loadings (Tests 1 to 7, discussed in **Sections 4.2.1** to **4.2.4**), and step changes in reactor loading (Test 8, discussed in **Section 4.2.5**). A one hour monitoring period was conducted prior to each testing event to verify initial process conditions. A stress (in the form of a dosage (spike) of concentrated reactor feedstock) was applied following this period, and the process was monitored (liquid phase parameters and off-gas N_2O concentrations) until it had returned to its initial state, approximately 3 hours after each spiking test. Specific details with regards to the applied perturbances will be provided in the respective results sections.

Liquid phase parameters (with the exception of DO) were monitored at a variable frequency, with the highest sampling frequency occurring at the start of the tests (during the most dynamic part of the response). The sampling frequency decreased over time as the rate of process change decreased. Liquid phase parameters were analysed using standard wet chemistry methods (APHA et al. 1995). DO and off-gas N_2O concentrations were monitored continuously by direct reading instruments (specific instrument and operational details are provided in **Chapter 3**), with average concentrations being logged at 30 second intervals. Analytical techniques and specific method references are summarized in **Table 4-1**. Free nitrous acid concentrations (FNA) were calculated based on the pH dependent equilibrium with NO_2^- (Anthonisen et al. 1976).

Table 4-1 Analytical methods – stress response testing.

Parameter	Location	Frequency	Method
COD	Influent Effluent	Pre-test Variable	Method 5220 D APHA et al. (1995)
NH_4^+	Influent Effluent	Pre-test Variable	Nesslerization
NO_3^-	Influent Effluent	Pre-test Variable	Method 4500-NO_3^- E APHA et al. (1995)
NO_2^-	Influent Effluent	Pre-test Variable	Method 4500-NO_2^- B APHA et al. (1995)
N_2O	Off-gas	Continuous	Off-gas Analyser
DO	Aeration Tank	Continuous	Calibrated Probe
pH	Aeration Tank	Variable	Calibrated Probe
TSS	Aeration Tank	Pre-test	Method 2540 D APHA et al. (1995)
Flow	Influent	Post-test	Pump Calibration

Graphical comparison of response data is a subjective process, and as a result the interpretation of such an analysis can be quite variable. A quantitative analysis of the responses was conducted to increase objectivity and improve the comparison of different tests. This analysis consisted of calculating the area of the responses of interest and using that area as a measure of the response magnitude. Responses of interest included DO depletions and accumulations of N_2O, NH_4^+, NO_2^-, and FNA.

Calculation of the response areas required a baseline to form an upper or lower boundary for depletions and accumulations, respectively. The measured pre-test baseline conditions would normally be used in such an analysis. However, as will be seen in the results presented in **Section 4.2.1**, variation in process steady state (i.e. post-test steady state conditions not being the same as initial baseline conditions) were observed in many of the tests. Since it is not possible to determine if the variation is a result of the imposed stresses or an independent process fluctuation, nor the exact time at which the fluctuation occurred, an exact response area could not be determined. Instead, the response area was bounded by calculating the area using the initial baseline conditions and again with the final steady state conditions.

4.2 Results and Discussion

4.2.1 Stress Response – Spiking Events

Seven spiking events were conducted to gather the data required to characterize the off-gas N_2O stress response. The first four tests were conducted over a 5 day period, starting 5 days following reactor seeding (**Seed A**). Towards the end of the first group of tests, adaptation effects had become apparent (changes in floc settling properties and process response), and the reactor was reseeded (**Seed B**). Following an identical initial start up period (5 days), the remaining spiking events (**Tests 5**, **6**, and **7**) were performed along with the step change test (**Test 8**).

The primary parameter varied in the spiking events was the spike volume. It should be noted that the concentration of the specific components in the concentrated feed used for the spikes varied over the course of the sampling period. Thus, even for identical spike volumes, the amounts of substrate in the spike would vary. A summary of the spike tests along with the substrate loadings in the spikes is provided as **Table 4-2**.

Table 4-2 Summary of spiking events.

Sludge	Test	Days from Seeding	Spike Volume (mL)	Spike	
				COD (mg COD)	Ammonium (mg NH_4^+– N)
A	1	5	15	908	74.9
	2	6	15	869	61.7
	3	7	10	587	43.5
	4	10	7.5	473	32.2
B	5	5	7.0	421	29.7
	6	7	7.0	353	25.2
	7	9	15	855	56.3

The individual test results were utilized to assess two of the five control suitability criteria; response correlation to stress and timescale suitability. Combinations of these tests were utilized to assess two other criteria, in particular:

- reproducibility – **Tests 1**, **2**, and **5** (**Section 4.2.2**); and
- proportionality – **Tests 2**, **3**, and **4** (**Section 4.2.3**).

The final criterion, response sensitivity, was assessed using the step response test (**Section 4.2.5**). Results of each individual spike test are shown in **Figure 4-1** to **Figure 4-7**.

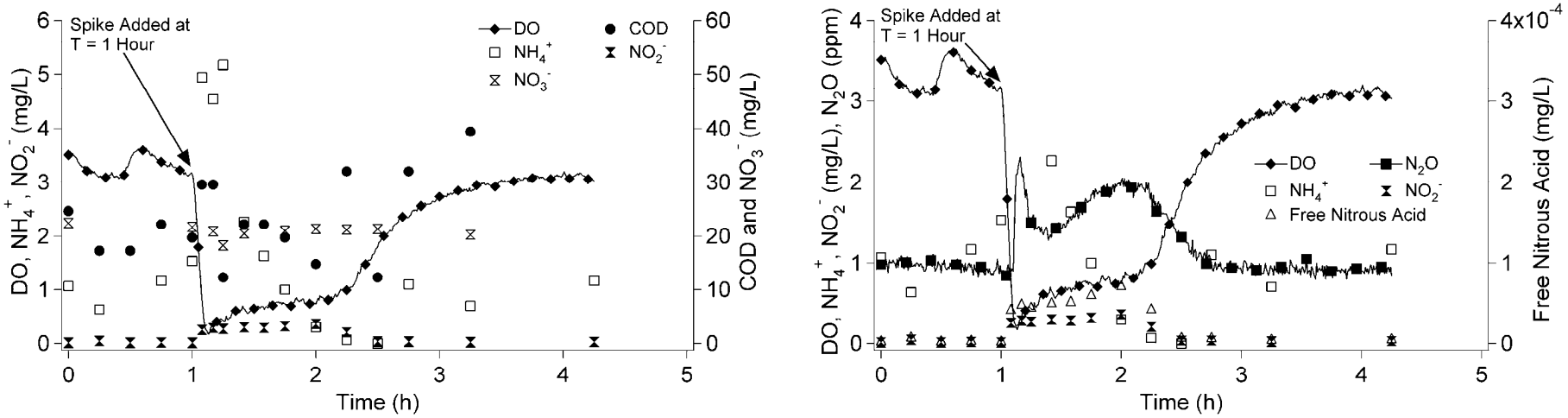


Figure 4-1 Stress response for a 15 mL concentrated feed shock load (Test 1); liquid phase response (left) and off-gas response (right).

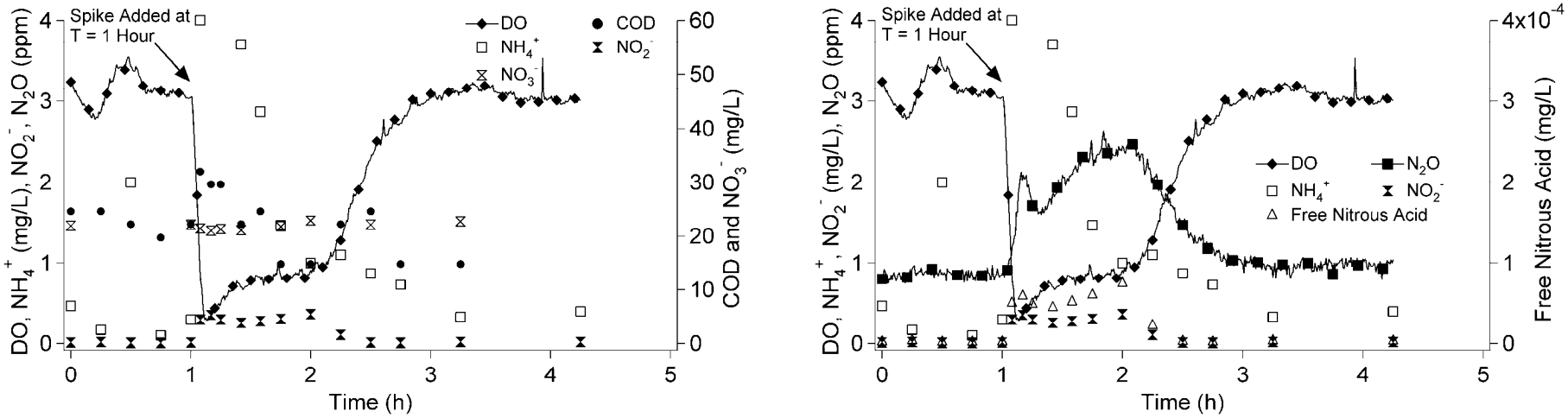


Figure 4-2 Stress response for a 15 mL concentrated feed shock load (Test 2); liquid phase response (left) and off-gas response (right).

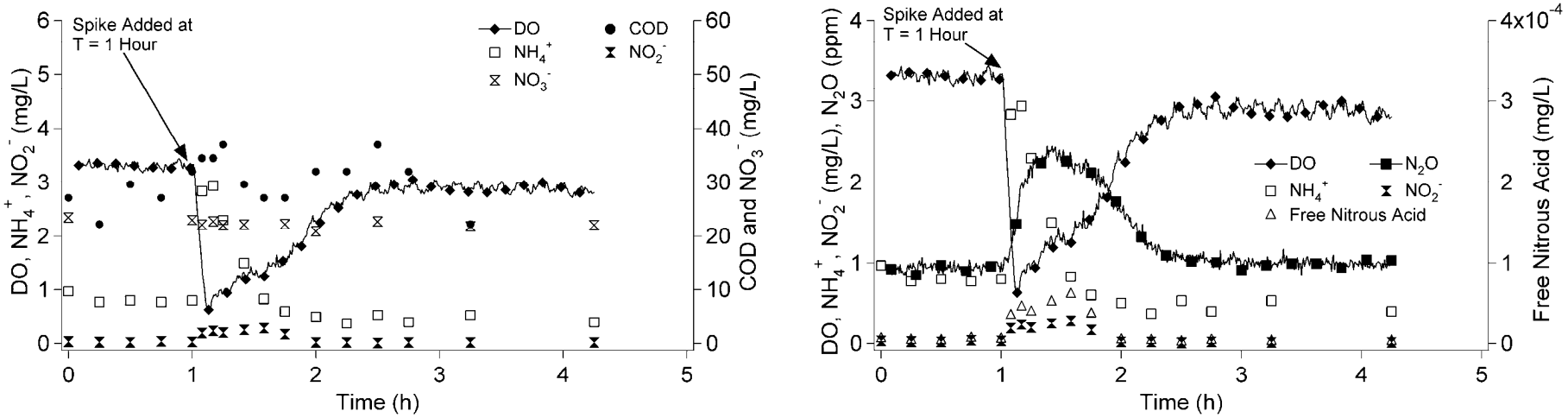


Figure 4-3 Stress response for a 10 mL concentrated feed shock load (Test 3); liquid phase response (left) and off-gas response (right).

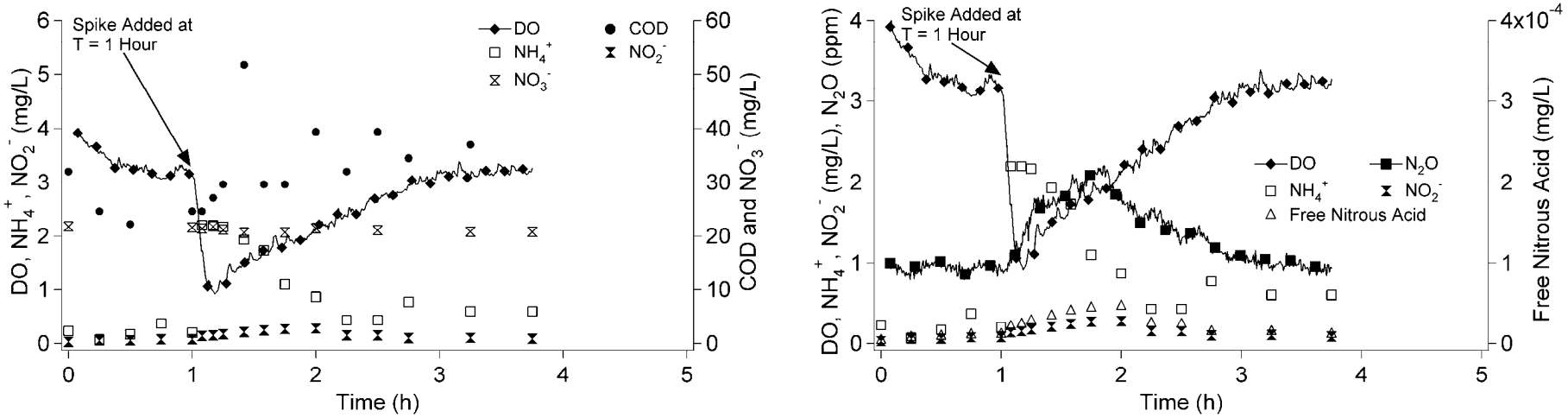


Figure 4-4 Stress response for a 7.5 mL concentrated feed shock load (Test 4); liquid phase response (left) and off-gas response (right).

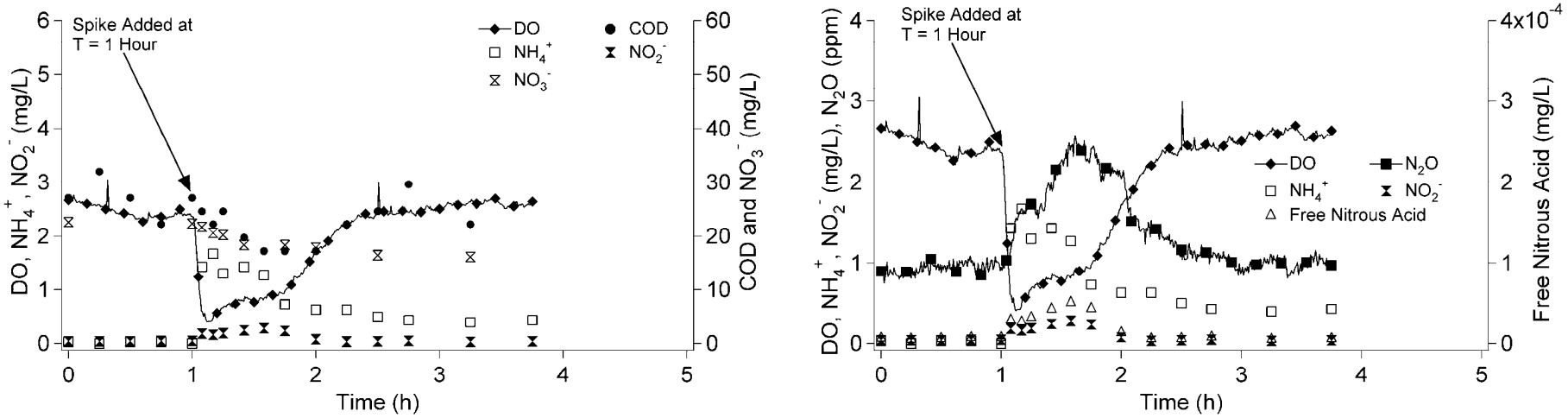


Figure 4-5 Stress response for a 7 mL concentrated feed shock load (Test 5); liquid phase response (left) and off-gas response (right).

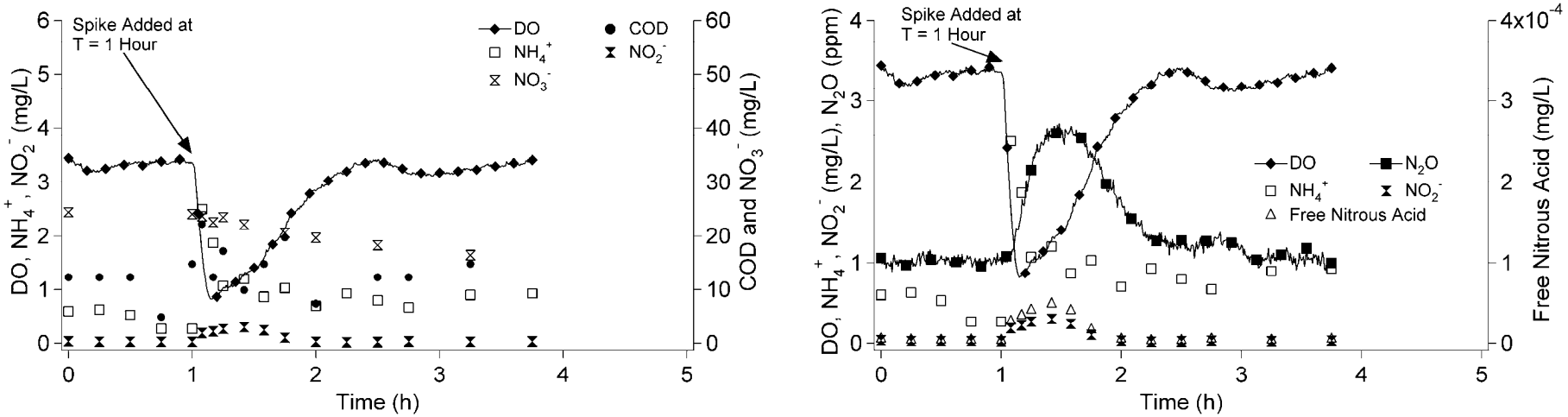


Figure 4-6 Stress response for a 7 mL concentrated feed shock load, reduced DO (Test 6); liquid phase response (left) and off-gas response (right).

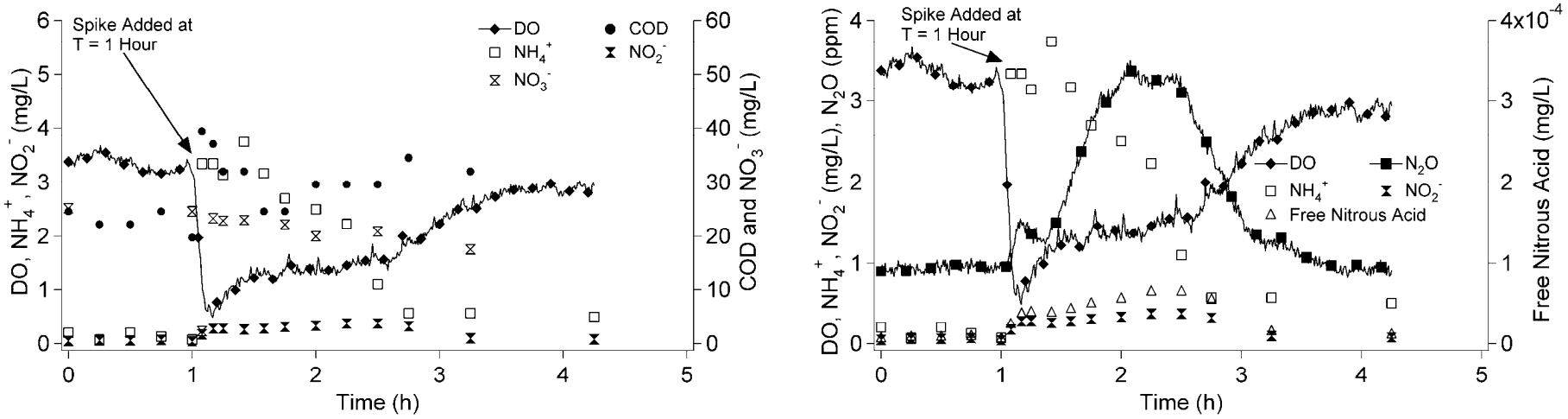


Figure 4-7 Stress response for a 15 mL concentrated feed shock load (Test 7); liquid phase response (left) and off-gas response (right).

Overall, the DO profiles presented in **Figure 4-1** to **Figure 4-7** had very similar forms. A typical DO depletion profile has been subdivided into regions of interest and is presented as **Figure 4-8**, below.

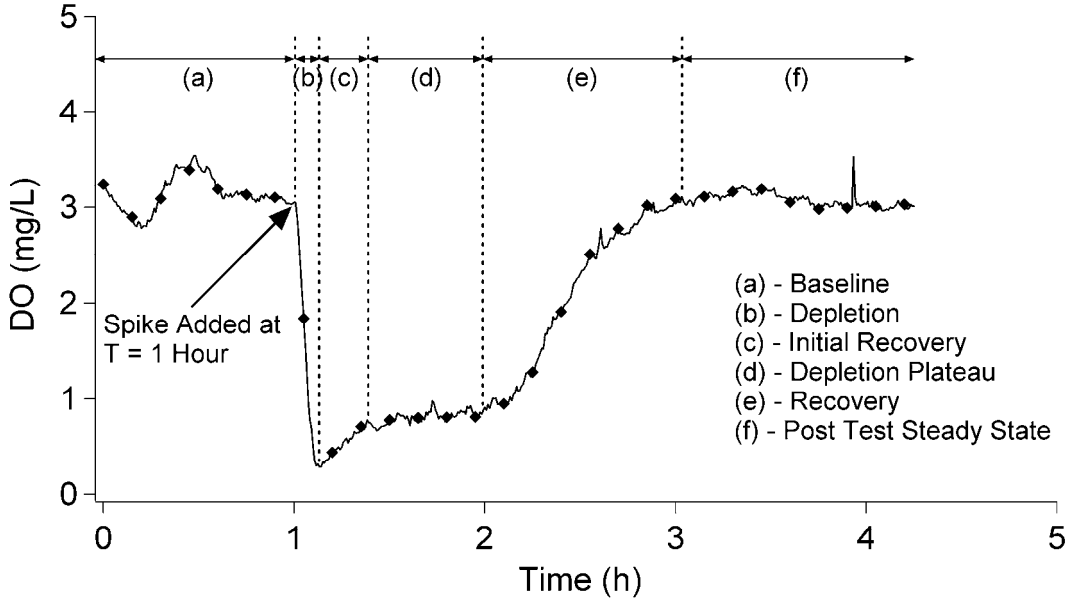


Figure 4-8 Dissolved oxygen depletion profile.

The first part of the profile **(a)** represents the initial baseline conditions. Following the application of a spike, an increase in DO uptake occurs as the bacteria respond to the added substrate, resulting in a very rapid decrease in DO concentrations **(b)**. As the DO decreases, substrate limitation results in inhibition of autotrophic bacteria, which continues to increases with decreasing DO until the oxygen uptake rate is equivalent to the aeration rate and the DO reaches a minimum concentration (within 8 to 11 minutes). The inhibition likely continues to increase after the minimum point as nitrite builds up, resulting in a small increase in the DO concentration **(c)**. Following this initial recovery, the DO concentration then increases at a much slower rate while the bacteria consume the excess substrate which has accumulated in the reactor. For smaller spikes, (**Test 3** and **4**), this increase was gradual, while for larger spikes (**Tests 1**, **2**, and **5**) a "depletion plateau" **(d)** of very slow DO increase persisted for approximately one hour. Once the bacteria consume the excess substrate, the oxygen uptake rate decreases and DO increases **(e)** until it reaches steady state conditions **(f)**.

If the DO depletion is viewed as a metabolic stress on the system, the off-gas N_2O profile is the measured response to that stress. The off-gas N_2O stress response is rapid, occurring within 4 to 8 minutes of the application of the stress. The timescale of this response is thus shorter than the typical timescale of aeration setpoint changes which are on the order of 15 to 30 minutes (Olsson and Newell 1999). A 5 to 10 minutes measurement response has been identified in the literature as being ideal for online process control (Lynggaard-Jensen 1999; Lynggaard-Jensen et al. 1996; Thomsen and Kisbye 1996). It can thus be concluded that on the basis of timescales, off-gas N_2O emissions are suitable for aeration control. Furthermore, as seen in **Figure 4-1** to **Figure 4-7**, the off-gas N_2O concentrations quickly returned to baseline conditions once the stress on the system had ended. Thus off-gas N_2O emissions satisfy **Criteria #1** and **#2**, namely the response occurs only in the presence of a process stress and occurs on a timescale suitable for process control.

While off-gas N_2O emissions loosely fit as an oxidative stress indicator, the actual stresses in the system are more complex, as seen when looking at the remaining liquid phase data. If the appearance of off-gas N_2O is strictly a function of the oxygen stress in the reactor, it would be expected that N_2O concentration would peak at the minimum DO concentration and then decrease as the DO increased. However, this was not the case. In all of the spike tests (**Tests 1** to **7**), the off-gas N_2O concentrations continued to increase after the DO had started to recover from the minimum value, with peak concentrations occurring on the DO depletion plateau.

Considering the other liquid phase parameters, the off-gas N_2O emissions did not appear to be strongly linked to the NH_4^+ concentrations. NH_4^+ is a significant metabolic inhibitor at concentrations greater than 10 mg/L and 1 mg/L for AOB and NOB, respectively (Hagopian and Riley 1998; Jianlong and Ning 2004). The measured NH_4^+ concentrations in the reactor did not increase above 5.2 mg/L, thus significant direct inhibition of AOB (which would result in a stronger link between NH_4^+ concentrations and process stress) would not likely occur. Instead, the role of NH_4^+ would be an indirect one via increasing the metabolic oxygen uptake and subsequent DO depletion, or the direct inhibition of NOB which would result in accumulation of NO_2^-.

A much stronger correlation existed between NO_2^-/FNA and off-gas N_2O concentrations. The location of the maximum off-gas N_2O concentrations as well as the start of the decline to baseline conditions correlated quite strongly to the maximum and initial decline for NO_2^- and FNA concentrations.

This observed correlation corresponds to the current mechanistic understanding presented in the literature (which was reviewed in **Section 2.1**). N_2O generation is believed to be an alternative metabolic pathway which is only initiated when a metabolic stress such as DO depletion or the presence of an inhibitory substance renders it favourable. Hence, the DO depletion acts to switch on the potential for the alternative pathway, and as such the linkage between off-gas N_2O and dissolved oxygen concentrations would not be a direct one. In addition to requiring favourable inhibitory conditions, NO_2^- (or FNA) is required as a substrate for the reaction (Shiskowski and Mavinic 2006). As the limiting substrate for the reaction, it would be expected that, as was observed in the experimental work, the generation rate (and correspondingly the off-gas concentrations) would follow the substrate concentration closely. While NH_4^+ is also a substrate for the reaction, it would not be expected to correlate strongly to the N_2O generation (other than as a source of oxidative stress) since it would likely be in excess.

The analysis to this point has been quite subjective in nature. A more objective assessment of the stresses and responses, in the form of an area analysis, was used to gain further understanding into the nature of the response. Results of this assessment for each of the spiking events are provided as **Table 4-3**. In addition to the process responses in terms of the accumulation and depletions, initial baseline and post test steady state conditions are provided for each of the parameters of interest. The percentile deviations between these initial and final conditions have been included to facilitate assessment of process variability during the testing period.

Table 4-3 Summary of stress responses to spiking events.

			Test ID						
			1	**2**	**3**	**4**	**5**	**6**	**7**
Test Conditions									
Temperature (°C)			20.9	21.8	22.9	22.7	25.6	24.4	25.8
MLSS (mg/L)			4665	4869	4299	3626	4868	3088	2260
Spike volume (mL)			15	15	10	7.5	7.0	7.0	15
Spike COD (mg)			908	869	587	473	421	353	855
Spike ammonium (mg)			74.9	61.7	43.5	32.2	26.7	25.2	56.3
Spike oxygen cemand (mg)			1251	1151	786	620	556	468	1112
Continuously Monitored Parameters									
DO	Concentration (mg/L)	Baseline	3.17	3.14	3.32	3.22	2.38	3.36	3.22
		Steady state	3.10	3.08	2.90	3.20	2.60	3.30	2.88
		Deviation (%)	2.2	2.0	12.6	0.7	8.5	1.8	10.6
	Depletion (mg•h/L)	Maximum	4.07	3.36	2.23	2.10	1.95	1.78	3.88
		Minimum	3.85	3.23	1.56	2.06	1.54	1.67	3.01
		Range (%)	5.3	3.7	29.9	2.3	20.7	6.4	22.3
N_2O	Concentration (ppm)	Baseline	0.91	0.86	0.93	0.95	0.97	1.03	0.96
		Steady state	0.92	0.97	1.00	0.98	0.99	1.05	0.94
		Deviation (%)	0.4	12.1	6.9	3.1	2.7	1.5	1.3
	Accumulation (ppm•h)	Maximum	1.20	1.87	1.25	1.22	1.29	1.37	3.06
		Minimum	1.19	1.64	1.14	1.16	1.23	1.34	3.03
		Range (%)	0.6	12.4	8.9	1.8	4.0	2.4	1.0
Liquid Phase Parameters									
NH_4^+	Concentration (mg/L)	Baseline	1.10	0.61	0.82	0.21	0.02	0.46	0.13
		Steady state	1.17	0.37	0.44	0.60	0.42	0.92	0.50
		Deviation (%)	5.7	39.6	45.8	65.6	95.2	49.8	73.3
	Accumulation (mg•h/L)	Maximum	1.41	2.84	0.94	1.77	1.61	1.08	4.30
		Minimum	1.36	2.38	0.64	1.03	0.79	0.25	3.36
		Range (%)	3.6	16.3	31.5	42.0	50.8	76.8	21.8
NO_2^-	Concentration (mg/L)	Baseline	0.018	0.011	0.027	0.058	0.040	0.028	0.054
		Steady state	0.027	0.017	0.015	0.093	0.032	0.028	0.075
		Deviation (%)	32.0	35.4	44.4	38.0	18.9	1.0	27.9
	Accumulation (mg•h/L)	Maximum	0.37	0.35	0.17	0.25	0.18	0.16	0.53
		Minimum	0.35	0.34	0.16	0.18	0.16	0.16	0.47
		Range (%)	6.6	2.8	7.5	28.7	7.6	0.2	10.2
FNA	Concentration ($x10^{-6}$ mg/L)	Baseline	2.13	1.43	3.86	6.73	5.40	3.34	6.27
		Steady state	3.39	2.31	2.43	10.7	4.57	3.44	9.50
		Deviation (%)	37.0	38.2	37.2	37.2	15.2	2.8	34.0
	Accumulation ($x10^{-5}$ mg•h/L)	Maximum	5.53	5.34	3.00	3.52	2.86	2.24	8.05
		Minimum	5.16	5.19	2.85	2.73	2.70	2.22	7.22
		Range (%)	6.7	2.8	5.3	22.6	5.6	0.6	10.2

The process was for the most part stable with regards to DO and off-gas N_2O concentrations. There was less than 8% variation from the initial baseline conditions to the final steady state for all the tests with the exception of **Test 3** and **7** for DO (12.6% and 10.6% deviation, respectively), and **Test 2** for off-gas N_2O (13.7% deviation). Much higher deviations were observed between baseline and post test steady state concentrations for the measured liquid phase parameters (NH_4^+, NO_2^-, and FNA), on the order of 32% to 49% with some outliers.

There does not appear to be a consistent trend with regards to the observed deviations, i.e. in some tests the baseline concentration was lower than the post test steady state concentration, while in others it was higher. This lack of a trend suggests that the deviations were not related to process timescales and were most likely a product of process instability/variability associated with the small scale of the pilot reactor. Furthermore, some of the baseline/steady state measurements for liquid phase parameters (NH_4^+ and NO_2^-/FNA) were near the limits of detection and small experimental errors could have a large percentile impact on the resultant concentrations.

With regards to the depletion/accumulation areas presented in **Table 4-3**, it should be noted that the liquid phase parameters (with the exception of DO) had a variable monitoring frequency and the data points were relatively coarsely spaced in comparison to the continuous monitoring data. As such, the area calculations for these parameters would be a coarse approximation of the accumulations and would be more useful in terms of assessing trends and proportionality instead of absolute values. Absolute values of the areas should not be interpreted directly since the magnitude of the responses can be influenced by a range of physical and operational parameters and could vary highly between processes. Instead, it is more appropriate to interpret the relative values of the parameters and relationships between then. These results will be interpreted in such a manner in **Sections 4.2.2**, **4.2.3**, and **4.2.4** to assess reproducibility, signal proportionality, and the effect of initial process conditions, respectively.

4.2.2 Response Stability

Stability of the process response was assessed using the results of three tests (**Tests 1**, **2**, and **5**) in which the process was perturbed with a 15 mL concentrated feed spike. Responses (DO and off-gas N_2O concentrations) for all three tests are compared in **Figure 4-9**, below.

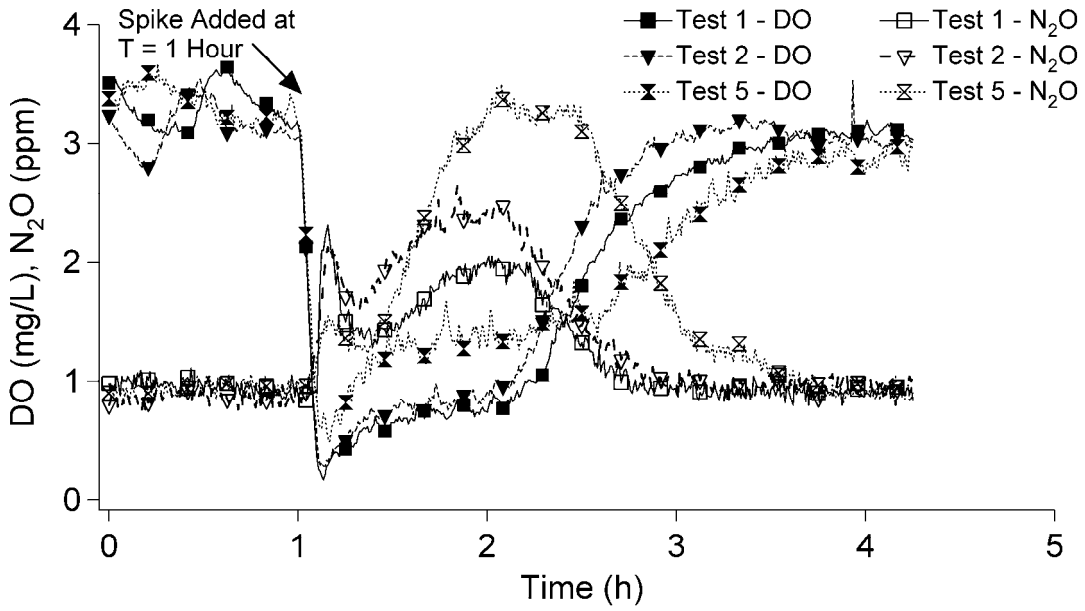


Figure 4-9 Stress response reproducibility using successive 15 mL feed spikes.

The response areas for DO depletions and off-gas N_2O accumulations are summarized in **Table 4-4**.

Table 4-4 Response reproducibility – area analysis.

		Test ID		
		1	**2**	**5**
Spike Loading	Oxygen demand (mg/L)	1251	1151	1112
DO Depletion (mg•h/L)	Maximum	4.06	3.36	3.88
	Minimum	3.85	3.23	3.05
	Average	3.96	3.29	3.44
	Range (%)	5.3	3.7	22.3
N_2O Accumulation (ppm•h)	Maximum	1.20	1.87	3.06
	Minimum	1.19	1.64	3.03
	Average	1.20	1.75	3.05
	Range (%)	0.6	12.4	1.0

DO profiles for **Tests 1** and **2** were quite consistent with regards to shape, with **Test 2** having a smaller net depletion as seen in the depletion areas presented in **Table 4-4**. This reduction in DO depletion (17% smaller) was somewhat larger than the reduction in loading (8% reduction from **Test 1** to **Test 2**). The DO deficits in **Tests 2** and **5** were not significantly different, with approximately 3% and 4% differences for the spike loading and resulting DO deficits, respectively. In terms of shape, the DO profile in **Test 3** was different from that of **Tests 1** and **2**, with a shallower deficit but a longer duration.

The observed off-gas N_2O accumulations were counter intuitive, with the greatest accumulation being observed at the lowest spike loading/DO depletion, and vice versa. There was a much higher variability in the off-gas N_2O accumulations, 61% between the highest and lowest accumulations. The shape of the off-gas N_2O profiles in **Tests 1** and **2** were quite similar, with an initial peak at the minimum DO followed by a gradual increase over the duration of the DO depletion plateau, after which there was a rapid decrease to the steady state concentration. **Test 5** had an off-gas N_2O profile which varied strongly from **Tests 1** and **2**, with a steady increase to the maximum concentration (no initial peak), and a much broader profile which corresponded to the broader DO profile.

Overall with regards to **Criterion #3** (reproducible response to stresses), there appeared to be a significant level of variability in the off-gas N_2O response, particularly between tests conducted on different seeds. It can not be definitively concluded from this work if the variability is inherent in the response or a function of other experimental factors, although in a stable microbial community it would be expected to have a fair degree of reproducibility.

It is possible that the variation in the off-gas N_2O responses represents a variability in the microbial populations between seeds (which were collected approximately 1.5 months apart). Alternatively these variations could be the result of the effects of successive spiking or adaptation to the synthetic feed/reactor operating conditions. These effects will be discussed further in **Section 4.2.3**.

4.2.3 Response Proportionality

Three sequential tests at decreasing spike volumes (**Tests 2**, **3**, and **4**) were conducted to assess the response proportionality to reactor loading. The DO and off-gas N_2O profiles for all three tests are presented in **Figure 4-10** for comparison.

The shapes of the DO profiles were as expected, with a shallower profile being observed at smaller spike loadings. Based on the results of the area analysis (**Table 4-5**, presented as a percentage of the average **Test 2** value), there was one deviation from the expected trend, with the depletion in **Test 4** being greater than that in **Test 3**. This is a function of depletion in **Test 3** having a larger range (approximately 30% between the minimum and maximum) due to the drift in the reactor DO from baseline to steady state, although the percentile depletion in **Test 4** is larger than the percentile load.

Off-gas N_2O responses had different shapes in all three tests, making visual comparison unreliable. The duration of the peaks decreased with decreasing load (quite similar to the shapes of the DO profiles), as did the peak off-gas N_2O concentrations. With regards to the net response (accumulation area), there was a decreasing trend **Tests 2** and **3** which corresponded well to the load. However, **Tests 3** and **4** did not have significantly different net responses, and similar to DO, there appeared to be an increased process response to the spike loading.

Table 4-5 Response proportionality – area analysis.

		Test ID		
		2	**3**	**4**
Spike loading*	Oxygen demand	100	68	54
DO Depletion*	Maximum	102	68	64
	Minimum	98	47	62
	Average	100	57	63
N_2O Accumulation*	Maximum	107	71	70
	Minimum	94	65	66
	Average	100	68	68

*Results are presented as a percentage of the average Test 2 value.

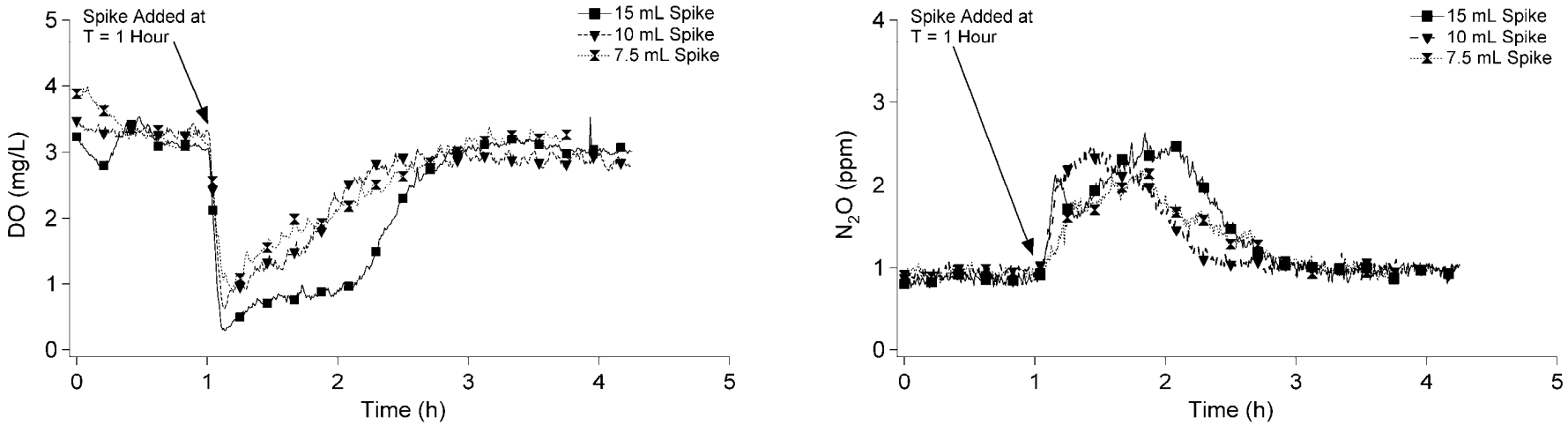


Figure 4-10 Stress response proportionality; DO response (left) and off-gas N_2O response (right).

Due to the variability noted in both this section and in the previous one, the entire dataset was analysed to assess proportionality. DO depletions and off-gas N_2O accumulations are presented as a function of spike loading in **Figure 4-11** and **Figure 4-12**, respectively.

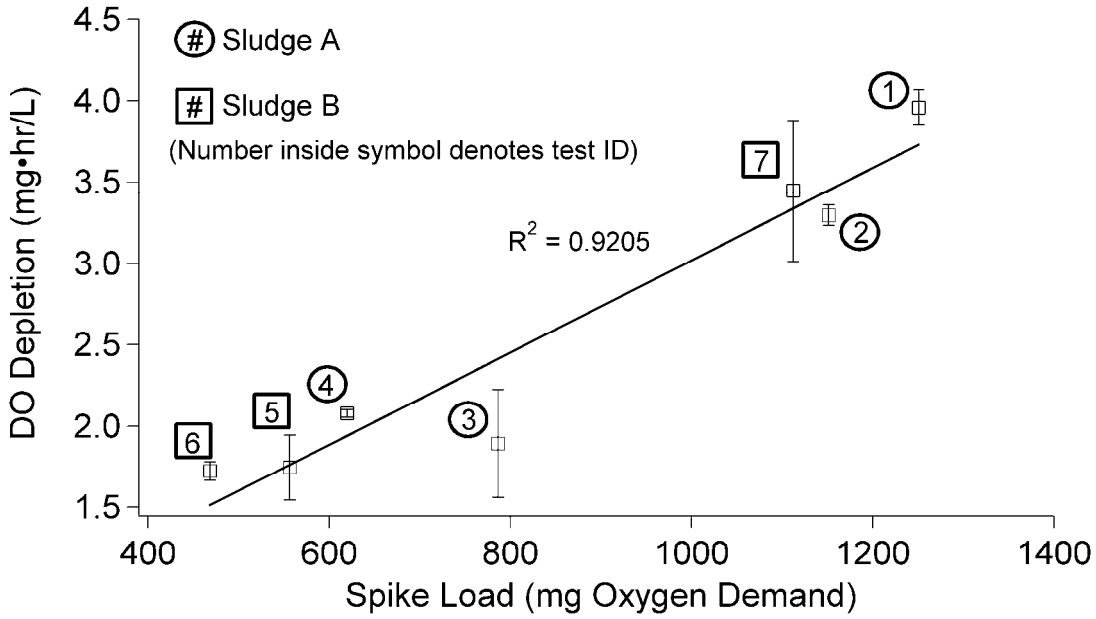


Figure 4-11 DO depletion as a function of shock loading magnitude.

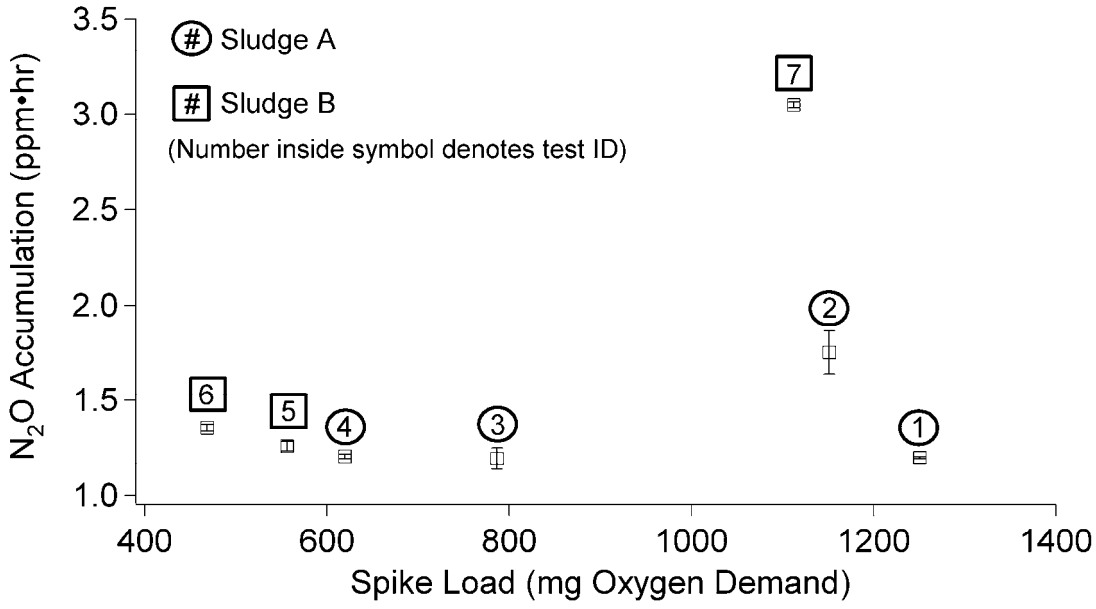


Figure 4-12 N_2O accumulation as a function of shock loading magnitude.

With regards to DO, a definite trend existed and the net response was proportional to the spike load, with one primary outlier (**Test 3** at 783 mg oxygen demand). The net off-gas N_2O response did not appear to have a proportional correlation to the spike load, indeed many of the net responses are relatively similar in magnitude. The off-gas N_2O results suggest the influence of other parameters than simply spike load. One way to assess the influence of other parameters is to look at off-gas N_2O yields normalized based on the spike load (oxygen demand) and reactor MLSS (a measure of biomass concentration).

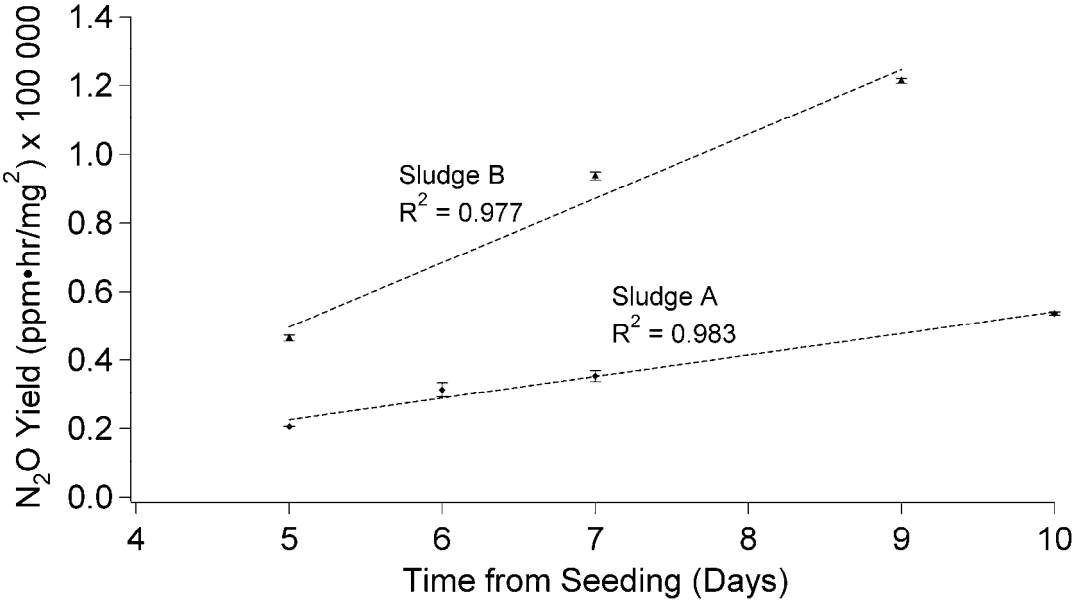


Figure 4-13 Temporal variation in off-gas N_2O yield.

Two things are apparent when looking at **Figure 4-13**. First, there is a significant difference in the yields for the two sludges, suggesting a variation in the biological makeup of the two seeds used to start up the reactor. It has been identified in literature that AOB populations can be influenced by seasonal effects (temperature) as well as operational parameters such as SRT and influent properties (Limpiyakorn et al. 2005; Siripong and Rittmann 2007). However, lacking microbiological analysis of the populations, such a difference can not be confirmed.

Secondly, a very strong linear correlation between N_2O yield and time from spiking (i.e. temporal effects) exists in the data. These effects could be the result of

adaptation to two forms of process stress. One source of stress would be the changed operational conditions from the full scale process to the lab scale reactor (for example changes in SRT, HRT and influent from a real wastewater to a synthetic one). These stresses would result in adaptive effects on the microbial community over time, with it being generally accepted that up to three times the SRT is required for a reactor to reach a new steady state. It is likely that while these adaptive changes would result in process instability, they may not be the dominant source of the temporal variation in the off-gas N_2O response. A second source of stress is the application of successive spikes which would exert a selective pressure that would favour the AOB best able to cope with repeated stress conditions of oxygen depletion. Thus the process would be selecting AOB best able to utilize the alternative metabolic pathway which results in the generation of N_2O. By selecting in this manner, it would be expected that there would be an increase in off-gas N_2O yield over time.

These yield results could account for the observed lack of proportionality in the off-gas N_2O emissions from **Test 4** compared to **Tests 2** and **3**. **Tests 2** and **3** were conducted on sequential days, while the final test (**Test 4**) was conducted three days later. Looking at **Figure 4-13**, the normalized N_2O yields for **Tests 2** and **3** were not significantly different, while that in **Test 4** was substantially higher, thus producing a larger response with a smaller spike loading.

Overall, the N_2O proportionality results are mixed with some data indicating proportionality with others indicated the presence of substantial temporal variations. The source of these variations needs to be further assessed, particularly to determine if they are a function of the experimental apparatus, in particular the synthetic feed, or are a product of the experimental methodologies (i.e. the act of perturbing the system with spikes produces changes in the system being investigated).

It is interesting to note that despite the mixed N_2O results, DO depletions showed a good level of proportionality. This is likely due to the nature of the oxygen demand load applied, which was approximately 75% organic carbon. Thus the resulting DO depletion is parimarly a function of organic carbon metabolism by heterotrophic bacteria, and as such the response would not be influenced in the same manner by

external factors as N_2O generation (which in this case is solely a product of autothropihc bacteria).

With regards to **Criterion #4** (response proportional to applied stress), further investigation is required to determine parameter suitability. In particular, investigation should be conducted for operation on real wastewater at full scale plants utilizing smaller perturbations such as step changes in a controlled system, as well as assessing long term (seasonal) variations on fully adapted processes.

4.2.4 Effect of Initial Conditions

For application to process control, as well as for the development of an off-gas N_2O correlation, it is important to know if the response is dependent on initial conditions, i.e. if the same stress is applied, will there be a similar stress response at different operating setpoints. This was assessed by applying 7 mL spikes to the process operating at two different aeration setpoints, the first with a baseline DO concentration of 2.5 mg/L (**Test 5**) and the second at 3.3 mg/L DO (**Test 6**). DO and off-gas N_2O profiles are provided for both tests in **Figure 4-14** for comparison.

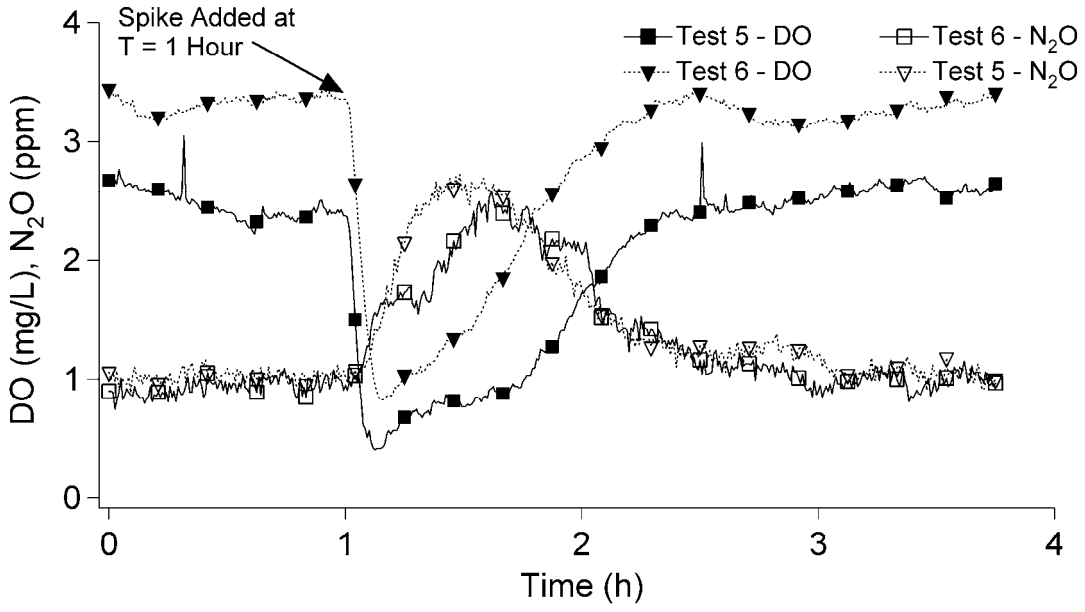


Figure 4-14 Evaluation of initial condition effects on stress response.

For the liquid phase DO concentrations, the profiles in the two tests were similar and for the most part offset by a consistent amount (with the exception of the initial minimum DO, where the profile in **Test 6** was closer to that in **Test 5** indicating a slightly stronger response). Based on the area analysis, there was no significant difference between the measured depletions, with the depletion range for **Test 6** being inside that for **Test 5**.

Off-gas N_2O profiles were quite similar as well, except the profile in **Test 6** had a much rounder peak and reached a maximum earlier than in **Test 5**, although the maximum values were similar. The shapes and maximum points were strongly correlated to the liquid phase NO_2^-/FNA concentrations (presented in **Figure 4-5** and **Figure 4-6**, respectively). Despite some variations in shape, the net responses were quite similar, being only 7% different. This indicated that while initial conditions do have some effect on the response, they appeared to be small and not likely to be significant over the normal operating range of a controlled process.

4.2.5 Stress Response – Feed Step Change

While spike tests provide useful dynamic data, another common test used to characterize process dynamics is the step response test. In a step response test, a step change is applied to one of the process input parameters and the resulting changes in process outputs as they approach a new steady state is observed. Step changes tend to be more representative of actual process control applications. Typically a single step is done during a test. However, due to the temporal variability observed in **Tests 1** to **7**, several consecutive steps were done in a single test (**Test 8**, presented as **Figure 4-15**) to allow for more consistent results.

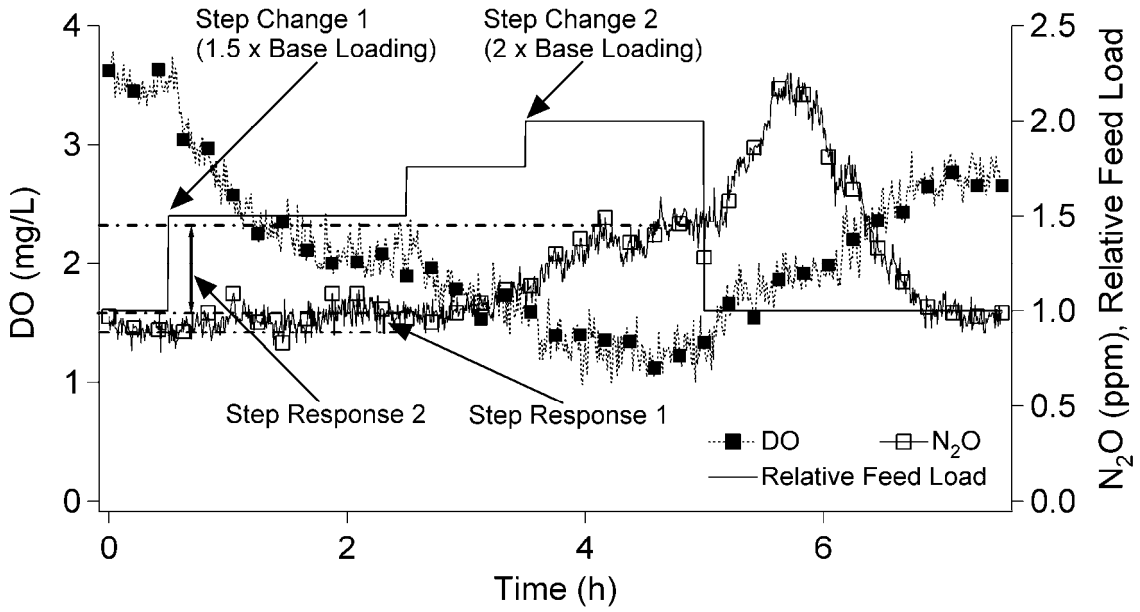


Figure 4-15 Stress response to a step change in influent feed concentration.

As seen in **Figure 4-15**, the process required approximately one hour to reach a new steady state following application of a step change. Three steps were applied, but for the purposes of this analysis the second and third steps will be lumped together into Step 2. The two steps (1 and 2) consisted of identical load increases, with Step 1 being an increase from full load to 150% of full load, and Step 2 being an increase from 150% to 200% of full load.

The off-gas N_2O response to Step 2 was much larger than that for Step 1. Likely this difference in response is due to the nature of DO inhibition of biological processes, which is Monod in form and not a linear correlation. Due to this form, above a certain bulk DO concentration the process is rather insensitive to changes in DO, thus changes in DO result in very small changes in the level of inhibition (and corresponding off-gas N_2O response). Once the bulk concentration decreases sufficiently, the sensitivity becomes larger and the inhibition increases at a greater rate with decreasing DO (and the process response becomes more significant). Based on the results presented in **Figure 4-15**, once the bulk DO concentration reaches approximately 2 mg/L, process inhibition (and correspondingly off-gas N_2O concentrations) became highly sensitive to changes in reactor DO. This in

agreement with Tallec et al. (2006a), who observed a trend of increasing N_2O generation with decreasing dissolved oxygen concentrations below 2 mg/L.

At the end of Step 2, after the process loading had been returned to the normal operating load, a rapid increase in off-gas N_2O concentrations was observed. Likely this is due to accumulation of NO_2^-/FNA and NH_4^+ during the step test associated with the process operating at an excessively high loading. At that point the process was beginning to fail significantly and this failure was exhibited in the off-gas N_2O concentrations.

In terms of application to process control, these results demonstrate that the stress response is sensitive to changes in process conditions in the normal operating range of an activated sludge process (**Criterion #5**). Furthermore, the off-gas N_2O signal was relatively stable at the operating setpoints, a requirement to be a suitable parameter for process control.

4.3 Summary

The dynamics of off-gas N_2O stress responses were assessed to determine the suitability of this parameter for process control applications. Off-gas N_2O emissions from nitrifying processes are believed to be a stress-response relationship in which AOB experiencing metabolic stress utilize an alternative metabolic pathway (that generates N_2O) as a survival mechanism. In general, the observed off-gas N_2O responses were in agreement with the prevailing mechanistic understanding of this process, with two conditions having to be satisfied for the alternative autotrophic metabolic pathway of interest to proceed and the subsequent stress response to be exhibited. Namely, there must be a source of process stress (for example a DO depletion caused by an increase in influent loading) and the presence of the limiting substrate for the alternative metabolic pathway (NO_2^- or possibly FNA) for the stress response to be generated.

Evaluation of this stress-response relationship was conducted against 5 key criteria, with the results summarized below in **Table 4-6**.

Table 4-6 Summary of off-gas N_2O suitability as a control parameter.

Criteria	Description	Comments
1	Presence correlated to stress	Strong correlation, only occurs in the presence of a DO depletion and NO_2^-/FNA accumulation
2	Timescale suitable for process control	Response timescale on the order of 4 to 8 minutes, faster than the timescale of aeration setpoint adjustment, thus suitable.
3	Reproducible response	Variability observed, however results inconclusive due to potential influences from other processes.
4	Proportional response	Some results proportional, however temporal variability in N_2O yield indicates presence of other influences.
5	Sensitivity suitable for process control	Response is suitably sensitive in the desired operational DO range.

Overall, off-gas N_2O concentrations met the majority of the criteria, indicating a strong potential for application as a non-invasive means of aeration process control for nitrifying activated sludge processes. Questions do however remain with regards to response proportionality and reproducibility, and further investigation is required into these areas.

In particular, the source of the apparent temporal effects on the off-gas N_2O yield needs to be investigated. Potential sources of these effects in the experimental setup utilized in this work included adaptation to the synthetic feed/reactor operating conditions, and adaptive effects/process instability associated with the application of successive spikes to the reactor.

To improve the assessment of the stress-response, it is recommended that future work be conducted utilizing a pilot or full scale process fed with real wastewater, and that the assessment be performed utilizing step response experiments (or diurnal feed loadings), which would provide conditions representative of normal process operation. This would serve to eliminate several sources of adaptive effects and allow the assessment of long term variability in the stress response due to seasonal population changes in full scale processes. An understanding of population changes would greatly increase understanding of the specific off-gas N_2O emissions and assist in identifying sources of variability. It is recommended that future work be supported by molecular analysis, particularly to identify and quantify AOB populations.

Finally, the results of the stress-response analysis provided the necessary data to allow the development of a liquid phase activated sludge process model and an off-gas N_2O model. This model development, along with its application to assess the potential benefits of non-invasive process control utilizing off-gas N_2O as a control parameter will be presented in the following chapter (**Chapter 5**).

Chapter 5 Process Simulation

With the suitability of off-gas N_2O concentrations as a process control parameter being demonstrated in **Chapter 4**, an aeration control concept was developed based on off-gas N_2O monitoring (presented in **Section 5.1.1**). A process simulation study was conducted to assess the performance of this control concept, as well as to quantify the potential benefits associated with its implementation. The work presented in this chapter will support the technical, environmental, and economic evaluation presented in **Chapter 6**.

The simulation work required the development of a data generator (simulated process) which was then utilized to evaluate specific operational and control scenarios of interest. This work was conducted in two phases; in the first phase, process simulation was performed using a data generator based on existing data obtained from Burgess et al. (2002b), hereinafter referred to as the "Cranfield data". In addition to providing relevant results that contributed to the study objectives, the work conducted in this phase served to identify data gaps and to improve the experimental design used to gather data for use in the second process simulation phase.

Simulations carried out in the second phase utilized a data generator based upon data collected from a laboratory scale activated sludge bioreactor (presented in **Chapter 4**), which will be refered to as the "UNSW data". Both datasets will be discussed in greater depth in **Section 5.2.1** and **5.3.1** for the Cranfield and UNSW datasets, respectively.

A discussion of the overarching simulation methodology utilized in this study, along with the proposed process control concept is provided as **Section 5.1**. Data generator development using Cranfield and UNSW data is presented in **Sections 5.2** and **5.3**, respectively. Simulations to evaluate the process control concept and quantify potential benefits are presented **Section 5.4**, and concluding remarks are provided in **Section 5.5**. It should be noted that portions of this chapter concerning the analysis conducted utilizing the Cranfield data has been published in Biotechnology and Bioengineering (Sivret et al. 2008).

5.1 Overarching Simulation Methodology

Evaluating the off-gas N_2O based aeration control concept required the development of a simulation package. This simulation package consisted of two primary interacting components: a process control algorithm (which included process monitoring and actuators), and a data generator (a simulated activated sludge process). The interactions between the simulator components are depicted in **Figure 5-1**.

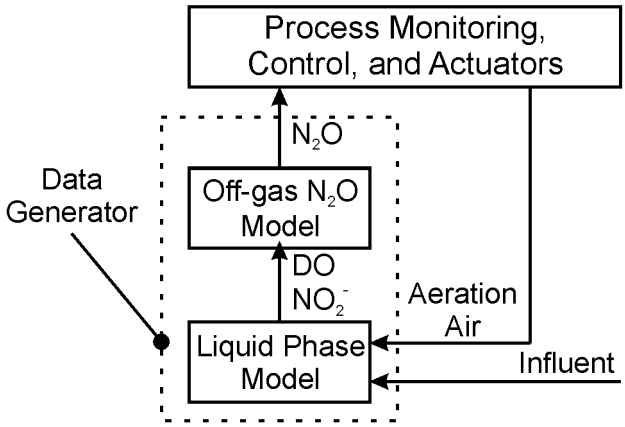


Figure 5-1 Simulation package components.

The liquid phase model utilizes influent and air supply data as inputs, generating a liquid phase output which is fed to the off-gas N_2O model. In turn, the off-gas N_2O model produces an off-gas N_2O concentration output that is passed to the process control algorithm which adjusts the aeration air supply to the liquid phase model based upon the process setpoint.

Process inputs (influent) were used to generate operating scenarios to evaluate the process control concept's effectiveness. All simulations were conducted using Matlab 7.0 (The MathWorks, Natick, MA, USA), Excel (Microsoft Corporation, Redmond, WA, USA), and simulators coded in LabVIEW (National Instruments, Austin, TX, USA). The two primary components (process control concept and the data generator) are discussed in the following subsections.

5.1.1 Off-gas N_2O Aeration Control Concept

The proposed aeration control concept was based upon the utilization of an off-gas N_2O signal as a surrogate for the inhibition dynamics of the autotrophic nitrifying bacteria in the bioreactor. It is proposed that the aeration to nitrifying activated sludge processes can be controlled based upon the level of metabolic inhibition experienced (indicated by off-gas N_2O concentrations). That is, an off-gas N_2O concentration corresponding to an acceptable level of process inhibition is selected as the operating setpoint, and this concentration is controlled using the air flow to the aeration system as a master control variable. This becomes a rather straightforward control concept (**Figure 5-2**), which does not require advanced process models or invasive process monitoring.

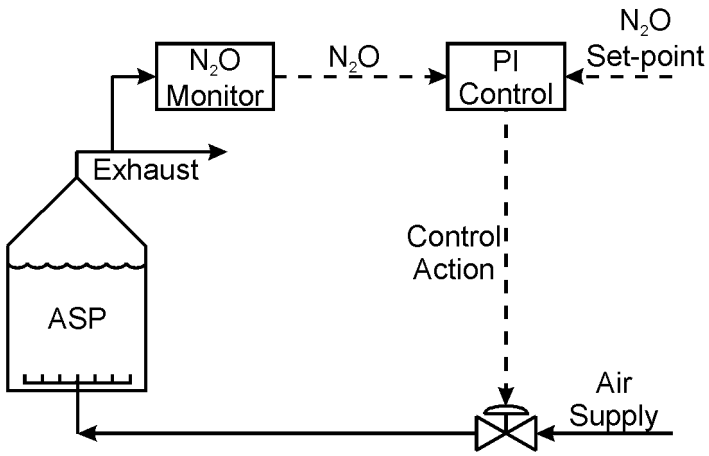


Figure 5-2 Off-gas N2O aeration control concept.

The aeration control concept was implemented as a PI control algorithm to control the airflow to the simulated bioreactor. For simulation purposes, an idealized control response was used (i.e. no response lags in control equipment), and suitable action was provided to the air supply valve to allow control of the system. The controller was tuned using the continuous cycling method with Ziegler-Nichols tuning parameter coefficients (Seborg et al. 2003).

5.1.2 Data Generator

A data generator was developed to provide a platform onto which to test the process control concept. This data generator consisted of two model components; a gas phase model to link the off-gas N_2O concentration to liquid phase properties, and a liquid phase model to determine the properties required by the off-gas model as a function of external stimuli, i.e. influent conditions and aeration.

The liquid phase activated sludge process model consisted of 4 sub models; a hydraulic model, a settling model, an aeration model, and a biological process model. This model also required a set of initial conditions which were selected based upon steady state operational data. The dataflow between the individual data generator subcomponents are illustrated in **Figure 5-3**.

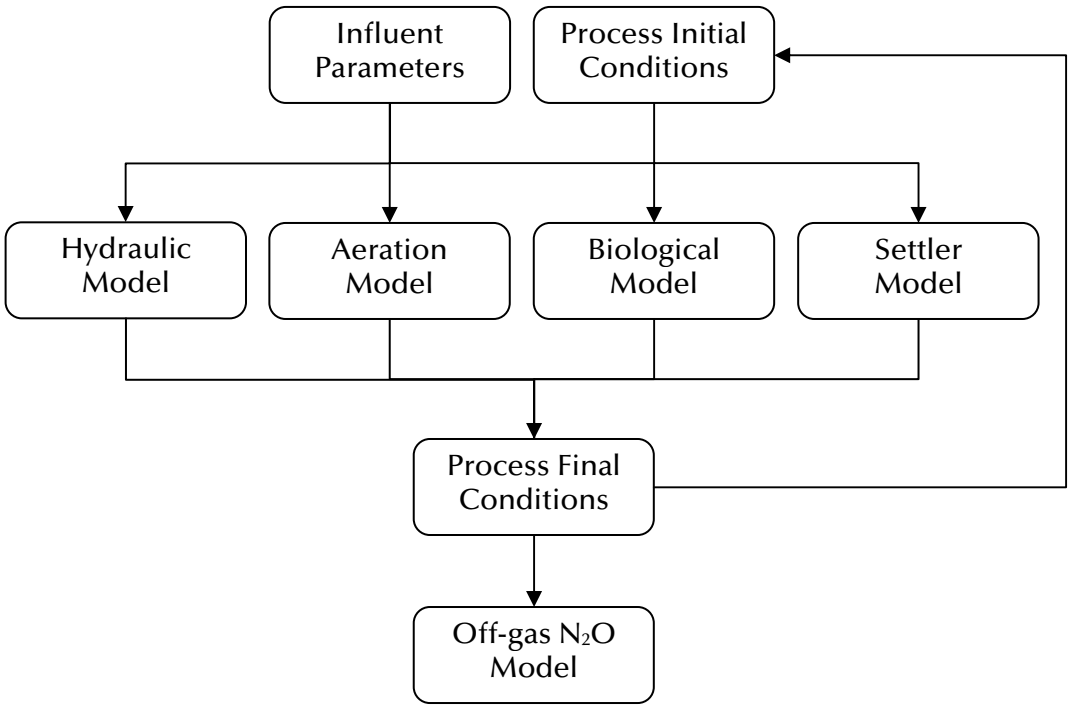


Figure 5-3 Data flows – data generator.

For the purposes of this work, the treatment process aeration tanks were assumed to be well mixed and were modelled as continuous stirred tank reactors (CSTRs). The validity of this assumption will be discussed in **Sections 5.2.2.2** and **5.3.2.2**. It was also assumed that the processes were operating at a hydraulic steady state, i.e.

the influent flow was equal to the effluent flow with no accumulation in the process. Since the treatment process influents were supplied from storage tanks using peristaltic feed pumps operating at constant flow rates, this assumption would be justified.

An idealized settling model was utilized. This model consisted of complete point separation of the solids and liquids inside the settler, with no sludge storage. This assumption is considered valid providing there is no substantial changes in suspended solid loadings and the bioreactor is at hydraulic steady state (Langergraber et al. 2004). The exact operating conditions of the settler used to generate the Cranfield data was not discussed in Burgess et al. (2002b), thus an idealized mode of settling was assumed for the process. The idealized settling assumption was verified for the UNSW settler.

No data was available with regards to the aeration system (particularly aeration configuration and mass transfer properties) in the bioreactors used to collect the Cranfield and UNSW data. An overall mass transfer coefficient was assumed, and the airflow was calibrated to provide an appropriate steady state DO concentration.

The biological component of the liquid phase model was developed based upon the ASM1 family of activated sludge biological process models (Henze et al. 2000). ASM1 was chosen as the process model since it has the largest pool of existing knowledge and conditions which would warrant the application of the more complex ASM3 model, such as significant anoxic or anaerobic zones (Langergraber et al. 2004) or high COD concentrations that would result in readily biodegradable COD storage being a dominant phenomena (Koch et al. 2000), did not exist.

Simplifying assumptions were made to customize the ASM1 model to the system being studied as well as to reduce computational demands. The modelled bioreactor operated in an aerobic mode only (as a nitrification process), thus the anoxic components of model were omitted. Furthermore, the determination of concentrations of inert organic matter (soluble and particulate forms) and particulate biomass decay products was not included in the final model. These substances only appear as products from the modelled processes and as such do not influence any of the state variables of interest. Finally, the alkalinity portion of

the model was omitted since the bioreactor pH remained relatively constant over the duration of the sampling events for both the Cranfield (Burgess et al. 2002b) and UNSW data.

The development and calibration of the remaining aspects of the biological models for both datasets were a function of the available data. Thus, the approaches varied amongst the two datasets and will be discussed separately in **Sections 5.2.2** and **5.3.2** for the Cranfield and UNSW data, respectively.

Currently, no predictive N_2O off-gas models exist in the literature for activated sludge processes. It was necessary to develop a correlation to generate N_2O profiles as a result of existing liquid phase conditions. Development of off-gas N_2O models for the Cranfield and UNSW data will be discussed in **Sections 5.2.3** and **5.3.3**, respectively.

5.2 Data Generator Development – Cranfield Data

5.2.1 Data Sources

Experimental data used in the development and validation of the stress response data generator were obtained from Burgess et al. (2002b). This data was generated during two experiments where shock loads of ammonia were applied to a pilot scale (300 L) activated sludge process and the process response (DO, effluent NH_3, and off-gas N_2O) was measured. As such, the data only describes off-gas N_2O concentrations as a function of changes in ammonia loading.

The bioreactor used in these experiments was operated at a 6 hour hydraulic retention time and a 12 day sludge retention time, and treated wastewater from the Cranfield University wastewater treatment plant with an average COD of 391 mg/L and ammonia concentration of 44.3 mg/L (Burgess et al. 2002b). It should be noted that the equilibrium between ammonia and ammonium at near-neutral pH is shifted strongly towards ammonium (Henze et al. 2000). Thus while the ASM model considers total soluble ammonia nitrogen (ammonia + ammonium), the ammonia portion is typically insignificant and the ASM models are typically written based on ammonium (Henze et al. 2000) As such, all ammonia data from literature was converted to ammonium and all soluble ammonia nitrogen concentrations were reported as ammonium.

It is important to note that the original purpose of these datasets were to evaluate the stress response relationships between off-gas N_2O and liquid phase conditions. These datasets were not developed considering the data needs associated with process modelling, and as a result there were a number of gaps from a process modelling perspective. The most notable data gap was the lack of a detailed influent characterisation, which is a key component of any model calibration exercise. This gap, along with a lack of COD profiles, limited the calibration and validation of the heterotrophic processes in the mechanistic model.

A number of assumptions were made with regards to the feed characteristics and initial bioreactor conditions to fill in the dataset to allow the application of a

biological process model. The wastewater feed was assumed to be of constant quality over the duration of the test (14 hours), and the COD fractionation was assumed based on fractionations for European wastewater obtained from Wichern et al. (2003). Influent characteristics used in the model as well as the respective data sources are summarized in **Table 5-1**.

Table 5-1 Influent characterisation - Cranfield data, Test 1.

Parameter		Value	Source
Q_{inf}	Influent flow (L/h)	50	Burgess et al. (2002b)
$S_{NH,I}$	Influent NH_4^+ (mg NH_4^+-N/L)	51	Burgess et al. (2002b)
COD_I	Influent total COD (mg COD/L)	362	Scaled from Burgess et al. (2002b) based on influent ammonium.
$S_{S,I}$	Influent readily biodegradable COD (mg COD/L)	72	20% of total influent COD Wichern et al. (2003)
$X_{S,I}$	Influent slowly biodegradable COD (mg COD/L)	81	50% of total influent COD Wichern et al. (2003)

5.2.2 Liquid Phase Component

5.2.2.1 Model Selection and Formulation

The primary purpose of the liquid phase model was to simulate DO profiles as a function of feed conditions and aeration. Two approaches were evaluated for simulating the reactions occurring in the liquid phase of the bioreactor. The first approach was a mechanistic model using ASM1 (Henze et al. 2000). A highly reduced ASM1-based model was developed as the second modelling approach in an effort to eliminate many of the modelling uncertainties associated with the mechanistic model.

Mechanistic ASM1 Model

The mechanistic ASM1 model was developed using the full ASM1 model matrix (Henze et al. 2000) and applying the simplifying modelling assumptions discussed in **Section 5.1.2**, namely:

- only aerobic processes were considered;
- inert organic matter was omitted;
- particulate decay products were omitted; and
- the alkalinity model component was omitted.

It should be noted that this model contains both heterotrophic and autotrophic processes. The final mechanistic biological model developed for the Cranfield data is presented in matrix form as **Table 5-2**.

Table 5-2 Mechanistic model matrix – ASM1.

Category	Process	Process State Variable									Rate
		S_S	X_S	X_H	X_A	S_O	S_{NO}	S_{NH}	S_{ND}	X_{ND}	
Het. processes	Aerobic growth	$-\frac{1}{Y_H}$		1		$-\frac{1-Y_H}{Y_H}$		$-i_{XB}$			$\mu_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{O,H}+S_O}\right)X_H$
Auto. processes	Aerobic growth				1	$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{XB}-\frac{1}{Y_A}$			$\mu_A\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_O}{K_{O,A}+S_O}\right)X_A$
Biomass decay	Decay (heterotrophic)		$1-f_P$	-1						$i_{XB}-f_P i_{XP}$	$b_H X_H$
	Decay (autotrophic)		$1-f_P$		-1					$i_{XB}-f_P i_{XP}$	$b_A X_A$
	Ammonification							1	-1		$k_a S_{ND} X_H$
	Hydrolysis – organics	1	-1								$k_h\left(\frac{\frac{X_S}{X_H}}{K_X+\frac{X_S}{X_H}}\right)\left[\left(\frac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\right]X_H$
	Hydrolysis – organic nitrogen								1	-1	$k_h\left(\frac{\frac{X_S}{X_H}}{K_X+\frac{X_S}{X_H}}\right)\left[\left(\frac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\right]\frac{X_H X_{ND}}{X_S}$

Reduced ASM1 Model

A highly reduced ASM1-based model was developed as the second modelling approach. This approach sought to eliminate many of the modelling uncertainties by minimizing the number of state variables modelled and mathematically fitting the reduced process parameters to the experimental data.

The full ASM1 model matrix (Henze et al. 2000) was used as a starting point for the reduced model development. This matrix was then reduced using several key assumptions. In addition to the assumptions discussed previously, it was assumed that the influent COD and NH_4^+ concentrations were relatively constant over the time period considered. Being less sensitive to reduced dissolved oxygen concentrations, heterotrophic bacteria would experience less variation in metabolic activity during the dissolved oxygen depletions. Therefore, under the assumed constant feed conditions, the dissolved oxygen demand associated with heterotrophic growth would be relatively constant. Since the process response to changes in air supply (and not specific air supply rates themselves) is of interest, the heterotrophic oxygen demand was neglected.

Furthermore, it was assumed that the bacterial populations would remain relatively stable over the course of the time period (14 hours), which eliminated the microbial population state variables. The final reduced model (presented in **Table 5-3**) had two key state variables (DO and NH_4^+), and considered three main processes: aeration, autotrophic growth, and ammonification.

Table 5-3 Reduced model matrix - Cranfield data.

Process	S_O	S_{NH}	Kinetics
Aeration	K_1		$\left(S_{O,S} - S_O\right)$
Autotrophic growth	$-K_2$	$-K_3$	$X_A\left(\frac{S_O}{S_O + K_{O,A}}\right)\left(\frac{S_{NH}}{S_{NH} + K_{NH}}\right)$
Ammonification		K_4	$\left(X_H + X_A\right)$

5.2.2.2 Model Calibration

Two different calibration methodologies were implemented for the process models. The mechanistic ASM1 model was calibrated in a more traditional manner, using a combination of sensitivity analysis and manual calibration based on process knowledge, while a mathematical calibration technique was applied to the reduced model.

ASM1 Model Calibration

Prior to the mechanistic model calibration, a sensitivity analysis was conducted to identify the parameters of key importance for calibration. In addition to assisting with model calibration, sensitivity analyses can assist in the development of sampling campaigns by focusing experimental effort on key parameters. The sensitivity analysis was conducted using a similar methodology to that used in several of the studies reviewed in **Section 2.2.2** (Makinia et al. 2005; Ni and Yu 2008).

Due to the form imparted on the activated sludge process model by the Monod kinetics used in the ASM1 biological model, model parameters can have different effects on steady state and dynamic model performance. Indeed, steady state calibration can often be achieved in a much simpler manner (using less calibration parameters) than dynamic calibration. To illustrate the differences between calibrating the two forms of the model, the sensitivity analysis was conducted in two parts, first only looking at steady state model predictions (neglecting process dynamics), and then assessing the dynamic performance of the model.

Steady State Model Calibration

To provide a basis on which to compare sensitivity, an initial model run had to be conducted using the default model parameters obtained from Henze et al. (2000) and the influent characterization presented in **Table 5-1**. The model parameters were then adjusted as needed until the steady state predictions matched those of the data set being fitted.

An adjustment to the autotrophic bacteria growth rate was required because the growth rate using the default values was too low and resulted in washout of the bacteria from the system and nitrification failure. Adjustments to the maximum

autotrophic bacteria growth rate have been required in other studies to account for low predictions of nitrification (Wichern et al. 2003). While applying ASM3 to six wastewater treatment plants, Wichern et al. (2003) used a maximum autotrophic bacteria growth rate of 1.6/d, which is similar to that used to fit this process. The default and modified parameters are presented in **Table 5-4**, with the modified parameters in bold.

Table 5-4 Steady state calibration of mechanistic model - Cranfield data.

Parameters		Units	ASM1 Default	Initial Calibration
Mass transfer parameters				
k_La	Aeration mass transfer coefficient	1/d	-	3.5
Stoichiometric coefficients				
Y_H	Heterotroph yield	g COD_{XH}/g COD_{XS}	0.67	0.67
Y_A	Autotroph yield	g COD_{XS}/g N_{SNH}	0.24	0.24
f_P	Fraction of biomass degrading to particulate products	-	0.08	0.08
i_{XB}	Biomass nitrogen content	g N/g COD_{XBM}	0.086	0.086
i_{XP}	Particulate product nitrogen content	g N/g COD_{XP}	0.06	0.06
Rate constants				
k_H	Hydrolysis rate constant	g X_S/(g X_H•d)	3	3
k_a	Ammonification rate constant	m^3/(g X_H•d)	0.08	0.08
μ_H	Heterotroph maximum growth rate	1/d	6	6
μ_A	Autotroph maximum growth rate	1/d	0.8	**1.4**
b_H	Heterotroph decay coefficient	1/d	0.62	0.62
b_A	Autotroph decay coefficient	1/d	0.62	0.62
Saturation constants				
K_{OH}	Heterotroph oxygen half-saturation constant	mg DO/L	0.2	0.2
K_{OA}	Autotroph oxygen half-saturation constant	mg N/L	1	1
K_{NH}	Ammonium half-saturation constant	mg DO/L	0.4	**0.75**
K_X	Hydrolysis half-saturation constant	g X_S/g X_H	0.03	0.03
K_S	Substrate half-saturation constant	mg COD/L	20	20

A comparison between the results of the calibrated model and the raw data is provided as **Figure 5-4**.

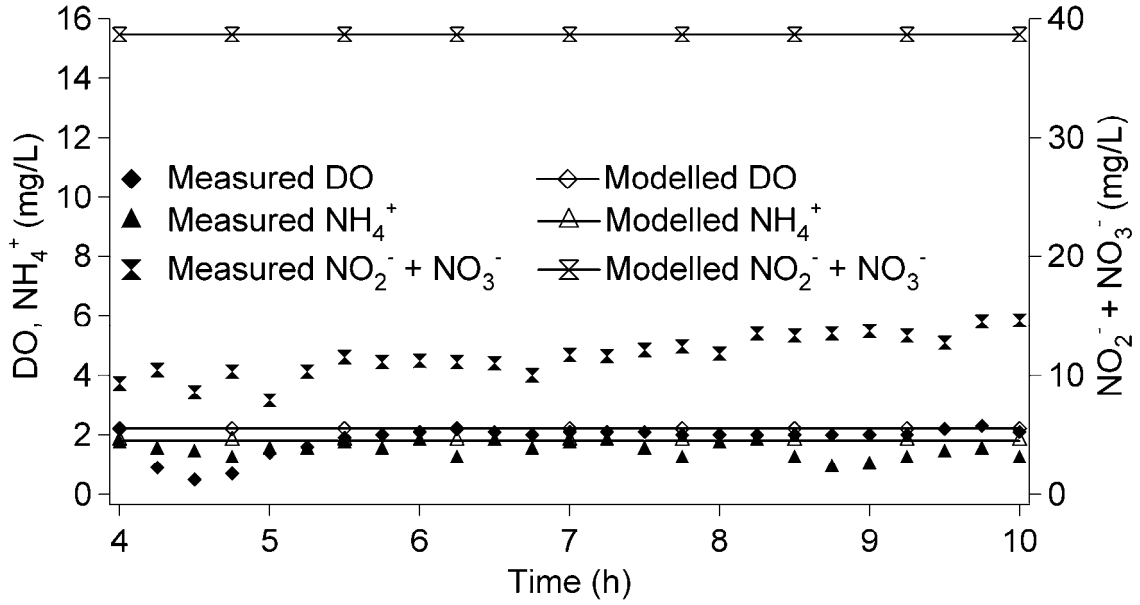


Figure 5-4 Steady state model calibration – Cranfield data.

In general, predicted steady state DO and NH_4^+ concentrations fit the measured data quite well, although there was a large discrepancy with regards to the NO_2^-/NO_3^- fit. While the exact reason for this discrepancy is not readily apparent at this time, it should be noted that the NO_2^-/NO_3^- concentrations were measured in the effluent from the reactor (following the settling tank), and thus it is possible that denitrification could be occurring in the settling tank, reducing the NO_2^-/NO_3^- concentrations in the effluent.

The calibrated model was then applied to a second dataset from Burgess et al. (2002b), with the predicted and measured results presented in **Figure 5-5**.

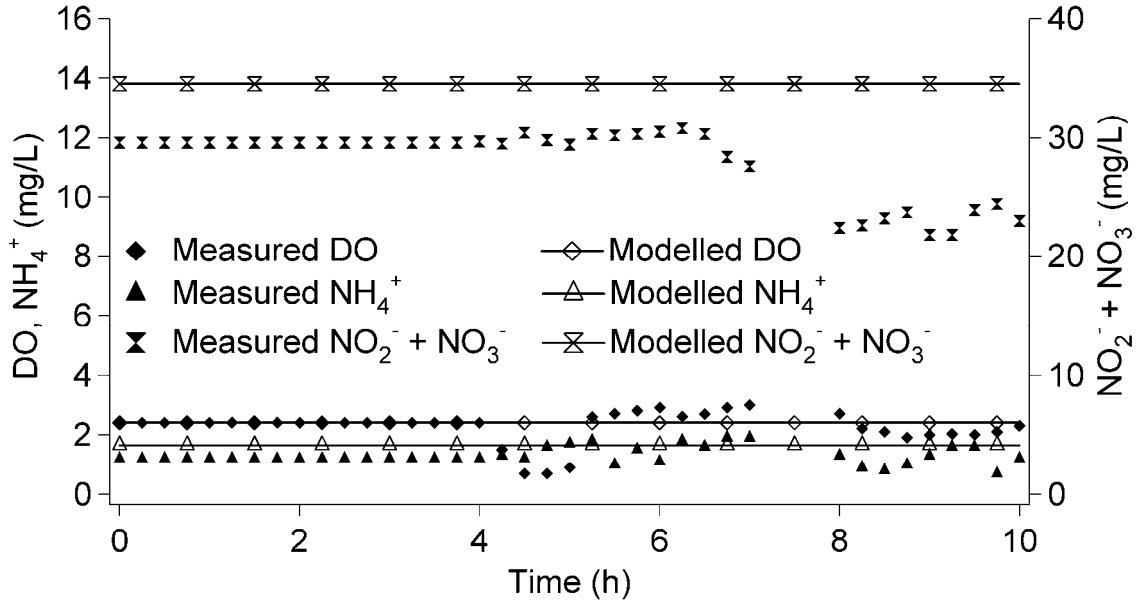


Figure 5-5 Steady state model evaluation using a second Cranfield data set.

The model provided a good prediction of the effluent NH_4^+ concentrations. NO_2^-/NO_3^- concentrations were over-predicted by the model, although to a lesser extent than in the first test. This closer fit is due to an increase in the measured NO_2^-/NO_3^- concentrations in the reactor effluent over those in the first data set.

Steady State Sensitivity Analysis

The steady state and dynamic sensitivity analyses consisted of varying each of the 16 model parameters over a range of values centred on those used in the steady state fitted model and observing the effect of these changes on the model outputs. Each parameter was varied individually, holding all other parameters constant at the calibration value. In some cases, particularly for several parameters related to autotrophic bacterial growth, the lower end of the analysis range was limited due to process stability (nitrifier washout).

Many of the model parameter influenced the DO concentrations as well as other state variables. Since the biological activity of aerobic microorganisms is strongly linked to DO concentrations, changes in this concentration would also influence many of the state variables. In practice, the steady state DO concentrations in the processes are generally controlled to a specific level, and it is therefore necessary to

differentiate between direct sensitivity associated with the parameter variation, and indirect sensitivity caused by the parameter's influence on DO concentrations.

A parameter variation range of +100% to -75% was investigated for the steady state sensitivity analysis. For each parameter variation, the effect on the DO concentration was first determined by running the model for approximately three times the SRT (40 days), which was sufficient for the modelled process to reach steady state conditions. This first set of modelling results was used to characterize the DO sensitivity. To remove the DO influence on parameter sensitivity, the model air flow was adjusted until the DO concentration in the reactor was close to that of the base condition, and the model was run until it once again reached steady state. These adjusted steady state values were used to determine the parameter sensitivity.

The steady state sensitivity was analysed in an objective manner based on the relative change in the model state variable to the change in the model parameters (van Veldhuizen et al. 1999):

$$S_{i,j} = \frac{\Delta Y_j / Y_j}{\Delta X_i / X_i}$$

Where $S_{i,j}$ is the normalized sensitivity coefficient for a specific state variable, Y_j is the state variable of interest, and X_i is the manipulated process parameter. Steady state sensitivities were ranked by applying the following classifications to the normalized sensitivity coefficients:

- Very Strong – $S_{i,j} > 1$
- Strong – $0.5 < S_{i,j} < 1$
- Moderate – $0.1 < S_{i,j} < 0.5$
- Minimal - $S_{i,j} < 0.1$

Plots of the effect of each parameter on each of the 9 state variables are presented as **Figure 5-6** and **Figure 5-7** (which show a parameter which influences a wide range

of state variables and one with limited influence, respectively), and as **Figures A-1** to **A-14** in **Appendix A**.

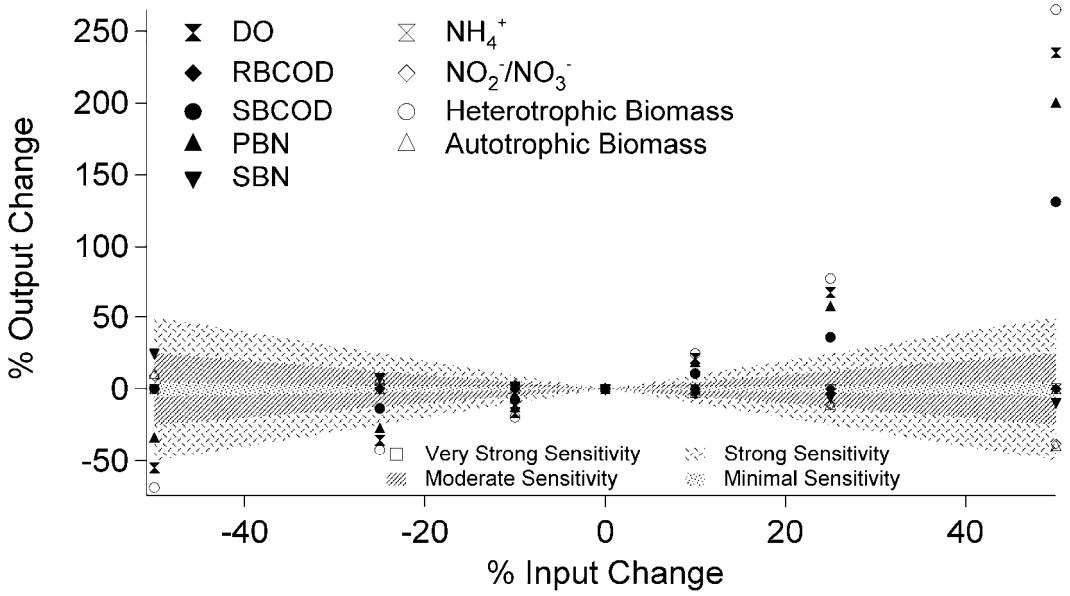


Figure 5-6 Effect of heterotrophic yield (Y_H) on system state variables.

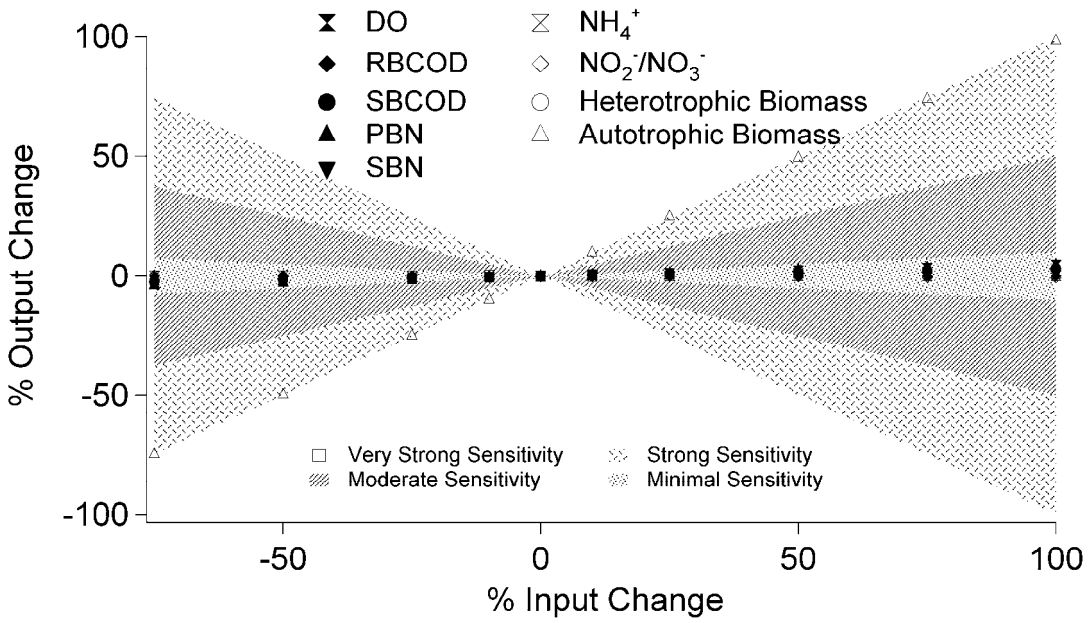


Figure 5-7 Effect of autotrophic yield (Y_A) on system state variables.

A wide variation in the influence of the parameters investigated on the model state variables was seen in the steady state sensitivity plots. Two of the parameters (Y_H

and b_H) were identified as being a significant influence on many of the state variables, while the remaining parameters either influenced a limited number of the model states (Y_A, i_{XB}, μ_H, μ_A, b_A, k_H, K_S, K_{OA}, K_{NH}, K_X and k_a), or had minimal influence (f_p, i_{XP}, and K_{OH}).

It should be noted that a model parameter limitation was encountered in the range of parameters investigated. The stoichiometric coefficients used to determine the amount of dissolved oxygen consumed during the reaction are of the following form for heterotrophic bacteria and autotrophic bacteria, respectively:

$$\frac{1-Y_H}{Y_H}$$

$$-\frac{4.57-Y_A}{Y_A}$$

As seen in these equations, for values of Y_H equal to 1 and Y_A equal to 4.57, this stoichiometric coefficient will be zero, indicating that no oxygen would be consumed during metabolism although growth and substrate utilization would continue. Indeed if the values were further increased the reactions would be modelled as producing oxygen instead of consuming it. Both scenarios would be unrealistic and produce meaningless model results. The autotrophic bacteria yield coefficient was varied over a range of 0.12 to 0.36 g COD_{XA}/g N_{SNH}, and was not near the limitation imposed by the stoichiometric coefficient. However, this limitation had to be considered for the sensitivity analysis for the heterotrophic bacteria yield coefficient since the default value for the coefficient presented in Henze et al, (2000) was 0.67 g COD_{XH}/g COD_{XS} and at +50% reaches a value of 1 g COD_{XH}/g COD_{XS}. The response to a 50% increase in this parameter has been included in the sensitivity analysis (**Figure 5-6**) for illustrative purposes only.

While not a limitation to the sensitivity and validity of the model, there was a practical limitation in the values for several of the model parameters related to the growth of autotrophic bacteria. In particular, excessively low maximum autotrophic biomass growth rates or high decay rates (μ_A and b_A, respectively) resulted in

insufficient levels of ammonium removal. There was a substantial increase in the predicted steady state concentration of ammonium (**Figure A-1**) at maximum autotrophic biomass growth rates below 4.5 d^{-1} (a 25% reduction below the default 6 d^{-1}), indicating nitrification failure. At high autotrophic bacteria decay rates, a decrease in the bacteria population in the reactor and a build-up in ammonium was observed (**Figure A-4**). This increase in ammonium could be attributed to the reduced capacity for removal due to the lower concentration of biomass in the reactor, and increased ammonium production through the decay processes applied to the biomass. These two parameters (μ_A in particular), are very important parameters to be considered during model calibration if the predicted level of ammonium removal/autotrophic biomass growth is too low.

The autotrophic bacteria yield coefficient (Y_A) had a significant influence on the concentration of autotrophic bacteria in the reactor, while at the same time the predicted effluent ammonium concentration was relatively insensitive to it (**Figure 5-7**). This result is counterintuitive since it would be expected that as the autotrophic bacteria population decreases the ammonium removal would begin to decrease as well. However, growth in biological systems occurs under substrate (in this case ammonium) limited conditions. That is the bacteria continue to increase their population until they reach a steady state where the amount of available substrate limits further increases in the population. The yield coefficient relates the amount of biomass produced to the amount of substrate metabolized, thus while a change in the yield coefficient affects the amount of biomass that can be supported by a given amount of substrate, it generally does not have a strong influence on the overall amount of substrate consumed.

Similar trends were observed in the corresponding heterotrophic bacteria kinetic parameters, μ_H and b_H (**Figure A-1** and **Figure A-3**, respectively), although these parameters could be varied over a larger range before substantial increases in the effluent readily biodegradable chemical oxygen demand were observed.

A summary of the model state variable sensitivities is presented as **Table 5-5**. It should be noted that the sensitivities for two of the autotrophic parameters (μ_A and b_A) are reported as those for most of the range investigated and neglect the

enhanced sensitivity that was observed at extreme values where changes resulted in instability in the autotrophic bacteria population.

Table 5-5 State variable sensitivities (steady state analysis - Cranfield data).

Parameter	State Variable								
	S_O	S_S	X_S	S_{NH}	S_{NO}	S_{ND}	X_{ND}	X_H	X_A
Y_H	■		■		▒	▨	■	■	
Y_A									■
μ_H		▒							
μ_A	▨			■					
b_H	▨	■	▒			▒	▒	▒	
b_A	▨			■					■
f_P	▨		▨				▨	▨	
i_{XB}	▨				▨	▒	▒		▨
i_{XP}									
k_a						■			
k_H							■		
K_{OH}		▨	▨				▨		
K_{OA}				▒					
K_S		■							
K_{NH}				■					
K_X			■				▒		

Legend	
Very strong $S_{i,j} > 1$	■
Strong $0.5 < S_{i,j} < 1$	▒
Moderate $0.1 < S_{i,j} < 0.5$	▨
Minimal $S_{i,j} < 0.1$	

Dynamic Sensitivity Analysis

As mentioned previously, model parameters can have different effects on steady state and dynamic performance. As a first step in the dynamic sensitivity analysis, the predictive power of the steady state calibrated model was assessed by running the model at steady state using the same influent conditions as presented previously in **Table 5-1**, and then subjecting the model to a pulse of NH_4^+. The model response was plotted for comparison with the data from Burgess et al. (2002b), and is presented as **Figure 5-8**.

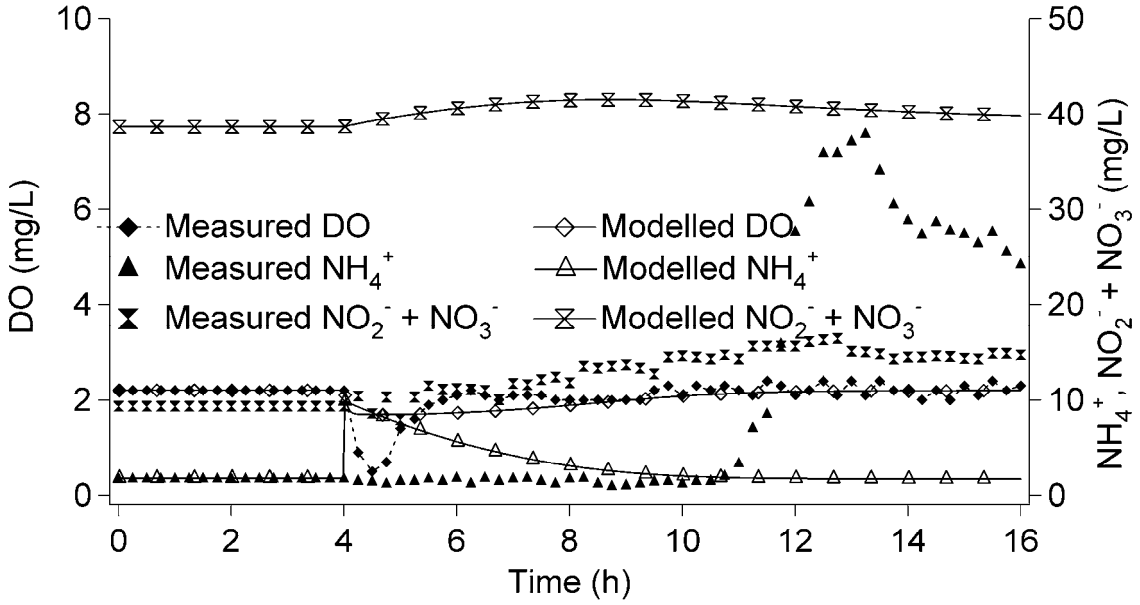


Figure 5-8 Dynamic performance of steady state fitted ASM1 - Cranfield data.

As seen in the above figure, the steady state calibrated model provides a poor fit of the DO and NH_4^+ concentration profiles. This is to be expected since steady state data do not contain dynamic information. Other attempts to utilize a steady state model for dynamic predictions (Plazl et al. 2001) have also concluded that they do not provide a suitable approximation of dynamic performance.

For the dynamic sensitivity analysis, a smaller parameter variation range of +50% to -50% was investigated. Using the steady state calibrated model, a 2.44 g spike of ammonium (identical to the one used in Burgess et al. (2002b)) was applied to the reactor at the four hour mark of the simulation and the resulting dynamic behaviour was observed. Dynamic sensitivity was analysed for a reduced set of variables (DO, NH_4^+ and NO_2^-/NO_3^-) based on available process dynamic data. Similar to the steady state sensitivity analysis, reactor DO concentrations were corrected to remove DO influence on parameter sensitivity.

An example of the dynamic sensitivity analysis plots produced during the analysis is provided as **Figure 5-9**. The dynamic sensitivity plots (for all three parameters) are included as **Figures A-15** to **A-30** in **Appendix A**.

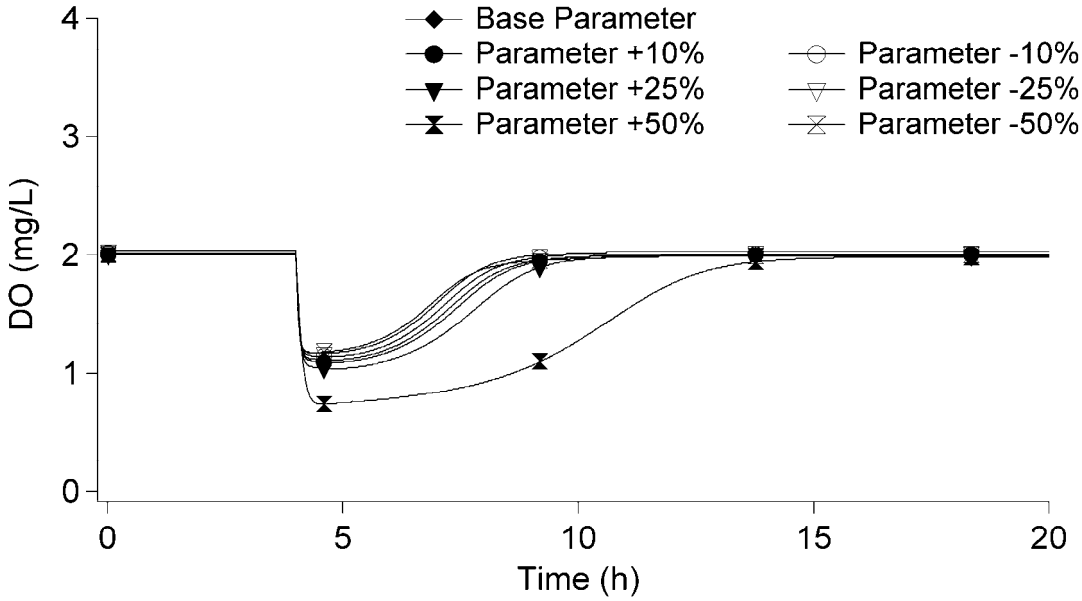


Figure 5-9 Effect of heterotrophic yield (Y_H) on dynamic DO response.

Ranking of dynamic sensitivity was performed in a more subjective manner than for the steady state sensitivities since the dynamic sensitivity involved the interpretation of changes in the response shape. Dynamic sensitivities were ranked as sensitive, slightly sensitive, or minimally sensitive in terms of the impact on response magnitude and speed (time to return to steady state). A summary of the model state variable sensitivities is provided as **Table 5-6**.

Table 5-6 State variable sensitivities (dynamic analysis - Cranfield data).

Parameter	State Variable					
	S_O		S_{NH}		S_{NO}	
	Response Speed	Response Magnitude	Response Speed	Response Magnitude	Response Speed	Response Magnitude
Y_H	■	■	▨			
Y_A						
μ_H						
μ_A	■	■	■	■	■	■
b_H						
b_A	■	■	■	■	■	■
f_P						
i_{XB}						
i_{XP}						
k_a						
k_H						
K_{OH}						
K_{OA}	■	▨		▨		▨
K_S						
K_{NH}	■	▨		▨		▨
K_X						

Legend	
Sensitive	■
Slightly sensitive	▨
Minimally sensitive	

The key parameters influencing the dynamic dissolved oxygen response were Y_H, μ_A, and b_H, while K_{OA} and K_{NH} were important with regards to the response speed. Dynamic ammonium and nitrate/nitrite responses were less sensitive to parameter changes, with substantial sensitivity being restricted to μ_A and b_A, and minor magnitude sensitivity to K_{OA} and K_{NH}.

A wide variation in the magnitude of the influence of the model parameters on the significant state variables (dissolved oxygen and ammonium) was observed, with the state variable predictions being relatively insensitive to a number of parameters. Key parameter sensitivities (both dynamic and steady state) are summarized in **Table 5-7**.

Table 5-7 Summary of key state variable sensitivities - Cranfield data.

State Variable	Sensitivity		
	Steady State	**Dynamic Response Speed**	**Dynamic Response Magnitude**
DO	Y_H, μ_A, b_H, b_A	Y_H, μ_A, b_A, K_{OA}, K_{NH}	Y_H, μ_A, b_A
NH_4^+	μ_A, b_A, K_{OA}, K_{NH}	μ_A, b_A	μ_A, b_A

Table 5-7 demonstrates that there is a reduced set of variables which needs to be considered for dynamic calibration. In addition, the steady state and dynamic sensitivities are quite different, that is many parameters which had strong influences on the steady state had minimal influences on the dynamic response, and vice-versa.

The list of sensitive parameters presented in **Table 5-7** compares favourably with those reported by Weijers and Vanrolleghem (1997). A statistical analysis conducted on an ASM model developed for a carousel type nitrogen removal facility (Weijers and Vanrolleghem 1997) produced a reduced set of sensitive parameters which included all the parameters listed in **Table 5-7** with 3 exceptions: μ_A, K_{NH}, and b_A. While the autotrophic decay rate (b_A) is an important parameter with regards to the autotrophic bacterial population in the bioreactor, it is considered too difficult to measure as a meaningful parameter (Henze et al. 2000), and is generally assigned a default value. The importance of μ_A and K_{NH} (and absence of sensitivity to μ_H and K_S) is likely linked to the perturbation being a pure ammonium spike and not including COD.

When considering the presented sensitivity results, it is important to note that the results are strongly dependent on the characteristics of the system being studied (such as hydraulic and sludge retention times, feed composition, and feed flow), and will not be representative of other system configurations. Also, the sensitivity analysis is conducted around a specific operating point and only considers the influence of changing a single parameter at a time. Conducting the sensitivity around another operating point could produce a different set of sensitivity results and changing multiple parameters simultaneously could have synergistic or antagonistic effects on the resulting change in the state variables.

Model Calibration

Using the results of the steady state and dynamic sensitivity analyses, the most sensitive parameters were identified and all non-sensitive parameters were set to the literature default values (Henze et al. 2000). The model was then manually calibrated to improve dynamic performance using the identified key sensitive parameters. Calibrated model parameters are presented in **Table 5-8**, with modified parameters in bold. A comparison between the output of the calibrated model and the raw data from Burgess et al. (2002b) is provided as **Figure 5-10**.

Table 5-8 Mechanistic model calibration - Cranfield data.

Parameters		Units	ASM1 Default	Steady State	Dynamic
Mass transfer parameters					
k_La	Aeration mass transfer coefficient	1/d	-	3.5	3.5
Stoichiometric coefficients					
Y_H	Heterotroph yield	g COD_{XH}/g COD_{XS}	0.67	0.67	**0.90**
Y_A	Autotroph yield	g COD_{XS}/g N_{SNH}	0.24	0.24	0.24
f_P	Fraction of biomass degrading to particulate products	-	0.08	0.08	0.08
i_{XB}	Biomass nitrogen content	g N/g COD_{XBM}	0.086	0.086	0.086
i_{XP}	Particulate product nitrogen content	g N/g COD_{XP}	0.06	0.06	0.06
Rate constants					
k_H	Hydrolysis rate constant	g X_S/(g X_H•d)	3	3	3
k_a	Ammonification rate constant	m^3/(g X_H•d)	0.08	0.08	0.08
μ_H	Heterotroph maximum growth rate	1/d	6	6	6
μ_A	Autotroph maximum growth rate	1/d	0.8	**1.4**	**1.35**
b_H	Heterotroph decay coefficient	1/d	0.62	0.62	**0.3**
b_A	Autotroph decay coefficient	1/d	0.62	0.62	**0.3**
Saturation constants					
K_{OH}	Heterotroph oxygen half-saturation constant	g DO/m^3	0.2	0.2	0.2
K_{OA}	Autotroph oxygen half-saturation constant	mg N/L	1	1	**0.8**
K_{NH}	Ammonium half- saturation constant	mg DOL	0.4	**0.75**	**1.5**
K_X	Hydrolysis half- saturation constant	g X_S/g X_H	0.03	0.03	0.03
K_S	Substrate half- saturation constant	mg COD/L	20	20	20

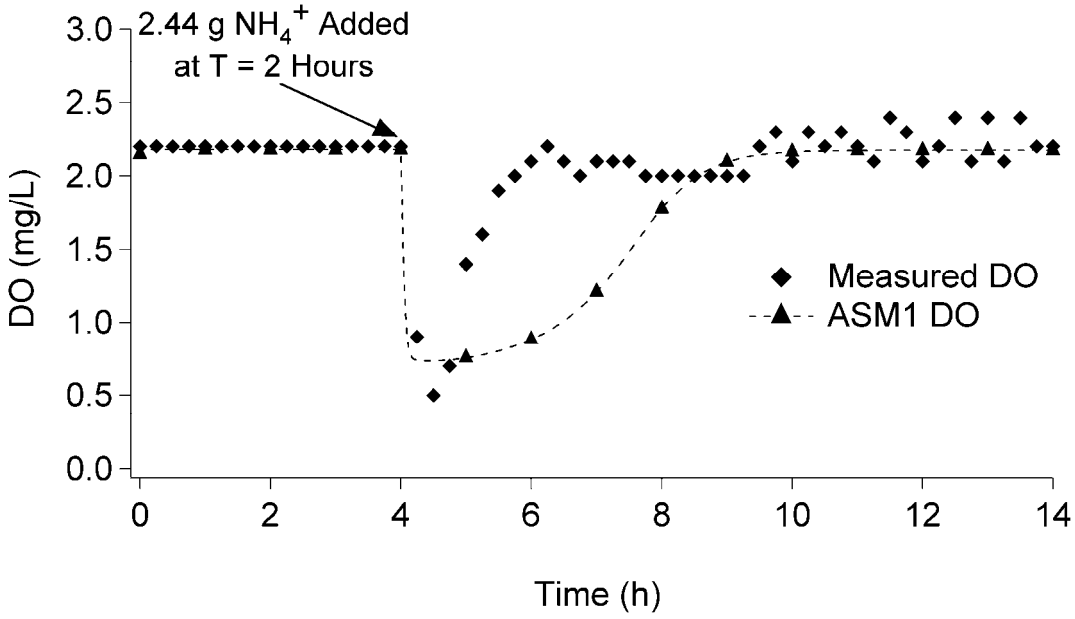


Figure 5-10 Mechanistic model calibration – Cranfield data: Burgess et al. (2002b).

As seen in **Figure 5-10**, the system response was quite aggressive (i.e. very fast bacterial metabolic response to the applied shock load) and the ASM1 model was not able to reproduce this effect accurately within a typical parameter space. While it was possible to fit the magnitude of the DO response to the spike, the response (return to steady state) was much slower than that measured.

The lack of concentration profiles for state variables related to heterotrophic processes was a limitation in the dataset. Heterotrophic processes have a strong influence on the DO profiles in the bioreactor and the inability to calibrate these processes increased uncertainty in the model predictions. Substantial changes were made to the heterotrophic bacteria yield coefficients as well as both the heterotrophic and autotrophic bacteria decay coefficients during calibration to fit the magnitude of the DO response. Since the response speed could not be calibrated, the overall amount of DO depletion in the bioreactor (i.e. the total area of the drop below steady state conditions) was predicted to be much larger than the measured value.

Overall the dynamic performance of the ASM1 model was not considered sufficient to represent conditions in the system being studied. This indicated that there were

other processes/phenomena such as non-ideal bioreactor hydraulics which were not accounted for in the mechanistic (ASM1) modelling.

Reduced Model Calibration

Reduced model calibration was conducted using a mathematical process, specifically a search routine was implemented in Matlab 7.0 (The MathWorks, Natick, MA) to minimize the residual prediction error. The influent profiles were input into the reduced model and the model parameters were mathematically optimized to minimize the residual errors between the predicted values and the experimental data set.

Unlike the mechanistic ASM1 model parameters, the reduced model parameters were determined based on purely mathematical fitting criteria with no restrictions on parameter values (other than being positive values). Reduced model parameters are presented in **Table 5-9**.

Table 5-9 Reduced model calibration - Cranfield data.

Parameter		Units	Mathematical Calibration
K_1	Aeration calibration parameter	1/d	0.203
K_2	Autotrophic oxygen consumption	mg DO/(L•d)	4.631
K_3	Autotrophic ammonium consumption	mg NH_4^+-N/(L•d)	8.577
K_4	Ammonification parameter	mg NH_4^+-N/(mg COD•d)	0.216
K_{OA}	Autotrophic biomass oxygen half-saturation coefficient	mg DO/L	0.00176
K_{NH}	Autotrophic biomass ammonium half-saturation coefficient	mg NH_{4+}-N/L	0.638

While it is not possible to assign any biological meaning to the parameters due to the mathematical nature of the model calibration employed, it is interesting to note that the calibration process selected a very low K_{OA} value. Essentially the reduced model neglected the effects of DO inhibition on process kinetics.

The reduced model response to the influent conditions, along with the experimental response data set is presented as **Figure 5-11**. The calibrated mechanistic ASM1 model response is also presented in this figure for comparison purposes.

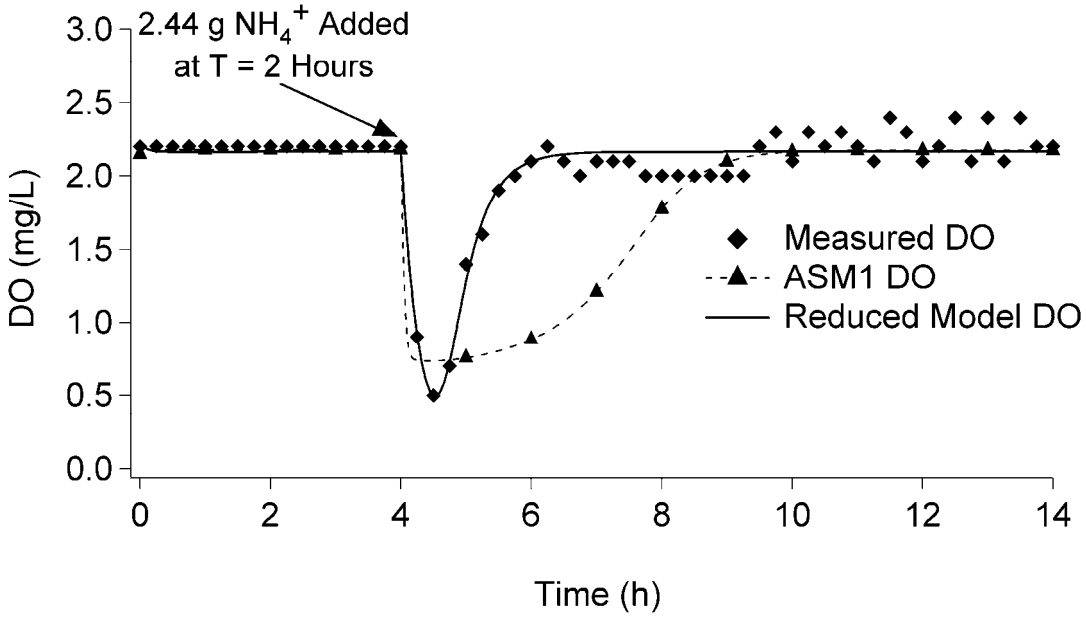


Figure 5-11 Reduced model calibration – Cranfield data: Burgess et al. (2002b).

Comparing the two sets of model results presented in **Figure 5-11**, the reduced model provides a much better representation of the DO response to system perturbation. Due to data limitations, the reduced model (which would account for these processes empirically) was selected as the basis for the liquid phase model component of the data generator.

5.2.3 Off-gas N_2O Model Component

While insights into the specific N_2O production mechanisms have been provided in recent years (Colliver and Stephenson 2000; Shiskowski and Mavinic 2006), these mechanisms remains an area of ongoing research and no thorough investigations of specific biokinetic parameters have been conducted. Thus, at the current state of knowledge with regards to this process (discussed in **Section 2.1**), a strict mechanistic modelling of N_2O generation is not feasible. As a result, an empirical model was developed to link the measured response (off-gas N_2O) to the applied stresses.

5.2.3.1 Model Development

The Cranfield data (Burgess et al. 2002b) indicated a strong correlation between metabolic stressors and off-gas N_2O concentrations, particularly depletions in the bioreactor DO concentrations (produced by rapid changes in feed NH_4^+ loadings or by changes in the rate of oxygen supply), as well as chemical inhibition by allylthiourea. For the data sets studied, no chemical inhibitors were added and it was assumed that depletions in DO concentrations would be the main metabolic stress present in the system. The developed model neglects the effects of chemical inhibitors. However, if these substances were present in the feed at relatively constant concentrations, the resulting inhibition would be expected to be relatively constant as well, and would be accounted for in the model calibration.

The initial N_2O off-gas model was developed for the Cranfield data using two components: a proportional component dependent on the bioreactor DO concentrations, and an offset component. NO_2^-/NO_3^- concentrations were reported as a sum (and also measured in reactor effluent and not inside the aeration tank), thus the role of NO_2^- (or FNA) could not be assessed. This model utilized an inversed switching function like those used in anoxic processes in the ASM family (Henze et al. 2000). The offset component was required since the switching function could not fit the baseline concentrations while at the same time fitting the shape of the dynamic portion of the response. The utilized model had the following form:

$$C_{N_2O} = \left(K_{N_2O,1} \left(\frac{K_{N_2O,2}}{S_O + K_{N_2O,2}} + K_{N_2O,3} \right) \right)$$

5.2.3.2 Model Calibration

Model fit coefficients were obtained using a search routine in Matlab 7.0 (The MathWorks, Natick, MA) to minimize the residual prediction error using the dissolved oxygen and N_2O data for the first NH_4^+ shock loading test presented in Burgess et al. (2002b). This model calibration would account for N_2O generation as a function of liquid phase DO concentrations, as well as N_2O stripping efficiency,

dilution effects and sensor properties. The fitted model ($K_{N2O,1}$ = 1.05, $K_{N2O,2}$ = 0.106, and $K_{N2O,3}$ = 0.046) is presented as **Figure 5-12**.

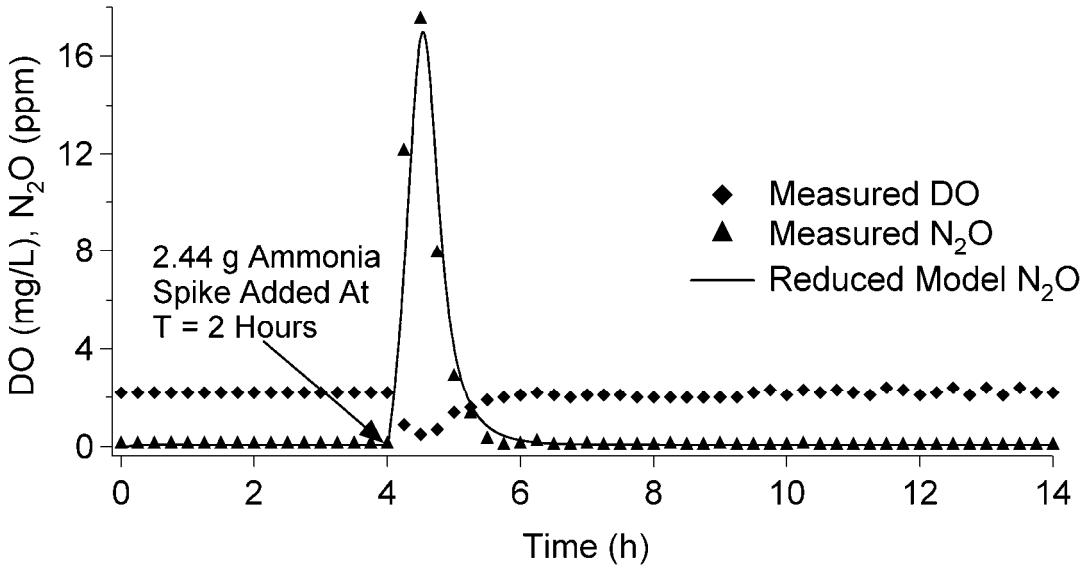


Figure 5-12 Fitted off-gas N_2O correlation using data from Burgess et al. (2002b).

It should be noted that the available experimental dataset began with the application of the NH_4^+ shock load to the bioreactor and did not contain a substantial characterisation of the initial steady state conditions. To enable an initial steady state calibration of the model prior to the application of the shock load it was necessary to assume that the initial conditions in the bioreactor were at steady state. The first four hours of simulation data are thus based on initial conditions, with the NH_4^+ shock load being applied at the fourth hour.

Overall the developed correlation provided a representation of the dynamics of the concentration of N_2O in the bioreactor off-gas that was within the experimental error of the measurements. There was some deviation on the decay portion of the response, with the correlation over-predicting the off-gas N_2O concentrations.

5.2.4 Data Generator Performance

As a verification of the data generator, the influent characteristics for the second set of NH_4^+ shock loading response data (an independent set of data collected following

sufficient process stabilization time) from Burgess et al. (2002b) were applied to the simulator and the predicted off-gas N_2O concentrations were compared to the measured values (**Figure 5-13**).

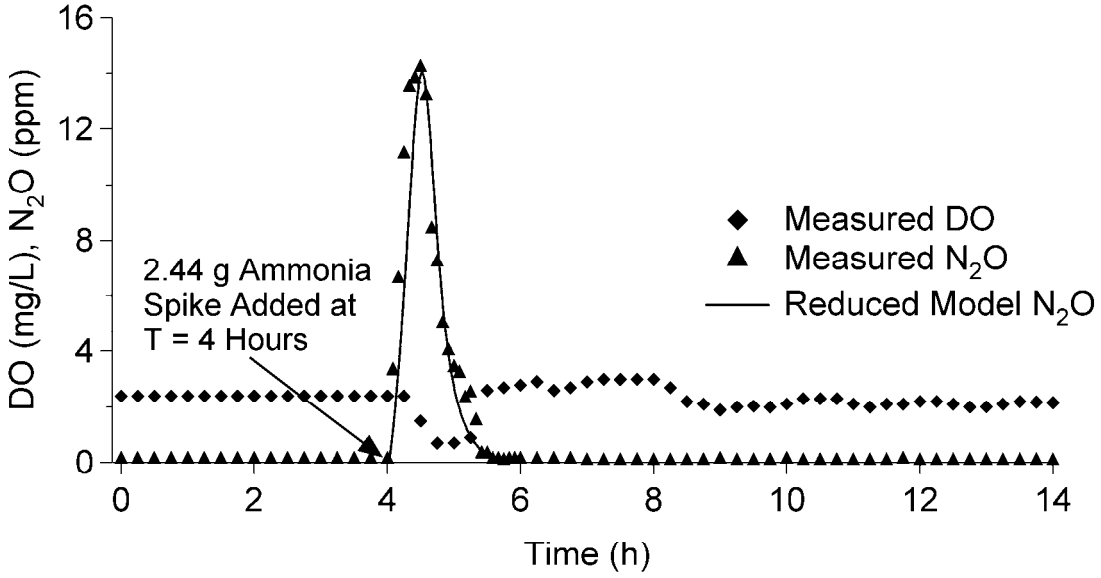


Figure 5-13 Simulation of off-gas N_2O concentrations during an NH_4^+ shock load based on data from Burgess et al. (2002b), Test 2.

Similar to observations during the N_2O off-gas model calibration, the off-gas N_2O predictions based on the liquid phase simulations provided a simulation of the measured data, although once again with some over prediction of the off-gas N_2O concentrations on the decay portion of the response.

5.3 Data Generator Development – UNSW Data

5.3.1 Data Sources

The UNSW data was collected from a 28.7 L activated sludge bioreactor that was operated on a continuous basis using a synthetic wastewater. Specific reactor operational details and an overview of the associated process/monitoring equipment are presented in **Chapter 3**.

Sampling campaigns were developed to support the development and validation of the process models used in the simulation study. The sampling campaign consisted of routine process monitoring and characterisation of process dynamics.

Routine process monitoring was conducted to verify process steady state prior to conducting experimental work, and to provide routine process operational data such as removal efficiencies, sludge retention times, and hydraulic retention times. A summary of typical process operating conditions is provided as **Table 5-10**.

Table 5-10 Operating conditions, UNSW activated sludge bioreactor.

Parameter	Units	Location	Average Value	Analysis Method
COD removal	%	Influent/effluent	93.9	Method 5220 D APHA et al. (1995)
NH_4^+ removal	%	Influent/effluent	98.3	Nesslerization
NO_3^-	mg/L	Effluent	22.9	Method 4500-NO_3^- E APHA et al. (1995)
NO_2^-	mg/L	Effluent	0.03	Method 4500-NO_2^- B APHA et al. (1995)
N_2O	mg/L	Off-gas	0.94	Off-gas analyser
DO	mg/L	Aeration tank	3.2	Calibrated probe
TSS	mg/L	Aeration tank	4240	Method 2540 D APHA et al. (1995)
pH	-	Aeration tank	7.21	Calibrated probe
Temperature	°C	Aeration tank	23.0	Calibrated probe
SRT	d	-	12	Calculated
HRT	hr	Aeration tank	16.9	Pump calibration

Dynamic process data was collected for a range of process initial conditions and perturbances. The results of **Test 2** were utilized for model calibration, and four tests

(representing independent operating conditions) were used for model validation. These tests are summarized in **Table 5-11**, and specific profile data has been presented in **Chapter 4**.

Table 5-11 Dynamic tests utilized for model calibration and validation.

Objective	Data Source	Comments
Model calibration	Test 2	Sludge A, base spike
Model validation	Test 1	Sludge A, base spike
	Test 3	Sludge A, reduced spike
	Test 5	Sludge B, reduced operating DO and spike
	Test 6	Sludge B, reduced spike

Tests 4 and **7** were not used for model validation purposes since both tests were near the end of the testing period with their respective sludges and, as discussed in **Chapter 4**, by that point the processes were demonstrating significant instability. Process model inputs were developed based upon the tests of interest and are presented in **Table 5-12**.

Table 5-12 Model scenario inputs, UNSW data.

		Units	Test 1	Test 2	Test 3	Test 5	Test 6
Reactor conditions	Sludge	-	A	A	A	B	B
	pH	-	7.23	7.20	7.15	7.17	7.23
	Temperature	(°C)	20.9	21.8	22.9	25.6	24.4
Influent	Flow	(L/hr)	1.71	1.73	1.73	1.67	1.63
	COD	(mg/L)	384	360	365	379	345
	RBCOD	(mg/L)	269	252	255	266	241
	SBCOD	(mg/L)	115	108	109	114	104
	NH_4^+	(mg/L)	31.7	25.5	27.0	26.8	24.6
	SBN	(mg/L)	8.1	7.6	7.7	8.0	7.2
	PBN	(mg/L)	3.5	3.2	3.3	3.4	3.1
	NO_3^-	(mg/L)	0.44	0.21	0.25	0.29	0.56
	NO_2^-	(mg/L)	0.06	0.07	0.07	0.06	0.05
Spike	COD	(mg/L)	908	869	587	421	353
	RBCOD	(mg/L)	636	608	411	295	247
	SBCOD	(mg/L)	272	261	176	126	106
	NH_4^+	(mg/L)	74.9	61.7	43.5	29.7	25.2
	SBN	(mg/L)	19.1	18.3	12.3	8.8	7.4
	PBN	(mg/L)	8.2	7.8	5.3	3.8	3.2

In developing these model inputs, assumptions had to be made with regards to the COD and biodegradable nitrogen fractions. RBCOD and SBCOD were assumed to

be 70% and 30% of the total influent COD, respectively. This assumption was based upon the synthetic feed composition (**Table 3-1**), which consisted primarily of easily biodegradable organic carbon compounds such as glucose. Based upon an assessment of the nitrogen containing compounds in the feed, non-ammonium nitrogen was estimated to be 3% of the influent COD, and the fractionation (into SBN and PBN) was assumed to follow the COD fractionation.

5.3.2 Liquid Phase Component

5.3.2.1 Model Selection and Formulation

The review of the mechanisms responsible for generation of N_2O by nitrifying bacteria (**Section 2.1**), indicated that liquid phase NO_2^- or FNA concentrations play a role as one of the reaction substrates. With the availability of a full liquid phase inorganic nitrogen speciation (NH_4^+, NO_2^-/FNA, and NO_3^-) in the experimental data, two-step nitrification models were investigated. These models allow for the prediction of these inorganic nitrogen species which could then be provided as an input to the off-gas N_2O generation model component of the data generator.

Liquid phase process modelling was once again approached from a mechanistic perspective. Two multistep nitrification models were utilized in this work, both based upon the ASM1 model. While several multistep ASM3 models are available, the ASM1 models were utilized due to the advantages associated with the ASM1 model base (discussed in **Section 5.1.2**).

The first model applied was ASM1 with the two-step nitrification modification proposed by Nowak et al. (1994), hereinafter referred to as "ASM1-Nowak". This modification consisted of separating the lumped nitrification processes (autotrophic growth and decay) and state variables (autotrophic biomass and NO_2^-/NO_3^- concentration) into individual components. In the case of the autotrophic components of the model, they were separated in AOB and NOB components. The Nowak et al. (1994) modification did not contain any other substantial changes to the ASM1 model base.

ASMN, proposed by Hiatt and Grady (2008a; 2008b) and discussed previously in **Section 2.2.3**, was utilized as the second two-step nitrification model. In addition to separating the lumped nitrification processes into AOB and NOB and allowing the prediction of NO_2^- and NO_3^- concentrations, this model contains several new processes and adjustments to the reaction mechanisms for AOB and NOB growth. New processes include mixotrophic growth of NOB, and assimilative NO_3^- reduction to NH_4^+. In ASMN, AOB and NOB growth utilize FA and FNA as growth substrates, respectively. This introduces pH dependence into the nitrification process rates.

The mechanistic models were developed by applying the simplifying modelling assumptions discussed in **Section 5.1.2**, namely:

- only aerobic processes were considered;
- inert organic matter was omitted; and
- particulate decay products were omitted.

Since the pH in the reactor was controlled via sodium carbonate addition, the alkalinity portions of the models were omitted. Additional assumptions were made in the development of the ASMN model; assimilative NO_3^- reduction to NH_4^+ was neglected since NH_4^+ was present in the reactor at all times during the simulation, and purely autotrophic NOB growth was assumed (mixotrophic growth was neglected).

The developed mechanistic models utilized in this work are presented in matrix form as **Table 5-13** and **Table 5-14** for ASM1-Nowak and ASMN, respectively.

Table 5-13 Mechanistic model matrix – ASM1-Nowak.

Category	Process	Process State Variable											Rate
		S_S	X_S	X_H	X_M	X_N	S_O	S_{NO2}	S_{NO3}	S_{NH}	S_{ND}	X_{ND}	
Het. Pocesses	Aerobic growth	$-\frac{1}{Y_H}$		1			$-\frac{1-Y_H}{Y_H}$			$-i_{XB}$			$\mu_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{O,H}+S_O}\right)X_H$
Auto. Processes	Aerobic growth (AOB)				1		$-\frac{3.43-Y_M}{Y_M}$	$\frac{1}{Y_M}$		$-i_{XB}-\frac{1}{Y_M}$			$\mu_M\left(\frac{S_O}{K_{O,M}+S_O}\right)\left(\frac{S_{NH}}{K_{NH,M}+S_{NH}}\right)X_M$
	Aerobic growth (NOB)					1	$-\frac{1.14-Y_N}{Y_N}$	$-\frac{1}{Y_N}$	$\frac{1}{Y_N}$	$-i_{XB}$			$\mu_N\left(\frac{S_O}{K_{O,N}+S_O}\right)\left(\frac{S_{NO2}}{K_{NO2,N}+S_{NO2}}\right)X_N$
Biomass Decay	Decay (heterotrophic)		$1-f_P$	-1								$i_{XB}-f_P i_{XP}$	$b_H X_H$
	Decay (AOB)		$1-f_P$		-1							$i_{XB}-f_P i_{XP}$	$b_M\left(\frac{S_O}{K_{O,M}+S_O}\right)X_M$
	Decay (NOB)		$1-f_P$			-1						$i_{XB}-f_P i_{XP}$	$b_N\left(\frac{S_O}{K_{O,N}+S_O}\right)X_N$
	Ammonification									1	-1		$k_a S_{ND} X_H$
	Hydrolysis – organics	1	-1										$k_h\left(\frac{\frac{X_S}{X_H}}{K_X+\frac{X_S}{X_H}}\right)\left[\left(\frac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\right]X_H$
	Hydrolysis – organic nitrogen										1	-1	$k_h\left(\frac{\frac{X_S}{X_H}}{K_X+\frac{X_S}{X_H}}\right)\left[\left(\frac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\right]\frac{X_H X_{ND}}{X_S}$

Table 5-14 Mechanistic model matrix – ASMN.

Category	Process	Process State Variable											Rate
		S_S	X_S	$X_{B,H}$	$X_{B,A1}$	$X_{B,A2}$	S_O	S_{NO3}	S_{NO2}	S_{NH}	S_{NS}	X_{NS}	
Het. Processes	Aerobic growth	$-\frac{1}{Y_H}$		1			$-\frac{1-Y_H}{Y_H}$			$-i_{N/XB}$			$\mu_H\left(\frac{S_S}{K_{S,1}+S_S}\right)\left(\frac{S_O}{K_{O,H1}+S_O}\right)X_{B,H}$
Auto. Processes	Aerobic growth (AOB)				1		$-\frac{3.43-Y_{A1}}{Y_{A1}}$		$\frac{1}{Y_{A1}}$	$-i_{N/XB}-\frac{1}{Y_{A1}}$			$\mu_{A1}\left(\frac{S_{FA}}{K_{FA}+S_{FA}+\frac{S_{FA}^2}{K_{I9FA}}}\right)\left(\frac{S_O}{K_{O.A1}+S_O}\right)\left(\frac{K_{I9FNA}}{K_{I9FNA}+S_{FNA}}\right)X_{B,A1}$
	Aerobic growth (NOB)					1	$-\frac{1.14-Y_{A2}}{Y_{A2}}$	$\frac{1}{Y_{A2}}$	$-\frac{1}{Y_{A2}}$	$-i_{N/XB}$			$\mu_{A2}\left(\frac{S_{FNA}}{K_{FNA}+S_{FNA}+\frac{S_{FNA}^2}{K_{I10FNA}}}\right)\left(\frac{S_O}{K_{O.A2}+S_O}\right)\left(\frac{K_{I10FA}}{K_{I10FA}+S_{FA}}\right)X_{B,A2}$
Biomass Decay	Decay (heterotrophic)		$1-f'_D$	-1								$i_{N/XB}-f'_D i_{N/XD}$	$b_{L,H}X_{B,H}$
	Decay (AOB)		$1-f'_D$		-1							$i_{N/XB}-f'_D i_{N/XD}$	$b_{L,A1}X_{B,A1}$
	Decay (NOB)		$1-f'_D$			-1						$i_{N/XB}-f'_D i_{N/XD}$	$b_{L,A2}X_{B,A2}$
	Ammonification									1	-1		$k_a S_{NS}X_{B,H}$
	Hydrolysis – organics	1	-1										$k_h\left(\frac{\frac{X_S}{X_{B,H}}}{K_X+\frac{X_S}{X_{B,H}}}\right)\left[\left(\frac{S_O}{K_{O,H1}+S_O}\right)+\eta_h\left(\frac{K_{O,H1}}{K_{O,H1}+S_O}\right)\left(\frac{\sum NO_x}{K_{:NO3}+\sum NO_x}\right)\right]X_{B,H}$
	Hydrolysis – organic nitrogen										1	-1	$k_h\left(\frac{\frac{X_S}{X_{B,H}}}{K_X+\frac{X_S}{X_{B,H}}}\right)\left[\left(\frac{S_O}{K_{O,H1}+S_O}\right)+\eta_h\left(\frac{K_{O,H1}}{K_{O,H1}+S_O}\right)\left(\frac{\sum NO_x}{K_{:NO3}+\sum NO_x}\right)\right]\frac{X_{B,H}X_{NS}}{X_S}$

5.3.2.2 Model Calibration

The two models were calibrated using a process identical to that used for the ASM1 calibration conducted in **Section 5.2.2.2** for the Cranfield data. Steady state and dynamic sensitivity analyses were conducted for each model, with the information obtained from these analyses being used to guide the manual calibration process.

ASM1-Nowak

Steady State Sensitivity Analysis

Unlike for the Cranfield data, the initial model run conducted using default model parameters obtained from literature (Nowak et al. 1994) and the influent characterization presented in **Table 5-12** provided a stable result. Thus, no parameter adjustment was required prior to conducting the steady state sensitivity analysis. The default model parameters utilized in the initial model run are presented in **Table 5-15**.

Identical to the ASM1 steady state sensitivity analysis, a parameter variation range of +100% to -75% was investigated and dissolved oxygen influences on parameter sensitivity were mitigated via air flow adjustment. Plots of the effect of each parameter on the model state variables of interest are presented as **Figures A-31** to **A-51** in **Appendix A**. A summary of the state variable sensitivities is presented as **Table 5-16**.

Similar to the Cranfield steady state analysis, parameter variation limitations were encountered for Y_H (instability at Y_H values greater than 1), as well as for low maximum specific autotrophic bacteria growth rates. Utilization of μ_M and μ_N values less than 50% of the default values resulted in loss of the respective bacterial populations and process failure. No limitation was encountered for the autotrophic decay rates (b_M, b_N) over the parameter range investigated.

Table 5-15 Preliminary calibration of ASM1-Nowak - UNSW data.

Parameters		Units	Parameter Value
Mass transfer parameters			
k_La	Aeration mass transfer coefficient	1/d	3.5
Stoichiometric coefficients			
Y_H	Heterotroph yield	g COD_{XH}/g COD_{XS}	0.67[1]
Y_M	AOB yield	g COD_{XM}/g N_{SNH}	0.18[3]
Y_N	NOB yield	g COD_{XN}/g N_{SNO2}	0.06[3]
f_P	Fraction of biomass degrading to particulate products	-	0.08[1]
i_{XB}	Biomass nitrogen content	g N/g COD_{XBM}	0.086[1]
i_{XP}	Particulate product nitrogen content	g N/g COD_{XP}	0.06[1]
Rate constants			
k_H	Hydrolysis rate constant	g X_S/(g X_H•d)	3[1]
k_a	Ammonification rate constant	m^3/(g X_H•d)	0.08[1]
μ_H	Heterotroph maximum growth rate	1/d	6[1]
μ_M	AOB maximum growth rate	1/d	2.0[2]
μ_N	NOB maximum growth rate	1/d	2.1[2]
b_H	Heterotroph decay coefficient	1/d	0.62[1]
b_M	AOB decay coefficient	1/d	0.43[2]
b_N	NOB decay coefficient	1/d	0.50[2]
Saturation constants			
$K_{O,H}$	Heterotroph oxygen half-saturation constant	g DO/m^3	0.2[1]
$K_{O,M}$	AOB Oxygen half-saturation constant	mg N/L	0.3[2]
$K_{O,N}$	NOB Oxygen half-saturation constant	mg N/L	0.6[2]
$K_{NH,M}$	AOB ammonium half-saturation constant	mg N/L	0.5[2]
$K_{NO2,N}$	NOB nitrite half-saturation constant	mg N/L	0.5[2]
K_X	Hydrolysis half-saturation constant	g X_S/g X_H	0.03[1]
K_S	Substrate half-saturation constant	mg COD/L	20[1]

[1] – ASM1 default value (Henze et al. 2000)

[2] – Nowak et al. (1994)

[3] – Hiatt and Grady (2008b)

Table 5-16 State variable sensitivities (steady state analysis - UNSW Data, ASM1-Nowak).

Parameter	State Variable										
	S_O	S_S	X_S	S_{NH}	S_{NO2}	S_{NO3}	S_{ND}	X_{ND}	X_H	X_M	X_N
Y_H											
Y_M											
Y_N											
μ_H											
μ_M											
μ_N											
b_H											
b_M											
b_N											
f_P											
i_{XB}											
i_{XP}											
k_a											
k_H											
K_{OH}											
K_{OM}											
K_{ON}											
K_S											
K_{NH}											
K_{NO2}											
K_X											

Legend	
Very strong $S_{i,j} > 1$	
Strong $0.5 < S_{i,j} < 1$	
Moderate $0.1 < S_{i,j} < 0.5$	
Minimal $S_{i,j} < 0.1$	

Once again, a wide variation in the influence of the parameters investigated on the model state variables was seen in the steady state sensitivity plots. Two of the parameters (Y_H and b_H) had significant influence on many of the state variables, while the remaining parameters influenced a more limited number of the model state variables, with the exception of f_P, i_{XP}, K_{OH}, K_{OM}, and K_{ON}, which had minimal influence.

Dynamic Sensitivity Analysis

The dynamic sensitivity was analysed over a parameter variation range of +50% to -50%. A spike containing organic carbon and nitrogen (**Test 2**, **Table 5-12**) was applied to the reactor at the four hour mark of the simulation and the resulting dynamic behaviour was observed. Dynamic sensitivity was analysed for DO, NH_4^+,

NO_2^-, and NO_3^-. Like the steady state sensitivity analysis, reactor DO concentrations were corrected to mitigate DO influences on parameter sensitivity.

Dynamic sensitivities were ranked in terms of the impact on response magnitude and speed (time to return to steady state). A summary of the model state variable sensitivities is provided as **Table 5-17**.

Table 5-17 State variable sensitivities (dynamic analysis – UNSW data, ASM1-Nowak).

Parameter	State Variable							
	S_O		S_{NH}		S_{NO2}		S_{NO3}	
	Response Speed	Response Magnitude	Response Speed	Response Magnitude	Response Speed	Response Magnitude	Response Speed	Response Magnitude
Y_H	■	■	■	■	■	■		▨
Y_M								
Y_N								
μ_H						▨		
μ_M		▨	■	▨	■	■		
μ_N					▨	■		▨
b_H					▨			
b_M			▨	■	■	■		
b_N					■	■		
f_P								
i_{XB}	▨		■	▨	■	■		▨
i_{XP}								
k_a								
k_H								
K_{OH}								
K_{OM}						▨		
K_{ON}						▨		
K_S								
K_{NH}			▨	▨		▨		
K_{NO2}					■	▨		
K_X								

Legend	
Sensitive	■
Slightly sensitive	▨
Minimally sensitive	

The key parameter influencing the dynamic DO response was Y_H. The dynamic NH_4^+ response was primarily sensitive to Y_H, in addition to response speed sensitivity to μ_M and i_{XP}, and response magnitude sensitivity to b_M. The dynamic NO_2^- response was sensitive to the greatest number of parameters, with speed and magnitude sensitivity to Y_H, μ_M , b_M, b_N, and i_{XP}, as well as speed sensitivity to K_{NO2} and

magnitude sensitivity to μ_N. Dynamic NO_3^- responses were rather insensitive to parameter changes, with only minor magnitude sensitivity being observed for several parameters. Overall, DO was less sensitive dynamically than in the ASM1 model calibration for the Cranfield data, while NH_4^+ and NO_2^- were sensitive to an increased number of model parameters.

Key parameter sensitivities (both dynamic and steady state) are summarized for the primary state variables of interest in **Table 5-18**.

Table 5-18 Summary of state variable sensitivities – UNSW data, ASM1-Nowak.

State Variable	Sensitivity		
	Steady State	**Dynamic Response Speed**	**Dynamic Response Magnitude**
DO	Y_H, b_H, f_P	Y_H	Y_H
NH_4^+	μ_M, K_{NH}	Y_H, μ_M, i_{XB}	Y_H, b_M
NO_2^-	μ_N, b_N, K_{NO2}	Y_H, μ_M, b_M, b_N, i_{XB}, K_{NO2}	Y_H, μ_M, μ_N, b_M, b_N, i_{XB}
NO_3^-	Y_H, b_H, i_{XP}, i_{XB}	-	-

As seen in **Table 5-18**, the majority of the state variables had sensitivity in at least one form to the Y_H, which would thus be of particular importance in model calibration. The remaining parameters of interest from a sensitivity perspective were primarily associated with the AOB and NOB growth/decay processes. It is interesting to note that while NO_3^- concentrations displayed some steady state sensitivity, they were relatively insensitive from a dynamic perspective.

Model Calibration

Using the results of the steady state and dynamic sensitivity analyses, the model was manually calibrated to improve dynamic performance. Calibrated model parameters are presented in **Table 5-19**, with modified parameters in bold. A comparison between the output of the calibrated model and the raw data is provided as **Figure 5-14**.

Table 5-19 ASM1-Nowak calibration – UNSW data.

Parameters		Units	Initial	Calibrated
Mass transfer parameters				
k_La	Aeration mass transfer coefficient	1/d	3.5	**3.1**
Stoichiometric coefficients				
Y_H	Heterotroph yield	g COD_{XH}/g COD_{XS}	0.67[1]	**0.64**
Y_M	AOB yield	g COD_{XM}/g N_{SNH}	0.18[3]	0.18
Y_N	NOB yield	g COD_{XN}/g N_{SNO2}	0.06[3]	0.06
f_P	Fraction biomass degrading to particulate products	-	0.08[1]	0.08
i_{XB}	Biomass nitrogen content	g N/g COD_{XBM}	0.086[1]	0.086
i_{XP}	Particulate product nitrogen content	g N/g COD_{XP}	0.06[1]	0.06
Rate constants				
k_H	Hydrolysis rate constant	g X_S/(g X_H•d)	3[1]	**15**
k_a	Ammonification rate constant	m^3/(g X_H•d)	0.08[1]	**0.1608**
μ_H	Heterotroph maximum growth rate	1/d	6[1]	**3.8**
μ_M	AOB maximum growth rate	1/d	2.0[2]	**1.6**
μ_N	NOB maximum growth rate	1/d	2.1[2]	**3**
b_H	Heterotroph decay coefficient	1/d	0.62[1]	0.62
b_M	AOB decay coefficient	1/d	0.43[2]	0.43
b_N	NOB decay coefficient	1/d	0.50[2]	0.50
Saturation constants				
$K_{O,H}$	Heterotroph oxygen half-saturation constant	g DO/m^3	0.2[1]	0.2
$K_{O,M}$	AOB oxygen half-saturation constant	mg N/L	0.3[2]	**0.5**
$K_{O,N}$	NOB oxygen half-saturation constant	mg N/L	0.6[2]	0.6
$K_{NH,M}$	AOB ammonium half-saturation constant	mg N/L	0.5[2]	0.5
$K_{NO2,N}$	NOB nitrite half-saturation constant	mg N/L	0.5[2]	0.5
K_X	Hydrolysis half-saturation constant	g X_S/g X_H	0.03[1]	0.03
K_S	Substrate half-saturation constant	mg COD/L	20[1]	20

[1] – ASM1 default value (Henze et al. 2000)

[2] – Nowak et al. (1994)

[3] – Hiatt and Grady (2008b)

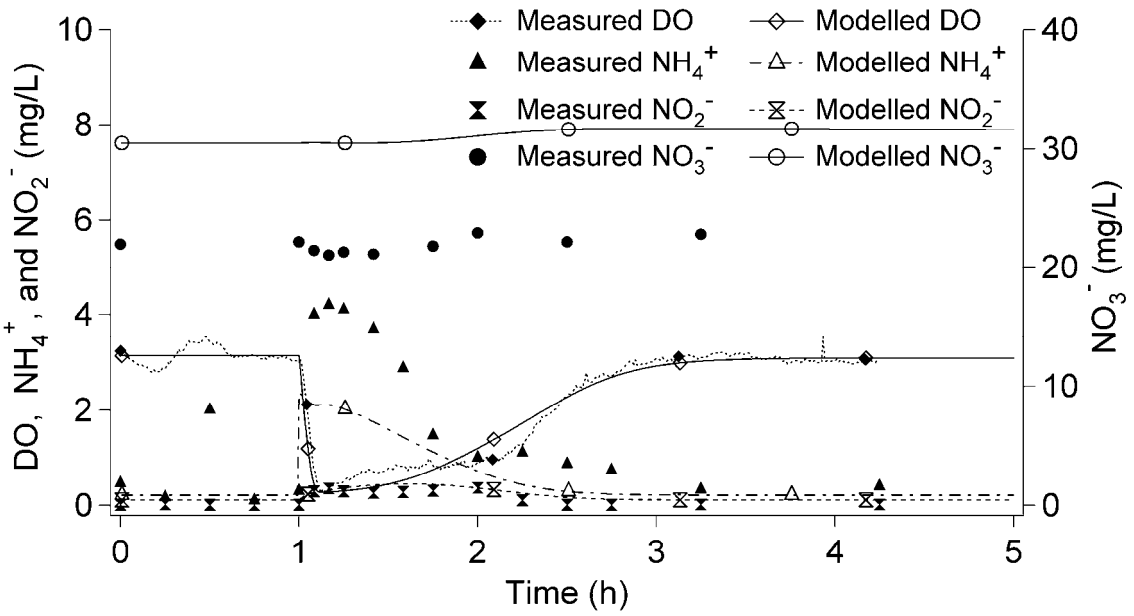


Figure 5-14 Calibrated ASM1-Nowak model.

Several parameters were adjusted in fitting the model to the UNSW data, in particular many of the hydrolysis/ammonification parameters were changed in increase the rate of substrate regeneration (primarily to improve the NH_4^+ fit and broaden the DO depletion). Adjustments were also made to many of the AOB and NOB growth parameters to calibrate the NO_2^- response.

The model provided a good representation of the DO profile in the reactor, matching the initial decay and final rise to steady state. There was some discrepancy in the fit during the DO depletion plateau, which the model form could not capture, instead providing a more gradual return to steady state. The initial increase in the NH_4^+ profile following the application of the spike was substantially under-predicted. While the predictive capacity was poor for this parameter, it is likely that the source is experimental, and not a mechanistic limitation of the model. Based upon the NH_4^+ content of the applied spike, the magnitude of the NH_4^+ response was nearly twice that expected.

One possibility is the presence of non-ideal reactor hydraulics which could cause poor dispersion of the spike through the reactor, increasing the observed concentration in the effluent. However, based on observations of mixing in the reactor (DO profiling and reactor spiking), the reactor was well mixed with minimal

dead zones, and it is unlikely that non-ideal flow of the required magnitude exists. Another possibility is enhanced hydrolysis and ammonification resulting from the high operating MLSS in the reactor. The reactor was seeded using recycled activated sludge and a fairly high initial operating MLSS (on the order of 4500 mg/L) was used. This MLSS and the corresponding biomass COD was substantially higher than those predicted by the steady state process model, thus it is possible that there is an added NH_4^+ and organic carbon input from this decaying "excess" biomass.

Predicted effluent NO_3^- concentrations were substantially higher (on the order of 50% greater) than the measured values. Due to the insensitivity of NO_3^- concentrations to the model parameters, significant adjustment was not possible. The process model provided an acceptable representation of the dynamic NO_2^- concentrations, although with some over prediction of the steady state concentrations.

Overall, despite the poor predictive capacity for NH_4^+ and NO_3^-, the performance of the ASM1-Nowak model was acceptable for the primary parameters of interest for the off-gas N_2O model component of the data generator (DO and NO_2^-).

ASMN

Steady State Sensitivity Analysis

Similar to ASM1-Nowak, a stable result was obtained from the initial ASMN model run that was conducted using default model parameters obtained from literature (Hiatt and Grady 2008b) along with the influent characterization presented in **Table 5-12**. No parameter adjustment was required prior to conducting the steady state sensitivity analysis, and the default model parameters utilized in the initial model run are presented in **Table 5-20**.

Table 5-20 Preliminary calibration of ASMN - UNSW data.

Parameters		Units	Value
Mass transfer parameters			
k_La	Aeration Mass Transfer Coefficient	1/d	3.5
Stoichiometric coefficients			
Y_H	Heterotroph yield	mg COD_{XH}/mg COD_{XS}	0.6
Y_{A1}	AOB yield	mg COD_{XA1}/mg N	0.18
Y_{A2}	NOB yield	mg COD_{XA2}/mg N	0.06
f'_D	Fraction of biomass degrading to debris	-	0.08
$i_{N/XB}$	Active biomass nitrogen content	mg N/mg COD_{XB}	0.086
$i_{N/XD}$	Biomass debris nitrogen content	mg N/mg COD_{XD}	0.06
Rate constants			
k_h	Hydrolysis rate constant	mg COD_{XS}/(mg COD_{XH}•d)	2.208
k_a	Ammonification rate constant	L/(mg COD_{XH}•d)	0.1608
μ_H	Heterotroph maximum growth rate	1/d	6.25
μ_{A1}	AOB maximum growth rate	1/d	0.78
μ_{A2}	NOB maximum growth rate	1/d	0.78
$b_{L,H}$	Heterotroph decay coefficient	1/d	0.408
$b_{L,A1}$	AOB decay coefficient	1/d	0.096
$b_{L,A2}$	NOB decay coefficient	1/d	0.096
Saturation constants			
$K_{O,H1}$	Heterotroph oxygen half-saturation constant	mg DO/L	0.1
$K_{O,A1}$	AOB oxygen half-saturation constant	mg DO/L	0.6
$K_{O,A2}$	NOB oxygen half-saturation constant	mg DO/L	1.2
K_{FA}	FA half-saturation constant	mg N/L	0.0075
K_{FNA}	FNA half-saturation constant	mg N/L	0.0001
K_{I9FA}	AOB growth FA inhibition coefficient	mg N/L	1
K_{I9FNA}	AOB growth FNA inhibition coefficient	mg N/L	0.1
K_{I10FA}	NOB growth FA inhibition coefficient	mg N/L	0.2
K_{I10FNA}	NOB growth FNA inhibition coefficient	mg N/L	0.04
K_{NO3}	Heterotroph nitrate half-saturation constant	mg N/L	0.2
K_X	Hydrolysis half-saturation constant	mg X_S/mg $X_{B,H}$	0.15
$K_{S,1}$	Substrate half-saturation constant	mg COD/L	20

The steady state sensitivity analysis was conducted using an identical procedure to that used for ASM1-Nowak. The parameter variation limitations were identical to those observed for the ASM1-Nowak model, with instability at Y_H values greater than

1, as well as at μ_{A1} and μ_{A2} values less than 50% of the defaults. No limitation was encountered for the autotrophic decay rates (b_M, b_N) over the parameter range investigated. Plots of the effect of each parameter on each of the model state variables of interest are presented as **Figures A-73** to **A-97** in **Appendix A**. A summary of the state variable sensitivities is presented as **Table 5-21**.

Table 5-21 State variable sensitivities (steady state analysis - UNSW data, ASMN).

Parameter	State Variable										
	S_O	S_S	X_S	S_{NH}	S_{NO2}	S_{NO3}	S_{ND}	X_{ND}	X_H	X_M	X_N
Y_H	■		■			▨		■	■	▨	▨
Y_{A1}										▩	
Y_{A2}											▩
μ_H		▩									
μ_{A1}				▩							
μ_{A2}					▩						
b_H	▨	■	▨			▨	■	▨	▨	▨	▨
b_{LA1}				▩						▩	
b_{LA2}					▩						▩
f_d	▨		▨					▨			
$i_{N/XB}$						▨	■	■			▨
$i_{N/XP}$											
k_a							▩				
k_H			▩					▩			
K_{OH}											
K_{OA1}				▨							
K_{OA2}					▨						
K_S		■									
K_{FA}				▩							
K_{FNA}					■						
K_{I9FA}											
K_{I9FNA}											
K_{I10FA}											
K_{I10FNA}											
K_X			▩					▩			

Legend	
Very strong $S_{i,j} > 1$	■
Strong $0.5 < S_{i,j} < 1$	▩
Moderate $0.1 < S_{i,j} < 0.5$	▨
Minimal $S_{i,j} < 0.1$	

The model state variables in the ASMN model were generally less sensitive to parameter changes than those in the ASM1-Nowak model. Y_H and b_H continued to have a significant influence on many of the state variables, while the remaining parameters influenced a more limited number of the model state variables, with the

exception of f_d, $i_{N/XP}$, K_{OH}, K_{OA1}, K_{OA2}, K_{I9FA}, K_{I9FNA}, K_{I10FA}, and K_{I10FNA}, which had minimal influence.

Dynamic Sensitivity Analysis

The dynamic sensitivity analysis of the ASMN model was conducted using a procedure identical to that used for the ASM1-Nowak model. A summary of the model state variable sensitivities is provided as **Table 5-22**.

Table 5-22 State variable sensitivities (dynamic analysis – UNSW data, ASMN).

Parameter	State Variable							
	S_O		S_{NH}		S_{NO2}		S_{NO3}	
	Response Speed	Response Magnitude	Response Speed	Response Magnitude	Response Speed	Response Magnitude	Response Speed	Response Magnitude
Y_H	■	■	■	■	■	■	▨	▨
Y_{A1}			▨	▨		▨		
Y_{A2}					▨	▨		
μ_H								
μ_{A1}	▨		■	▨	■	■		
μ_{A2}					■	■	▨	
b_H								
b_{LA1}			■	▨		▨		
b_{LA2}					▨	▨		
f_d								
$i_{N/XB}$	▨		▨	▨	■	■	▨	▨
$i_{N/XP}$								
k_a								
k_H								
K_{OH}								
K_{OA1}				▨		▨		
K_{OA2}					▨	▨		
K_S								
K_{FA}				▨	■	▨		
K_{FNA}					▨	▨		
K_{I9FA}								
K_{I9FNA}								
K_{I10FA}								
K_{I10FNA}								
K_X								

Legend	
Sensitive	■
Slightly sensitive	▨
Minimally sensitive	

Similar to the steady state sensitivity analysis results, the ASMN model was less dynamically sensitive to model parameters (and sensitive to a number of different parameters) than the ASM1-Nowak model. The key parameter influencing the dynamic DO response was Y_H. The dynamic NH_4^+ response was primarily sensitive to Y_H, in addition to response magnitude sensitivity to μ_M and b_{LA1}. The dynamic NO_2^- response was sensitive to the greatest number of parameters, with speed and magnitude sensitivity to Y_H, μ_{A1}, μ_{A2}, and $i_{N/XB}$, as well as speed sensitivity to K_{FA}. Like the ASM1-Nowak model, dynamic NO_3^- responses were rather insensitive to parameter changes, with only minor magnitude and speed sensitivity being observed for several parameters.

Key parameter sensitivities (both dynamic and steady state) are summarized for the primary state variables of interest in **Table 5-23**.

Table 5-23 Summary of state variable sensitivities - UNSW data, ASMN.

State Variable	Sensitivity		
	Steady State	**Dynamic Response Speed**	**Dynamic Response Magnitude**
DO	Y_H, b_H, f_d	Y_H	Y_H
NH_4^+	μ_{A1}, b_{LA1}, K_{OA1}, K_{FA}	Y_H, μ_{A1}, b_{LA1}	Y_H
NO_2^-	μ_{A2}, b_{LA2}, K_{OA2}, K_{FNA}	Y_H, μ_{A1}, μ_{A2}, $i_{N/XB}$	Y_H, μ_{A1}, μ_{A2}, $i_{N/XB}$, K_{FA}
NO_3^-	Y_H, b_H, $i_{N/XB}$	-	-

As seen in **Table 5-23** (and similar to ASM1-Nowak), the majority of the state variables had sensitivity in at least one form to Y_H, which would be of particular importance in model calibration. The remaining parameters of interest from a sensitivity perspective were primarily associated with the AOB and NOB growth/decay processes, and NO_3^- concentrations were relatively insensitive from a dynamic perspective.

Model Calibration

Using the results of the steady state and dynamic sensitivity analyses, the model was manually calibrated to improve dynamic performance. Calibrated model parameters are presented in **Table 5-24**, with modified parameters in bold. A comparison between the output of the calibrated model and the raw data is provided as **Figure 5-15**.

Table 5-24 ASMN calibration - UNSW data.

Parameters		Units	Initial	Calibrated
Mass transfer parameters				
k_La	Aeration mass transfer coefficient	1/d	3.5	3.5
Stoichiometric coefficients				
Y_H	Heterotroph yield	mg COD_{XH}/mg COD_{XS}	0.6	**0.57**
Y_{A1}	AOB yield	mg COD_{XA1}/mg N	0.18	0.18
Y_{A2}	NOB yield	mg COD_{XA2}/mg N	0.06	0.06
f'_D	Fraction biomass degrading to debris	-	0.08	0.08
$i_{N/XB}$	Active biomass nitrogen content	mg N/mg COD_{XB}	0.086	**0.04**
$i_{N/XD}$	Biomass debris nitrogen content	mg N/mg COD_{XD}	0.06	0.06
Rate constants				
k_h	Hydrolysis rate constant	mg COD_{XS}/(mg COD_{XH}•d)	2.208	2.208
k_a	Ammonification rate constant	L/(mg COD_{XH}•d)	0.1608	0.1608
μ_H	Heterotroph maximum growth rate	1/d	6.25	**2**
μ_{A1}	AOB maximum growth rate	1/d	0.78	**1.8**
μ_{A2}	NOB maximum growth rate	1/d	0.78	**1.8**
$b_{L,H}$	Heterotroph decay coefficient	1/d	0.408	0.408
$b_{L,A1}$	AOB decay coefficient	1/d	0.096	0.096
$b_{L,A2}$	NOB decay coefficient	1/d	0.096	0.096
Saturation constants				
$K_{O,H1}$	Heterotroph oxygen half-saturation constant	mg DO/L	0.1	**0.05**
$K_{O,A1}$	AOB oxygen half-saturation constant	mg DO/L	0.6	**1.6**
$K_{O,A2}$	NOB oxygen half-saturation constant	mg DO/L	1.2	**0.9**
K_{FA}	FA half-saturation constant	mg N/L	0.0075	**0.002**
K_{FNA}	FNA half-saturation constant	mg N/L	0.0001	**0.00005**
K_{I9FA}	AOB growth FA inhibition coefficient	mg N/L	1	1
K_{I9FNA}	AOB growth FNA inhibition coefficient	mg N/L	0.1	0.1
K_{I10FA}	NOB growth FA inhibition coefficient	mg N/L	0.2	0.2
K_{I10FNA}	NOB growth FNA inhibition coefficient	mg N/L	0.04	0.04
K_{NO3}	Heterotroph nitrate half-saturation constant	mg N/L	0.2	0.2
K_X	Hydrolysis half-saturation constant	mg X_S/mg $X_{B,H}$	0.15	0.15
$K_{S,1}$	Substrate half-saturation constant	mg COD/L	20	20

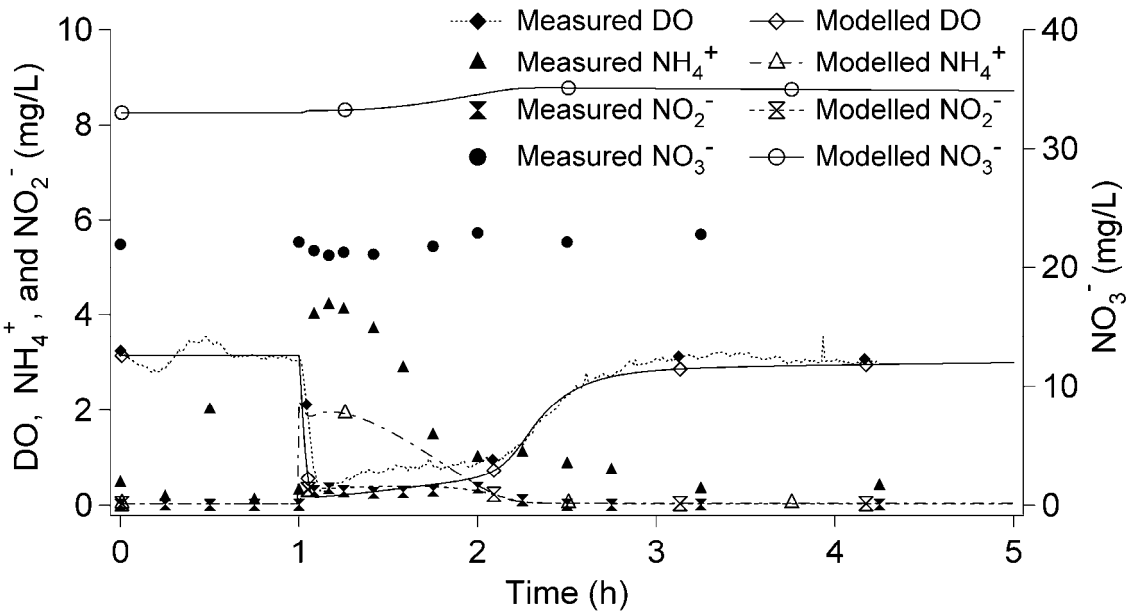


Figure 5-15 Calibrated ASMN model.

Several parameters were adjusted in fitting the model to the UNSW data; in particular many of the oxygen half-saturation constants and the heterotrophic yield were adjusted to improve the fit of the DO profile. Adjustments were also made to many of the AOB and NOB growth parameters to calibrate the NO_2^- response.

The model provided a good representation of the DO profile in the reactor, matching the initial decay and final rise to steady state. There was some discrepancy in the fit during the DO depletion plateau, which the model over predicted. Similar to the ASM1-Nowak model, the initial increase in the NH_4^+ profile following the application of the spike was substantially under-predicted. This further supports the possibility that the source of this deviation is experimental in nature and not a mechanistic limitation of the model. Predicted effluent NO_3^- concentrations were once again substantially higher (on the order of 50% greater) than the measured values. The process model provided a good representation of both the dynamic and steady state NO_2^- concentrations.

Like the ASM1-Nowak model, ASMN's predicative capacity for the primary parameters of interest for the off-gas N_2O model component of the data generator (DO and NO_2^-) was suitable for application as the data generator's liquid phase model component.

5.3.2.3 Liquid Phase Model Comparison and Selection

Model performance was evaluated by applying the calibrated ASM1-Nowak and ASMN models to simulate the process responses to the inputs for **Tests 1**, **3**, **5**, and **6** (**Table 5-12**). These tests were conducted at different operating points (initial DO conditions), as well as with variable process stimuli (spike volumes), and allowed an independent assessment of the model's performance. Key process responses of interest for the off-gas N_2O model are presented along with the measured data for comparison purposes as **Figure 5-16** and **Figure 5-17** for DO and NO_2^-, respectively.

In general, the DO profile fits using both models were of fairly similar quality, with the largest depletions predicted by the calibrated ASMN model. The ASMN model outperformed the ASM1-Nowak model in **Test 1**, where there was a significant DO depletion plateau. In **Tests 3** and **5**, in which there was a more linear increase in DO from the minimum up to the final steady state conditions, the ASM1-Nowak model had the smallest level of depletion over-prediction and best performance. It should be noted that there was a significant difference between the initial and post-test steady state DO concentrations in these tests, indicating a shift in the process state. It is quite possible that there are additional DO dynamics incorporated into the observed response (i.e. the observed response is not solely due to the applied disturbance). Dynamic DO depletions in **Test 6** were under-predicted by the ASMN-Nowak model, while the ASMN model had a more mixed performance, initially over-predicting the DO depletion then under-predicting the depletion during the recovery period to steady state.

The ASMN model provided a very good representation of the steady state NO_2^- concentrations (**Figure 5-17**), which were consistently over-predicted by the ASM1-Nowak model. With regards to the dynamic portion of the response, both models over-predicted the peak NO_2^- concentrations in **Tests 1**, **3**, and **5**. The ASMN model had the smallest amount of over-prediction of the two models and better captured the shape of the NO_2^- peak in **Test 1**, although it did not reproduce the slope of the NO_2^- peak in **Tests 3** and **5**. For **Test 6**, the NO_2^- peak predicted by ASMN was much narrower than the measured value and the prediction was quite poor, while a much better representation was obtained by the ASM1-Nowak model.

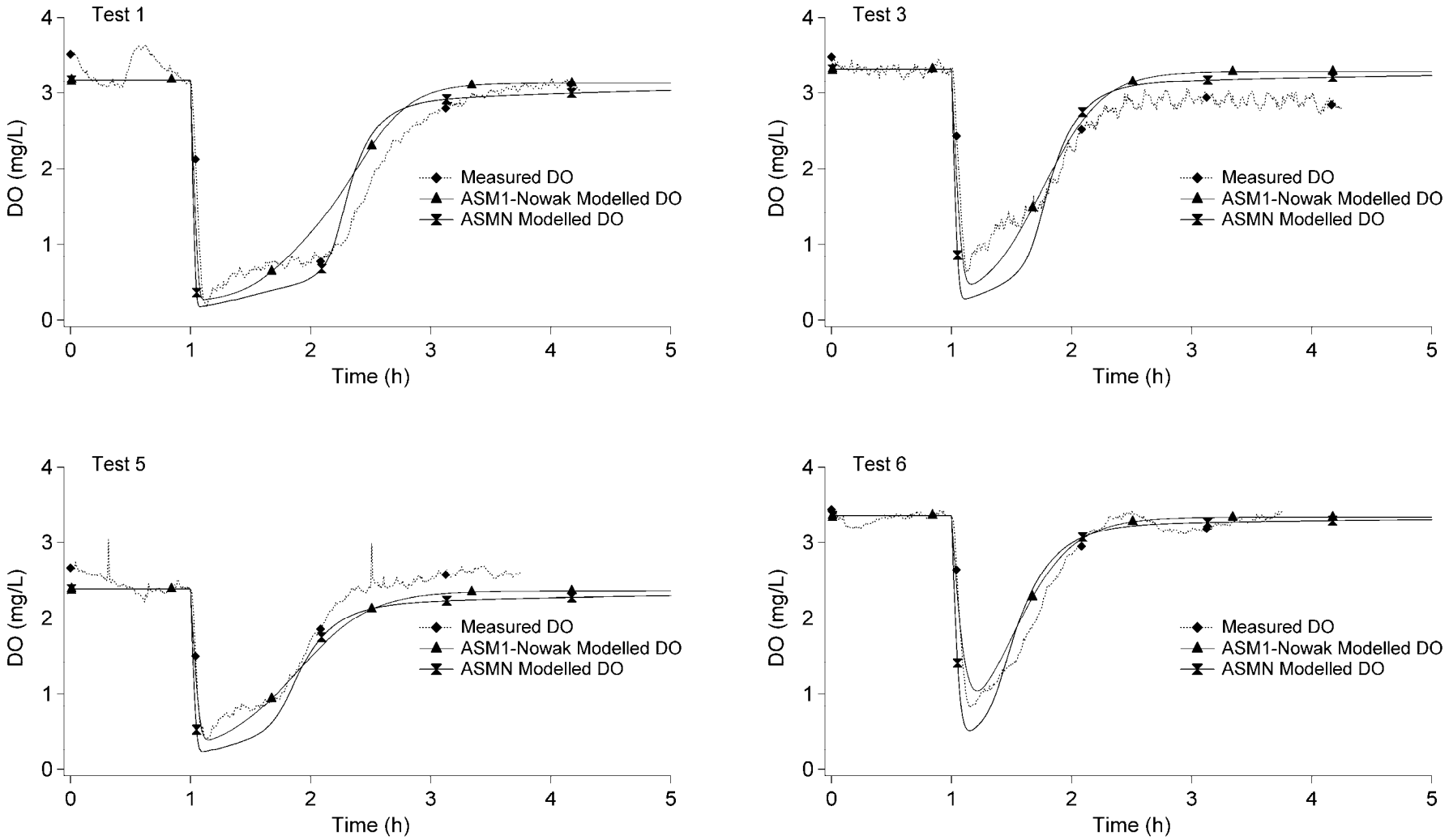


Figure 5-16 Comparison of modelled DO responses with UNSW data.

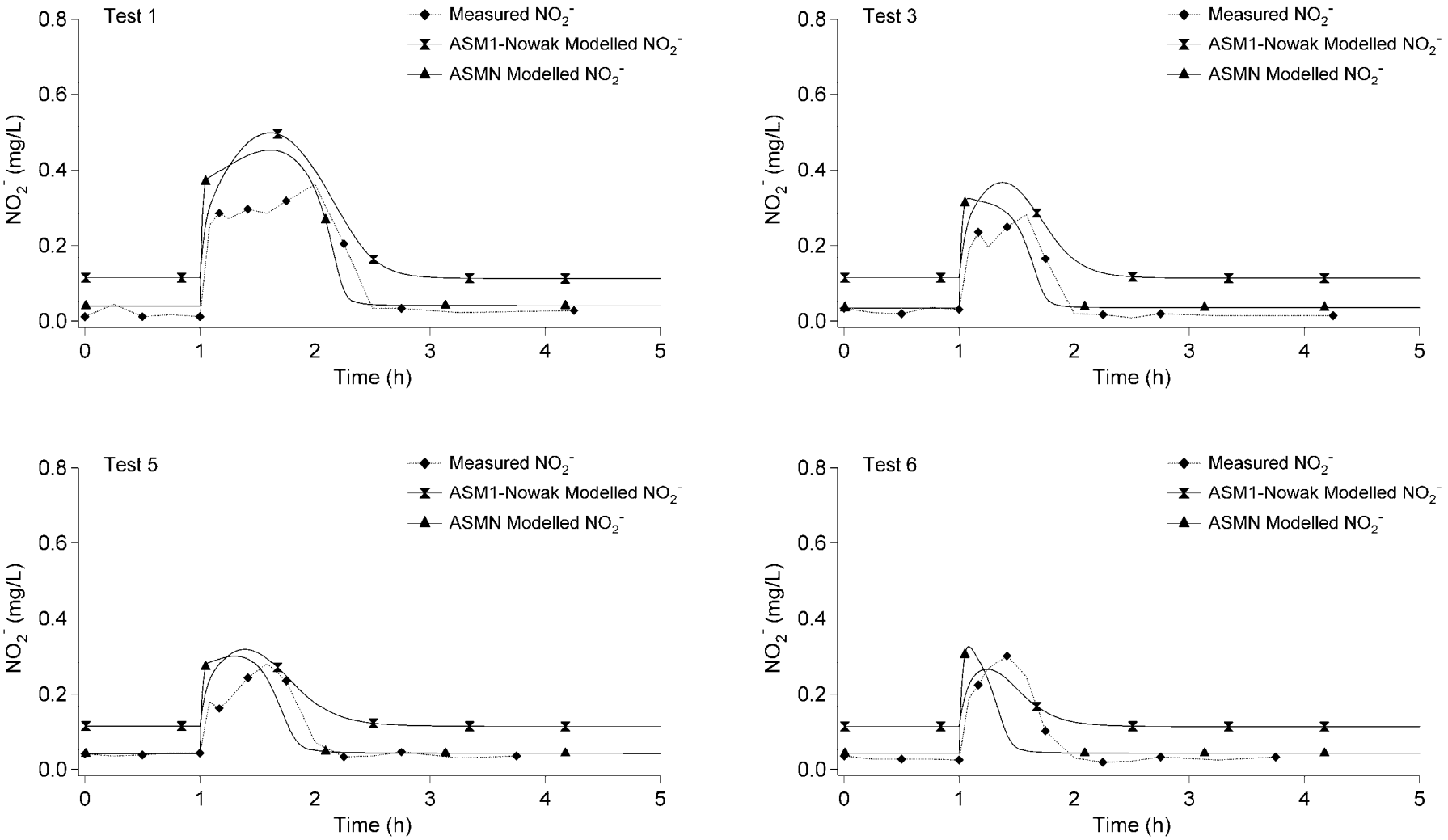


Figure 5-17 Comparison of modelled NO_2^- responses with UNSW data.

Overall, the ASMN model had better performance than the ASM1-Nowak model, with improved capture of the dynamic shape of the DO depletion, and providing a better prediction of NO_2^- concentrations. It is likely that this improved predictive capacity is a result of the changes to the process kinetics for AOB and NOB growth in ASMN, although it is entirely possible that the improved predictive capacity is simply a function of having additional parameters available for calibration/fitting. Due to its superior performance, the ASMN model was selected as the liquid phase model for the data generator.

5.3.3 Off-gas N_2O Model Component

An off-gas model was developed for the UNSW data to link the measured response (off-gas N_2O) to the liquid phase reactor conditions. The model was based upon the off-gas N_2O model developed for the Cranfield data (**Section 5.2.3**), with a number of modifications.

5.3.3.1 Model Development

The Cranfield off-gas N_2O model was developed based upon the observation of a direct correlation between off-gas N_2O concentrations and liquid phase DO concentrations, and consisted of a proportional component with an inverse switching function for DO concentration and an offset component. The offset component was required since the switching function could not fit the baseline concentrations while at the same time fitting the shape of the dynamic portion of the response. As a result, the Cranfield off-gas N_2O model lacked sensitivity at higher DO concentrations. This model was further limited by NO_2^- and NO_3^- concentrations in the process data being reported as a sum (as well as being measured in the reactor effluent), and as such the data could not be assessed for any correlation to NO_2^-/FNA.

Off-gas N_2O concentrations in the UNSW data (**Chapter 4**) were less dependent on reactor DO concentrations, which primarily acted as a switching function. Furthermore, a strong dependence on NO_2^-/FNA was also observed. Both of these aspects correspond well with the current mechanistic understanding of the aerobic

autotrophic N_2O generation mechanism. Due to the strong NO_2^-/FNA dependence, the Cranfield off-gas N_2O model was not able to provide a good representation of the off-gas N_2O concentrations for the UNSW reactor.

With the availability of liquid phase NO_2^- and NO_3^- data, it was possible to assess other forms of off-gas N_2O models. A range of models were evaluated including various combinations of Monod style dependencies on DO, FNA, and NH_4^+. Overall, the best performance was obtained from a model with two terms; the first term was a direct FNA proportionality (dominant in the dynamic portion of the response) and the second term was a DO inhibition proportionality factor (dominant in the steady state portion of the response, at high DO concentrations). Incorporation of NH_4^+ concentrations into the off-gas models did not improve the predictive capacity, likely due to NH_4^+ being the excess substrate for the alternative metabolic pathway producing the off-gas N_2O. The off-gas N_2O model utilized for the UNSW data had the following form:

$$C_{N_2O} = K_{DO,1}\left(\frac{K_{DO,2}}{S_O + K_{DO,2}}\right) + K_{FNA,1}(S_{FNA})$$

Utilization of a DO dependent steady state fitting parameter allowed for broader model applicability. As seen in the data presented in **Chapter 4**, off-gas N_2O concentrations are sensitive to DO concentration changes even at higher DO concentrations (greater than 3 mg/L). It is possible that this sensitivity is a result of the presence of NO_2^- in local zones of higher concentration within the activated sludge flocs. Even small changes in bulk DO concentrations would influence DO profiles within the flocs, producing zones of localized oxygen stress, resulting in AOB utilizing alternative metabolic pathways which produce N_2O.

It is important to note that while parameter selection and some of the model forms are based on biological process knowledge, the model was developed purely from a data fitting perspective and is in fact more a correlation analysis than an in-depth modelling exercise.

5.3.3.2 Model Calibration

Model parameters were obtained by fitting the proposed model to DO, NO_2^-, and N_2O data for **Test 2**. The fitted model ($K_{DO,1}$ = 1, $K_{DO,2}$ = 20, and $K_{FNA,1}$ = 20000) is presented as **Figure 5-18**.

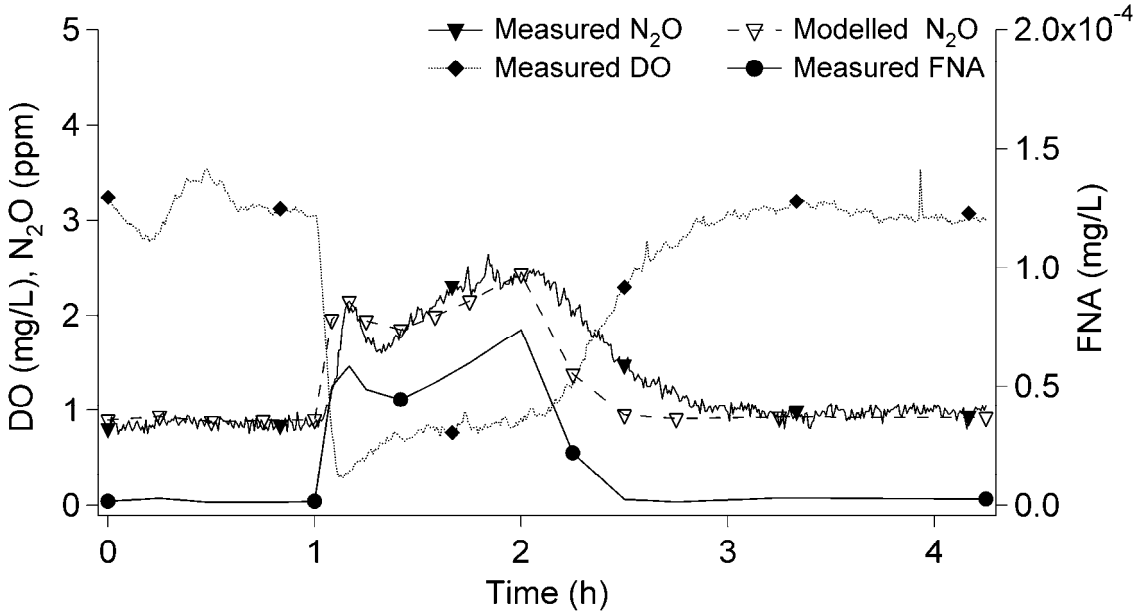


Figure 5-18 Calibrated off-gas N_2O model.

Overall, the developed model provided a good representation of the off-gas N_2O concentration dynamics. There was some deviation on the decay portion of the response, with the model under-predicting off-gas N_2O concentrations. During the period of process stress, some N_2O would be accumulating in the liquid phase. It is possible that the higher off-gas N_2O concentrations during the decay portion of the response is a result of the accumulated liquid phase N_2O being stripped to the process off-gas by the aeration air.

Capturing the dynamics of the decay portion of the response would likely require the development of a mechanistic N_2O model, which is beyond the scope of this work. A mechanistic model could consist of the addition of two new state variables to the ASM model matrix (liquid and gas phase N_2O concentration), along with process rates and stoichiometric coefficients for the autotrophic production of liquid phase N_2O, mass transfer of liquid phase N_2O to the aeration air, and liquid phase N_2O oxidation at elevated DO concentrations. However, additional

clarification and understanding of the specific mechanisms involved in this process are required before the development of such a model becomes feasible.

5.3.3.3 Off-gas N_2O Model Performance

The performance of the calibrated off-gas N_2O model was assessed by applying the model to the measured liquid phase data (DO and NO_2^-) for **Tests 1**, **3**, **5**, and **6** and comparing the predicted off-gas N_2O concentrations with the measured values. These results are presented as **Figure 5-19**.

For **Tests 1**, **3**, **5** and **6**, the shape of the predicted off-gas N_2O profile matched the measured shape quite well, although there were some discrepancies with regards to over prediction of the N_2O peak for **Test 1**, and under-prediction of the peaks and decay (discussed in the previous section) for **Tests 3** and **5** and **6**. The predictive capacity was quite poor for **Test 6**, in which the off-gas N_2O profile was substantially longer (over twice as long as the predicted value). The substantial over-prediction in **Test 6** is a function of the FNA profile, which deviated from the forms in **Tests 1** and **3**, being much shorter than the DO depletion.

Variability in the model performance corresponded to the temporal variations in the off-gas N_2O stress response observed in **Chapter 4**. The model form assumed a constant stress-response relationship, and was not capable of representing changes in this relationship. Thus, the predictions corresponded to the observed trend of increasing N_2O yield per amount of applied stress, over-predicting the N_2O profile for the test conducted before the calibration test (**Test 1**), and under-predicting the N_2O profiles for tests conducted afterwards (**Tests 3**, **5**, and **6**).

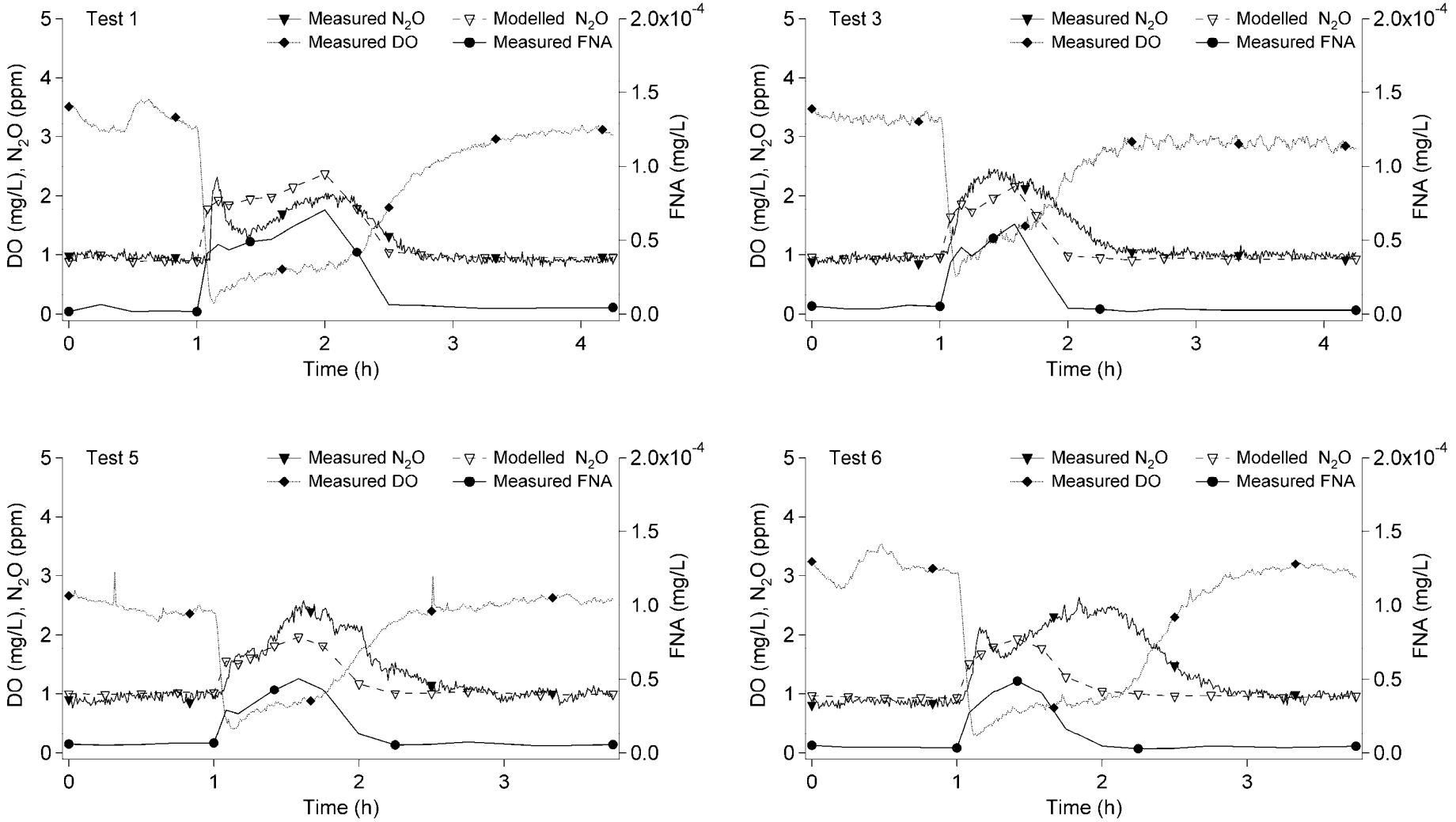


Figure 5-19 Comparison of modelled N_2O responses with UNSW data.

5.3.4 Data Generator Performance

Process inputs for the calibration data set (**Test 2**) were applied to the data generator (consisting of the ASMN liquid phase model and the off-gas N_2O model) to predict the off-gas N_2O profile (**Figure 5-20**). The data generator was successful at predicting the initial and post tests steady state components of the off-gas N_2O profile, as well as capturing the initial rise and most of the dynamic profile. However, as discussed previously, the data generator did not capture the decay portion of the response, predicting an earlier return to steady state.

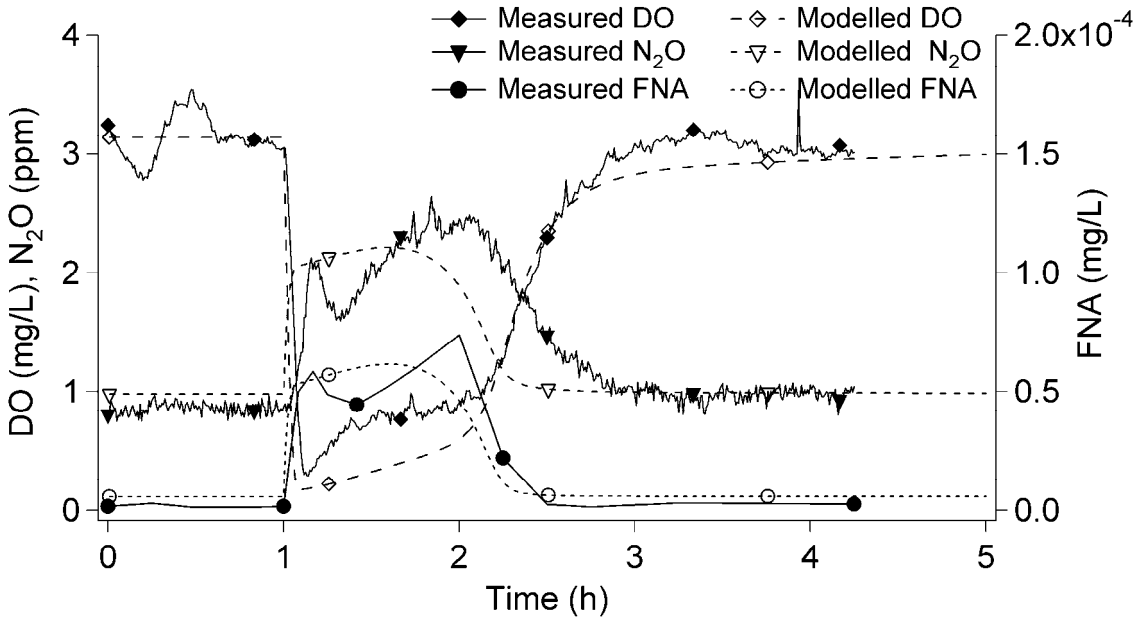


Figure 5-20 Data generator evaluation - Test 2, UNSW data.

Data generator performance was then evaluated by feeding the process inputs for a series of independent operating scenarios (**Table 5-11** and **Table 5-12**). Predicted and measured off-gas N_2O profiles, as well as liquid phase profiles of components of interest, are presented as **Figure 5-21**. The off-gas N_2O profiles produced by the data generator reflect a combination of the limitations of its individual components, with a reduced and compressed off-gas N_2O response being generated.

Assessment of response quality was complicated by the observed temporal variability in the off-gas N_2O stress response. It is likely that this variability (and potentially process instability) is responsible for a substantial proportion of the

prediction errors. Despite the variable performance seen in **Figure 5-21**, the data generator successfully reproduces the fundamental stress response dynamics, and as such will be utilized in **Section 5.4** to evaluate the proposed control concept.

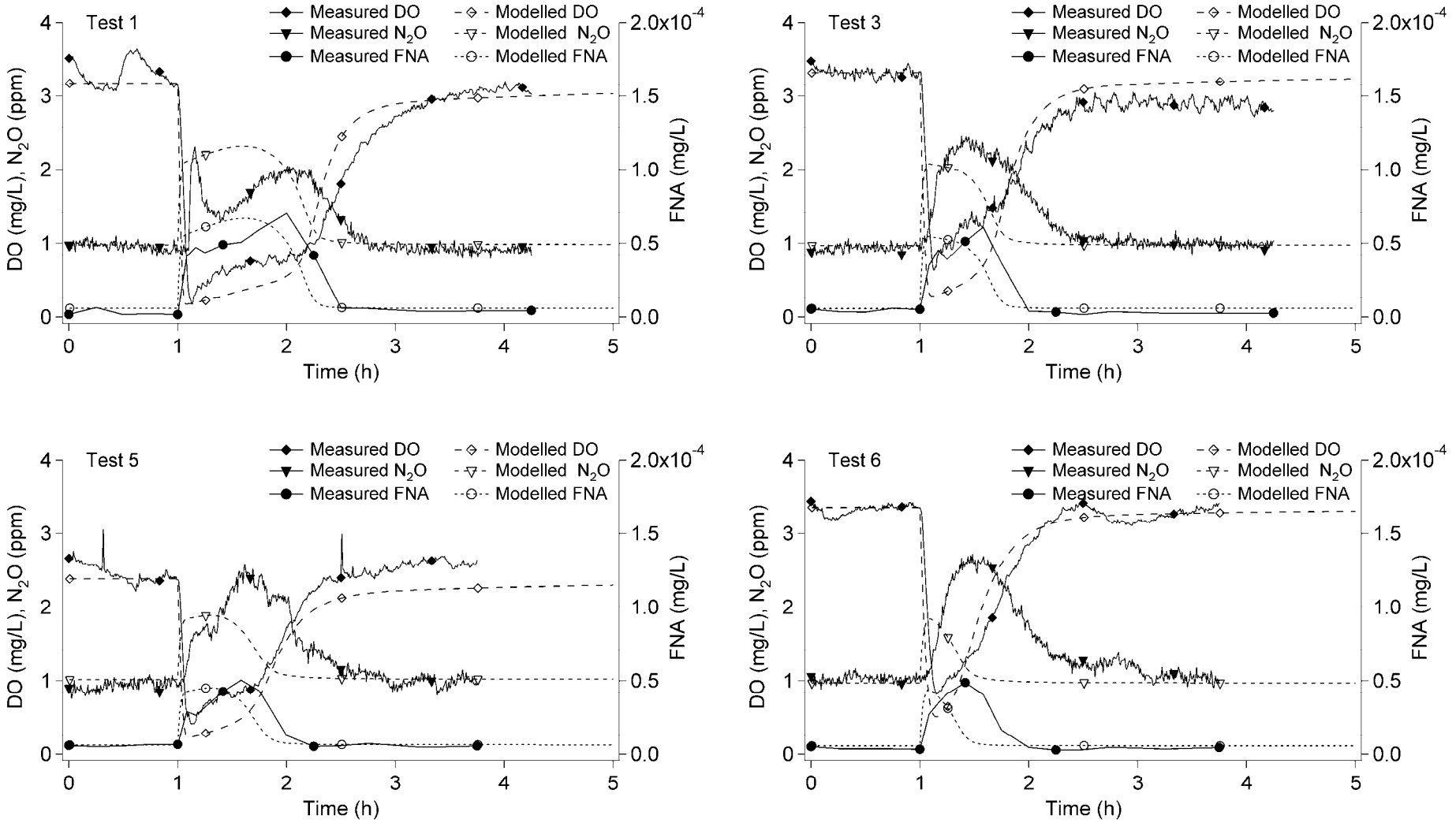


Figure 5-21 Data generator performance evaluation – UNSW data.

5.4 Process Control Concept Evaluation

The final step of the simulation study was to evaluate the proposed aeration control concept. This evaluation was conducted utilizing a PI control algorithm attached to the data generators developed for both the Cranfield and UNSW data sets. The controller was tuned using the continuous cycling method with Ziegler-Nichols tuning parameter coefficients (Seborg et al. 2003).

Evaluation using the Cranfield data generator was restricted to a control feasibility assessment due to limitations in the source dataset. The UNSW data generator was utilized to assess control concept feasibility, as well as to quantify potential operational benefits associated with application of the control concept. Feasibility evaluations will be presented in **Sections 5.4.1** and **5.4.2** for the Cranfield and UNSW processes, respectively. Benefits associated with the application of the developed control concept will be quantified in **Section 5.4.3**.

5.4.1 Cranfield Data

The feasibility of the proposed aeration control concept was evaluated for several operating scenarios. Since the reactors were operated at a hydraulic steady state the effects of process flow variations were not assessed, the focus was instead on variations of influent parameter concentrations. Two forms of concentration variation were evaluated, spikes and diurnal variations. Spikes allow for the assessment of the process response and controller effectiveness with regards to short term events (shock loadings). Diurnal variations in feed concentration are more representative of routine process operation and provide a basis to evaluate the long term effectiveness and benefits of process control implementation.

Conditions for the shock loading scenario were based upon those for **Test 1** from Burgess et al. (2002b), in particular a 41 mg/L influent NH_4^+ concentration and a 2.44 g NH_4^+ shock loading. For the second control evaluation scenario, a diurnal NH_4^+ concentration variation was input to the data generator. This NH_4^+ input profile was generated from a normalized diurnal variation pattern (**Figure 5-22**) based upon

literature (Metcalf and Eddy 2003). The input diurnal NH_4^+ concentration was based around an average concentration of 41 mg/L.

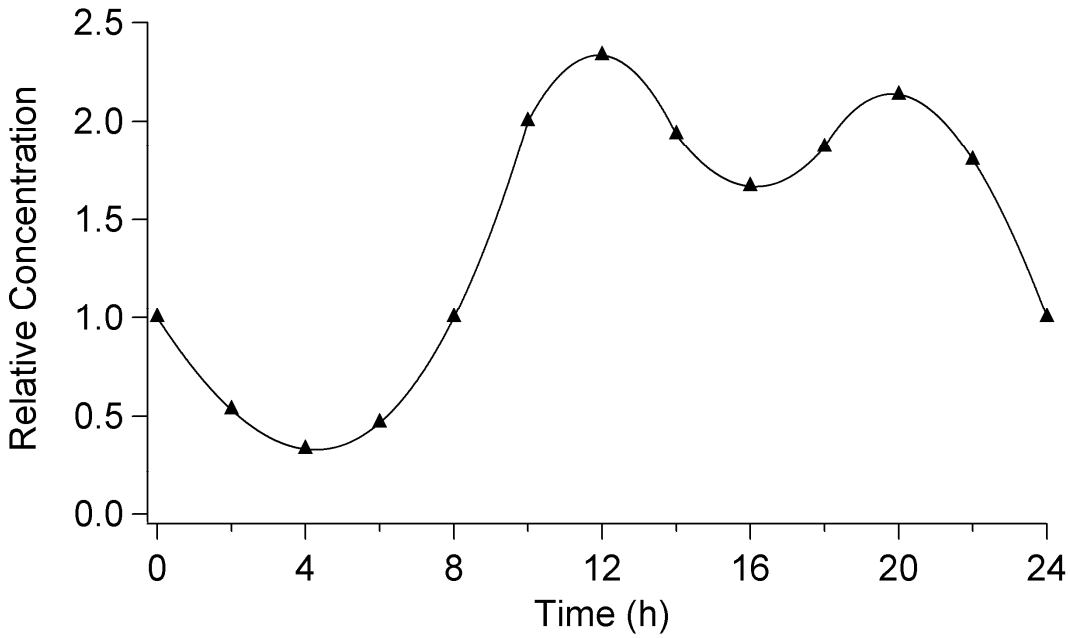


Figure 5-22 Normalized diurnal variation.

Process Control Evaluation

The response of the controlled process to two forms of stimuli is presented as **Figure 5-23** for NH_4^+ shock loading, and **Figure 5-24** and **Figure 5-25** for simulated diurnal variations in the influent NH_4^+ concentrations. Relative airflow is also presented in these figures, and is taken relative to the base airflow at steady state conditions. An N_2O setpoint of 0.2 ppm was used for this analysis. This setpoint was chosen to provide a similar level of autotrophic metabolic inhibition (and thus nitrification efficiency) as that presented in the experimental data. It should be noted that since the diurnal profile was based on average NH_4^+ concentrations in the experimental data and the process setpoint was unchanged from experimental conditions, the total air usage over the time period investigated would be equal for both the controlled and uncontrolled scenarios.

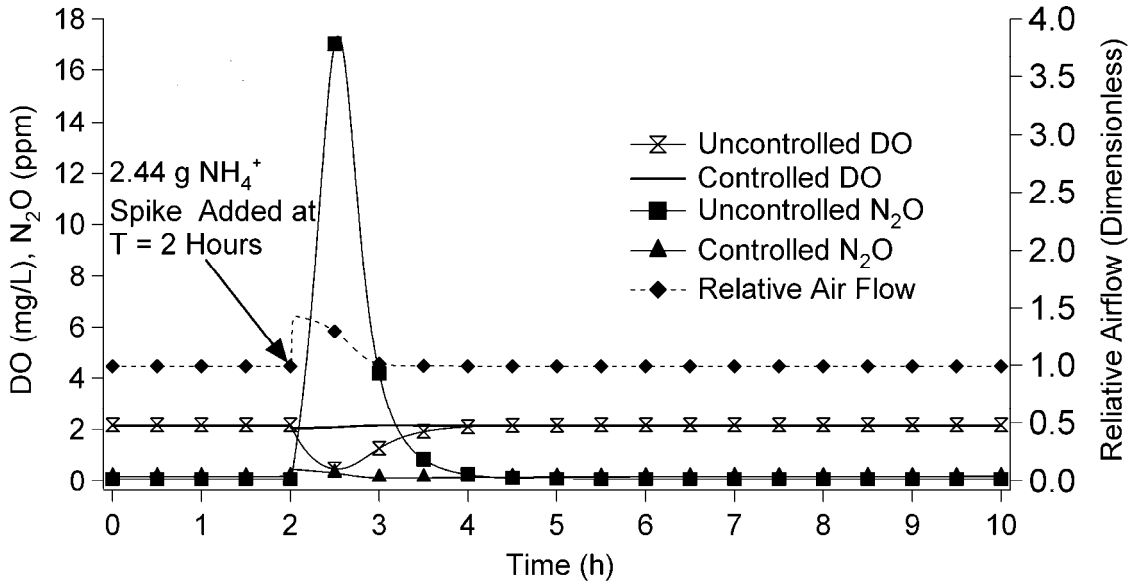


Figure 5-23 Controlled and uncontrolled process response to an NH_4^+ shock load – Cranfield data generator.

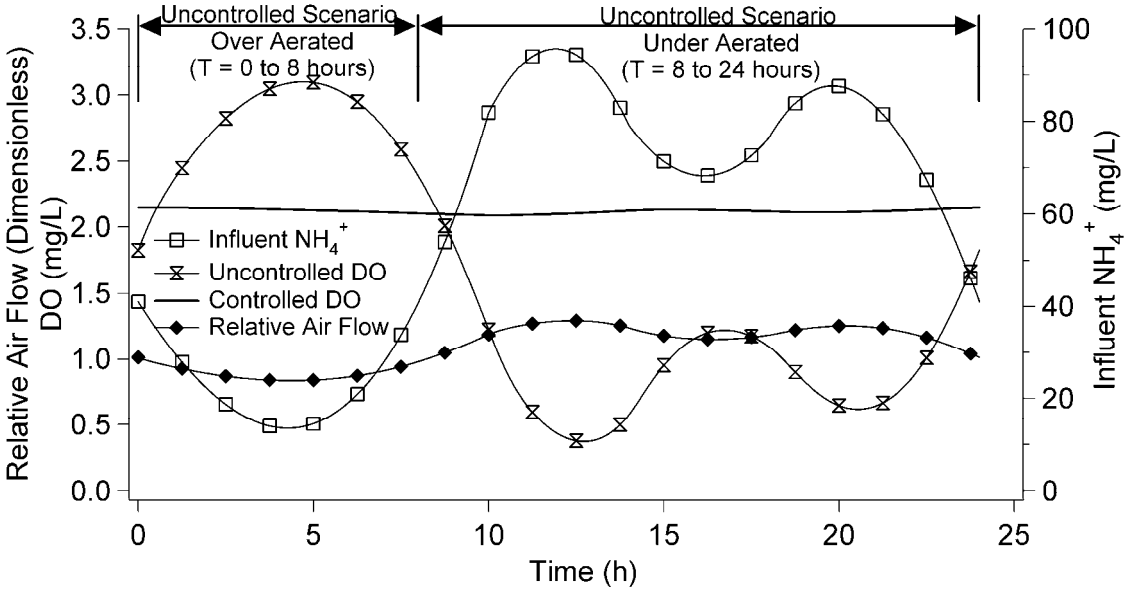


Figure 5-24 Controlled and uncontrolled process DO response to diurnal NH_4^+ loading variations – Cranfield data generator.

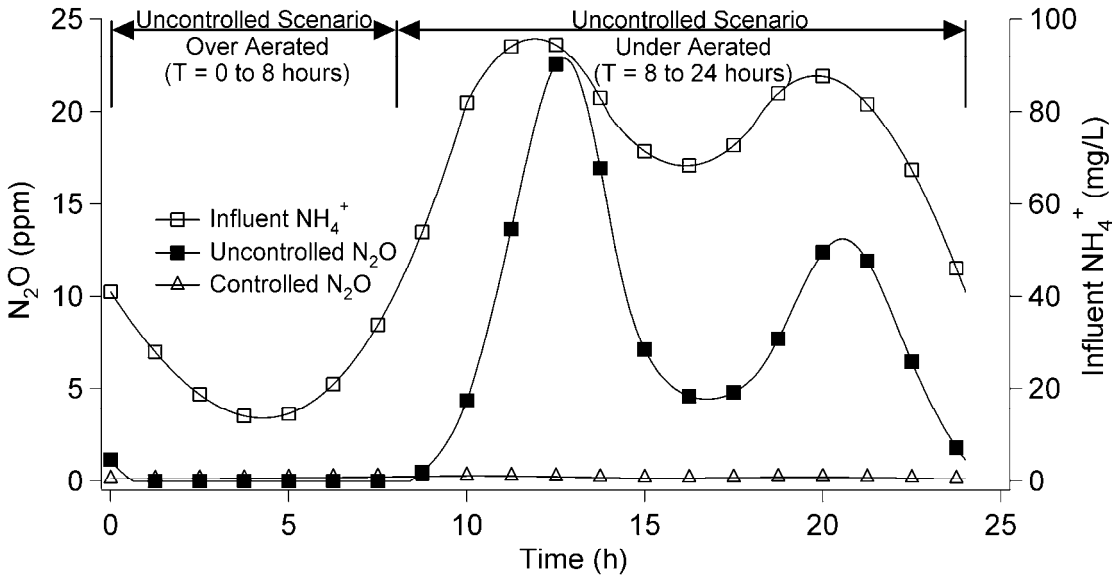


Figure 5-25 Controlled and uncontrolled process off-gas N_2O response to diurnal NH_4^+ loading variations – Cranfield data.

For both of the studied scenarios, changes in influent NH_4^+ loading resulted in changes in off-gas N_2O concentrations which initiated a control action, i.e. a change in the aeration air supply flow. The process control method implemented in this simulation was successful in maintaining the processes at the desired operating setpoint. These results demonstrated that off-gas N_2O concentrations used as a surrogate for autotrophic bacterial metabolic inhibition has the potential to provide a means of controlling bioreactor aeration air supply and promote stable operation by minimizing periods of significant inhibition (indicated by elevated off-gas N_2O concentrations).

For uncontrolled operation during diurnal variations (**Figure 5-24** and **Figure 5-25**), the wastewater was over-aerated for the first eight hours (DO concentration increasing above the steady state concentration). Hence energy was wasted during this time period and excess operating cost was incurred. During the following 16 hours the uncontrolled plant was under-aerated, resulting in DO depletion in the bioreactor and reduced nitrification efficiency. By applying off-gas based process control the aeration was reduced during low loading periods and increased during higher loadings, matching the aeration supply with the metabolic demand and achieving a more efficient use of aeration air.

5.4.2 UNSW Data

The feasibility of the proposed aeration control concept was evaluated with the UNSW data generator using a similar methodology as that employed for the Cranfield data generator. Both spikes (short term events) and diurnal influent concentration variations (long term/routine process operation) were utilized to evaluate the controller performance.

Conditions for the shock loading scenario were based upon the influent properties for **Test 2** (**Table 5-12**), with a shock load of approximately 50% of the spike applied in **Test 2** input into the data generator. The second control evaluation scenario utilized a diurnal feed concentration variation based upon the influent properties for **Test 2** scaled around the normalized diurnal variation pattern presented in **Figure 5-22**. It should be noted that the spikes and diurnal variations utilized in this analysis included all feed components, and not just NH_4^+ like in the Cranfield data generator based assessment.

The response of the controlled process to two forms of stimuli is presented as **Figure 5-26** for shock loading, and **Figure 5-27** and **Figure 5-28** for diurnal variations in the influent concentrations. Only influent NH_4^+ variations are presented in the plot (as a reference), but other influent components did undergo a similar variation during the investigated scenarios. Relative airflow is also presented in these figures, and is taken relative to the base airflow at steady state conditions. An N_2O setpoint of 1 ppm was used for this analysis.

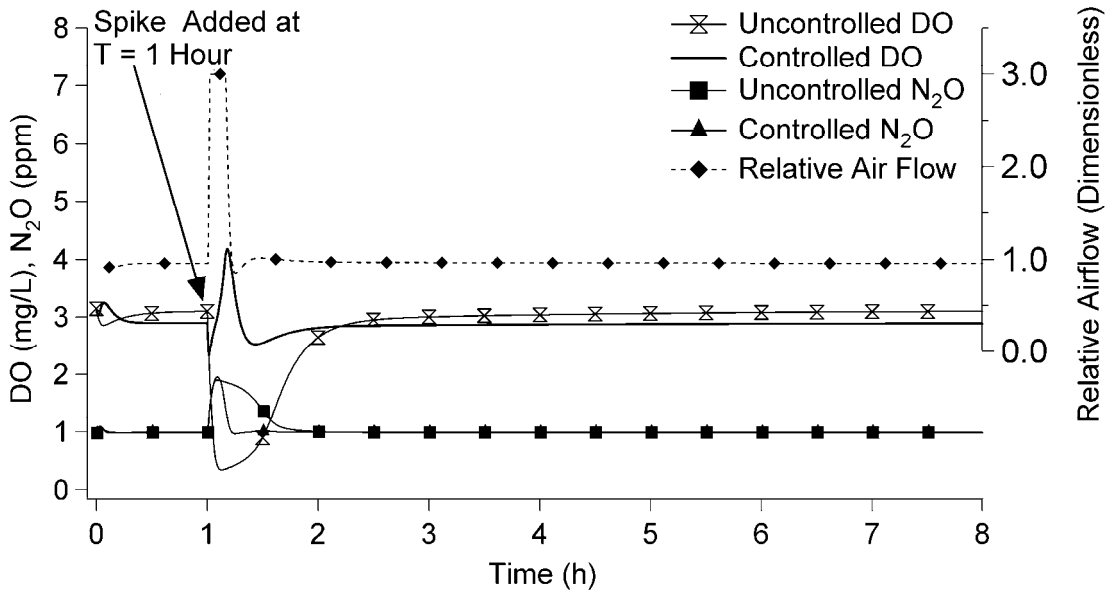


Figure 5-26 Controlled and uncontrolled process response to an NH_4^+ shock load – UNSW data generator.

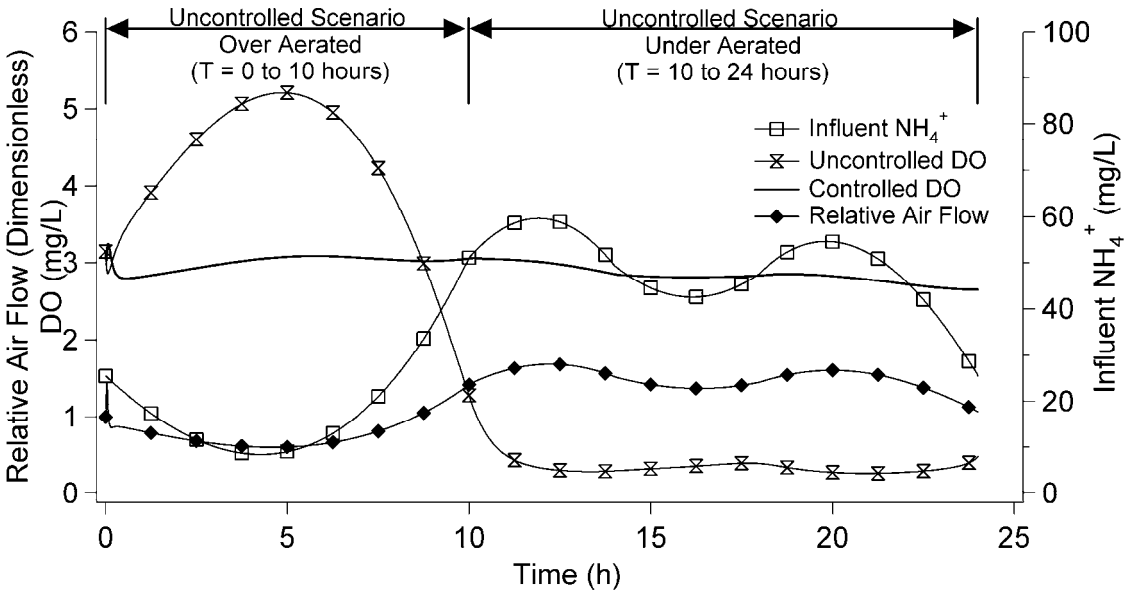


Figure 5-27 Controlled and uncontrolled process DO response to diurnal NH_4^+ loading variations – UNSW data generator.

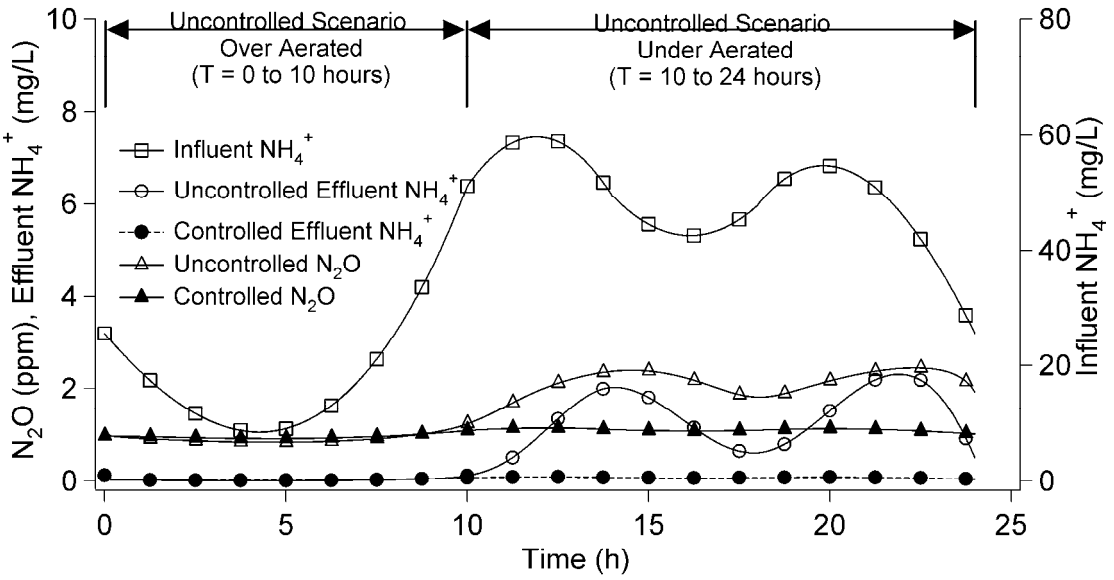


Figure 5-28 Controlled and uncontrolled process off-gas N_2O response to diurnal NH_4^+ loading variations – UNSW data.

The implemented process control concept was successful in maintaining the process at the desired operating setpoint. Furthermore, as seen in **Figure 5-28**, it was successful at averting nitrification failure (preventing the build-up of NH_4^+ inside the reactor), and provided better matching of the aeration supply with the metabolic demand, achieving a more efficient use of aeration air. Using combined changes to all process influent components (carbon and nitrogen), these results demonstrated that while the stress response is limited to AOB bacteria, the control concept is also able to maintain suitable environmental conditions for the heterotrophic bacteria, and would be suitable for combined carbon and nitrogen removal processes.

Unlike the previous evaluation using the Cranfield data generator, the implemented process control was not able to mitigate the magnitude of the initial off-gas N_2O peak (although it was able to substantially reduce the duration of the response), and there was some overshoot in the reactor DO. These differences are a function of the form of the off-gas N_2O model. For the Cranfield data generator, the dynamic component of the off-gas N_2O model was dependent on DO concentrations only, and as such the stress response was extremely quick and allowed for very fine control of the aeration air supply. The off-gas N_2O model in the UNSW data generator utilized FNA as the dominant term for the response during dynamic

conditions, introducing biokinetics into the stress response relationship. While this is a more realistic representation of the processes involved, the biokinetics adds deadtime into the process response. While many methods exist to address the effects of deadtime on feedback control, a full exploration of these techniques (other than adjusting the algorithm integral action) is beyond the scope of this work.

5.4.3 Estimate of Benefits

Quantification of the process inputs and outputs relative to other conventional modes of process operation (in particular DO based aeration control and constant air flow operation) was required to support the evaluation of the environmental and economic feasibility of the proposed process control concept (presented in **Chapter 6**). Aeration and process emission quantification for each of the operation modes was conducted by process simulation utilizing the diurnal feed input from **Section 5.4.2**.

Operation with off-gas N_2O based aeration control was simulated using the process simulator from **Section 5.4.2**, while operation with DO based aeration control was simulated using the data generator developed in **Section 5.3** connected to a feedback PI control algorithm (DO as the monitored value and aeration airflow as the manipulated variable). As with previous work, an idealized control response was used and the controller was tuned using the continuous cycling method with Ziegler-Nichols tuning parameter coefficients (Seborg et al. 2003). Constant air flow operation (referred to as uncontrolled operation) was simulated using the base data generator developed in **Section 5.3**, with no added control algorithms.

The evaluation was conducted in two parts; the first part focused on the assessment of relative aeration requirements for the three modes of operation, while the objective of the second part was to evaluate control system performance in terms of process emissions.

Aeration Requirements

Aeration requirements were assessed for all three modes of operation at a moderate DO concentration (~2 mg/L). To compare the aeration requirements, it was

necessary that each of the processes be operated at an equivalent level of performance. Average NH_4^+ removal was selected as the performance parameter since it is a key indicator of process efficiency for nitrification processes, and its emission is often regulated. While NO_2^- is also an important operational parameter and subject to regulation, the opportunity exists to remove it downstream in the denitrification component of the overall process, and as such is not a critical operational parameter for the purpose of this assessment.

The 2 mg/L DO concentration was used for the DO based aeration control setpoint, and the other processes operating points were set based on achieving an equivalent average NH_4^+ removal. A summary of the process inputs (aeration) and outputs (total mass flows and emission concentrations) is provided as **Table 5-25**, and process response profiles are presented in **Figure 5-30**.

Table 5-25 Evaluation of aeration requirements – moderate DO (2 mg/L) operation.

Control type		DO control	N_2O control	Uncontrolled
Setpoint		DO = 2 mg/L	N_2O = 1.1 ppm	N/A
Total air input (L)		4697	4594	5904
Net process outputs				
NH_4^+ (mg)		2.95	2.83	2.86
NO_2^- (mg)		2.59	2.47	2.51
N_2O (mg)		18.0	18.0	17.2
Emission concentrations				
NH_4^+ (mg/L)	Average	0.07	0.07	0.07
	Maximum	0.12	0.11	0.15
	Minimum	0.02	0.2	0.01
DO (mg/L)	Average	1.99	1.79	3.30
	Maximum	2.08	2.10	5.94
	Minimum	1.93	1.52	1.39
NO_2^- (mg/L)	Average	0.06	0.06	0.06
	Maximum	0.10	0.09	0.12
	Minimum	0.02	0.02	0.01
N_2O (mg/L)	Average	1.10	1.10	1.05
	Maximum	1.23	1.19	1.30
	Minimum	0.96	0.99	0.82

Application of process control achieved substantial reductions in the amount of aeration required to achieve similar levels of nitrification efficiency. Reductions (compared to uncontrolled operation) on the order of 20.4% and 22.2% were achieved through the utilization of DO and off-gas N_2O based aeration control,

respectively. The off-gas N_2O based aeration control concept was slightly more efficient, requiring less aeration and achieving slightly lower net emissions of NH_4^+ and NO_2^-.

The above analysis is quite restrictive in nature due to the evaluation criteria. To broaden the assessment, controller performance was was evaluated for a range of operating points using the efficiency based criterion proposed by Vrecko et al. (2006). As seen in **Figure 5-29**, both control concepts were quite similar in terms of performance and consistently outperformed operation with constant aeration flow.

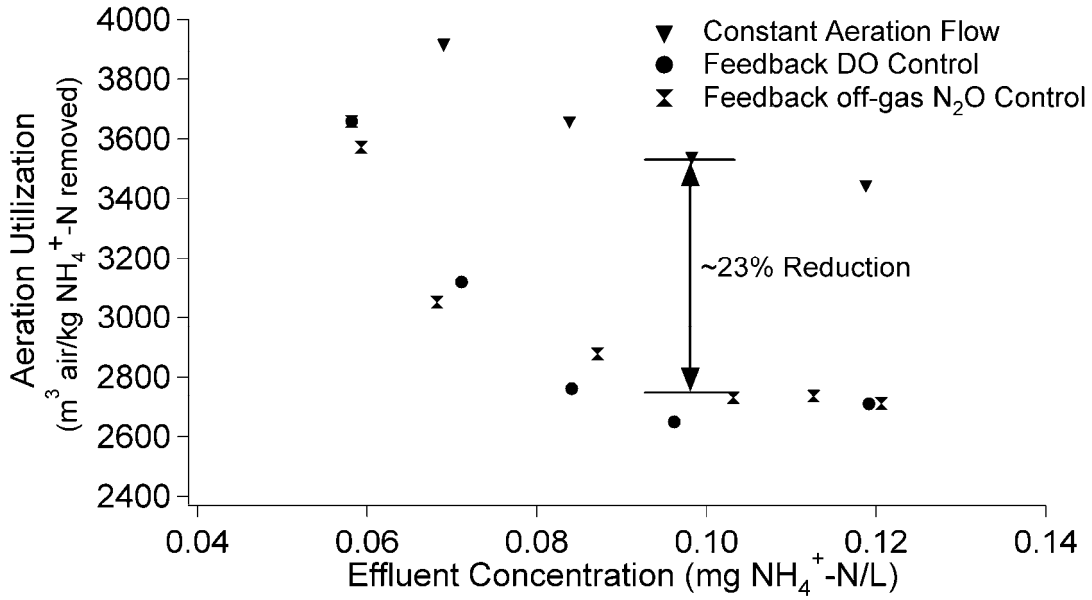


Figure 5-29 Comparison of Aeration Utiliziation

Based on the response profiles presented in **Figure 5-30**, both forms of aeration control had similar performance during periods of low loading. Off-gas N_2O based aeration control provided better mitigation of peak response concentrations (NH_4^+, NO_2^-, and off-gas N_2O) during periods of elevated loading. This improved performance is likely due to a more aggressive application of aeration, with the off-gas N_2O control concept allowing process DO concentrations to increase during periods of elevated loading (stress) and decrease during periods of low loading.

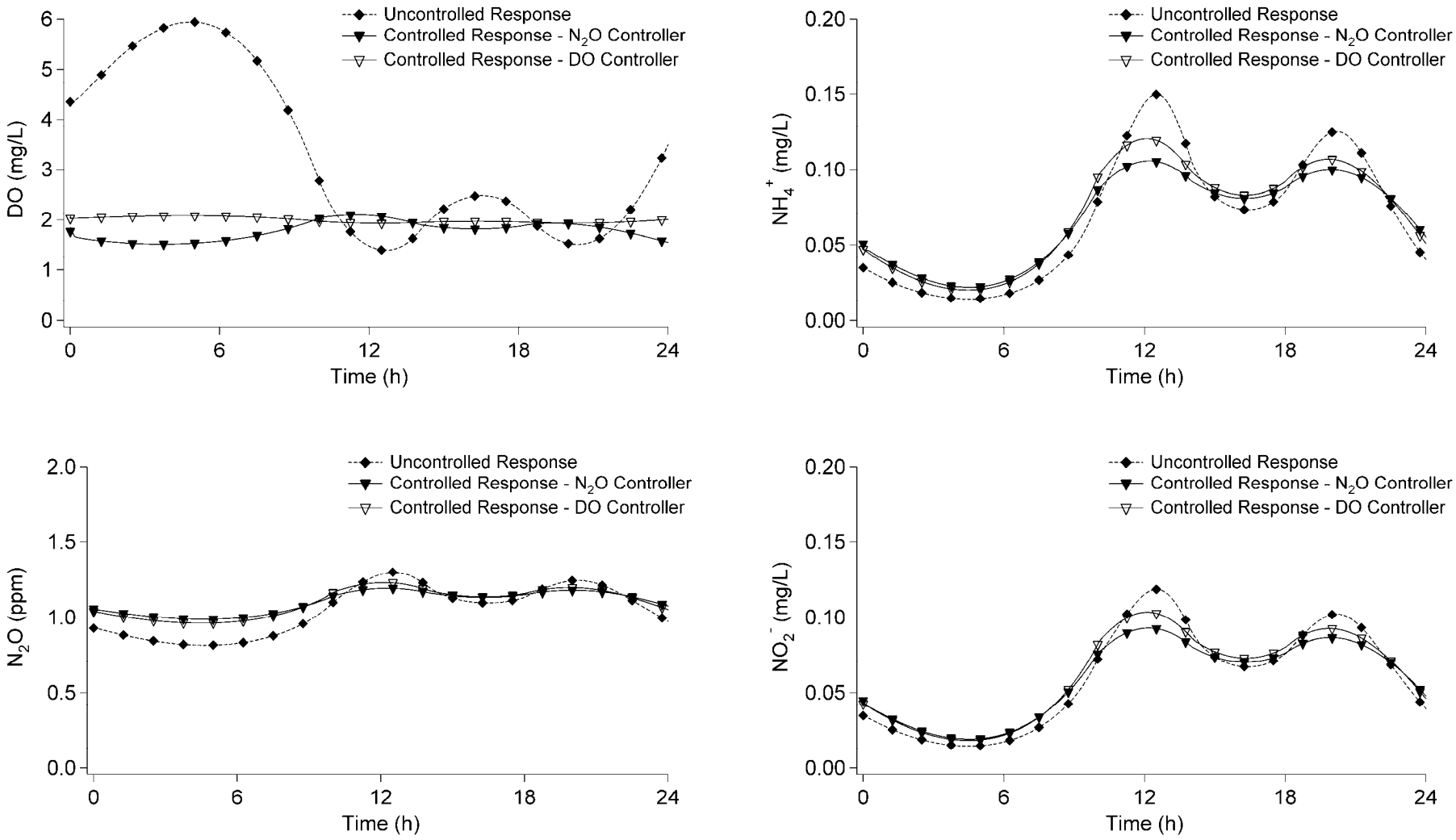


Figure 5-30 Process response - moderate DO (2 mg/L) operation.

Process Emissions

Controller performance with regards to process emissions was evaluated from the perspective of process manipulation efficiency. That is, controller performance was assessed based on ability to control undesirable process emissions using the same amount of aeration air supply (the manipulated variable). Differences in process emissions would be a result of the matching between aeration supply and demand.

Two sets of operating conditions were selected for this evaluation; high DO operation (3 mg/L) and low DO operation (1 mg/L). These conditions were used as the setpoint for the process with DO based aeration control, and the net aeration requirement was determined. This aeration requirement was then applied for the remaining two processes to determine appropriate setpoints (off-gas N_2O concentration and air flow rate for off-gas N_2O based aeration control and constant airflow operation, respectively). A summary of the process inputs, outputs and emission concentrations for high DO operation is provided as **Table 5-26**, and response profiles are presented in **Figure 5-31**.

Table 5-26 Evaluation of control performance – high DO (3 mg/L) operation.

Control type		DO control	N_2O control	Uncontrolled
Setpoint		DO = 3 mg/L	N_2O = 0.9963 ppm	N/A
Total air input (L)		5510	5510	5510
Net process outputs				
NH_4^+ (mg)		2.41	2.41	3.47
NO_2^- (mg)		2.27	2.27	2.84
N_2O (mg)		17.0	17.0	17.8
Emission concentrations				
NH_4^+ (mg/L)	Average	0.06	0.06	0.08
	Maximum	0.10	0.09	0.21
	Minimum	0.02	0.02	0.01
DO (mg/L)	Average	2.95	2.95	2.94
	Maximum	3.09	3.15	5.76
	Minimum	2.86	2.69	0.94
NO_2^- (mg/L)	Average	0.05	0.05	0.07
	Maximum	0.09	0.09	0.15
	Minimum	0.02	0.02	0.01
N_2O (mg/L)	Average	1.04	1.04	1.09
	Maximum	1.15	1.14	1.42
	Minimum	0.92	0.92	0.82

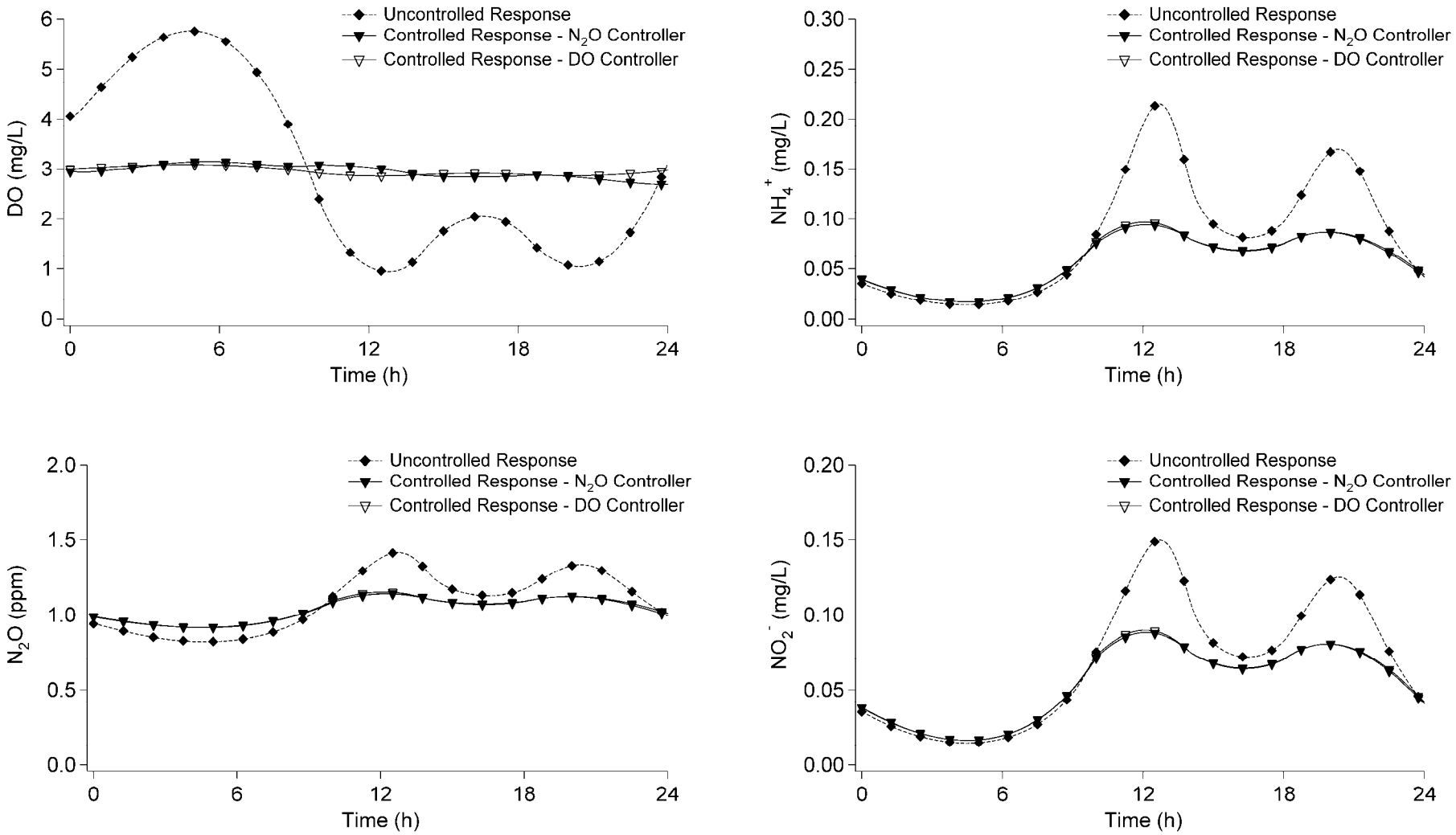


Figure 5-31 Process response - high DO (3 mg/L) operation.

Both forms of aeration control had similar performance in terms of net process emissions, achieving reductions relative to the uncontrolled scenario of 31%, 20%, and 4.5% for NH_4^+, NO_2^-, and off-gas N_2O, respectively. The dynamic profiles for the controlled processes (**Figure 5-31**) were also quite similar, with little significant difference between the emission concentrations of the parameters of interest. It can also be seen from this plot that emission reductions were predominately a result of better control during the elevated loading parts of the diurnal influent variation, with the controlled and uncontrolled response profiles being similar during the low loading periods.

A second controller performance evaluation was conducted at a lower operating DO concentration (1 mg/L). A summary of the process inputs, outputs and emission concentrations is provided as **Table 5-27**, and process response profiles are presented in **Figure 5-32**.

Table 5-27 Evaluation of control performance – low DO (1 mg/L) operation.

Control type		DO control	N_2O control	Uncontrolled
Setpoint		DO = 1 mg/L	N_2O = 1.258 ppm	N/A
Total air input (L)		4074	4074	4074
Net process emissions				
NH_4^+ (mg)		4.93	5.00	124.92
NO_2^- (mg)		3.66	3.73	14.84
N_2O (mg)		20.0	20.2	33.3
Emission concentrations				
NH_4^+ (mg/L)	Average	0.12	0.12	3.00
	Maximum	0.22	0.16	8.66
	Minimum	0.02	0.05	0.02
DO (mg/L)	Average	1.02	0.89	1.65
	Maximum	1.12	1.34	4.80
	Minimum	0.95	0.36	0.18
NO_2^- (mg/L)	Average	0.09	0.09	0.36
	Maximum	0.15	0.12	0.84
	Minimum	0.02	0.05	0.02
N_2O (mg/L)	Average	1.22	1.24	2.04
	Maximum	1.43	1.32	3.57
	Minimum	1.02	1.13	0.85

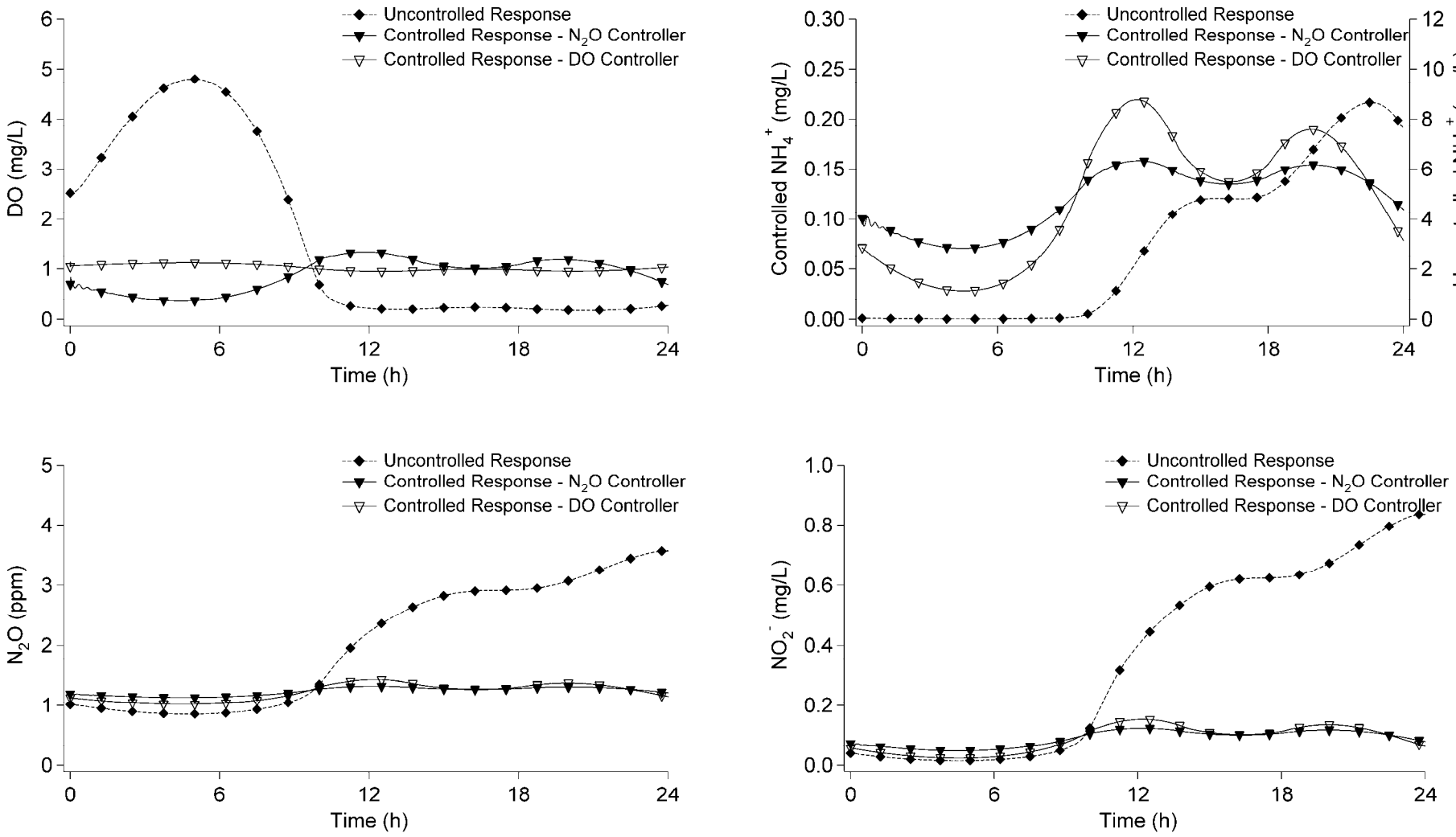


Figure 5-32 Process response - low DO (~ 1 mg/L) operation.

Both forms of aeration control had similar performance in terms of net process emissions (< 2% difference), achieving reductions relative to the uncontrolled scenario on the order of 96%, 75%, and 40% for NH_4^+, NO_2^-, and off-gas N_2O, respectively. These large emissions reductions were due to the significant nitrification inhibition experienced by the uncontrolled process during periods of elevated loading, where removal efficiency decreased to 66%.

It is interesting to note that while the overall performance of the two controllers was quite similar, differences existed between the response profiles. Off-gas N_2O based aeration control provided a more dampened variation in the NH_4^+ response, with increased NH_4^+ concentrations during the reduced loading portion of the diurnal variation, and much reduced concentrations during the period of elevated loading. While the NO_2^- and off-gas N_2O concentration profiles were quite similar, DO based aeration control provided profiles with smaller levels of variation.

Overall, the results indicated that off-gas N_2O based aeration control was capable of providing an equivalent level of process control and operational benefits as conventional DO based aeration control. The controlled process responses were similar at DO concentrations of 3 mg/L, with off-gas N_2O aeration control providing better mitigation of peak NH_4^+ emission concentrations as the operating DO decreased.

The controlled processes were able to provide high levels of NH_4^+ removal even at reduced operating DO concentrations. Compared to a process operating at 3 mg/L, operation at 2 mg/L and 1 mg/L utilized approximately 16.5% and 35.5% less aeration air, respectively. These reductions represent substantial energy and cost savings. However, it should be noted that this assessment does not include other practical considerations related to activated sludge process operation at low DO concentrations, such as sludge settling properties. In addition to process control, the application of off-gas N_2O monitoring for low DO processes could enhance process operation by providing real-time knowledge of process metabolic status which could enhance decision making processes.

While the results of this analysis are quite favourable, it should be noted that they are dependent on the off-gas N_2O model component of the process simulator. The

lack of a mechanistic model for off-gas N_2O generation as an AOB stress response is a limitation for this work. Furthermore, the simulation results would be dependent on process operating conditions, influent properties (concentrations and variations), and process biokinetics. Due to all these dependences, as well as the lack of a mechanistic off-gas N_2O model, field trials (preferably at pilot or full scale) are necessary to provide a thorough assessment of the off-gas N_2O based aeration control concept, and explore any practical limitations encountered during reduced DO operation.

5.5 Summary

An aeration control concept was developed based on the utilization of off-gas N_2O concentrations as a real-time indicator of nitrification inhibition dynamics, and aeration flow as the master control variable. This process control concept was tested on two simulated activated sludge processes based upon independent datasets (Cranfield and UNSW data) to demonstrate its feasibility and to estimate application benefits (in terms of aeration and emission reductions) to support the environmental and economic evaluation components of **Chapter 6**.

The application of off-gas N_2O based aeration control to both of the simulated activated sludge processes was tested by subjecting the controlled processes to short term influent variations (shock loadings) and diurnal variations of influent concentrations (representing normal process variation). Results of these simulations (presented in **Sections 5.4.1** and **5.4.2** for the Cranfield and UNSW processes, respectively) demonstrated the effectiveness of this form of aeration control, which was able to maintain the processes at the desired operating setpoints and avert nitrification failure by providing better matching between aeration supply and metabolic demand.

Performance of off-gas N_2O based aeration control was compared with conventional DO based aeration control and constant airflow operation (uncontrolled operation) to provide an estimate of the benefits of applying this control technique. Aeration reductions (relative to the uncontrolled process) on the order of 20.4% and 22.2% were achieved through the utilization of DO and off-gas N_2O based aeration control, respectively.

The performance of both forms of aeration control was demonstrated to be similar in terms of control efficiency (i.e. ability to control undesirable process emissions using the same amount of aeration air supply). Net emission reductions (relative to the uncontrolled process) were dependent on the operating DO, with the application of process control having the greatest benefits at lower operating DO concentrations where influent fluctuations result in significant inhibition in the

uncontrolled process. Emission reductions ranged from 31% to 96% for NH_4^+, 20% to 75% for NO_2^-, and 4.5% to 40% for off-gas N_2O.

Overall, while both forms of aeration control were shown to be quite similar in terms of performance, the off-gas N_2O based aeration control concept was slightly more efficient, utilizing less aeration and providing better mitigation of peak response concentrations during periods of elevated loading. Furthermore, its performance improved relative to DO based aeration control when the operating DO concentrations were decreased, likely due to enhanced matching of aeration supply and demand as well as more aggressive application of aeration.

Enhanced aeration control could allow for reductions in the typical factors of safety applied to operating DO concentrations for full scale activated sludge processes. Operation at reduced DO concentrations could achieve substantial savings in aeration (up to 35.5% for operation at 1 mg/L DO compared to 3 mg/L), although other practical aspects related to activated sludge process operation at low DO concentrations need to be considered in evaluating the feasibility of such an application.

While the results of the analysis were quite favourable and have demonstrated the potential benefits of enhanced aeration control via off-gas N_2O monitoring, the lack of a mechanistic model for off-gas N_2O generation and observed temporal variations in the off-gas N_2O stress response introduce uncertainty into the simulation results. Furthermore, the results of this analysis are highly dependent on process operating conditions, influent properties (concentrations and variations), and process biokinetics. Field trials are necessary to provide a thorough assessment of the proposed off-gas N_2O aeration control concept and investigate several of the practical implementation issues which will be discussed in the technical evaluation component of **Chapter 6**.

Chapter 6 Aeration Control Concept Evaluation

In **Chapter 5**, a non-invasive off-gas N_2O monitoring based process control concept was proposed for nitrifying activated sludge processes. A basic feedback implementation of this concept was evaluated and potential benefits (in terms of aeration efficiency and effluent quality) were quantified. With potential benefits having been demonstrated through process simulation, the next step was to evaluate the concept at pilot scale. While full application of the control concept was beyond the scope of this work, technical and economic/environmental evaluations of the proposed control concept were conducted to support future implementation.

The technical evaluation (**Section 6.1**) was conducted to identify potential technical limitations and aspects requiring further investigation and development. This evaluation was split into two components; physical implementation of the process monitoring element of the control system (**Sections 6.1.1**), and implementation of specific aeration control strategies utilizing this concept (**Section 6.1.2**). Finally, an economic and environmental evaluation of the implementation of off-gas N_2O monitoring based aeration control strategies was conducted to identify potential benefits to provide motivation for future work. The results of this evaluation are presented in **Section 6.2**.

6.1 Technical Evaluation

6.1.1 Off-gas N_2O Monitoring Implementation

As the first part of the process control chain, process monitoring has a strong influence on the overall success of any implemented control strategy. In particular, process monitoring must be representative, accurate, reliable, and have a suitable response time. Off-gas monitoring systems typically consist of three distinct components, namely sample collection, conditioning, and analysis (**Figure 6-1**).

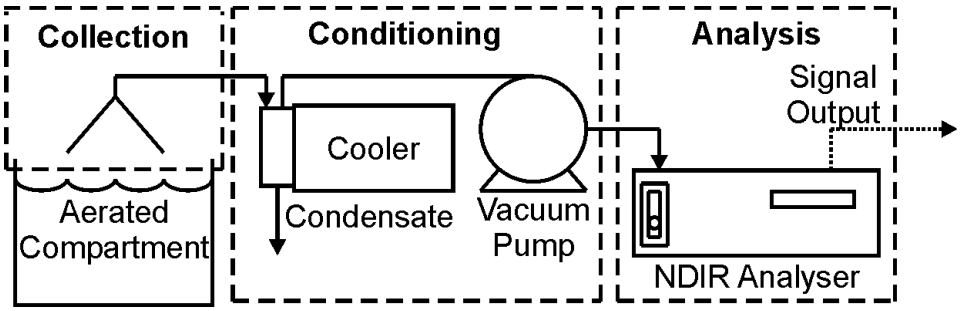


Figure 6-1 Process off-gas monitoring system.

The individual components of the system utilized in this work have been discussed in depth in **Section 3.2**. This assessment will instead focus on broader implementation issues which are relevant regardless of the specific equipment type.

Sample Collection

While the off-gas analyser and sample conditioning system can be utilized at pilot and full scale directly, modifications to the sample collection system will be required to make the transition. For the laboratory scale bioreactor it was feasible to place a hood over the aerated portion of the process and collect the majority of the off-gas, with the sample being withdrawn from the headspace created in the hood. This method of gas collection would not be feasible from a practical perspective for full-scale processes.

A more feasible approach is the utilization of smaller hoods to collect a localized off-gas sample for analysis. Examples of the application of this approach for off-gas

analysis from wastewater treatment aeration tanks have been presented in the literature (Benckiser et al. 1996; Clark 2000; Sumer et al. 1995). Two primary approaches have been utilized; floating hoods (Benckiser et al. 1996; Sumer et al. 1995) and partially submerged fixed hoods (Clark 2000).

The use of floating and fixed sample collection hoods has the advantage of obtaining the off-gas sample directly from the wastewater, minimizing dilution of the sample by the outside atmosphere. However, none of the sampling events reported in the literature were conducted on long term bases, and thus do not address fouling concerns related to the contact between the sample collection hood and the wastewater. While not as significant as for direct sampling techniques where filtration is required, material transported by bio-aerosols (generated as the aeration air bubbles through the wastewater) would impinge and accumulate on the inside the hood, requiring periodic cleaning. Furthermore, the potential exists for foam to accumulate inside the hood during foaming events, which could clog the collection system or in the worst case foul the sample conditioning and analysis equipment. Lacking a long-term onsite evaluation of the operation of these collection systems, fouling severity and the associated maintenance requirements cannot be determined, although the potential exists to mitigate some of these shortcomings through improved sample hood design.

An alternative sample collection technique would be the use of hoods suspended above the wastewater, creating a truly non-invasive monitoring system. While there would still be some fouling due to bio-aerosol material transport, it would likely be less significant than for direct contact sample collection systems, and the non-invasive system would be much less susceptible to foaming. However, elevating the hood introduces the potential for atmospheric intrusion into the sample, resulting in some sample dilution and a corresponding loss of sensitivity. The significance of this intrusion would need to be assessed through application on a full-scale process.

The specific location of the sample hoods within the process is an important technical consideration. As noted by Clark (2000), the ideal location for the sample hoods would be in the centre of the aeration lane. This would serve to reduce the impact of non-ideal flow around edges of the process and improve response time. While it would be possible to install floating hoods in such a location, the

installation of fixed or suspended hoods in the centre of processes would likely be difficult and costly. It is likely that fixed or suspended hoods would be located near the edges of the reactor for practical purposes, allowing easy access for maintenance and cleaning (Clark 2000). It should be noted that proximity to the edge of the aeration lanes could be an added concern for suspended hoods since here would be a greater potential for atmospheric intrusion.

Overall, the sample collection system utilized for off-gas N_2O monitoring is relatively simple in nature, with no mechanical components to wear. This system would be fairly low maintenance compared to conventional invasive liquid phase process monitoring techniques. While there is a need for further evaluation and development (particularly with regards to air intrusion and the impacts of fouling and foaming for non-invasive and invasive sample collection techniques, respectively), the system appears to be feasible from a technical standpoint.

Sample Conditioning

The sample conditioning component of the process is utilized to remove moisture and protect the upstream instrumentation. Peltier type gas coolers have a long history of application for industrial gas emission sampling, and as a result have been developed to the point where they are fairly low maintenance and highly reliable. The gas cooler utilized in this study did not require any significant maintenance during 2 years of continuous operation. While there is a requirement for periodic emptying of the condensate trap, it is possible to connect the trap to a control valve to automatically empty the trap at predefined intervals.

One issue of concern which arose during operation was condensation in the tubing used to transport the off-gas from the collection system to the conditioner. This issue was seasonal in nature, being most significant during the winter (reduced ambient temperature). The presence of condensate in the tubing has two primary effects; it creates a greater pressure drop in the system, increasing the demand on the sample pump, and it causes the sample gas to be sparged before going to the analyser, potentially capturing some of the analyte of interest and reducing the system accuracy. Condensation would be increasingly significant for full scale applications with longer sample lines. Two potential solutions are moving the sample conditioning system closer to the process (shortening the lines), and heating

and/or insulating the sample line to prevent condensation. While heating the sample lines would increase operating costs, with the small gas flows required by the analyser (<1 L/min), combined with proper tube insulation it would likely be a relatively small increase. Heating the lines would allow for more flexibility in terms of installation, and allow a centralized conditioning system to be used.

Analysis

Off-gas analysis was conducted using a NDIR based continuous emissions monitor (CEM). These monitors are readily available, and have a long history of application in industrial settings (particularly in the petroleum and power industries) to continuously monitor emissions from a wide range of processes. As such, they have seen substantial refinement and are well suited to the demands of industrial applications.

Providing the other components of the sampling system (sample pump, conditioning system, and flow/pressure regulation) are operating properly, these analysers are extremely reliable and require minimal maintenance. Furthermore, the instruments are very stable and do not require frequent recalibration. While calibration checks were performed on the analyser in the lab unit on a weekly basis, the unit was extremely stable and only required recalibration on a monthly basis (a 5 minute procedure). While more frequent verification and calibration is desirable for a full scale application, the associated time demand can be reduced substantially through automation. CEMs are suitable for integration into existing data collection and control systems. With the installation of control valves to switch between calibration gases and the off-gas sample flow, the entire calibration process can be automated. Routine calibration checks (and recalibration if required) can be conducted automatically, and the instrument can be set to report any faults or excessive deviations from the calibration to ensure that maintenance is conducted in a timely fashion and minimize periods of instrument failure.

6.1.2 Process Control Application

Consideration will next be given to the means in which the data generated by the off-gas N_2O monitoring system could be incorporated into aeration control strategies. As discussed previously, off-gas N_2O concentrations act as an indicator of the metabolic status of autotrophic bacteria. The presence of N_2O in the off-gas indicates AOB metabolic inhibition and is fundamentally similar to NH_4^+, whose presence is also an indicator of metabolic inhibition (albeit a more indirect indicator). It is thus possible to utilize off-gas N_2O monitoring as a replacement for NH_4^+ monitoring in many of the control strategies reviewed in **Section 2.4.3** (in particular direct feedback control, feedback supervisory control, and feedback control to supplement feedforward control strategies).

As an indicator of process overloading, off-gas N_2O monitoring could form the basis for process capacity control strategies to tailor the active volume (capacity) to match the demand. It could be used as a decision making parameter in a rule (or fuzzy) based control strategy to turn on or off additional aerated volume as needed, or to manage the nitrification rates in each of the compartments to extend activity across the entire plant capacity in a method similar to that proposed by Sahlmann et al. (2004).

Since this technique is monitoring metabolic status and not a specific wastewater property, it cannot be utilized for influent based feedforward control strategies. Furthermore, at the current state of knowledge with regards to off-gas N_2O generation (discussed in **Section 2.1**), strict mechanistic modelling is not feasible and off-gas N_2O monitoring would not be suitable as a basis for model predictive control (MPC) strategies (although a very basic form could be utilized if a stable correlation is developed on a site specific basis).

While the majority of the control strategies discussed to this point utilize off-gas N_2O monitoring in a supervisory role (providing setpoints to subordinate controllers), the opportunity exists for a shift in the operating paradigm of the individual compartments. Existing processes utilize DO feedback controllers as subordinate controllers, implementing setpoints based on a desired operating efficiency. As DO is an indirect and rough measure of operating efficiency, the

potential exists to achieve a finer level of control by directly controlling the inhibition (and hence nitrification efficiency) using an off-gas N_2O based feedback control strategy directly manipulating the aeration flow rate (similar to the control strategy evaluated in **Chapter 5**). This form of control would also remove the requirement for invasive liquid phase sensors in the individual aerated compartments.

While the potential exists to incorporate this monitoring technique into a wide range of control strategies, a number of issues must be considered prior to implementation, in particular the applicability of the control strategy to specific processes, and response stability.

Applicability

A primary limitation with off-gas N_2O monitoring based control strategies is the dependence on the presence of AOB to generate the stress response of interest. These control strategies would not be applicable to anaerobic or anoxic processes, or to aerobic processes which support a minimal AOB population.

While the data presented in Burgess et al. (2002b) described the off-gas N_2O response as a function of NH_4^+ shock loadings, it did not address the simultaneous changes in both COD and NH_4^+ loadings, which are commonly seen in wastewater treatment processes. These forms of combined loading changes were addressed in **Chapter 4**, and it was demonstrated that the autotrophic stress response was sufficiently sensitive to detect these loading changes. Since AOB are more sensitive to inhibition by reduced DO concentrations than heterotrophic bacteria, control of combined COD removal and nitrification processes using AOB stress responses would provide appropriate conditions for the growth of heterotrophic bacteria.

As discussed in **Section 2.1.4**, a broad range of bacteria and mechanisms can produce N_2O, which can be stripped to the off-gas by aeration, producing a mixed off-gas signal. In situations where a large portion of the off-gas N_2O is produced by processes which cannot be controlled by changes in aeration flow (such as the inhibition of nitrifying bacteria by chemical substances, or heterotrophic denitrification), the controllability of the process will be limited.

Burgess et al. (2002b) presented data demonstrating that an N_2O stress response was obtained following the application of chemical inhibitors (allylthourea) that specifically block the normal metabolic pathways of nitrifying autotrophic bacteria. Since the stress response is being initiated by the chemical inhibitors and not associated with reduced DO concentrations, aeration does not provide a means of controlling the process. Thus N_2O based control strategies would not have control authority in those situations and would provide excess aeration. For processes where chemical inhibitors are an operational issue, the simultaneous application of DO and off-gas N_2O monitoring along with a form of pattern recognition may be required to identify these forms of process upset and implement appropriate remedial actions.

N_2O generation by heterotrophic denitrification is not a concern for sequential processes where denitrification follows nitrification. It is however a concern for predenitrification processes where an anoxic zone precedes the aerobic nitrification zone. Since there is no sparging of the anoxic zone by aeration air, a significant amount of the N_2O generated by incomplete heterotrophic denitrification would remain in the liquid phase until it reached the aerobic zone where it would be sparged into the off-gas, generating a false positive AOB inhibition signal. This signal would result in the controller increasing the aeration supply to the first compartment, providing excess aeration.

A further concern is the potential for a cascading effect in which the increase in aeration associated with N_2O production by heterotrophic denitrification results in an increased level of DO being sent to the anoxic zone by the internal recycle flow. The increased loading of DO would further inhibit the heterotrophic denitrification, producing more N_2O and resulting in greater increases in aeration. This cycle would continue until the controller saturates (i.e. reaches maximum aeration flow), and denitrification would be compromised. While this scenario is indeed relevant for very small processes like laboratory scale and onsite decentralised bioreactors, for large processes with multiple individually controlled compartments it would not likely be an issue, with the excess N_2O being sparged from the liquid phase fairly quickly and would be expected to only influence the first aerated compartment. The magnitude of these effects needs to be investigated at pilot scale in a multi-compartment reactor prior to application at full scale. In the event that N_2O

emissions associated with heterotrophic denitrification significantly interfere with off-gas N_2O based controls strategies, it is possible that having a small aerobic zone operated at a constant air flow rate to sparge any accumulated N_2O prior to entering the controlled aeration zones could eliminate the interference.

Finally, it should be noted that since the off-gas N_2O monitoring technique is dependent on N_2O being stripped from the liquid phase by the aeration air, the monitoring system will not receive data in the event of an aeration failure. Aeration failures would have to be detected separately in a fully automated facility.

Response Stability

The long-term stability of the off-gas N_2O stress response (in terms the N_2O generation rate relative to the level of AOB inhibition) is essential in the development of off-gas N_2O monitoring based control strategies. These strategies require the selection of off-gas N_2O setpoints which correspond to a desired level of AOB inhibition (and hence process performance), and any variation in the relationship between the two would have a negative impact on the quality of control.

Results of the stress response analysis presented in **Chapter 4** raise questions with regards to the stability of the stress response. A very strong temporal effect existed in the collected data, although it could not be definitively concluded if the variability was inherent in the response or a function of other experimental factors. Variability was also observed between the responses obtained using two samples of activated sludge collected from the same process (and at the same sampling location) approximately 5 weeks apart, suggesting a variation in the biological makeup in the process. These results highlight potential seasonal effects which may need to be accounted for in control strategy development. Long-term investigation is required at pilot or full scale to determine if these temporal variations do indeed exist, and to assess their magnitude and impact on off-gas N_2O monitoring based control strategies.

As the link between the liquid and gas phase N_2O concentrations, changes in N_2O mass transfer rates could have an impact on the magnitude of the observed stress responses for a given level of AOB metabolic inhibition. Specifically, changes in aeration flow to the compartments could change the characteristics of the aerator

bubble patterns (size and quantify), altering the N_2O mass transfer rate. In addition, changes in aeration flow rates would also effect the dilution of the N_2O transferred to the process off-gas. The results presented in **Chapter 4** were conducted at a constant aeration rate to isolate the data from these effects, thus no conclusion can be reached with regards to their importance. No published assessment of these effects is currently available in the literature, and future work is required to determine if mass transfer effects introduced by aeration air flow changes have any significant detrimental impacts on off-gas N_2O monitoring based control strategies.

6.1.3 Technical Feasibility

The off-gas N_2O monitoring system would be a relatively simple addition to existing wastewater treatment processes. Other than requiring a weatherproof shelter and power, the conditioning and analysis system can be installed "off the shelf" and requires significantly less maintenance than conventional invasive process monitors. Some technical challenges remain with regards to sample collection and conveyance to the conditioning system, and further development is required at full scale to assess and address the effects of aerosol fouling, foaming, and sample condensation.

From a control strategy perspective, the potential exists to apply off-gas N_2O monitoring as the basis for a range of aeration control strategies including feedback control (both direct control and in a supervisor role) and process capacity (aeration volume) control. Off-gas N_2O monitoring is not suitable for influent based feedforward control strategies, and at the current level of mechanistic knowledge it is not suitable for advanced MPC strategies. With a dependence on the presence of AOB, this monitoring technique would not be a suitable as a basis for aeration control strategies for anaerobic or anoxic processes, nor for aerobic processes which support a minimal population of autotrophic bacteria. However, the results presented in **Chapter 4** demonstrate that it would be a suitable basis to develop aeration control strategies for combined COD removal and nitrification processes.

Some controllability concerns exist with regards to N_2O generation associated with predenitrification processes and chemical inhibitors, as well as with regards to the

long-term stability of the off-gas N_2O stress response and impacts of changes in mass transfer properties associated with aeration flows. Long-term investigation is required at pilot or full scale to determine the level of significance associated with each of these concerns and to develop appropriate form of mitigation where required.

6.2 Economic and Environmental Evaluation

While the potential for non-invasive aeration control using off-gas N_2O monitoring has been demonstrated in **Chapter 5**, a need exists to extend investigation from simulation and lab-scale environments to pilot and full scale processes. In addition to investigating the technical issues outlined in **Section 6.1.3**, an important part of any pilot or full scale work would be to provide further clarification of the potential environmental and economic benefits associated with improved aeration control.

The objective of the following economic and environmental evaluation is to identify potential benefits that could provide motivation for further research, development, and eventual uptake of this aeration control technique. Furthermore, this evaluation is intended to provide some direction for future work to explore these benefits.

6.2.1 Economic Evaluation

Economics are a very strong driver for operational decisions in wastewater treatment plants. Indeed, it has been indicated that the primary rationale for the installation of process control and automation has been to realize energy, consumable and labour cost savings (Hill et al. 2002). Potential economic benefits associated with the implementation of off-gas N_2O monitoring based process control strategies can be grouped into four main categories:

- instrumentation costs;
- energy savings;
- process capital investment; and
- improved compliance.

Cost savings associated with each of these aspects will be discussed in the following subsections. An in-depth cost based analysis was beyond the scope of this work. With the high level of variability introduced by the site and process specific nature of construction and operating/maintenance costs, an in-depth analysis would be of limited benefit without data from a full scale application of the aeration control

technique being evaluated. Economic benefits will instead be discussed in a more qualitative manner.

Instrumentation Costs

A range of costs are associated with process instrumentation, in particular instrument acquisition, equipment installation, and operating costs. With regards to off-gas N_2O monitoring equipment, the NDIR analyser and sample conditioning equipment (gas cooler, pressure/volume flow control) cost on the order of $8000 to $14000 AUD, which is similar in magnitude to the reported acquisition costs for existing liquid phase nutrient sensors (Winkler et al. 2004). In terms of installation costs, there would likely be a fairly similar level of investment required for physical infrastructure and services. Installation of the sample hood would have a similar cost as installation of liquid phase sensors into aeration lanes, although specific design and installation of hoods remains to be determined and the ultimate design would have an impact on the installation cost.

The primary difference between off-gas N_2O monitoring and invasive liquid phase monitoring techniques is operating cost. With minimal requirements for analyser maintenance, and ease of operation, it is likely that off-gas N_2O monitoring would achieve a significant reduction in maintenance costs compared to conventional liquid phase monitoring techniques. The primary source of ongoing maintenance would be cleaning the sample collection hood, but this needs to be evaluated at full scale to assess fouling issues for various configurations and estimate maintenance requirements.

Energy Savings

In assessing potential energy savings associated with improved aeration control, it is useful to put these costs in perspective against the overall wastewater treatment plant costs. Gratziou et al. (2005) developed cost functions to predict costs for a range of wastewater treatment processes constructed in Greece. These functions indicated that for wastewater treatment plants based on conventional activated sludge processes, construction cost ranged from 58.8% to 64.6% of the total costs, with operational and maintenance costs accounting for the remainder (Gratziou et al. 2005).

For medium sized plants of 10000 to 100000 population equivalent (pe), operational and maintenance costs break down to 56% personnel costs, 28% energy costs, and 16% for maintenance and chemical costs (Gratziou et al. 2005; Tsagarakis et al. 2003). The breakdown of these costs is dependent on the size of the plant, as economies of scale exist, in particular with regards to personnel costs. Based on a survey of Greek wastewater treatment plant costs, Tsagarakis et al. (2003) determined that for plants over 100000 pe, the operation and maintenance cost distribution shifts towards energy costs (47% personnel costs, 36% energy costs, 17% chemical and maintenance) . This trend was also confirmed by Gratziou et al. (2005).

With energy costs on the order of 36% of total facility operating costs (and increasing in importance with plant size), improved control of energy consumption at wastewater treatment plants has the potential to realize significant operating cost reductions. Compressors (for aeration) and pumps (bulk wastewater flow, sludge waste, and internal recycle pumps for predenitrification) are the primary energy consumers at wastewater treatment plants which have potential to be controlled. Indeed, aeration has been identified as the single largest energy consuming component of most biological wastewater treatment processes, and has been reported to be on the order of 50% of the total plant-wide energy consumption (Ferrer et al. 1998; Ingildsen et al. 2002), although for some plants aeration can have an even higher relative energy demand, approaching 60% to 80% of total plant-wide energy consumption (Chachuat et al. 2005a; Hamilton et al. 2006).

The possibility exists to achieve reductions in aeration energy requirements both through improvements in the operation of compressors which supply the pressurized air to the headers (**Section 2.4.3.4**), as well as in the supply of aeration to the bioreactors (**Section 2.4.3.1** to **2.4.3.3**). These savings are on the order of 10% for improved compressor control (Alex et al. 2002; Hewitt 1996), and 6-28% for enhanced aeration control (**Section 2.4.4**). A basic feedback off-gas N_2O based aeration control strategy was evaluated in **Chapter 5** and demonstrated to have slightly superior performance to constant setpoint DO based feedback strategy (~2% improvement), although the potential exists for improved reductions for operation at reduced DO concentrations, as well as through control strategy refinement or the application of more advanced control strategies such as those outlined in **Section 6.1.2**.

Based on these estimates, upwards of 18 to 30% of total wastewater treatment plant operating costs are associated with aeration. The combination of both compressor and aeration control could result in savings on the order of 5-10% of total plant-wide operating costs. Thus increases in aeration efficiency through improved control have the potential to have a significant impact on plant operating budgets.

In considering these numbers, it should be noted that cost analyses are site specific in nature, with a high level of variability in the specific cost components. For example, as noted by Tsagarkis (2003), personnel costs range between 24-48% in Europe, but can reach up to 70% in developing countries. Furthermore, the majority of economic data was reported for conventional activated sludge processes and not predenitrification processes. For predenitrification processes, it would be expected that energy costs would be an even larger component of operating costs, in particular due to increased oxygen demands associated with nitrification as well as additional pumping costs for internal recycle flows. A need thus exists to further clarify economic benefits associated with improved aeration control for predenitrification processes.

Process Capital Investment

Improved aeration control has been recognized as an efficient means of increasing facility throughput without increasing reactor size, i.e. capital cost investment (Vanrolleghem et al. 1994; Vanrolleghem and Lee 2003), allowing the deferment of process capacity upgrades. Furthermore, if incorporated at the design stage for new wastewater treatment plants, improved aeration control could allow for reduced reactor size, reducing both construction costs and land requirements.

Improved Compliance

Improved process control also has the potential to provide enhanced effluent quality, which will be discussed in **Section 6.2.2**. While there are substantial environmental benefits associated with these improvements, there can also be an associated economic value. The primary economic benefit in most jurisdictions is the avoidance of fines for failure to comply with effluent discharge regulations (which are often variable based on the regulatory body, as well as with the severity and frequency of infractions).

However, in some European jurisdictions a taxation style approach is applied to the regulation of wastewater effluent discharges (Stare et al. 2007; Vanrolleghem and Gillot 2002). In these regulatory regimes, charges are assigned on a per kg of pollutant emitted basis, with a base rate for emissions up to an established discharge threshold, and increased rates for emission exceeding the threshold. Thus, a financial incentive exists to not only comply with emission guidelines, but also to minimize emissions.

6.2.2 Environmental Evaluation

Assessment of environmental benefits associated with improved wastewater treatment plant process control has traditionally focused on regulated liquid phase pollutants. While these pollutants are indeed important, in a regulatory environment which is becoming increasingly concerned with greenhouse gas emissions (and moving towards full process emission accounting), the control of gas phase emissions are also of interest.

Both liquid and gas phase emissions will be discussed. However, similar to the economic assessment, emissions are highly dependent on process and operating conditions, and the relative importance of specific pollutants is dependent on local regulatory priorities. Thus specific emissions will not be discussed, and this evaluation will be conducted in a qualitative manner to highlight issues of interest for future research and evaluation.

Liquid Phase Emissions

The pollutants of primary interest for BNR processes are NH_4^+ (a cause of eutrophication and removed through nitrification), and NO_2^-/NO_3^- (toxic to marine life and removed through denitrification). Since this work focuses on nitrification process, this discussion will be limited to NH_4^+. As seen in the literature (summarized in **Table 2-7**), as well as in the results presented in **Section 5.4.3**, improved aeration control allows substantial reductions in both average and peak NH_4^+ emissions and maintains treatment integrity during episodic events such as rain storms or intermittent/accidental industrial discharges.

While there has been a move in some jurisdictions towards continuous monitoring for discharge flow rates and volumes, there remains a dependence on grab sampling to assess compliance for specific pollutants (Bogue et al. 1999). This allows more flexibility and room for deviation from regulated emission limits, particularly when compliance is measured on an average emissions concentration basis.

With increasing uptake and confidence in online instrumentation, it is only a matter of time before wastewater regulations will follow suit with air emission regulations for large sources and adopt continuous emission monitoring. Process performance would be transparent in a continuously monitored regulatory environment, with any violation of discharge limits being identified and reported. As such, a premium would be placed on improved performance and ensuring compliance at any given time and advanced control would become a fundamental component of wastewater treatment plants.

Gas Phase Emissions

While gas phase emissions are not traditionally a concern for wastewater treatment plants (with the exception of odour emissions), gas phase emissions from anthropogenic processes are receiving increased levels of scrutiny (especially those emissions identified as greenhouse gases), with a gradual movement towards establishing some form of emission regulation. Two forms of gas phase emissions are possible from BNR processes; direct process emissions, and indirect emissions associated with activities supporting the operation of the process (commonly the energy used to operate process equipment such as compressors and pumps).

Direct process emissions of interest from BNR processes include a range of oxidized nitrogen compounds (NO, NO_x, N_2O) produced by both aerobic and anoxic processes (discussed in **Section 2.1**). While NO and NO_x are of primarily of interest as conventional air contaminants, their production is primarily associated denitrification processes and is beyond the scope of this work. Off-gas N_2O emissions are of particular interest as it is a potent greenhouse gas. N_2O has a 100 year global warming potential of 296, thus a 1 kg emission has an equivalent contribution to global warming as a 296 kg emission of CO_2 when considered over a 100 year time interval (Intergovernmental Panel on Climate Change 2001).

Off-gas N_2O monitoring based nitrification control offers many benefits in a regulatory environment where these emissions are of interest. As demonstrated in **Chapter 4** and in the literature (Burgess et al. 2002a; Burgess et al. 2002b; Butler et al. 2005; Butler et al. 2009; Stuetz et al. 2003), off-gas N_2O emissions from nitrification processes are strongly dependent on influent and process operating conditions. As a result, these emissions can vary significantly from process to process, introducing significant uncertainty into emissions estimates using standardized emission factors. Off-gas N_2O monitoring eliminates that uncertainty, improving the accuracy of emissions reporting and allowing plants to gain benefits in terms of emission reductions due to improved process operation. There also may be a use for off-gas N_2O monitoring to verify denitrification efficiency and confirm that the process is reaching completion, i.e. producing N_2 and not N_2O.

Furthermore, if implemented as a control strategy (as seen in **Chapter 5**), off-gas N_2O monitoring would allow for the direct control of off-gas N_2O emission from nitrification processes. While this control would be useful on its own, benefits would be maximized through incorporation into a multicriteria control strategy to achieve an optimal balance between gas phase emissions, liquid phase emissions, and operating costs. Control of off-gas N_2O emissions could also be important for emerging BNR processes such as OLAND, CANON, SHARON, and Anammox. These processes require operation at suboptimal conditions that could result in significant off-gas N_2O emissions.

Indirect emissions are of importance in a total emission accounting regulatory regime, which is quite likely for greenhouse gas emissions. While indirect emissions are associated with a range of activities including sludge and chemical transportation, the primary indirect emissions of interest for nitrification processes are gas phase emissions from the power plants that generate the electricity required to operate compressors and pumps. These emissions include both conventional air contaminants such as SO_2, NO_x, and particulate matter, as well as CO_2 emissions (a greenhouse gas). It should be noted that the associated indirect emissions are highly dependent on the type of power plant supplying the electricity (e.g. coal, oil, natural gas, nuclear, solar, wind, or hydroelectric).

As the single largest energy consuming component of most biological wastewater treatment processes (Ferrer et al. 1998; Ingildsen et al. 2002), aeration is responsible for a significant portion of indirect emissions associated with energy generation. In **Section 6.2.1**, energy savings associated with increases in aeration efficiency through improved control were estimated to be upwards of 18 to 30%. Reductions in energy consumption would have corresponding reductions in indirect emissions, and the potential exists for significant reductions in wastewater treatment plant carbon footprints through the application of improved aeration control.

6.3 Summary

It has been demonstrated that aeration control for BNR through non-invasive off-gas N_2O monitoring is technically feasible and offers environmental and economic benefits, including reduced operating costs and process capital investment, improved compliance with discharge guidelines, and reductions in direct and indirect emissions. However, several gaps exist which must be addressed before this control technique can be applied to full scale processes.

Some concerns exist with regards to process controllability (due to N_2O generation associated with predenitrification processes and chemical inhibitors), as well as with the long-term stability of the off-gas N_2O stress response and impacts of changes in mass transfer properties associated with variations in aeration flow rate. Furthermore, technical challenges remain for sample collection and conveyance to the conditioning system, particularly in relation to the impacts of fouling, foaming, and sample condensation.

Long-term investigation is required at pilot or full scale to determine the level of significance associated with each of these concerns and to develop appropriate forms of mitigation where required. A need also exists to develop clear quantifications of the economic and environmental benefits associated with the implementation of improved aeration control on predenitrification processes.

Chapter 7 Conclusions and Recommendations

This research study detailed the development and evaluation of a non-invasive process monitoring based aeration control strategy for nitrification processes. The control strategy was based on off-gas N_2O monitoring. During the course of the research, the following key objectives were achieved:

- the operation of activated sludge nitrification processes was examined experimentally (**Chapter 4**) and through literature review (**Section 2.1**) to evaluate off-gas N_2O emissions under normal operating conditions and during process upset scenarios;
- a model for off-gas emissions from the studied nitrification processes was developed to correlate these emissions to liquid phase process parameters;
- a nitrification process control concept was proposed; and
- the proposed control concept was evaluated to determine the feasibility of implementation, cost effectiveness and associated environmental benefits.

A summary of the key results obtained in this work is presented as **Section 7.1**. Recommendations are provided in **Section 7.2** for future work to address identified knowledge gaps and limitations in the proposed aeration control technique.

7.1 Key Results

The dynamics of off-gas N_2O stress responses were assessed in **Chapter 4** using a laboratory scale nitrification process to determine their suitability for process control applications. Observed off-gas N_2O responses were in agreement with the prevailing mechanistic understanding of this process, with a source of process stress and the presence of the limiting substrate for the alternative metabolic pathway (NO_2^- or possibly FNA) being required for the stress response to be generated.

Evaluation of this stress-response relationship was conducted against 5 key criteria, with the results summarized in **Table 7-1**.

Table 7-1 Off-gas N2O monitoring suitability as a control parameter.

Criteria	Description	Comments
1	Presence correlated to stress	Strong correlation, only occurs in the presence of a DO depletion and NO_2 /FNA accumulation
2	Timescale suitable for process control	Response timescale on the order of 4 to 8 minutes, faster than the timescale of aeration setpoint adjustment, thus suitable.
3	Reproducible response	Variability observed, however results inconclusive due to potential influences from other processes.
4	Proportional response	Some results proportional, however temporal variability in N_2O yield indicates presence of other influences.
5	Sensitivity suitable for process control	Response is suitably sensitive in the desired operational DO range.

Overall, off-gas N_2O concentrations met the majority of the criteria, indicating a strong potential for application as a non-invasive means of aeration process control for nitrifying activated sludge processes. However, some questions did arise in relation to response proportionality and reproducibility, which will be summarized in **Section 7.2**.

A simple feedback aeration control strategy was developed in **Chapter 5** based on the utilization of off-gas N_2O concentrations as a real-time indicator of nitrification inhibition dynamics, and aeration flow as the master control variable. The control strategy was evaluated using two simulated activated sludge processes based upon independent datasets (Cranfield and UNSW data) which were subjected to short

term influent variations (shock loadings) and diurnal variations of influent concentrations (representing normal process variation).

Overall, application of the control strategy provided better matching between aeration supply and metabolic demand, allowing the process to be maintained at the desired operating setpoints and averting nitrification failure. Performance of an off-gas N_2O based aeration control strategy was demonstrated to be similar to DO based feedback aeration control, although the off-gas N_2O based aeration control concept was slightly more efficient, utilizing less aeration and providing better mitigation of peak response concentrations during periods of elevated loading. Furthermore, its performance improved relative to DO based aeration control when the operating DO concentrations were decreased, likely due to enhanced matching of aeration supply and demand as well as more aggressive application of aeration.

Aeration reductions (relative to the uncontrolled constant aeration flow process) on the order of 20.4% and 22.2% were achieved through the utilization of DO and off-gas N_2O based aeration control, respectively. Emission reductions were estimated to be on the order of 31% to 96% for NH_4^+, 20% to 75% for NO_2^-, and 4.5% to 40% for off-gas N_2O, with a strong dependence on the operating DO concentration. However, as observed in **Section 2.4.4**, care must be taken in utilizing these results due to the site and process specific nature of the results as well as limitations in existing process control strategy evaluation methodologies (discussed in **Section 7.2**).

A technical, economic and environmental evaluation the off-gas N_2O monitoring based control technique (**Chapter 6**) indicated that the control of BNR aeration through non-invasive off-gas N_2O monitoring is technically feasible and has the potential to offer significant environmental and economic benefits. Potential benefits include reductions in operating costs and process capital investment, as well as improved compliance with effluent discharge guidelines and reductions in both direct and indirect emissions of gaseous pollutants including greenhouse gases.

7.2 Limitations and Recommendations for Future Work

While the potential of off-gas N_2O based aeration control strategies to provide enhanced operation and economic/environmental benefits has been demonstrated, a number of research questions remain to be addressed. These questions are based on knowledge gaps identified in the literature review, as well as the evaluation of off-gas N_2O based aeration control. A summary of residual research questions based on the literature review, along with recommendations for future work is provided as **Table 7-2**.

In the evaluation of the off-gas N_2O based aeration control technique, a number of key knowledge gaps were identified which must be addressed to allow further implementation at pilot and full scale. In particular:

- temporal effects on off-gas N_2O yield and long-term stability;
- effect of microbiological population changes on off-gas N_2O emissions;
- impact of N_2O generated by non-AOB sources on process controllability;
- effects of changes in aeration flows on off-gas N_2O signals;
- design of off-gas sample collection equipment and assessment of maintenance and operational issues; and
- quantification of economic and environmental benefits associated with control strategy implementation.

As discussed in **Chapter 4**, a number of limitations are associated with experimental work conducted on laboratory scale bioreactors operating on synthetic wastewaters, in particular poor process stability and impacts of microbiological populations. Future work must move towards long-term field trials using pilot and full scale processes operating on real wastewater to address these limitations. Full scale application would allow investigation of practical implementation issues related to sample collection and allow a comprehensive assessment of the stability of the off-gas N_2O stress response.

It is recommended that future work focus on step response experiments or diurnal influent fluctuations instead of spike tests to eliminate adaptive effects associated

with the application of repeated stresses which are not a part of normal operation. Furthermore, future studies should be supported by microbial analysis to identify and quantify the dynamics of the AOB populations, which would greatly increase our understanding of off-gas N_2O emissions and assist in identifying any sources of observed variability. Additional studies relating to the operation of activated sludge processes at low DO concentrations should also be investigated to assess the feasibility of such an application for improved nitrogen removal in emerging BNR processes.

Overall, while off-gas N_2O monitoring based aeration control techniques have the potential to provide a significant economic and environmental benefits, a number of research questions remain to be answered and there is much room for continued research and development in this area.

Table 7-2 Literature review - residual knowledge gaps and recommendations for future work.

Topic	Knowledge Gap/Limitation	Recommended Future Work
BNR mechanisms and N_2O emissions	Limited knowledge of aerobic denitrification reaction mechanisms, substrates, and electron donors/acceptors.	Further evaluation of the role of nitrous acid as an electron acceptor for nitrifier denitrification.
	Lack of N_2O emissions data from emerging alternative nitrogen removal processes.	Pilot and full scale monitoring of off-gas N_2O emissions, evaluation of net greenhouse gas emissions from alternative nitrogen removal processes.
	Poor understanding of the importance of nitrifier denitrification in off-gas N_2O emissions as well as the influence of specific operational parameters.	Investigation of emissions from full scale processes combined with molecular analyses of AOB populations.
	Poor comparability of aerobic denitrification and N_2O generation data.	Standardize methodologies or develop best practices for data collection and emissions assessment.
Activated sludge process modelling	Lack of consensus with regards to calibration goals and requirements	Consolidation of the existing range of calibration protocols into a unified protocol.
	Limited understanding of long-term model calibration stability.	Long-term evaluation of process models applied to full scale processes, with specific focus on the duration of model calibrations.
	No existing mechanistic off-gas models for aerobic processes.	Investigation of mechanisms responsible for generation of liquid phase N_2O and of processes linking liquid phase conditions to off-gas emissions.
Non-invasive process monitoring	Effects of temporal variability of wastewater and microbiological communities on non-invasive process monitoring techniques and lack of full scale application.	Assessment long term stability and robustness of non-invasive monitoring techniques applied to full scale wastewater treatment processes.
	Limited assessment of the applicability of non-invasive monitoring techniques for process control.	Continued research and development of non-invasive techniques such as off-gas N_2O and CO_2 monitoring and their application in control strategies.
Aeration control	Poor comparability of benefits associated with improved process control.	Replace the evaluation component of the COST protocol with a practical procedure with an established basis for comparison. Develop easily interpreted performance criteria such as those based on aeration utilization.
	Limitation of process control uptake due to perception issues.	Establish a movement from simulation based studies to pilot and full scale applications to provide clear demonstrations of the benefits associated with improved control (in a quantitative manner) and address instrumentation and other practical concerns.
	Limitations in process control uptake due to barriers associated with process equipment and instrumentation.	Demonstrate and communicate the benefits associated with the application of an integrated design approach for process control and instrumentation.

Abeliovich A. 1992. Transformations of ammonia and the environmental impact of nitrifying bacteria. Biodegradation(3):255-64.

Ahn YH. 2006. Sustainable nitrogen elimination biotechnologies: A review. Process Biochemistry 41(8):1709-1721.

Alex J, To TB, Hartwig P. 2002. Improved design and optimization of aeration control for WWTPs by dynamic simulation. Water Science and Technology 45(4-5):365-372.

Amano K, Kageyama K, Watanabe S, Takemoto T. 2002. Calibration of model constants in a biological reaction model for sewage treatment plants. Water Research 36(4):1025.

Ameer Q, Adeloju SB. 2005. Polypyrrole-based electronic noses for environmental and industrial analysis. Sensors and Actuators B: Chemical 106(2):541.

Andersen JH, Schluter L, Aertebjerg G. 2006. Coastal eutrophication: recent developments in definitions and implications for monitoring strategies. Journal of Plankton Research 28(7):621-628.

Anderson DM, Glibert PM, Burkholder JM. 2002. Harmful algal blooms and eutrophication: Nutrient sources, composition, and consequences. Estuaries 25(4B):704-726.

Anthonisen AC, Loehr RC, Prakasam TBS, Srinath EG. 1976. Inhibition of nitrification by ammonia and nitrous acid. Journal Water Pollution Control Federation 48(5):835-852.

APHA, AWWA, WEF. 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed. Eaton AD, Clesceri LS, Greenberg AE, editors. Baltimore: AHPA/AWWA/WEF.

Argaman Y, Papkov G. 1995. A Steady-State Model For The Single Sludge Activated-Sludge System - 2. Model Application. Water Research 29(1):147-153.

Avcioglu E, Karahan-Gul O, Orhon D. 2003. Estimation of stoichiometric and kinetic coefficients of ASM3 under aerobic and anoxic conditions via respirometry. Water Science and Technology 48(8):185-194.

Balku S, Berber R. 2006. Dynamics of an activated sludge process with nitrification and denitrification: Start-up simulation and optimization using evolutionary algorithm. Computers & Chemical Engineering 30(3):490-499.

Balslev P, LynggaardJensen A, Nickelsen C. 1996. Nutrient sensor based real-time on-line process control of a wastewater treatment plant using recirculation. Water Science and Technology 33(1):183-192.

Baranao PA, Hall ER. 2004. Modelling carbon oxidation in pulp mill activated sludge systems: calibration of Activated Sludge Model No 3. Water Science and Technology 50(3):1-10.

Beaumont HJE, Hommes NG, Sayavedra-Soto LA, Arp DJ, Arciero DM, Hooper AB, Westerhoff HV, van Spanning RJM. 2002. Nitrite reductase of Nitrosomonas europaea is not essential for production of gaseous nitrogen oxides and confers tolerance to nitrite. Journal Of Bacteriology 184(9):2557-+.

Beline F, Martinez J, Chadwick D, Guiziou F, Coste CM. 1999. Factors affecting Nitrogen Transformations and Related Nitrous Oxide Emissions from Aerobically Treated Piggery Slurry. Journal of Agricultural Engineering Research 73(3):235.

Benckiser G, Eilts R, Linn A, Lorch HJ, Sumer E, Weiske A, Wenzhofer F. 1996. N2O emissions from different cropping systems and from aerated, nitrifying and denitrifying tanks of a municipal waste water treatment plant. Biology and Fertility of Soils 23(3):257-265.

Benes O, Spanjers H, Holba M. 2002. Respirometry techniques and activated sludge models. Water Science and Technology 46(4-5):1-6.

Bennett EM, Carpenter SR, Caraco NF. 2001. Human impact on erodable phosphorus and eutrophication: A global perspective. Bioscience 51(3):227-234.

Bernat K, Wojnowska-Baryla I. 2007. Carbon source in aerobic denitrification. Biochemical Engineering Journal 36(2):116-122.

Blackburne R, Vadivelu VM, Yuan ZG, Keller J. 2007. Determination of growth rate and yield of nitrifying bacteria by measuring carbon dioxide uptake rate. Water Environment Research 79(12):2437-2445.

Bloch H. 2001. EU policy on nutrients emissions: legislation and implementation. Water Science and Technology 44(1):1-6.

Bock E, Schmidt I, Stuven R, Zart D. 1995. Nitrogen loss caused by denitrifying nitrosomonas cells using ammonium or hydrogen as electron-donors and nitrite as electron-acceptor. Archives of Microbiology 163(1):16-20.

Bogue R, Marshallsay DR, Scott M, Thomas C, Whitworth C. 1999. On-line Instrumentation Standards and Practices. In: Industry UW, editor: UK Water Industry Reserach Limited.

Boller M. 1997. Small wastewater treatment plants -- A challenge to wastewater engineers. Water Science and Technology 35(6):1.

Bonastre A, Ors R, Capella JV, Fabra MJ, Peris M. 2005. In-line chemical analysis of wastewater: Present and future trends. Trac-Trends In Analytical Chemistry 24(2):128-137.

Bourgeois W, Burgess JE, Stuetz RM. 2001. On-line monitoring of wastewater quality: a review. Journal of Chemical Technology and Biotechnology 76(4):337-348.

Bourgeois W, Gardey G, Servieres M, Stuetz RM. 2003a. A chemical sensor array based system for protecting wastewater treatment plants. Sensors and Actuators B: Chemical 91(1-3):109-116.

Bourgeois W, Hogben P, Pike A, Stuetz RM. 2003b. Development of a sensor array based measurement system for continuous monitoring of water and wastewater. Sensors and Actuators B: Chemical 88(3):312-319.

Bourgeois W, Romain AC, Nicolas J, Stuetz RM. 2003c. The use of sensor arrays for environmental monitoring: interests and limitations. Journal of Environmental Monitoring 5(6):852-860.

Bourgeois W, Stuetz RM. 2002. Use of a chemical sensor array for detecting pollutants in domestic wastewater. Water Research 36(18):4505-4512.

Bro R. 2006. Review on Multiway Analysis in Chemistry - 2000-2005. Critical Reviews in Analytical Chemistry 36(3-4):279-293.

Brouwer H, Bloemen M, Klapwijk B, Spanjers H. 1998. Feedforward control of nitrification by manipulating the aerobic volume in activated sludge plants. Water Science and Technology 38(3):245-254.

Burgess JE, Colliver BB, Stuetz RM, Stephenson T. 2002a. Dinitrogen oxide production by a mixed culture of nitrifying bacteria during ammonia shock loading and aeration failure. Journal of Industrial Microbiology & Biotechnology 29(6):309-313.

Burgess JE, Stuetz RM, Morton S, Stephenson T. 2002b. Dinitrogen oxide detection for process failure early warning systems. Water Science and Technology 45(4-5):247-254.

Butler MD, Stephenson T, Stokes L, Stuetz RM. 2005. Dinitrogen oxide detection for nitrification failure early warning systems. Water Science and Technology 52(8):249-256.

Butler MD, Wang YY, Cartmell E, Stephenson T. 2009. Nitrous oxide emissions for early warning of biological nitrification failure in activated sludge. Water Research 43(5):1265-1272.

Cadet C, Beteau JF, Carlos Hernandez S. 2004. Multicriteria control strategy for cost/quality compromise in Wastewater Treatment Plants. Control Engineering Practice 12(3):335.

Canhoto O, Magan N. 2005. Electronic nose technology for the detection of microbial and chemical contamination of potable water. Sensors and Actuators B: Chemical 106(1):3-6.

Canhoto OF, Magan N. 2003. Potential for detection of microorganisms and heavy metals in potable water using electronic nose technology. Biosensors and Bioelectronics 18(5-6):751-754.

Carlsson B, Rehnstrom A. 2002. Control of an activated sludge process with nitrogen removal - a benchmark study. Water Science and Technology 45(4-5):135-142.

Cecil D. 2003. Controlling nitrogen removal using redox and ammonium sensors. Water Science and Technology 47(11):109-114.

Chachuat B, Roche N, Latifi MA. 2005a. Long-term optimal aeration strategies for small-size alternating activated sludge treatment plants. Chemical Engineering and Processing 44(5):593-606.

Chachuat B, Roche N, Latifi MA. 2005b. Optimal aeration control of industrial alternating activated sludge plants. Biochemical Engineering Journal 23(3):277-289.

Chandran K, Smets BF. 2000. Applicability of two-step models in estimating nitrification kinetics from batch respirograms under different relative dynamics of ammonia and nitrite oxidation. Biotechnology and Bioengineering 70(1):54-64.

Chandran K, Smets BF. 2005. Optimizing experimental design to estimate ammonia and nitrite oxidation biokinetic parameters from batch respirograms. Water Research 39(20):4969-4978.

Checchi N, Marsili-Libelli S. 2005. Reliability of parameter estimation in respirometric models. Water Research 39(15):3686-3696.

Clark E. 2000. The use of nitrous oxide (N2O) off-gas monitoring as an indicator of nitrification failure in an activated sludge process. [MSc.]. Cranfield: Cranfield University.

Cloern JE. 2001. Our evolving conceptual model of the coastal eutrophication problem. Marine Ecology-Progress Series 210:223-253.

Colliver BB, Stephenson T. 2000. Production of nitrogen oxide and dinitrogen oxide by autotrophic nitrifiers. Biotechnology Advances 18(3):219-232.

Cox CD. 2004. Statistical Distributions of Uncertainty and Variability in Activated Sludge Model Parameters. Water Environment Research 76(6):2672.

de Beer D, Schramm A. 1999. Micro-environments and mass transfer phenomena in biofilms studied with microsensors. Water Science and Technology 39(7):173-178.

de Figueiredo DR, Azeiteiro UM, Esteves SM, Goncalves FJM, Pereira MJ. 2004. Microcystin-producing blooms - a serious global public health issue. Ecotoxicology and Environmental Safety 59(2):151-163.

Devisscher M, Ciacci G, Fe L, Benedetti L, Bixio D, Thoeye C, De Gueldre G, Marsili-Libelli S, Vanrolleghem PA. 2006. Estimating costs and benefits of advanced control for wastewater treatment plants - the MAgIC methodology. Water Science and Technology 53(4-5):125-132.

Dewettinck T, Van Hege K, Verstraete W. 2001. The electronic nose as a rapid sensor for volatile compounds in treated domestic wastewater. Water Research 35(10):2475-2483.

Dold PL, Ekama GA, Marais GVR. 1980. A general model for the activated sludge process. Progess in Water Technology 12(6):47-77.

Dundee L, Hopkins DW. 2001. Different sensitivities to oxygen of nitrous oxide production by Nitrosomonas europaea and Nitrosolobus multiformis. Soil Biology & Biochemistry 33(11):1563-1565.

Eikelboom DH. 2000. Process Control of Activated Sludge Plants by Microscopic Investigation. London: IWA Publishing. 156 p.

Ekman M. 2008. Bilinear black-box identification and MPC of the activated sludge process. Journal of Process Control 18(7-8):643-653.

Ekman M, Bjorlenius B, Andersson M. 2006. Control of the aeration volume in an activated sludge process using supervisory control strategies. Water Research 40(8):1668-1676.

Falconer IR. 2005. Is there a human health hazard from microcystins in the drinking water supply? Acta Hydrochimica Et Hydrobiologica 33(1):64-71.

Ferrer J, Morenilla JJ, Bouzas A, Garcia-Usach F. 2004. Calibration and simulation of two large wastewater treatment plants operated for nutrient removal. Water Science and Technology 50(6):87-94.

Ferrer J, Rodrigo MA, Seco A, Penya-roja JM. 1998. Energy saving in the aeration process by fuzzy logic control. Water Science and Technology 38(3):209-217.

Ficara E, Musumeci A, Rozzi A. 2000. Comparison and combination of titrimetric and respirometric techniques to estimate nitrification kinetics parameters. Water SA 26(2):217-224.

Fikar M, Chachuat B, Latifi MA. 2005. Optimal operation of alternating activated sludge processes. Control Engineering Practice 13(7):853-861.

Fogelman S, Zhao HJ, Blumenstein M. 2006. A rapid analytical method for predicting the oxygen demand of wastewater. Analytical and Bioanalytical Chemistry 386(6):1773-1779.

Galloway JN, Dentener FJ, Capone DG, Boyer EW, Howarth RW, Seitzinger SP, Asner GP, Cleveland CC, Green PA, Holland EA and others. 2004. Nitrogen cycles: past, present, and future. Biogeochemistry 70(2):153-226.

Galluzzo M, Ducato R, Bartolozzi V, Picciotto A. 2001. Expert control of DO in the aerobic reactor of an activated sludge process. Computers & Chemical Engineering 25(4-6):619-625.

Gardner JW, Bartrlett PN. 1999. Electronic Noses Principles and Applications. Oxford: Oxford University Press.

Gardner JW, Shin HW, Hines EL, Dow CS. 2000. An electronic nose system for monitoring the quality of potable water. Sensors and Actuators B: Chemical 69(3):336-341.

Gejlsbjerg B, Frette L, Westermann P. 1998. Dynamics of N2O production from activated sludge. Water Research 32(7):2113-2121.

Gernaey KV, van Loosdrecht MCM, Henze M, Lind M, Jorgensen SB. 2004. Activated sludge wastewater treatment plant modelling and simulation: state of the art. Environmental Modelling & Software 19(9):763.

Goschnick J, Koronczi I, Frietsch M, Kiselev I. 2005. Water pollution recognition with the electronic nose KAMINA. Sensors and Actuators B: Chemical 106(1):182.

Grady CPL, Smets BF, Barbeau DS. 1996. Variability in kinetic parameter estimates: A review of possible causes and a proposed terminology. Water Research 30(3):742-748.

Gratziou M, Ekonomou S, Tsalkatidou M. 2005. Cost analysis and evaluation of urban sewage processing units. Water Science and Technology: Water Supply 5(6):155-162.

Guisasola A, Sin G, Baeza JA, Carrera J, Vanrolleghem PA. 2005. Limitations of ASM1 and ASM3: a comparison based on batch oxygen uptake rate profiles from different CD full-scale wastewater treatment plants. Water Science and Technology 52(10-11):69-77.

Gujer W, Henze M, Mino T, van Loosdrecht M. 1999. Activated Sludge Model No. 3. Water Science and Technology 39(1):183.

Habermeyer P, Sanchez A. 2005. Optimization of the intermittent aeration in a full-scale wastewater treatment plant biological reactor for nitrogen removal. Water Environment Research 77(3):229-233.

Hack M, Wiese J. 2006. Trends in instrumentation, control and automation and the consequences on urban water systems. Water Science and Technology 54(11-12):265-272.

Hagopian DS, Riley JG. 1998. A closer look at the bacteriology of nitrification. Aquacultural Engineering 18(4):223.

Hamilton R, Braun B, Dare R, Koopman B, Svoronos SA. 2006. Control issues and challenges in wastewater treatment plants. IEEE Control Systems Magazine 26(4):63-69.

Hellinga C, Vanrolleghem P, van Loosdrecht MCM, Heijnen JJ. 1996. The potential of off-gas analyses for monitoring wastewater treatment plants. Water Science and Technology 33(1):13-23.

Helmer C, Kunst S. Simultaneous nitrification/denitrification in an aerobic biofilm system; 1997 Jul 21-23; Berkeley, California. Pergamon-Elsevier Science Ltd. p 183-187.

Henze M, Gujer W, Mino T, van Loosdrecht M. 2000. Activated Sludge Models ASM1, ASM2, ASM2D and ASM3. London: International Water Association Publishing. 121 p.

Hewitt C. 1996. Programmable aeration control system reduces plant energy costs. Water Engineering & Management 143(5):30-33.

Hiatt WC, Grady CPL. 2008a. Application of the Activated Sludge Model for Nitrogen to Elevated Nitrogen Conditions. Water Environment Research 80(11):2134-2144.

Hiatt WC, Grady CPL. 2008b. An Updated Process Model for Carbon Oxidation, Nitrification, and Denitrification. Water Environment Research 80(11):2145-2156.

Hill RD, Manross RC, Davidson EV, Palmer TM, Ross MC, Nutt SG. 2002. Sensing and Control Systems: A Review of Municipal and Industrial Experiences. Alexandria: Water Environment Research Foundation.

Holenda B, Domokos E, Rédey Á, Fazakas J. 2008. Dissolved oxygen control of the activated sludge wastewater treatment process using model predictive control. Computers & Chemical Engineering 32(6):1270-1278.

Holman JB, Wareham DG. 2005. COD, ammonia and dissolved oxygen time profiles in the simultaneous nitrification/denitrification process. Biochemical Engineering Journal 22(2):125-133.

Hooper AB, Vannelli T, Bergmann DJ, Arciero DM. 1997. Enzymology of the oxidation of ammonia to nitrite by bacteria. Antonie Van Leeuwenhoek International Journal of General and Molecular Microbiology 71(1-2):59-67.

Hu Z-r, Wentzel MC, Ekama GA. 2003. Modelling biological nutrient removal activated sludge systems--a review. Water Research 37(14):3430.

Hulsbeek JJW, Kruit J, Roeleveld PJ, van Loosdrecht MCM. 2002. A practical protocol for dynamic modelling of activated sludge systems. Water Science and Technology 45(6):127-136.

Huntington R. 1998. Twenty years development of ICA in a water utility. Water Science and Technology 37(12):27-34.

Husmann M, Orth H, Schlegel S, Teichgraber B. 1998. Application of process control for improved nitrogen removal. Water Science and Technology 38(3):263-269.

Hwang S, Jang K, Jang H, Song JY, Bae W. 2006. Factors affecting nitrous oxide production: A comparison of biological nitrogen removal processes with partial and complete nitrification. Biodegradation 17(1):19-29.

Iacopozzi I, Innocenti V, Marsili-Libelli S, Giusti E. 2007. A modified Activated Sludge Model No. 3 (ASM3) with two-step nitrification-denitrification. Environmental Modelling & Software 22(6):847-861.

Inamori Y, Wu XL, Mizuochi M. 1997. N2O producing capability of Nitrosomonas europaea, Nitrobacter winogradskyi and Alcaligenes faecalis. Water Science and Technology 36(10):65-72.

Ingildsen P, Jeppsson U, Olsson G. 2002. Dissolved oxygen controller based on on-line measurements of ammonium combining feed-forward and feedback. Water Science and Technology 45(4-5):453-460.

Ingildsen P, Olsson G. 2002. Exploiting online in-situ ammonium, nitrate and phosphate sensors in full-scale wastewater plant operation. Water Science and Technology 46(4-5):139-147.

Ingildsen P, Wendelboe H. 2003. Improved nutrient removal using in situ continuous on-line sensors with short response time. Water Science and Technology 48(1):95-102.

Intergovernmental Panel on Climate Change. Climate Change 2001: The Scientific Basis. Houghton JT, Ding Y, Griggs DJ, Noguer M, van der Linden PJ, Dai X, Maskell K, Johnson CA, editors; 2001; Cambridge, UK. Cambridge University Press.

Iranpour R, Zermeno M, Rad H, Oh S, Gumar D. 1999. Cocurrent biological nitrification and denitrification in wastewater treatment - Discussion. Water Environment Research 71(6):1261-1262.

Islam KA, Newell B, Lant P. 1999. Advanced process control for biological nutrient removal. Water Science and Technology 39(6):97-103.

Itokawa H, Hanaki K, Matsuo T. 1996. Nitrous oxide emission during nitrification and denitrification in a full-scale night soil treatment plant. Water Science and Technology 34(1-2):277-284.

Itokawa H, Hanaki K, Matsuo T. 2001. Nitrous oxide production in high-loading biological nitrogen removal process under low COD/N ratio condition. Water Research 35(3):657-664.

Jardine CG, Gibson N, Hrudey SE. 1999. Detection of odour and health risk perception of drinking water. Water Science and Technology 40(6):91-98.

Jenkins D, Richard MG, Daigger GT. 2004. Manual on the Cause and Control of Activated Sludge Bulking, Foaming, and Other Solid Separation Problems, 3. London: IWA Publising. 190 p.

Jeong HS, Lee SH, Shin HS. 2007. Feasibility of on-line measurement of sewage components using the UV absorbance and the neural network. Environmental Monitoring and Assessment 133(1-3):15-24.

Jeppsson U. 1996. Modelling Aspects of Wastewater Treatment Processes [Ph.D. Thesis]. Lund: Lund Institute of Technology.

Jeppsson U, Pons MN. 2004. The COST benchmark simulation model - current state and future perspective. Control Engineering Practice 12(3):299-304.

Jetten MSM, Cirpus I, Kartal B, van Niftrik L, van de Pas-Schoonen KT, Sliekers O, Haaijer S, van der Star W, Schmid M, van de Vossenberg J and others. 2005. 1994-2004: 10 years of research on the anaerobic oxidation of ammonium. Biochemical Society Transactions 33:119-123.

Jetten MSM, Strous M, van de Pas-Schoonen KT, Schalk J, van Dongen U, van de Graaf AA, Logemann S, Muyzer G, van Loosdrecht MCM, Kuenen JG. 1998. The anaerobic oxidation of ammonium. FEMS Microbiology Reviews 22(5):421-437.

Jianlong W, Ning Y. 2004. Partial nitrification under limited dissolved oxygen conditions. Process Biochemistry 39(10):1223-1229.

Kaelin D, Rieger L, Eugster J, Rottermann K, Banninger C, Siegrist H. 2008. Potential of in-situ sensors with ion-selective electrodes for aeration control at wastewater treatment plants. Water Science and Technology 58(3):629-637.

Kalker TJJ, van Goor CP, Roeleveld PJ, Ruland MF, Babuska R. 1999. Fuzzy control of aeration in an activated sludge wastewater treatment plant: Design, simulation and evaluation. Water Science and Technology 39(4):71-78.

Kampschreur MJ, Tan NCG, Kleerebezem R, Picioreanu C, Jetten MSM, Loosdrecht MCM. 2008a. Effect of dynamic process conditions on nitrogen oxides emission from a nitrifying culture. Environmental Science & Technology 42(2):429-435.

Kampschreur MJ, van der Star WRL, Wielders HA, Mulder JW, Jetten MSM, van Loosdrecht MCM. 2008b. Dynamics of nitric oxide and nitrous oxide emission during full-scale reject water treatment. Water Research 42(3):812-826.

Kappeler J, Gujer W. 1992. Estimation Of Kinetic-Parameters Of Heterotrophic Biomass Under Aerobic Conditions And Characterization Of Waste-Water For Activated-Sludge Modeling. Water Science and Technology 25(6):125-139.

Karahan-Gul O, van Loosdrecht MCM, Orhon D. 2003. Modification of Activated Sludge Model no. 3 considering direct growth on primary substrate. Water Science and Technology 47(11):219-225.

Karner DA, Standridge AJH, Harrington GW, Barnum RP. 2001. Microcystin algal toxins in source and finished drinking water. Journal American Water Works Association 93(8):72-81.

Kester RA, deBoer W, Laanbroek HJ. 1997. Production of NO and N2O by pure cultures of nitrifying and denitrifying bacteria during changes in aeration. Applied And Environmental Microbiology 63(10):3872-3877.

Khin T, Annachhatre AP. 2004. Novel microbial nitrogen removal processes. Biotechnology Advances 22(7):519-532.

Koch G, Kuhni M, Gujer W, Siegrist H. 2000. Calibration and validation of activated sludge model no. 3 for Swiss municipal wastewater. Water Research 34(14):3580-3590.

Koch G, Kuhni M, Rieger L, Siegrist H. 2001a. Calibration and validation of an ASM3-based steady-state model for activated sludge systems--part II: : prediction of phosporous removal. Water Research 35(9):2246-2255.

Koch G, Kuhni M, Siegrist H. 2001b. Calibration and validation of an ASM3-based steady-state model for activated sludge systems--part I: : prediction of nitrogen removal and sludge production. Water Research 35(9):2235-2245.

Krause K, Bocker K, Londong J. 2002. Simulation of a nitrification control concept considering influent ammonium load. Water Science and Technology 45(4-5):413-420.

Krishna C, Van Loosdrecht MCM. 1999. Substrate flux into storage and growth in relation to activated sludge modeling. Water Research 33(14):3149.

Kristensen GH, Jansen JL, Jorgensen PE. 1998. Batch test procedures as tools for calibration of the activated sludge model - A pilot scale demonstration. Water Science and Technology 37(4-5):235-242.

Kuenen JG. 2008. Anammox bacteria: from discovery to application. Nature Reviews Microbiology 6(4):320-326.

Kuenen JG, Robertson LA. Combined nitrification-denitrification processes; 1994 Apr 18-21; Wageningen, Netherlands. p 109-117.

Langergraber G, Rieger L, Winkler S, Alex J, Wiese J, Owerdieck C, Ahnert M, Simon J, Maurer M. 2004. A guideline for simulation studies of wastewater treatment plants. Water Science and Technology 50(7):131-138.

Langergraber G, Wuchty M, Fleischmann N, Lechner M. 2003. Rapid automated detection of nitrification kinetics using respirometry. Water Science and Technology 47(2):149-155.

Larsen LH, Damgaard LR, Kjaer T, Stenstrom T, Lynggaard-Jensen A, Revsbech NP. 2000. Fast responding biosensor for on-line determination of nitrate/nitrite in activated sludge. Water Research 34(9):2463-2468.

Lee TT, Wang FY, Newell RB. 2006. Advances in distributed parameter approach to the dynamics and control of activated sludge processes for wastewater treatment. Water Research 40(5):853-869.

Li B, Bishop P. 2003a. Structure-function dynamics and modeling analysis of the micro-environment of activated sludge floc. Water Science and Technology 47(11):267-273.

Li B, Bishop PL. 2003b. Modeling of the microenvironment of activated sludge floc with experimental and theoretical methods. Journal of Environmental Engineering and Science 2(1):27-37.

Limpiyakorn T, Shinohara Y, Kurisu F, Yagi O. 2005. Communities of ammonia-oxidizing bacteria in activated sludge of various sewage treatment plants in Tokyo. FEMS Microbiology Ecology 54(2):205-217.

Liu XH, Peng Y, Wu CY, Akio T, Peng YZ. 2008. Nitrous oxide production during nitrogen removal from domestic wastewater in lab-scale sequencing batch reactor. Journal of Environmental Sciences-China 20(6):641-645.

Love NG, Bott CB. 2000. A Review and Needs Survey of Upset Early Warning Devices. Alexandria: Water Environment Research Foundation. 104 p.

Love NG, Bott CB. 2002. Evaluating the role of microbial stress response mechanisms in causing biological treatment system upset. Water Science and Technology 46(1-2):11-18.

Lukasse LJS, Keesman KJ, Klapwijk A, van Straten G. 1999. A comparison of NH4/NO3 control strategies for alternating activated sludge processes. Water Science and Technology 39(4):93-102.

Lynggaard-Jensen A. 1999. Trends in monitoring of waste water systems. Talanta 50(4):707-716.

Lynggaard-Jensen A, Eisum NH, Rasmussen I, Jacobsen HS, Stenstrom T. 1996. Description and test of a new generation of nutrient sensors. Water Science and Technology 33(1):25-35.

Makinia J, Rosenwinkel KH, Phan LC. 2006. Modification of ASM3 for the determination of biomass adsorption/storage capacity in bulking sludge control. Water Science and Technology 53(3):91-99.

Makinia J, Rosenwinkel KH, Spering V. 2005. Long-term simulation of the activated sludge process at the Hanover-Gummerwald pilot WWTP. Water Research 39(8):1489-1502.

Makinia J, Wells SA. 2000a. A general model of the activated sludge reactor with dispersive flow--I. model development and parameter estimation. Water Research 34(16):3987-3996.

Makinia J, Wells SA. 2000b. A general model of the activated sludge reactor with dispersive flow--II. model verification and application. Water Research 34(16):3997-4006.

Mao J, Jiang X-Q, Yang L-Z, Zhang J, Qiao Q-Y, He C-D, Yin S-X. 2006. Nitrous Oxide Production in a Sequence Batch Reactor Wastewater Treatment System Using Synthetic Wastewater. Pedosphere 16(4):451-456.

Martins AMP, Pagilla K, Heijnen JJ, van Loosdrecht MCM. 2004. Filamentous bulking sludge - a critical review. Water Research 38(4):793-817.

Meijer SCF, van Loosdrecht MCM, Heijnen JJ. 2001. Metabolic modelling of full-scale biological nitrogen and phosphorus removing wwtp's. Water Research 35(11):2711-2723.

Melcer H. 1999. Full scale experience with biological process models - Calibration issues. Water Science and Technology 39(1):245-252.

Metcalf L, Eddy H. 2003. Wastewater Engineering: Treatment and Reuse, 4th ed. Tchobanoglous G, Burton FL, Stensel HD, editors. Boston: McGraw-Hill.

Meyer U, Popel HJ. 2003. Fuzzy-control for improved nitrogen removal and energy saving in WWT-plants with pre-denitrification. Water Science and Technology 47(11):69-76.

Muñoz C, Rojas D, Candia O, Azocar L, Bornhardt C, Antileo C. 2009. Supervisory control system to enhance partial nitrification in an activated sludge reactor. Chemical Engineering Journal 145(3):453-460.

Murphy RB, Young BR, Kecman V. 2009. Optimising operation of a biological wastewater treatment application. ISA Transactions 48(1):93-97.

Mussati M, Gernaey K, Gani R, Jørgensen S. 2002. Computer aided model analysis and dynamic simulation of a wastewater treatment plant. Clean Technologies and Environmental Policy 4(2):100-114.

Nake A, Dubreuil B, Raynaud C, Talou T. 2005. Outdoor in situ monitoring of volatile emissions from wastewater treatment plants with two portable technologies of electronic noses. Sensors and Actuators B: Chemical 106(1):36-39.

Nataraja M, Qin Y, Seagren EA. 2006. Ultraviolet spectrophotometry as an index parameter for estimating the biochemical oxygen demand of domestic wastewater. Environmental Technology 27(7):789-800.

Ng ANL, Kim AS. 2007. A mini-review of modeling studies on membrane bioreactor (MBR) treatment for municipal wastewaters. Desalination 212(1-3):261-281.

NHMRC, NRMMC. 2004. Australian Drinking Water Guidelines 2004. Commonwealth of Australia.

Ni BJ, Yu HQ. 2008. Simulation of heterotrophic storage and growth processes in activated sludge under aerobic conditions. Chemical Engineering Journal 140(1-3):101-109.

Noda N, Kaneko N, Milkami M, Kimochi Y, Tsuneda S, Hirata A, Mizuochi M, Inamori Y. 2003. Effects of SRT and DO on N2O reductase activity in an anoxic-oxic activated sludge system. Water Science and Technology 48(11-12):363-370.

Nowak O, Svardal K, Schweighofer P. The dynamic behavior of nitrifying activated-sludge systems influenced by inhibiting waste-water compounds; 1994 Aug 22-24; Copenhagen, Denmark. p 115-124.

Nuhoglu A, Keskinler B, Yildiz E. 2005. Mathematical modelling of the activated sludge process--the Erzincan case. Process Biochemistry 40(7):2467-2473.

Nyberg U, Andersson B, Aspegren H. 1996. Experiences with on-line measurements at a wastewater treatment plant for extended nitrogen removal. Water Science and Technology 33(1):175-182.

Ogawa S, Sugimoto I. 2002. Detecting odorous materials in water using quartz crystal microbalance sensors. Water Science and Technology 45(4-5):201-206.

Oh J, Silverstein J. 1999. Oxygen inhibition of activated sludge denitrification. Water Research 33(8):1925-1937.

Olsson G. 2006. Instrumentation, control and automation in the water industry - state-of-the-art and new challenges CD. Water Science and Technology 53(4-5):1-16.

Olsson G, Newell B. 1999. Wastewater Treatment Systems: Modelling, Diagnosis and Control. London: IWA Publishing. 750 p.

Onkal-Engin G, Demir I, Engin SN. 2005. Determination of the relationship between sewage odour and BOD by neural networks. Environmental Modelling & Software 20(7):843-850.

Ossenbruggen PJ, Spanjers H, Klapwik A. 1996. Assessment of a two-step nitrification model for activated sludge. Water Research 30(4):939-953.

Palmer T, Ross M, Nutt SG. 2002. Measuring ammonia with online analyzers. Water Engineering & Management 149(7):34-39.

Papen H, Vonberg R, Hinkel I, Thoene B, Rennenberg H. 1989. Heterotrophic nitrification by *Alcaligenes-faecalis* - $NO2^-$, $NO3^-$, N_2O, and NO production in exponentially growing cultures. Applied and Environmental Microbiology 55(8):2068-2072.

Petersen B, Gernaey K, Devisscher M, Dochain D, Vanrolleghem PA. 2003. A simplified method to assess structurally identifiable parameters in Monod-based activated sludge models. Water Research 37(12):2893-2904.

Philips S, Wyffels S, Sprengers R, Verstraete W. 2002. Oxygen-limited autotrophic nitrification/denitrification by ammonia oxidisers enables upward motion towards more favourable conditions. Applied Microbiology and Biotechnology 59(4-5):557-566.

Piotrowski R, Brdys MA, Konarczak K, Duzinkiewicz K, Chotkowski W. 2008. Hierarchical dissolved oxygen control for activated sludge processes. Control Engineering Practice 16(1):114-131.

Plazl I, Koloini T, Levstek M, Burica O, Strazar M. 2001. ASM1 limitations for modeling of wastewater treatment processes. Acta Chimica Slovenica 48(4):625-636.

Pochana K, Keller J. 1999. Study of factors affecting simultaneous nitrification and denitrification (SND). Water Science and Technology 39(6):61-68.

Pochana K, Keller J, Lant P. 1999. Model development for simultaneous nitrification and denitrification. Water Science and Technology 39(1):235-243.

Pons M-N, Potier O. 2004. Control strategy robustness with respect to hydraulics. Control Engineering Practice 12(3):349-356.

Poth M. 1986. Dinitrogen production from nitrite by a Nitrosomonas isolate. Applied and Environmental Microbiology 52(4):957-959.

Poth M, Focht DD. 1985. N-15 kinetic-analysis of N2O production by Nitrosomonas europaea: an examination of nitrifier denitrification. Applied and Environmental Microbiology 49(5):1134-1141.

Reznik L. 1997. Fuzzy Controllers Handbook. Oxford: Newnes. 240 p.

Rieger L, Langergraber G, Thomann M, Fleischmann N, Siegrist H. 2004a. Spectral in-situ analysis of NO2, NO3, COD, DOC and TSS in the effluent of a WWTP. Water Science and Technology 50(11):143-152.

Rieger L, Thomann M, Joss A, Gujer W, Siegrist H. 2004b. Computer-aided monitoring and operation of continuous measuring devices. Water Science and Technology 50(11):31-39.

Robertson LA, Kuenen JG. 1984a. Aerobic denitrification - old wine in new bottles? Antonie Van Leeuwenhoek Journal of Microbiology 50(5-6):525-544.

Robertson LA, Kuenen JG. 1984b. Aerobic denitrification: a controversy revived. Archives of Microbiology 139(4):351-354.

Rodriguez-Mozaz S, Marco MP, de Alda MJL, Barcelo D. 2004. Biosensors for environmental applications: Future development trends. Pure and Applied Chemistry 76(4):723-752.

Ruiz G, Jeison D, Chamy R. 2003. Nitrification with high nitrite accumulation for the treatment of wastewater with high ammonia concentration. Water Research 37(6):1371-1377.

Russell SL, Marshallsay DR, MacCraith B, Devisscher M. 2003. Non-contact measurement of wastewater polluting load - the Loadmon project. Water Science and Technology 47(2):79-86.

Sahlmann C, Libra JA, Schuchardt A, Wiesmann U, Gnirss R. 2004. A control strategy for reducing aeration costs during low loading periods. Water Science and Technology 50(7):61-68.

Samuelsson P, Carlsson B. 2002. Control of the aeration volume in an activated sludge process for nitrogen removal. Water Science and Technology 45(4-5):45-52.

Samuelsson P, Halvarsson B, Carlsson B. 2005. Interaction analysis and control structure selection in a wastewater treatment plant model. IEEE Transactions On Control Systems Technology 13(6):955-964.

Samuelsson P, Halvarsson B, Carlsson B. 2007. Cost-efficient operation of a denitrifying activated sludge process. Water Research 41(11):2325-2332.

Schlegel S, Baumann P. 1996. Requirements with respect to on-line analyzers for N and P. Water Science and Technology 33(1):139-146.

Schmidt I. 2008. Nitric oxide: Interaction with the ammonia monooxygenase and regulation of metabolic activities in ammonia oxidizers. Nitric Oxide, Part F: Oxidative and Nitrosative Stress in Redox Regulation of Cell Signaling. p 121-135.

Schmidt I, Sliekers O, Schmid M, Bock E, Fuerst J, Kuenen JG, Jetten MSM, Strous M. 2003. New concepts of microbial treatment processes for the nitrogen removal in wastewater. FEMS Microbiology Reviews 27(4):481-492.

Schmidt I, Sliekers O, Schmid M, Cirpus I, Strous M, Bock E, Kuenen JG, Jetten MSM. 2002. Aerobic and anaerobic ammonia oxidizing bacteria - competitors or natural partners? FEMS Microbiology Ecology 39(3):175-181.

Schutze M, Campisano A, Colas H, Schilling W, Vanrolleghem PA. 2004. Real time control of urban wastewater systems - where do we stand today? Journal of Hydrology 299(3-4):335-348.

Seborg DE, Edgar TF, Mellichamp DA. 2003. Process Dynamics and Control, 2nd. New York: John Wiley & Sons. 736 p.

Seco A, Ribes J, Serralta J, Ferrer J. 2004. Biological nutrient removal model No.1 (BNRM1). Water Science and Technology 50(6):69-78.

Seitzinger SP, Harrison JA, Dumont E, Beusen AHW, Bouwman AF. 2005. Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of Global Nutrient Export from Watersheds (NEWS) models and their application. Global Biogeochemical Cycles 19(4):1-11.

Serralta J, Ribes J, Seco A, Ferrer J. 2002. A supervisory control system for optimising nitrogen removal and aeration energy consumption in wastewater treatment plants. Water Science and Technology 45(4-5):309-316.

Shiskowski DM. 2004. Investigation of nitrous oxide as a nitrification monitoring and aeration system control parameter in sequencing batch reactor wastewater treatment systems [Ph.D.]: The University of British Columbia (Canada).

Shiskowski DM, Mavinic DS. 2006. The influence of nitrite and pH (nitrous acid) on aerobic-phase, autotrophic N2O generation in a wastewater treatment bioreactor. Journal of Environmental Engineering and Science 5(4):273-283.

Shiskowski DM, Simm RA, Mavinic DS. 2004. An experimental procedure for identifying the aerobic-phase biological source of nitrous oxide in anoxic-aerobic wastewater treatment systems. Journal of Environmental Engineering and Science 3(6):549-553.

Shrestha NK, Hadano S, Kamachi T, Okura I. 2002. Dinitrogen production from ammonia by Nitrosomonas europaea. Applied Catalysis A: General 237(1-2):33-39.

Sin G, De Pauw DJW, Weijers S, Vanrolleghem PA. 2008. An efficient approach to automate the manual trial and error calibration of activated sludge models. Biotechnology and Bioengineering 100(3):516-528.

Sin G, Guisasola A, De Pauw DJW, Baeza JA, Carrera J, Vanrolleghem PA. 2005a. A new approach for modelling simultaneous storage and growth processes for activated sludge systems under aerobic conditions. Biotechnology and Bioengineering 92(5):600-613.

Sin G, Van Hulle SWH, De Pauw DJW, van Griensven A, Vanrolleghem PA. 2005b. A critical comparison of systematic calibration protocols for activated sludge models: A SWOT analysis. Water Research 39(12):2459-2474.

Sin G, Vanrolleghem PA. 2007. Extensions to modeling aerobic carbon degradation using combined respirometric-titrimetric measurements in view of activated sludge model calibration. Water Research 41(15):3345-3358.

Siripong S. 2005. Diversity assessment of nitrifying bacterial populations in wastewater activated sludge [Ph.D.]. United States -- Illinois: Northwestern University.

Siripong S, Rittmann BE. 2007. Diversity study of nitrifying bacteria in full-scale municipal wastewater treatment plants. Water Research 41(5):1110-1120.

Sivret EC, Peirson WL, Stuetz RM. 2008. Nitrous oxide monitoring for nitrifying activated sludge aeration control: a simulation study. Biotechnology And Bioengineering 101(1):109-118.

Sliekers AO, Haaijer SCM, Stafsnes MH, Kuenen JG, Jetten MSM. 2005. Competition and coexistence of aerobic ammonium- and nitrite-oxidizing bacteria at low oxygen concentrations. Applied Microbiology and Biotechnology 68(6):808-817.

Smets IY, Haegebaert JV, Carrette R, Van Impe JF. 2003. Linearization of the activated sludge model ASM1 for fast and reliable predictions. Water Research 37(8):1831-1851.

Smith VH, Tilman GD, Nekola JC. 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environmental Pollution 100(1-3):179-196.

Sorour MT, Bahgat LMF. 2004. Application of activated sludge models in traditionally operated treatment plants - A software environment overview. Water Quality Research Journal of Canada 39(3):294-302.

Spanjers H, Patry GG, Keesman KJ. 2002. Respirometry-based on-line model parameter estimation at a full-scale WWTP. Water Science and Technology 45(4-5):335-343.

Spanjers H, Vanrolleghem P. 1995. Respirometry As A Tool For Rapid Characterization Of Waste-water And Activated-Sludge. Water Science and Technology 31(2):105-114.

Stare A, Hvala N, Vrecko D. 2006. Modeling, Identification, and Validation of Models for Predictive Ammonia Control in a Wastewater Treatment Plant--A Case Study. ISA Transactions 45(2):159-174.

Stare A, Vrecko D, Hvala N, Strmcnik S. 2007. Comparison of control strategies for nitrogen removal in an activated sludge process in terms of operating costs: A simulation study. Water Research 41(9):2004-2014.

Stein LY, Arp DJ. 1998. Loss of ammonia monooxygenase activity in Nitrosomonas europaea upon exposure to nitrite. Applied And Environmental Microbiology 64(10):4098-4102.

Stricker A-E, Lessard P, Heduit A, Chatellier P. 2003. Observed and simulated effect of rain events on the behaviour of an activated sludge plant removing nitrogen. Journal of Environmental Engineering and Science 2(6):429-440.

Stuetz RM. 2004. Non-specific monitoring to resolve intermittent pollutant problems associated with wastewater treatment and potable supply. Water Science and Technology 49(9):137-143.

Stuetz RM, Burgess JE, Stephenson T. Non-invasive monitoring of wastewater nitrification failure. Proceedings AWA 20th Convention; 2003; Perth, Australia. p 8.

Stuetz RM, Fenner RA, Engin G. 1999a. Characterisation of wastewater using an electronic nose. Water Research 33(2):442-452.

Stuetz RM, George S, Fenner RA, Hall SJ. 1999b. Monitoring wastewater BOD using a non-specific sensor array. Journal of Chemical Technology and Biotechnology 74(11):1069-1074.

Suescun J, Ostolaza X, Garcia-Sanz M, Ayesa E. 2001. Real-time control strategies for predenitrification nitrification activated sludge plants biodegradation control. Water Science and Technology 43(1):209-216.

Sumer E, Weiske A, Benckiser G, Ottow JCG. 1995. Influence of environmental-conditions on the amount of N2O released from activated-sludge in a domestic waste-water treatment-plant. Experientia 51(4):419-422.

Svrcek C, Smith DW. 2004. Cyanobacteria toxins and the current state of knowledge on water treatment options: a review. Journal of Environmental Engineering and Science 3(3):155-185.

Swedish Environmental Protection Agency. 2002. Municipal Wastewater Treatment.

Swedish Environmental Protection Agency. 2004. Sweden's Environmental Objectives - are we getting there, de Facto 2004. Swedish Environmental Protection Agency.

Swedish Environmental Protection Agency. 2005. Sweden's Environmental Objectives - for the children, de Facto 2005. Swedish Environmental Protection Agency.

Tallec G, Garnier J, Billen G, Gousailles M. 2006a. Nitrous oxide emissions from secondary activated sludge in nitrifying conditions of urban wastewater treatment plants: Effect of oxygenation level. Water Research 40(15):2972-2980.

Tallec G, Garnier J, Billen G, Gousailles M. 2008. Nitrous oxide emissions from denitrifying activated sludge of urban wastewater treatment plants, under anoxia and low oxygenation. Bioresource Technology 99(7):2200-2209.

Tallec G, Garnier J, Gousailles M. 2006b. Nitrogen removal in a wastewater treatment plant through biofilters: nitrous oxide emissions during nitrification and denitrification. Bioprocess and Biosystems Engineering 29(5-6):323-333.

Thomas O, Baures E, Pouet MF. 2005. UV spectrophotometry as a non-parametric measurement of water and wastewater quality variability. Water Quality Research Journal of Canada 40(1):51-58.

Thomas O, Constant D. 2004. Trends in optical monitoring. Water Science and Technology 49(1):1-8.

Thomas O, Theraulaz F, Agnel C, Suryani S. 1996. Advanced UV examination of wastewater. Environmental Technology 17(3):251-261.

Thomsen HA, Kisbye K. 1996. N and P on-line meters: Requirements, maintenance and stability. Water Science and Technology 33(1):147-157.

Thomsen HA, Nielsen MK, Nielsen EH, Hansen NP. 1998. Load dependent control of BNR-WWTP by dynamic changes of aeration volumes. Water Science and Technology 37(12):157-164.

Tsagarakis KP, Mara DD, Angelakis AN. 2003. Application of cost criteria for selection of municipal wastewater treatment systems. Water Air and Soil Pollution 142(1-4):187-210.

Udert KM, Larsen TA, Gujer W. 2005. Chemical nitrite oxidation in acid solutions as a consequence of microbial ammonium oxidation. Environmental Science & Technology 39(11):4066-4075.

United Nations. 2002. World Ubanization Prospets The 2001 Revision. In: Department of Economic and Social Affairds PD, editor: United Nations.

United Nations. 2005. World Population Prospects The 2004 Revision, Highlights. In: Department of Economic and Social Affairds PD, editor: United Nations. p 105.

Vaiopoulou E, Melidis P, Kampragou E, Aivasidis A. 2005. On-line load monitoring of wastewaters with a respirographic microbial sensor. Biosensors and Bioelectronics 21(2):365-371.

van Loosdrecht MCM, Jetten MSM. 1998. Microbiological conversions in nitrogen removal. Water Science and Technology 38(1):1-7.

van Veldhuizen HM, van Loosdrecht MCM, Heijnen JJ. 1999. Modelling biological phosphorus and nitrogen removal in a full scale activated sludge process. Water Research 33(16):3459-3468.

Vanrolleghem P, Insel G, Petersen B, Sin G, De pauw D, Nopens I, Weijers S, Gernaey K. A comprehensive model calibration procedure for activated sludge models.; 1999a October 11-15, 2003; Los Angeles, CA, USA (on CD-ROM).

Vanrolleghem PA, Gillot S. 2002. Robustness and economic measures as control benchmark performance criteria. Water Science and Technology 45(4-5):117-126.

Vanrolleghem PA, Kong Z, Rombouts G, Verstraete W. 1994. An Online Respirographic Biosensor For The Characterization Of Load And Toxicity Of Wastewaters. Journal of Chemical Technology and Biotechnology 59(4):321-333.

Vanrolleghem PA, Lee DS. 2003. On-line monitoring equipment for wastewater treatment processes: state of the art. Water Science and Technology 47(2):1-34.

Vanrolleghem PA, Sin G, Van Hulle SWH, De Pauw DJW, van Griensven A. 2006. Reply to: Comment on "A critical comparison of systematic calibration protocols for activated sludge models: A SWOT analysis": Water Research (39) (2005) 2460-2474 by Denny Parker and Henryk Melcer. Water Research 40(15):2994-2996.

Vanrolleghem PA, Spanjers H, Petersen B, Ginestetf P, Takacs I. 1999b. Estimating (combinations of) Activated Sludge Model No. 1 parameters and components by respirometry. Water Science and Technology 39(1):195-214.

von Schulthess R, Gujer W. 1996. Release of nitrous oxide (N2O) from denitrifying activated sludge: Verification and application of a mathematical model. Water Research 30(3):521-530.

von Schulthess R, Kuhni M, Gujer W. 1995. Release of nitric and nitrous oxides from denitrifying activated-sludge. Water Research 29(1):215-226.

von Schulthess R, Wild D, Gujer W. 1994. Nitric And nitrous oxides from denitrifying activated-sldge at low-oxygen concentration. Water Science and Technology 30(6):123-132.

Vrecko D, Hvala N, Carlsson B. 2003. Feedforward-feedback control of an activated sludge process: a simulation study. Water Science and Technology 47(12):19-26.

Vrecko D, Hvala N, Stare A, Burica O, Strazar M, Levstek M, Cerar P, Podbevsek S. 2006. Improvement of ammonia removal in activated sludge process with feedforward-feedback aeration controllers. Water Science and Technology 53(4-5):125-132.

Wang C, Zeng Y, Lou J, Wu P. 2007. Dynamic simulation of a WWTP operated at low dissolved oxygen condition by integrating activated sludge model and a floc model. Biochemical Engineering Journal 33(3):217-227.

Weijers SR, Vanrolleghem PA. 1997. A procedure for selecting best identifiable parameters in calibrating activated sludge model no.1 to full-scale plant data. Water Science and Technology 36(5):69-79.

Weissenbacher N, Lenz K, Mahnik SN, Wett B, Fuerhacker M. 2007. Determination of activated sludge biological activity using model corrected CO2 off-gas data. Water Research 41(7):1587-1595.

Wichern M, Lubken M, Blomer R, Rosenwinkel KH. 2003. Efficiency of the Activated Sludge Model No. 3 for German wastewater on six different WWTPs. Water Science and Technology 47(11):211-218.

Wichern M, Obenaus F, Wulf P, Rosenwinkel KH. 2001. Modelling of full-scale wastewater treatment plants with different treatment processes using the Activated Sludge Model no. 3. Water Science and Technology 44(1):49-56.

Wicht H. 1996. A model for predicting nitrous oxide production during denitrification in activated sludge. Water Science and Technology 34(5-6):99-106.

Wild D, von Schulthess R, Gujer W. 1995. Structured Modeling Of Denitrification Intermediates. Water Science and Technology 31(2):45-54.

Winkler S, Rieger L, Saracevic E, Pressl A, Gruber G. 2004. Application of ion-sensitive sensors in water quality monitoring. Water Science and Technology 50(11):105-114.

World Health Organization. 2004. Guidelines for Drinking-water Quality, 3rd ed. Geneva: World Health Organization.

Wrage N, Velthof GL, Oenema O, Laanbroek HJ. 2004. Acetylene and oxygen as inhibitors of nitrous oxide production in Nitrosomonas europaea and Nitrosospira briensis: a cautionary tale. FEMS Microbiology Ecology 47(1):13-18.

Wrage N, Velthof GL, van Beusichem ML, Oenema O. 2001. Role of nitrifier denitrification in the production of nitrous oxide. Soil Biology and Biochemistry 33(12-13):1723-1732.

Yamanaka O, Obara T, Yamamoto K. 2006. Total cost minimization control scheme for biological wastewater treatment process and its evaluation based on the COST benchmark process. Water Science and Technology 53(4-5):203-214.

Yong M, Yong-Zhen P, Xiao-Lian W, Shu-Ying W. 2006. Intelligent control aeration and external carbon addition for improving nitrogen removal. Environmental Modelling & Software 21(6):821-828.

Yoo CK, Villez K, Van Hulle SWH, Vanrolleghem PA. 2008. Enhanced process monitoring for wastewater treatment systems. Environmetrics 19(6):602-617.

Zarrad W, Harmand J, Devisscher M, Steyer JP. 2004. Comparison of advanced control strategies for improving the monitoring of activated sludge processes. Control Engineering Practice 12(3):323-333.

Zheng H, Hanaki K, Matsuo T. 1994. Production Of Nitrous-Oxide Gas During Nitrification Of Waste-Water. Water Science and Technology 30(6):133-141.

Zumft WG. 1997. Cell biology and molecular basis of denitrification. Microbiology and Molecular Biology Reviews 61(4):533-616.

Appendix A - Figures

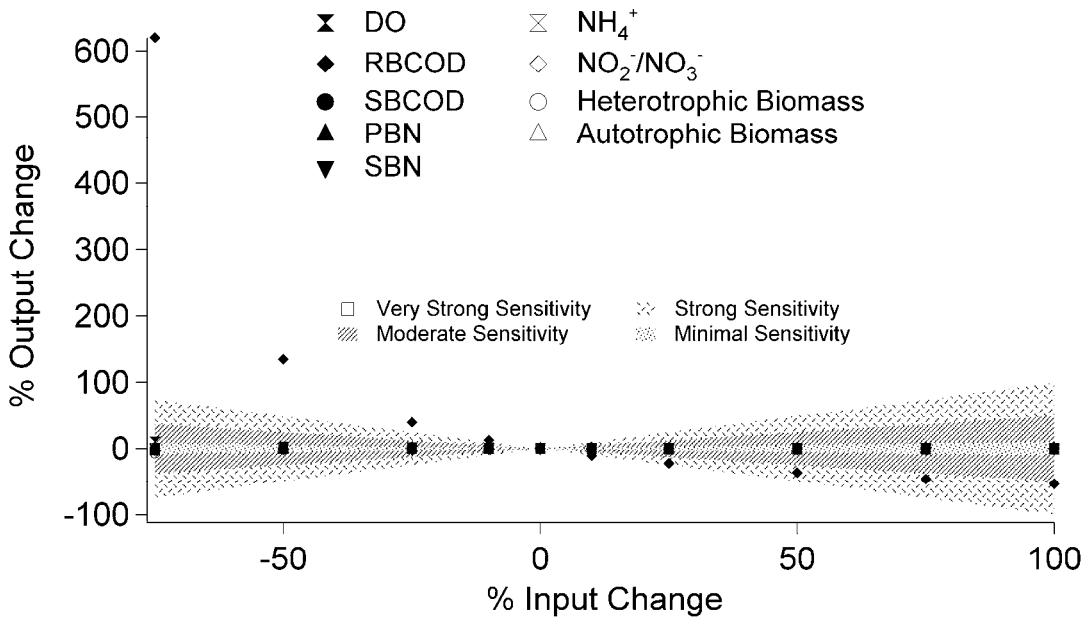


Figure A-1 Effect of heterotroph maximum specific growth rate (μ_H) on system state variables (ASM1 – Cranfield data).

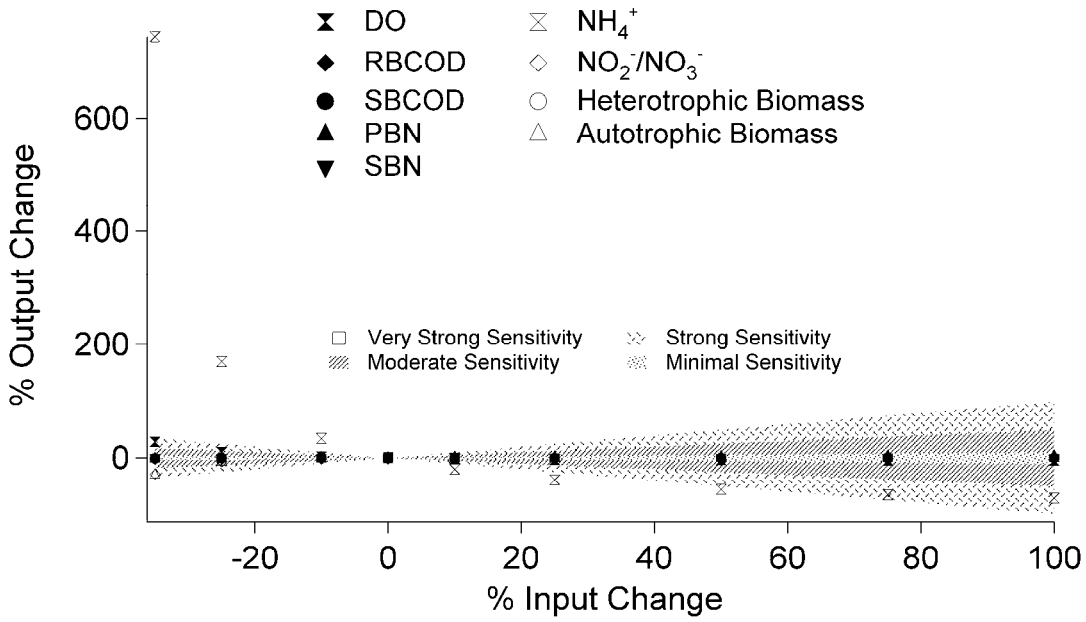


Figure A-2 Effect of autotroph maximum specific growth rate (μ_A) on system state variables (ASM1 – Cranfield data).

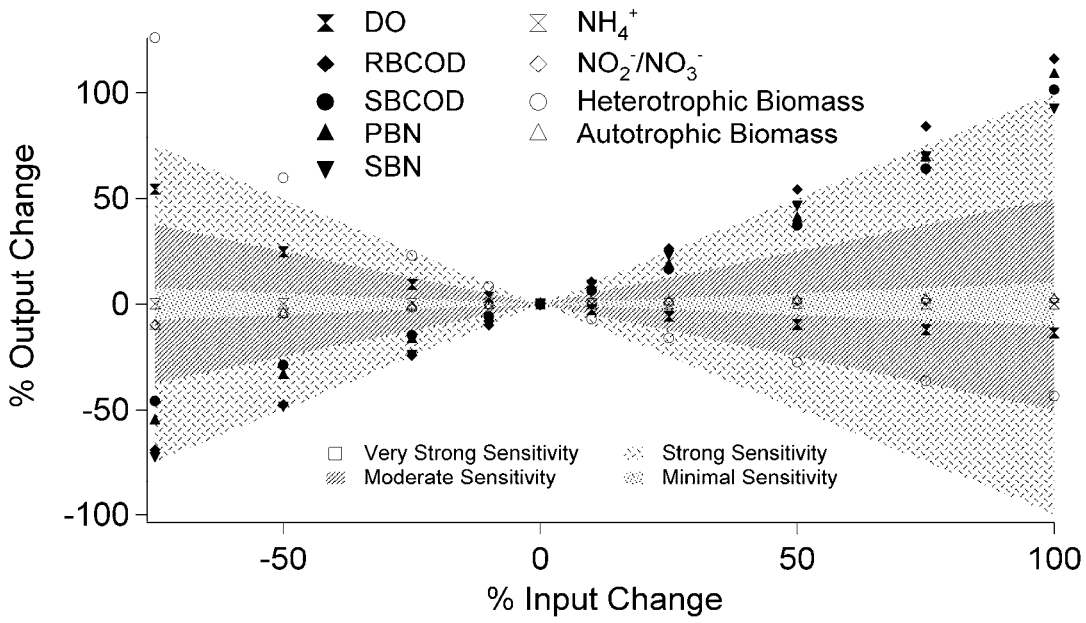
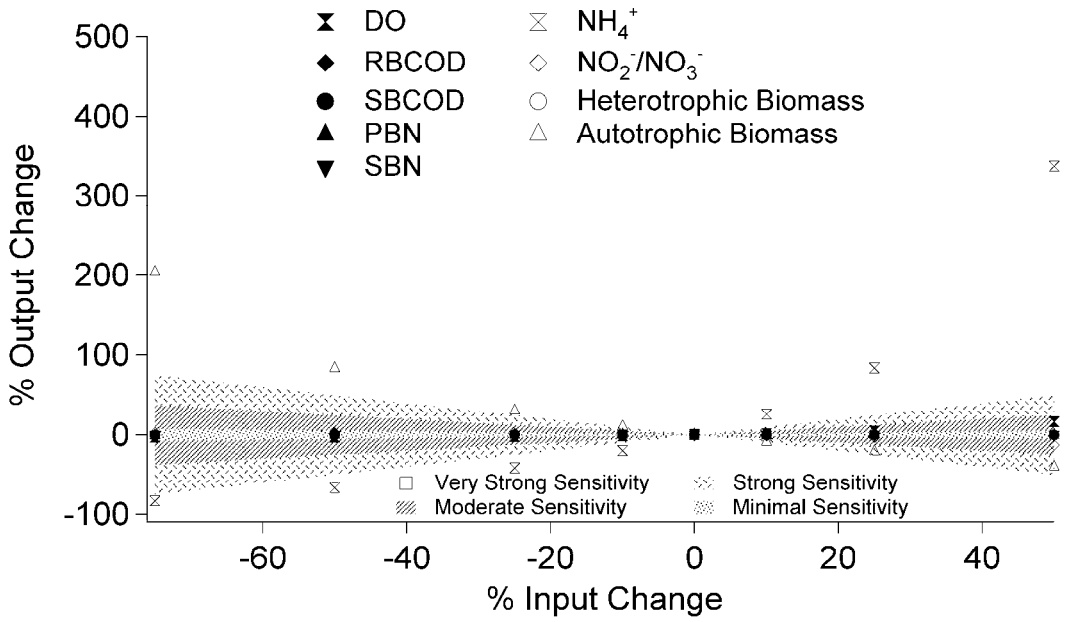


Figure A-3 Effect of heterotroph decay coefficient (b_H) on system state variables (ASM1 – Cranfield data).



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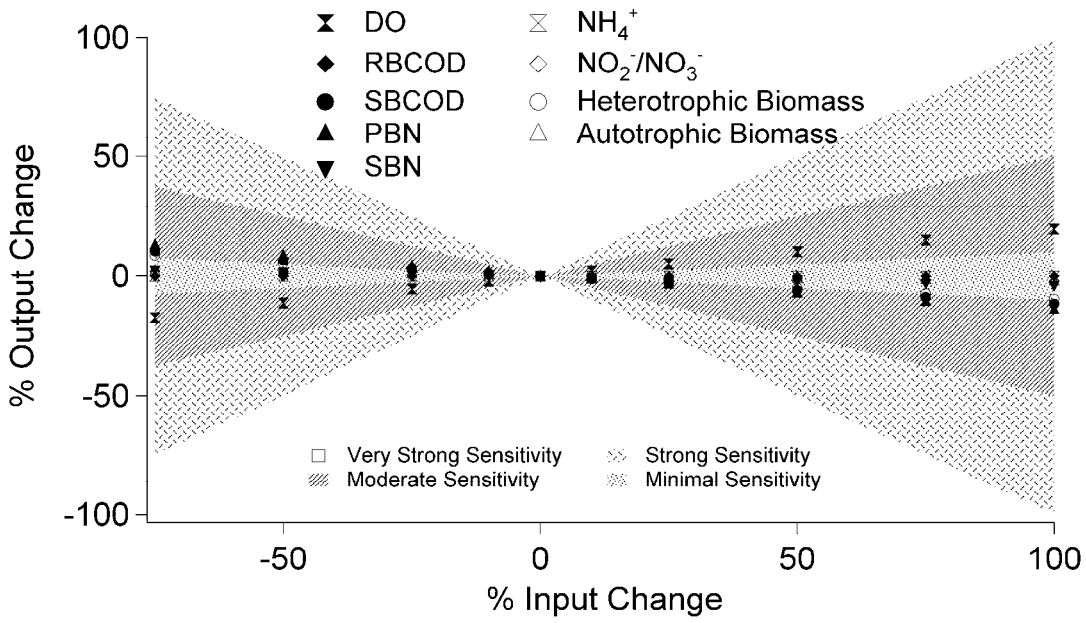

Figure A-5 Effect of biomass decay partitioning factor (f_p) on system state variables (ASM1 – Cranfield data).

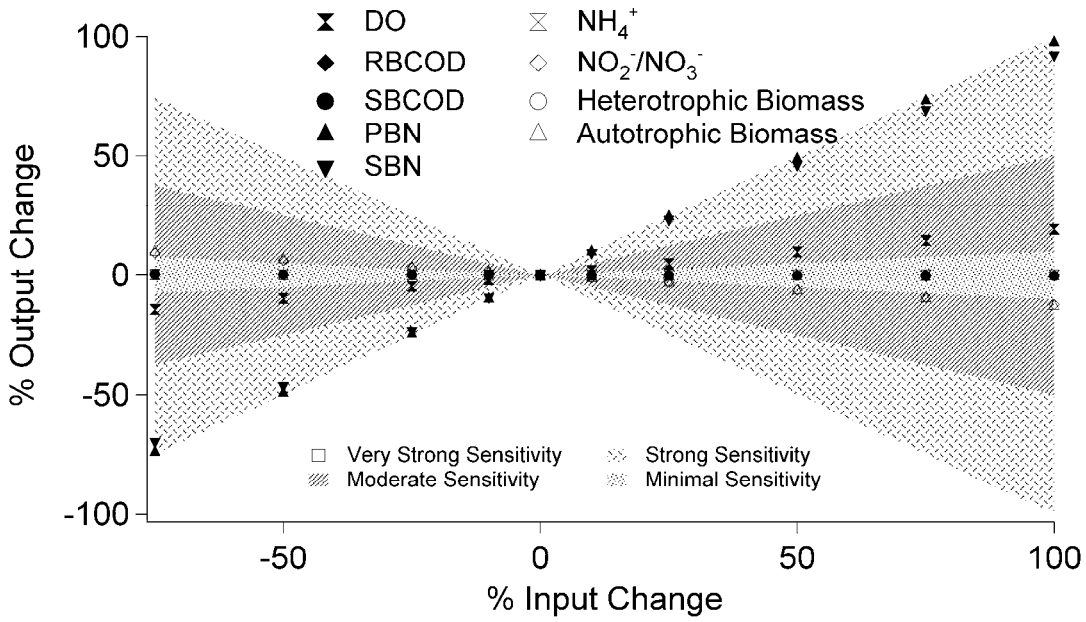

Figure A-6 Effect of biomass nitrogen fraction (i_{XB}) on system state variables (ASM1 – Cranfield data).

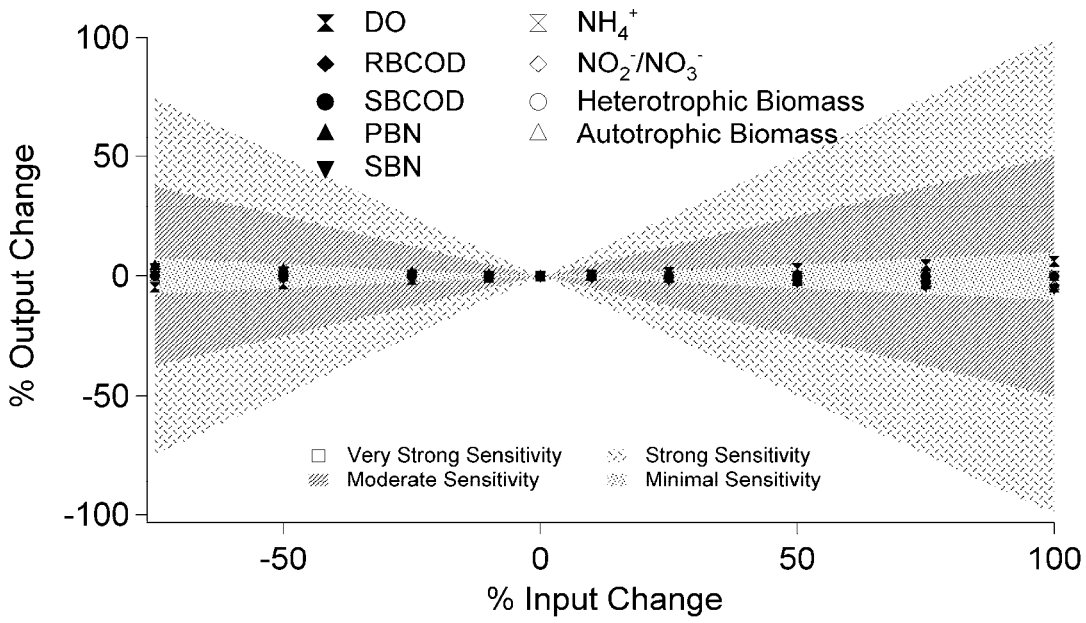

Figure A-7 Effect of particulate product nitrogen fraction (i_{XP}) on system state variables (ASM1 – Cranfield data).

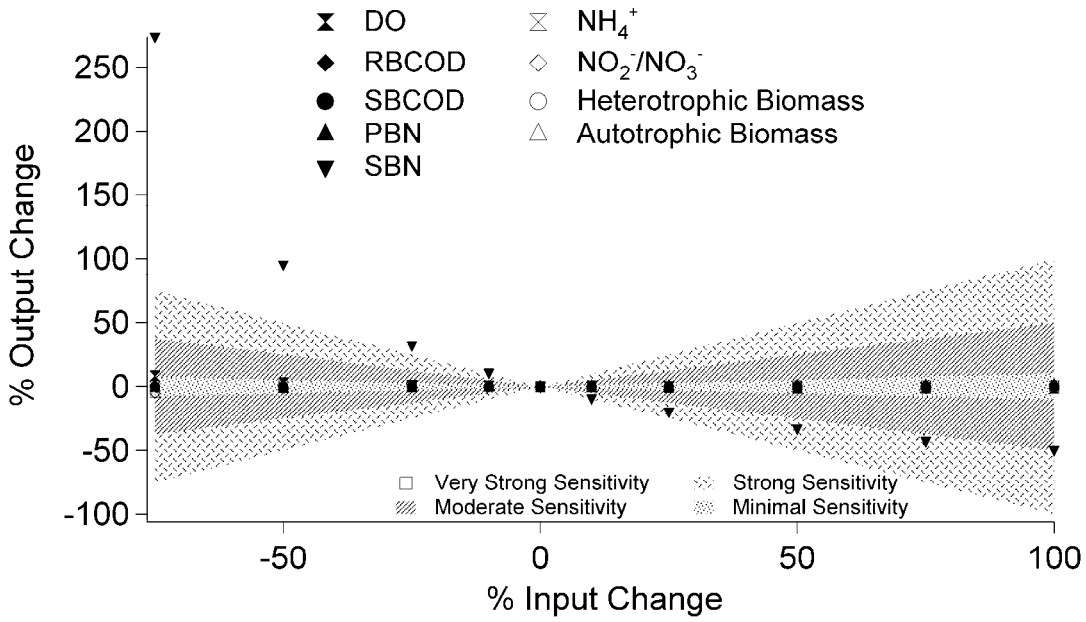

Figure A-8 Effect of ammonification rate (k_a) on system state variables (ASM1 – Cranfield data).

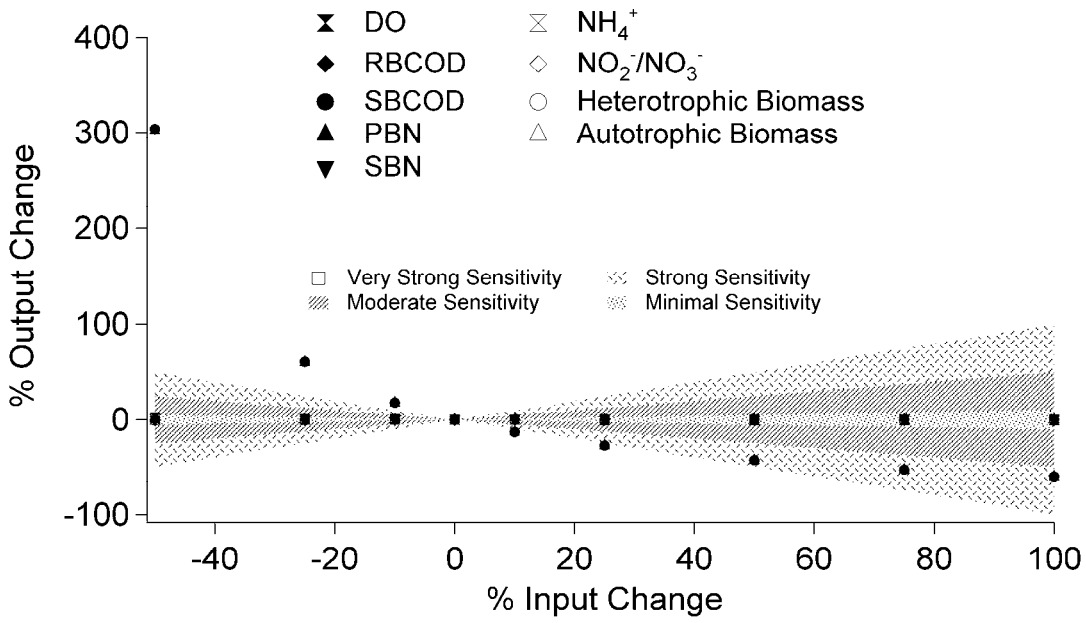

Figure A-9 Effect of maximum specific hydrolysis rate (k_H) on system state variables (ASM1 – Cranfield data).

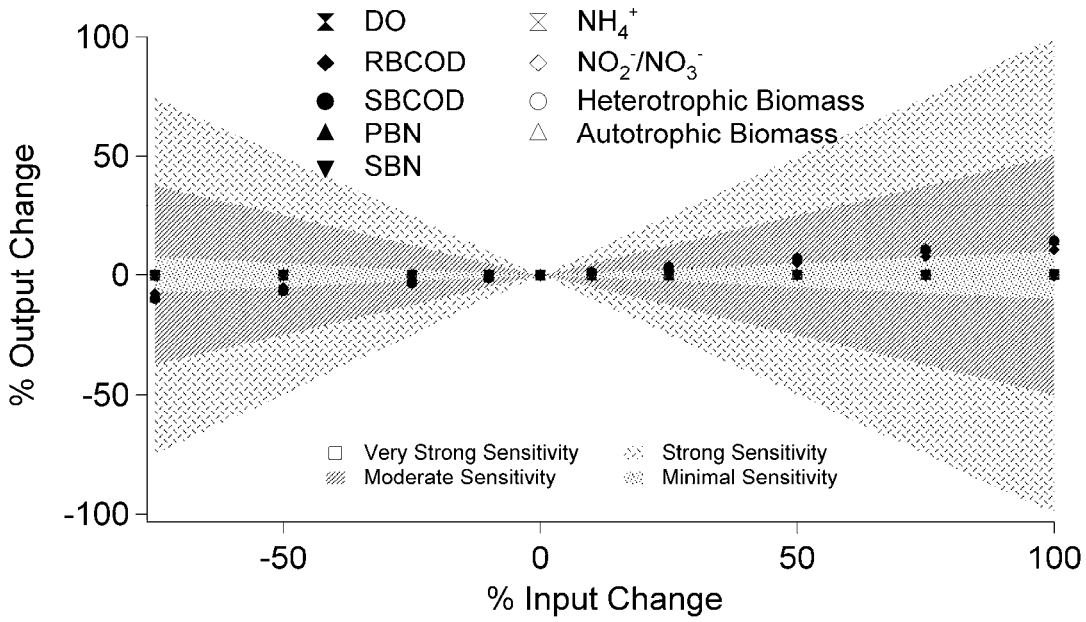

Figure A-10 Effect of heterotroph DO inhibition coefficient (K_{OH}) on system state variables (ASM1 – Cranfield data).

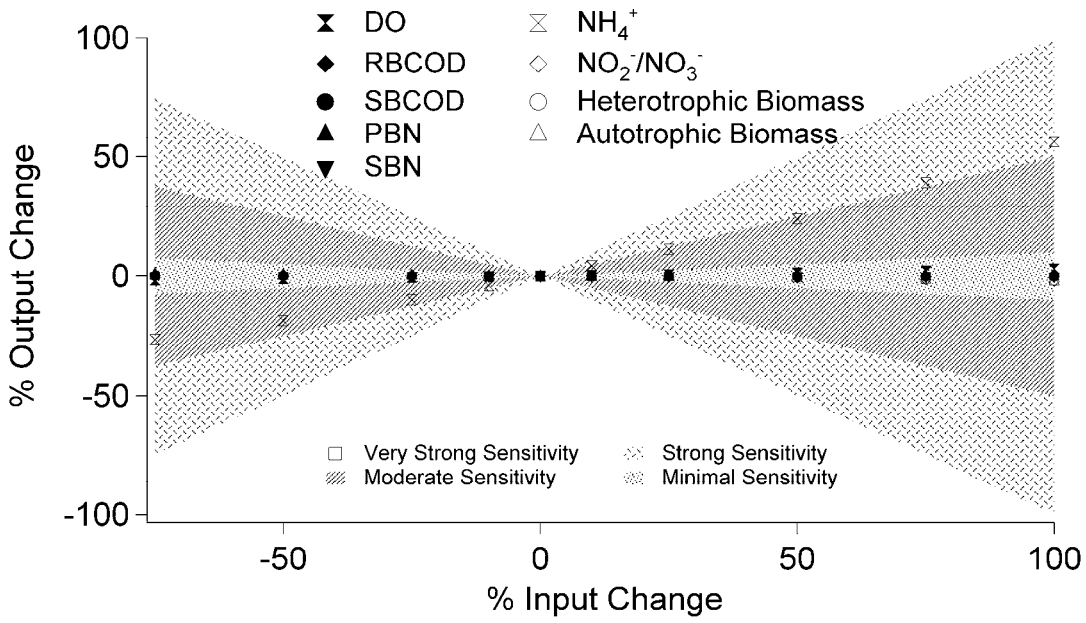

Figure A-11 Effect of autotroph DO inhibition coefficient (K_{OA}) on system state variables (ASM1 – Cranfield data).

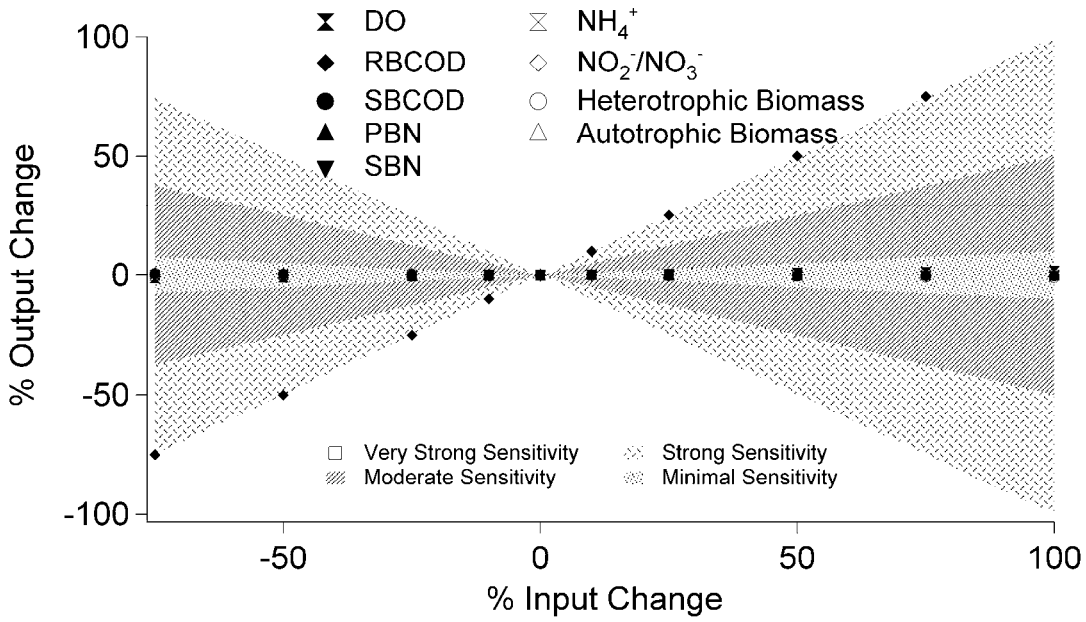

Figure A-12 Effect of heterotroph substrate inhibition coefficient (K_S) on system state variables (ASM1 – Cranfield data).

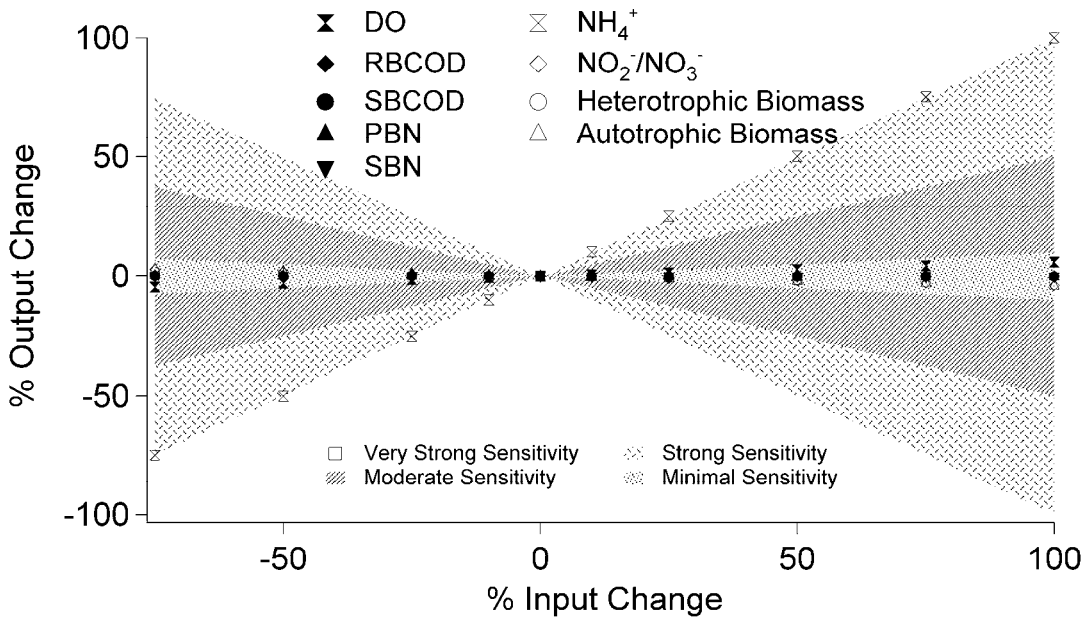

Figure A-13 Effect of autotroph ammonia inhibition coefficient (K_{NH}) on system state variables (ASM1 – Cranfield data).

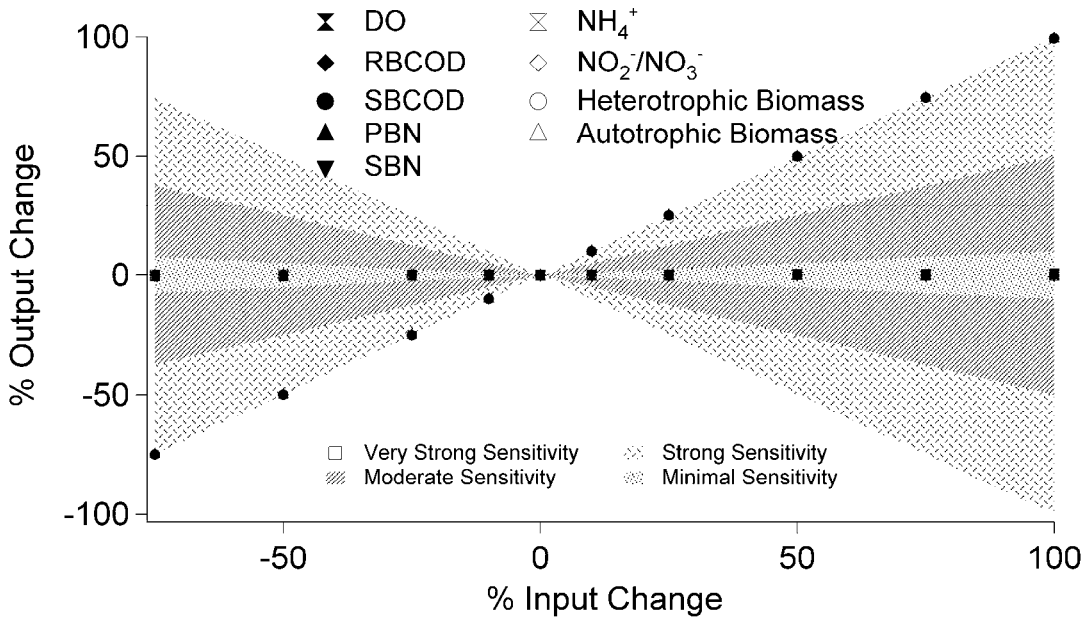

Figure A-14 Effect of hydrolysis half-saturation coefficient (K_X) on system state variables (ASM1 – Cranfield data).

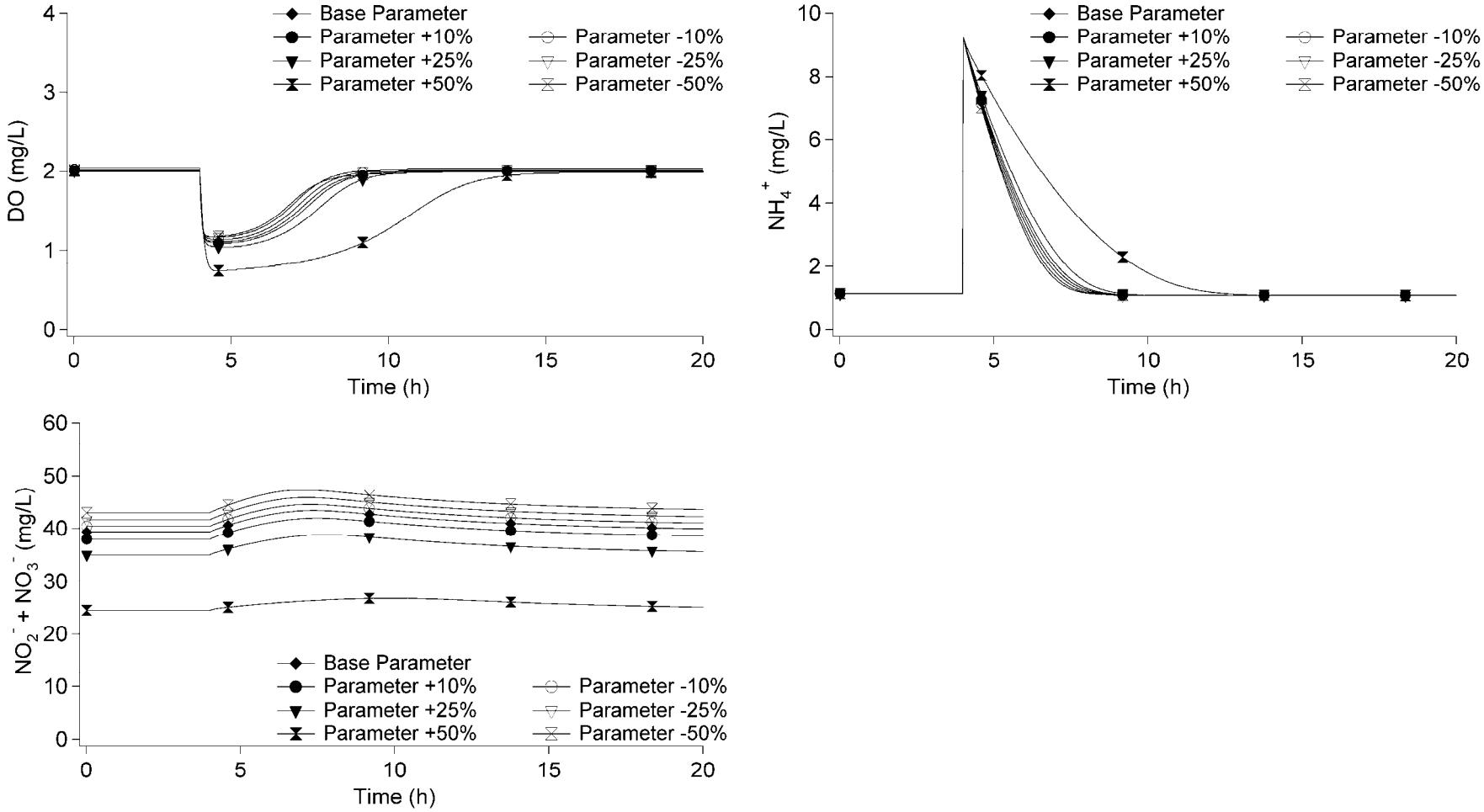

Figure A-15 Effect of heterotrophic yield (Y_H) on dynamic response (ASM1 – Cranfield data).

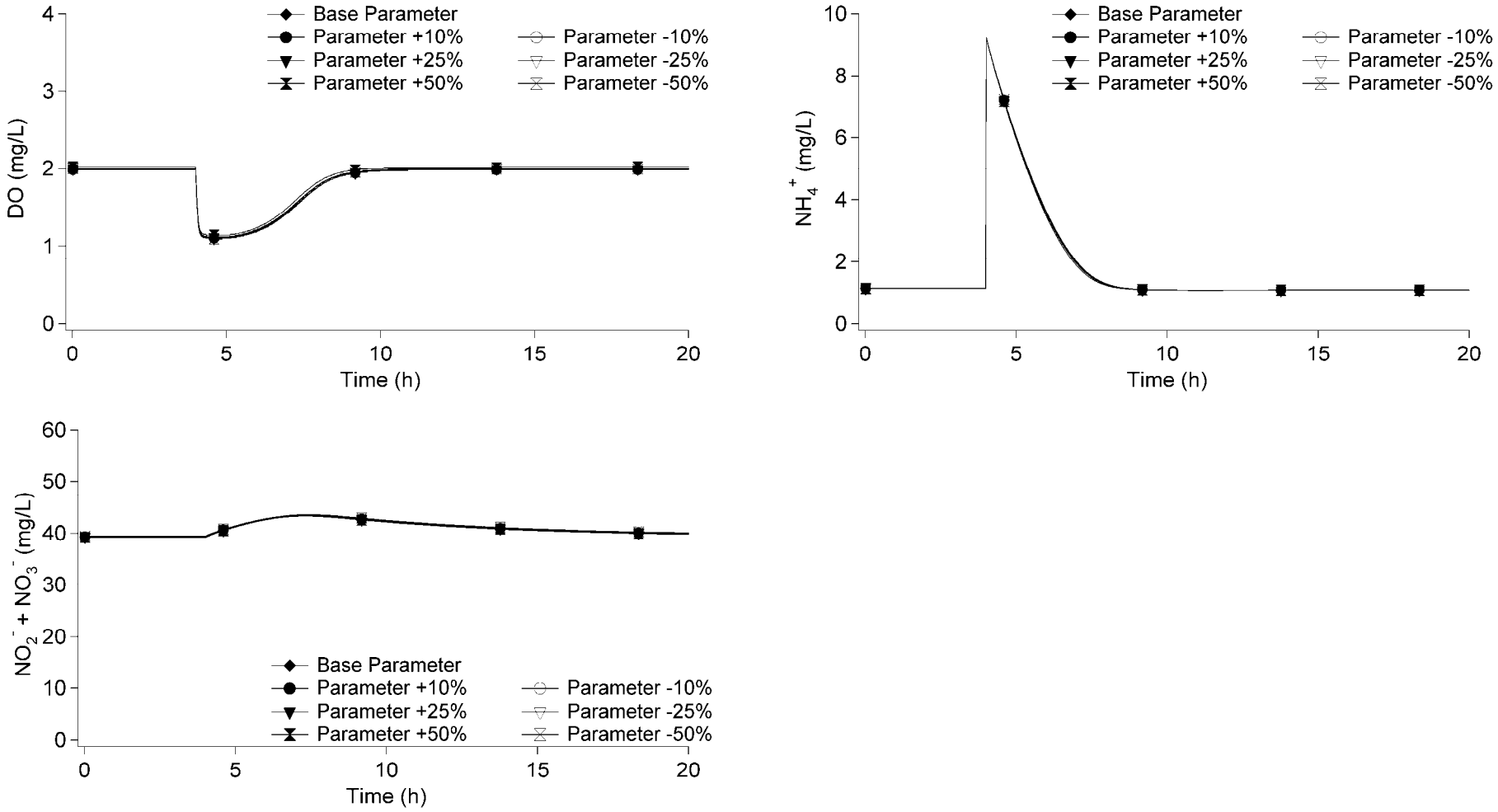

Figure A-16 Effect of autotrophic yield (Y_A) on dynamic response (ASM1 – Cranfield data).

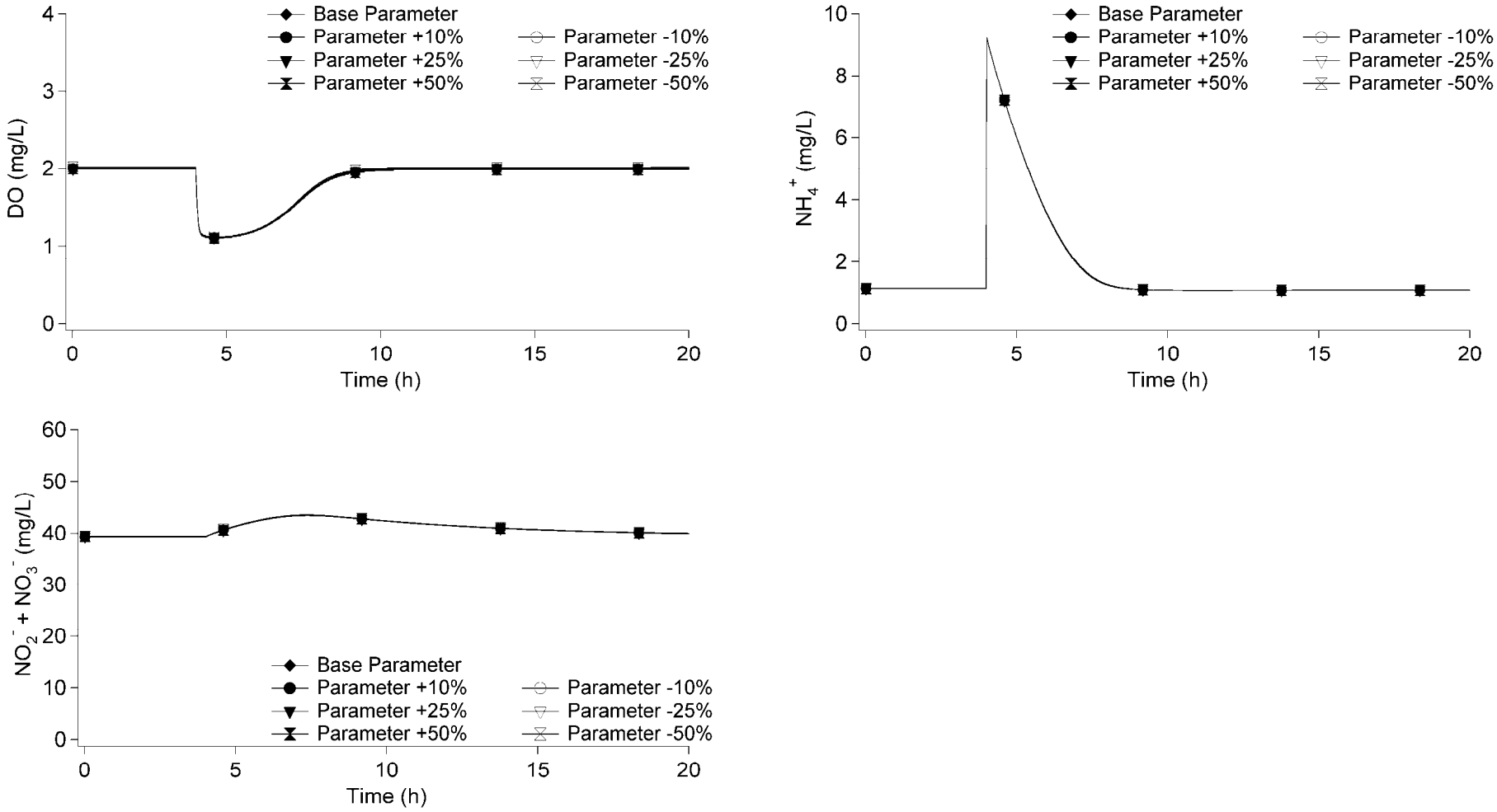

Figure A-17 Effect of heterotroph maximum specific growth rate (μ_H) on dynamic response (ASM1 – Cranfield data).

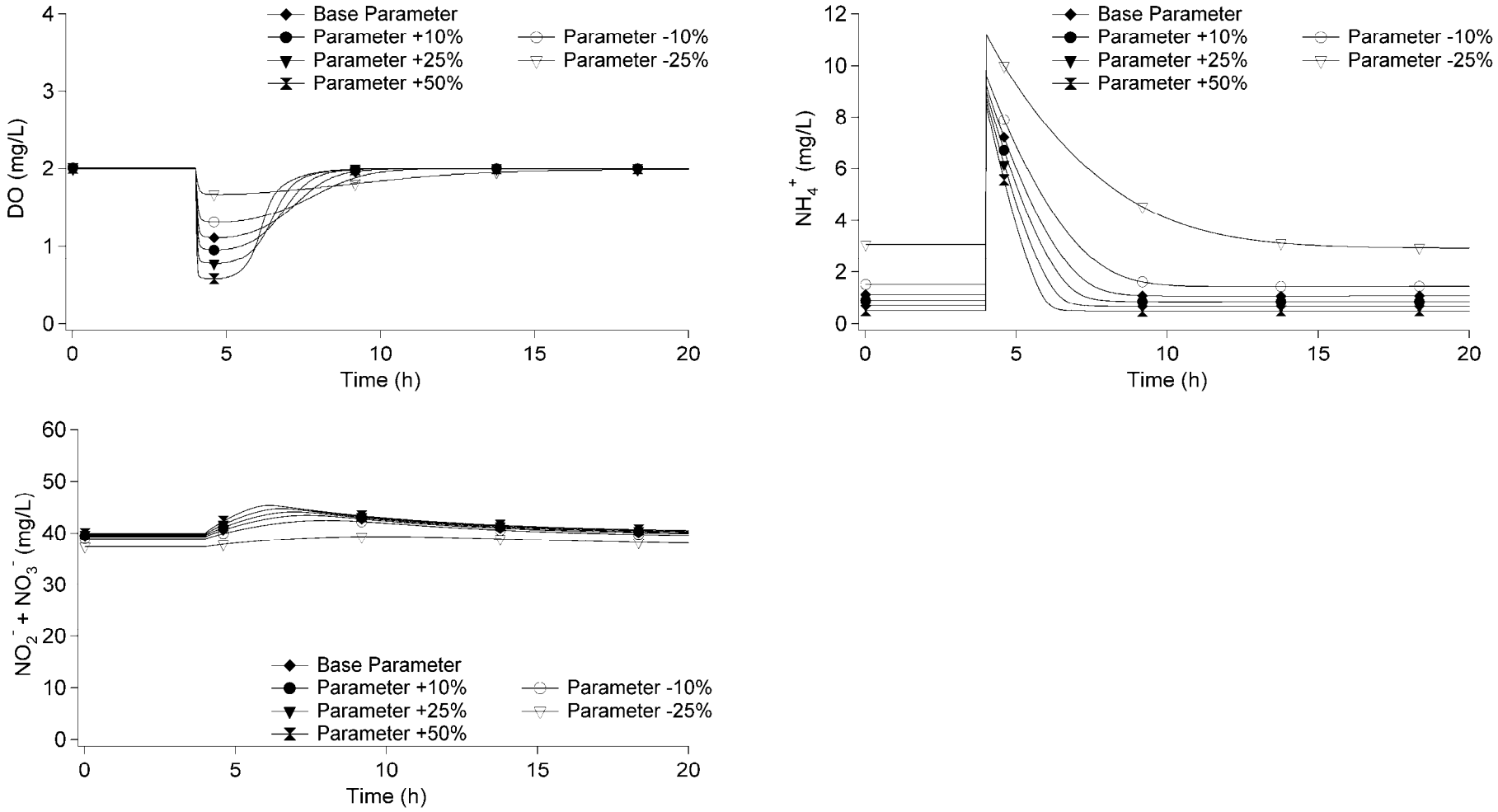

Figure A-18 Effect of autotroph maximum specific growth rate (μ_A) on dynamic response (ASM1 – Cranfield data).

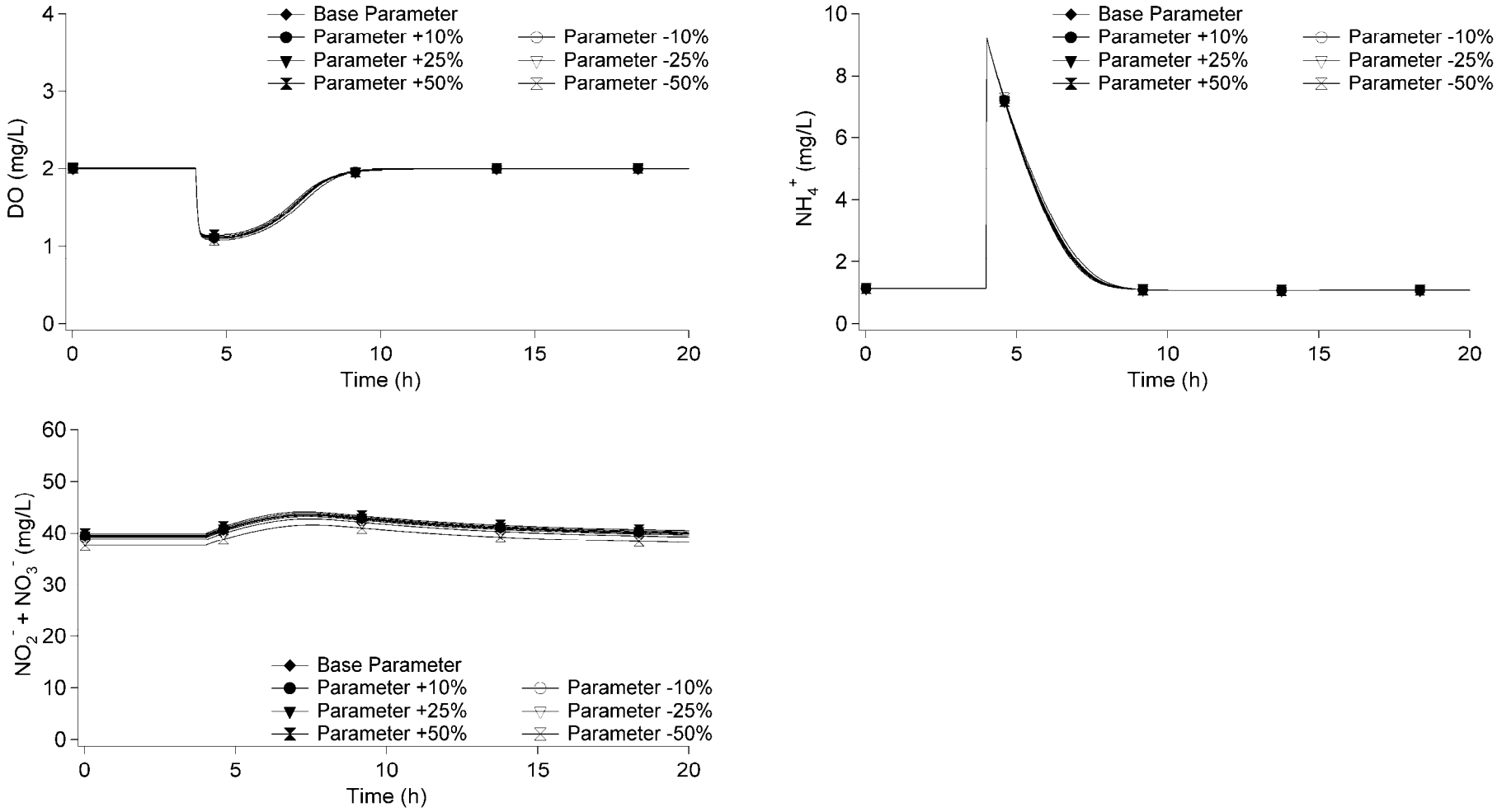

Figure A-19 Effect of heterotroph decay coefficient (b_H) on dynamic response (ASM1 – Cranfield data).

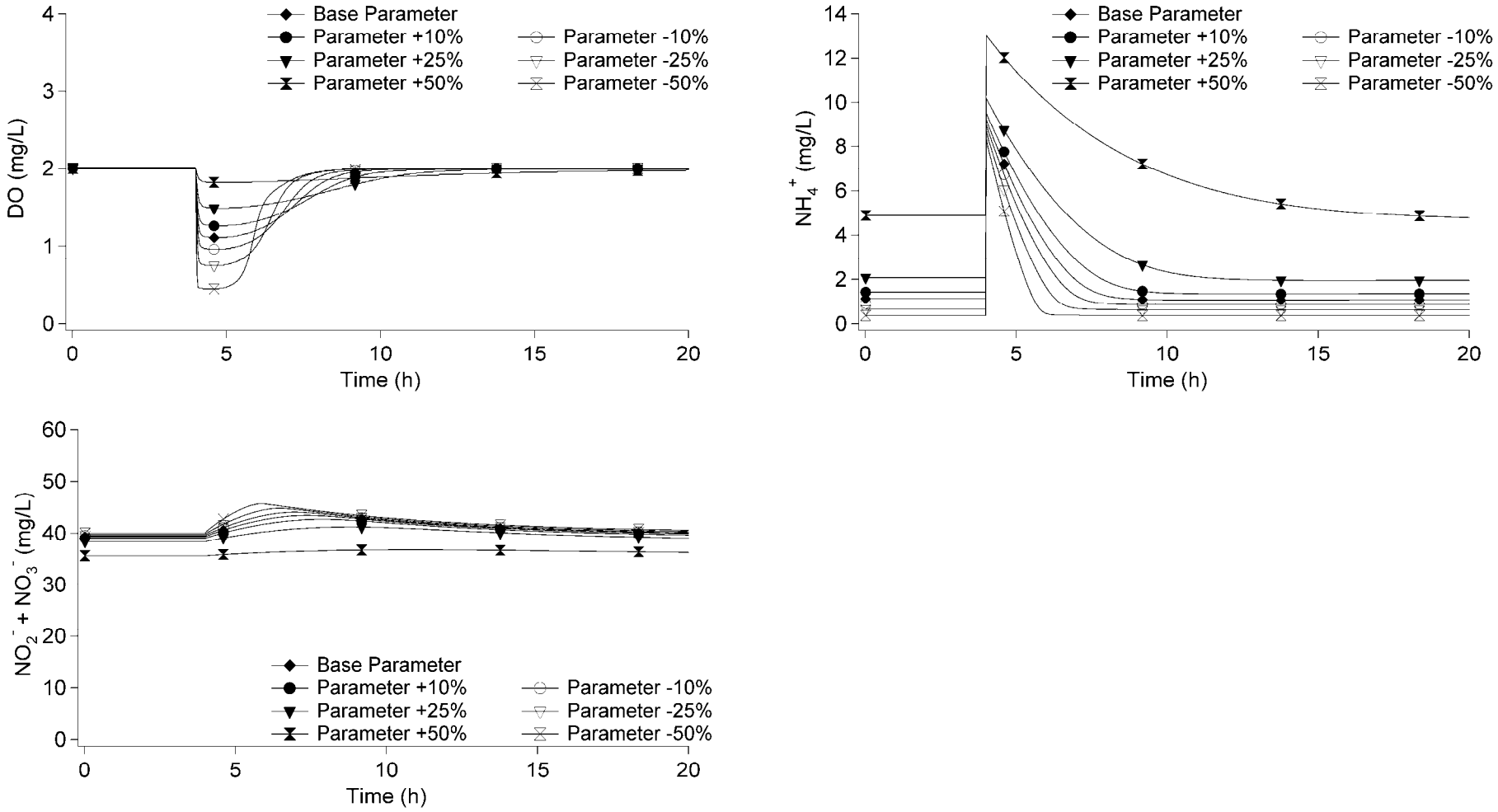

Figure A-20 Effect of autotroph decay coefficient (b_A) on dynamic response (ASM1 – Cranfield data).

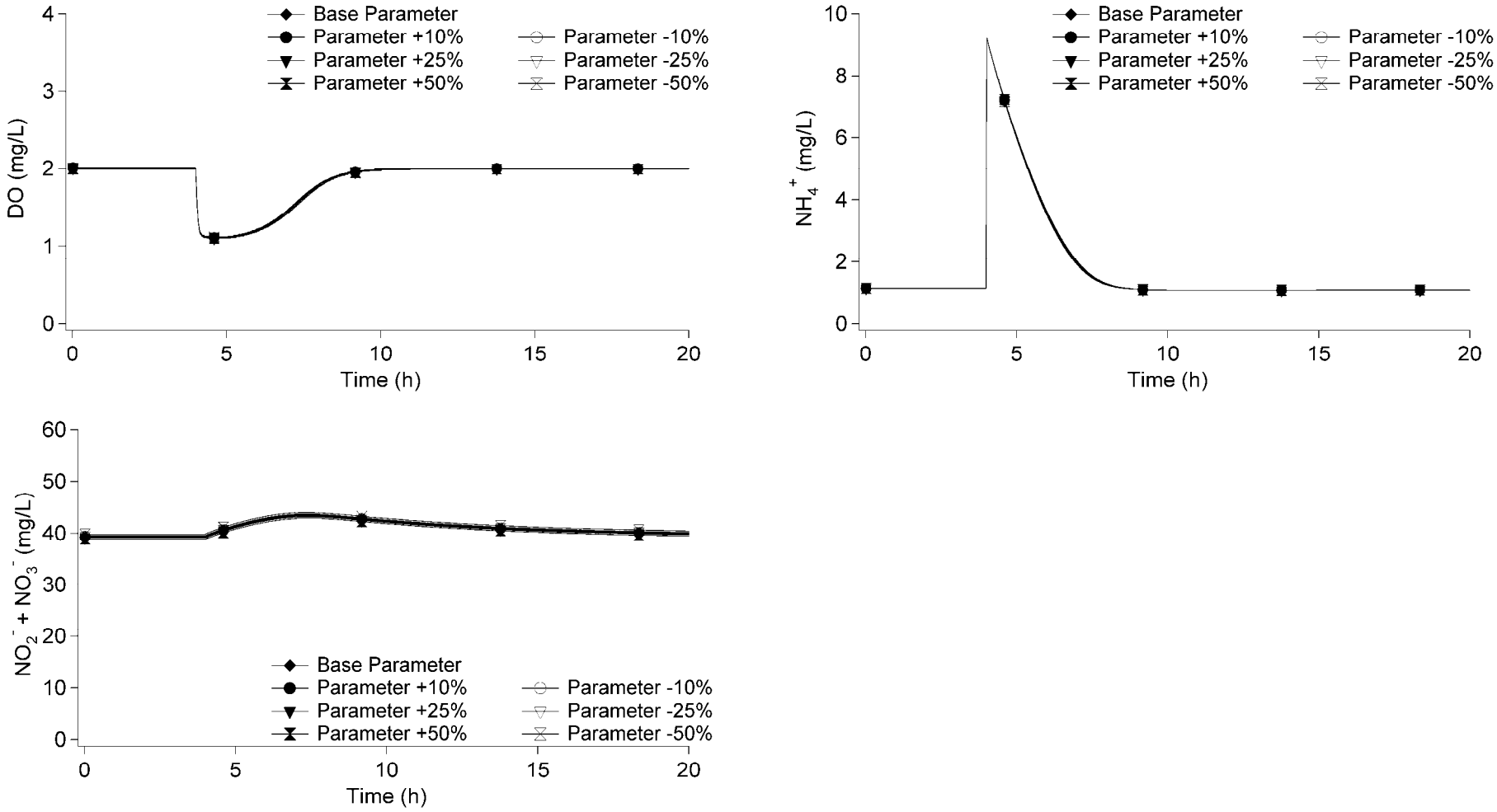

Figure A-21 Effect of biomass decay partitioning factor (f_p) on dynamic response (ASM1 – Cranfield data).

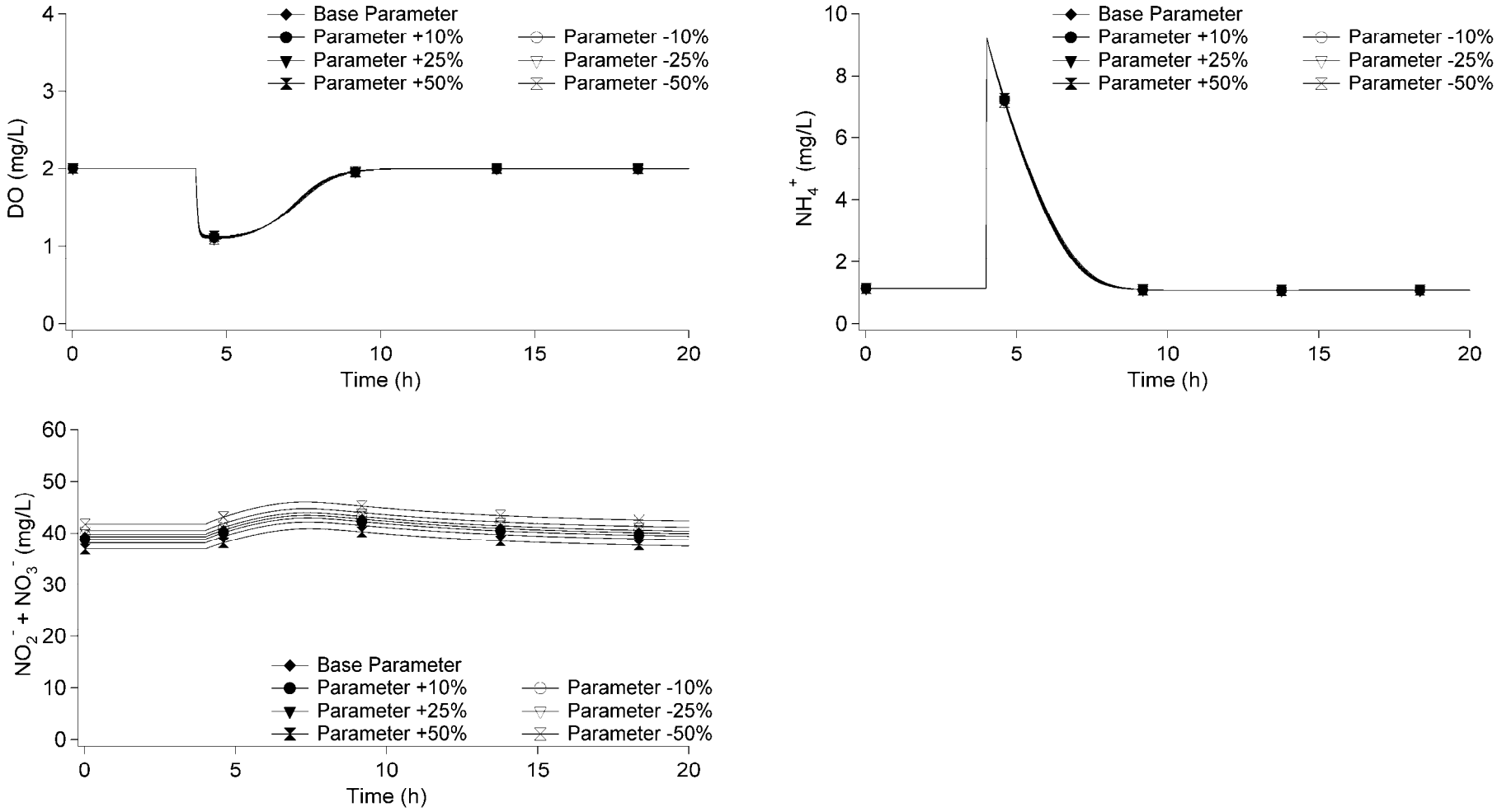

Figure A-22 Effect of biomass nitrogen fraction (i_{XB}) on dynamic response (ASM1 – Cranfield data).

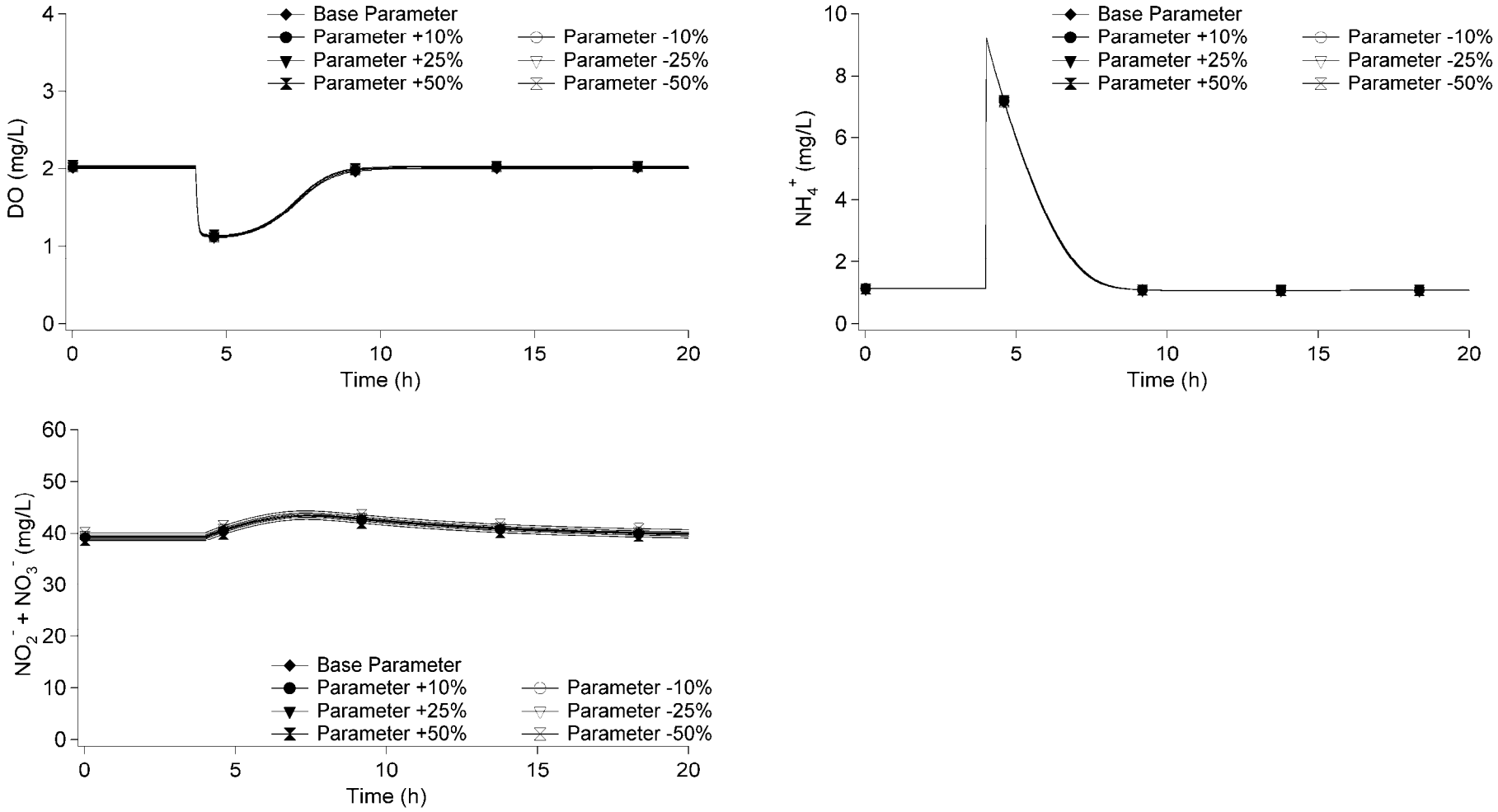

Figure A-23 Effect of particulate product nitrogen fraction (i_{XP}) on dynamic response (ASM1 – Cranfield data).

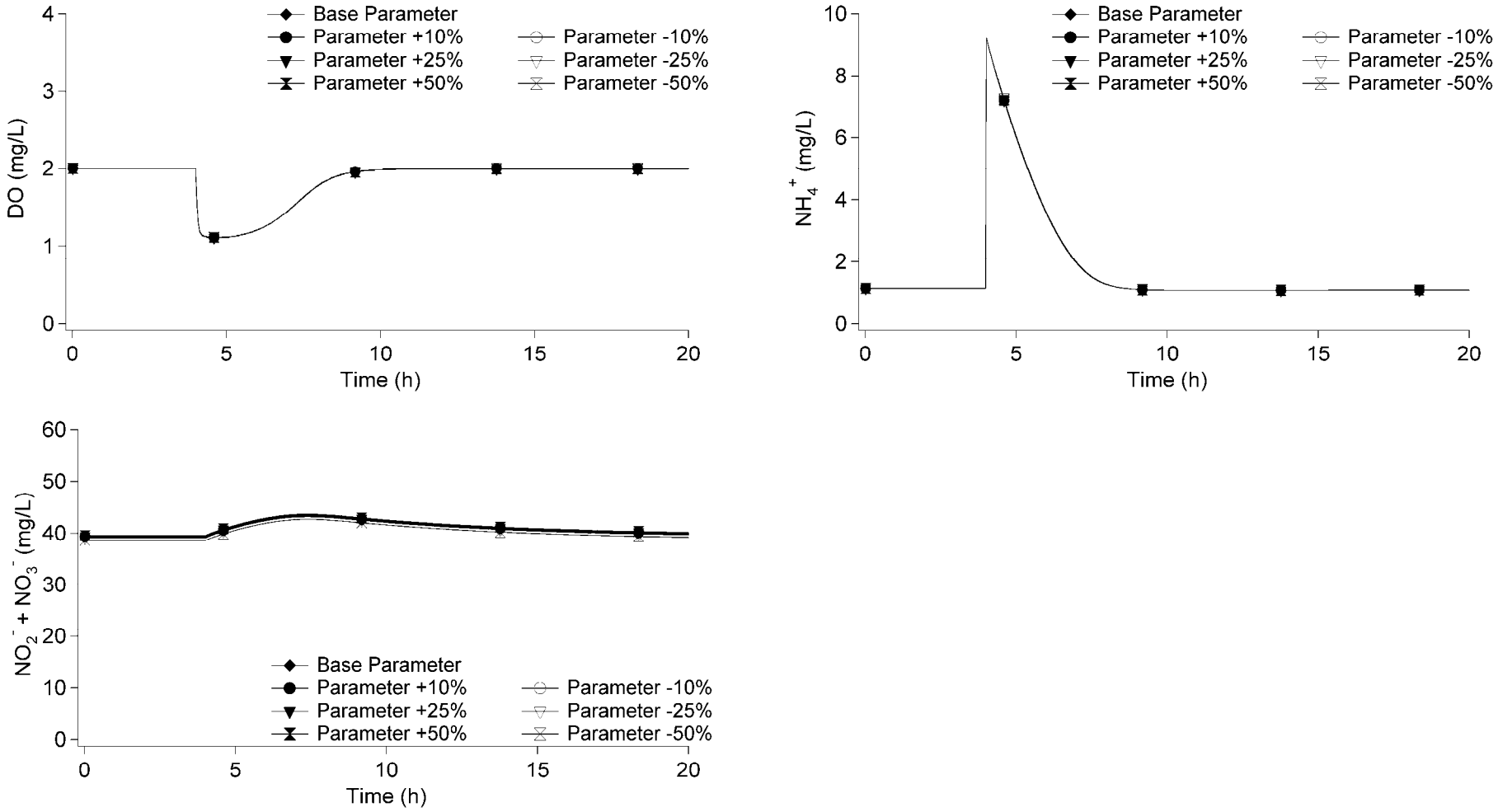

Figure A-24 Effect of ammonification rate (k_a) on dynamic response (ASM1 – Cranfield data).

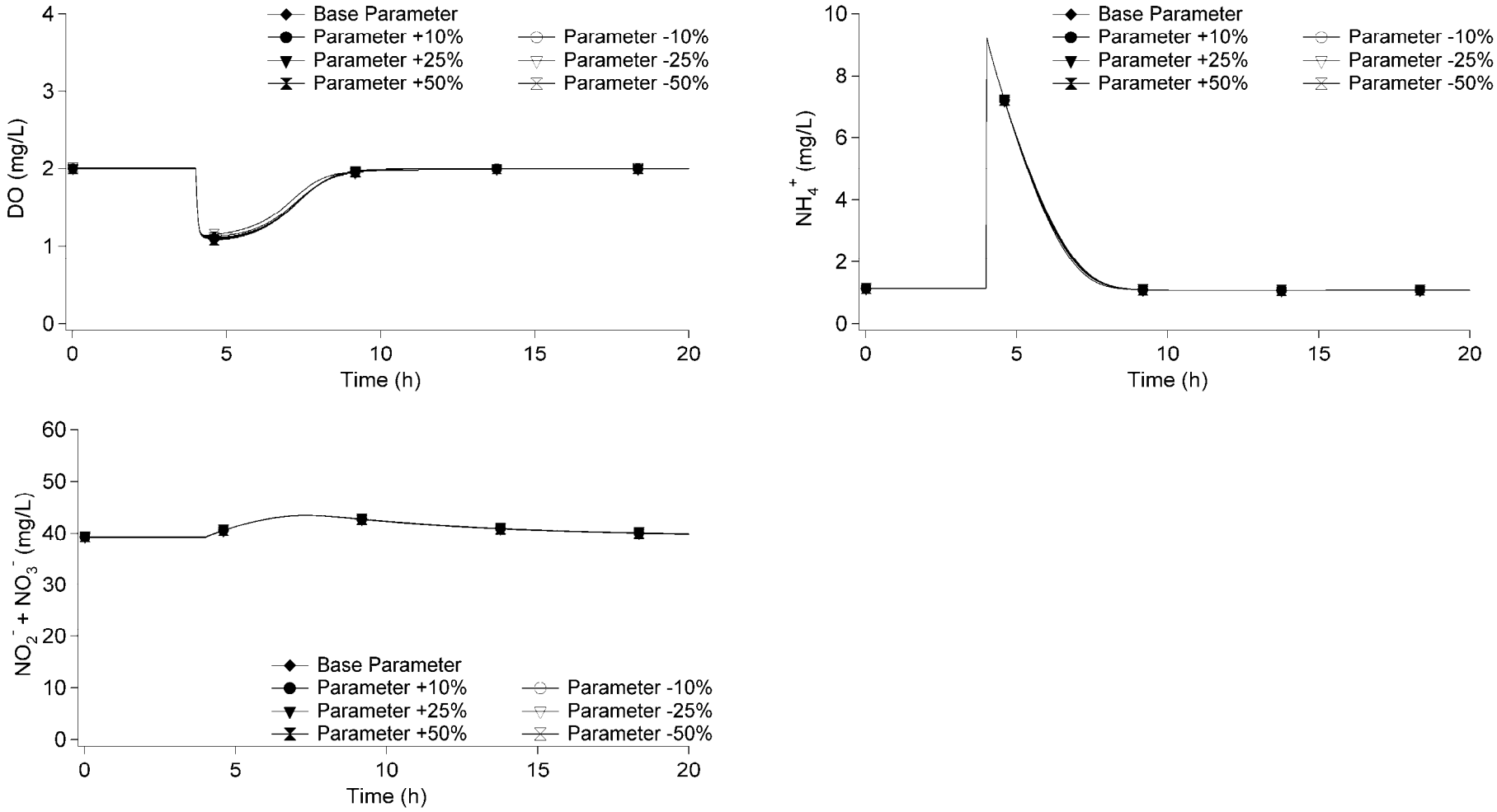

Figure A-25 Effect of maximum specific hydrolysis rate (k_H) on dynamic response (ASM1 – Cranfield data).

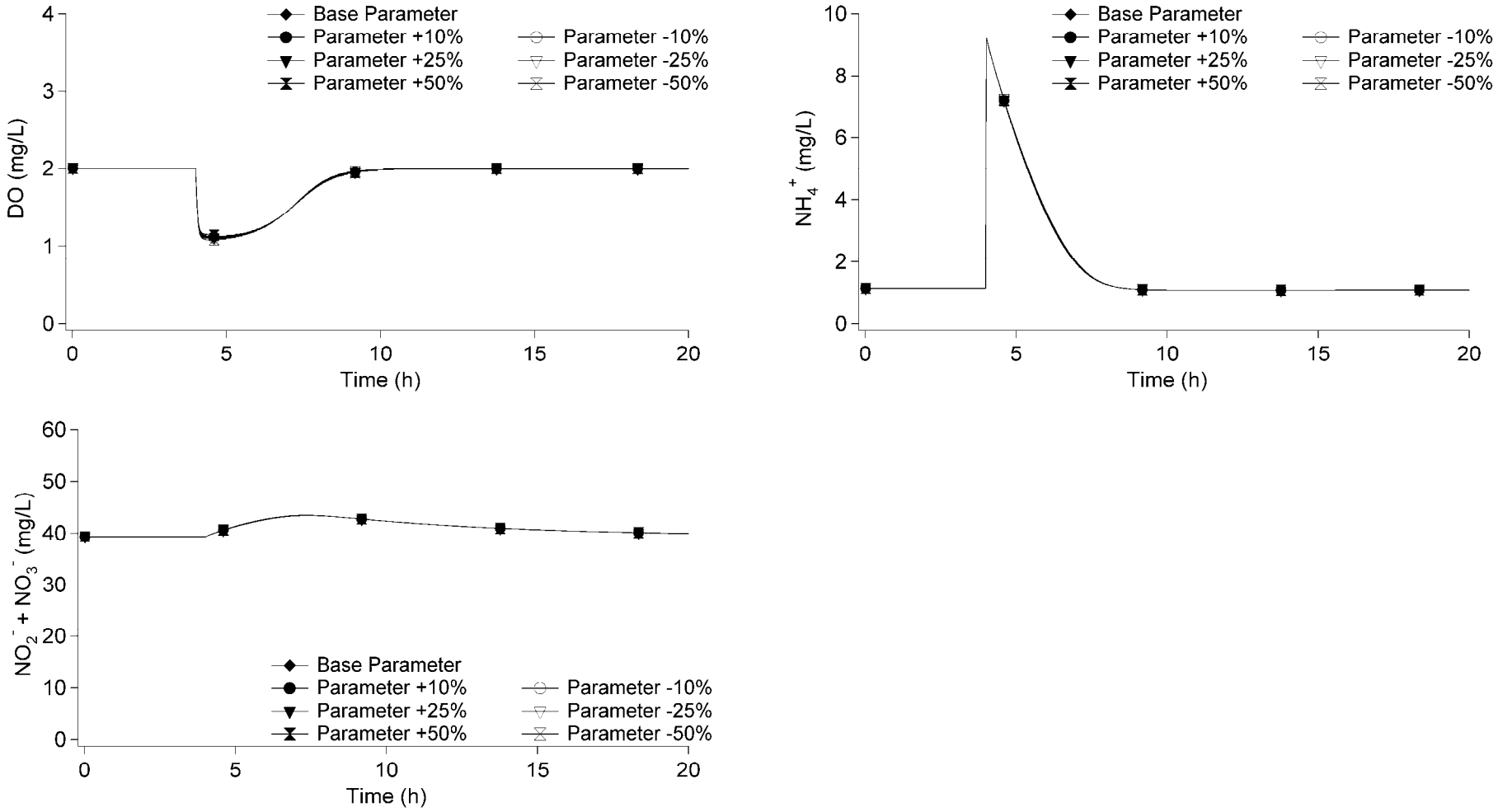

Figure A-26 Effect of heterotroph DO inhibition coefficient (K_{OH}) on dynamic response (ASM1 – Cranfield data).

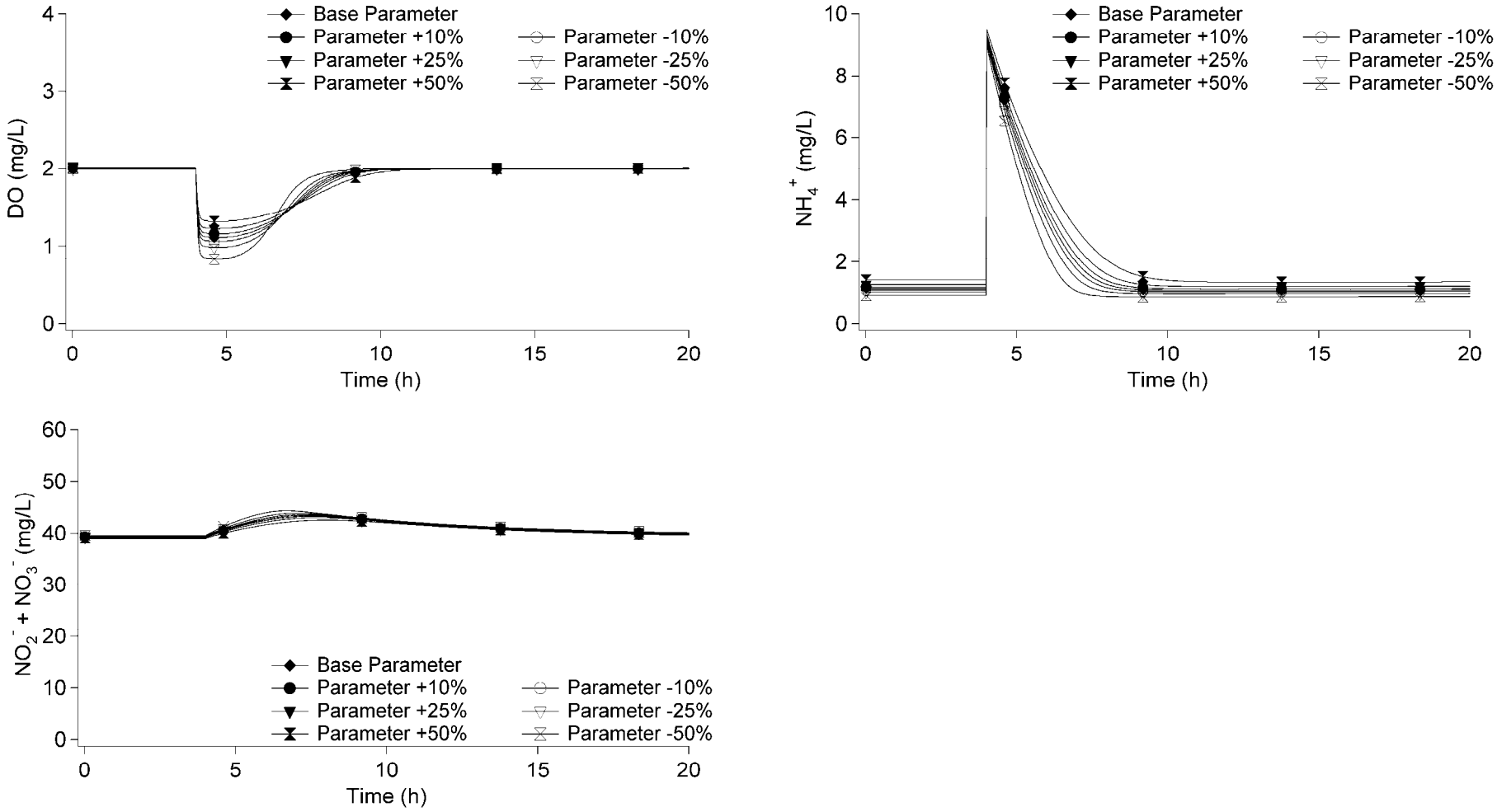

Figure A-27 Effect of autotroph DO inhibition coefficient (K_{OA}) on dynamic response (ASM1 – Cranfield data).

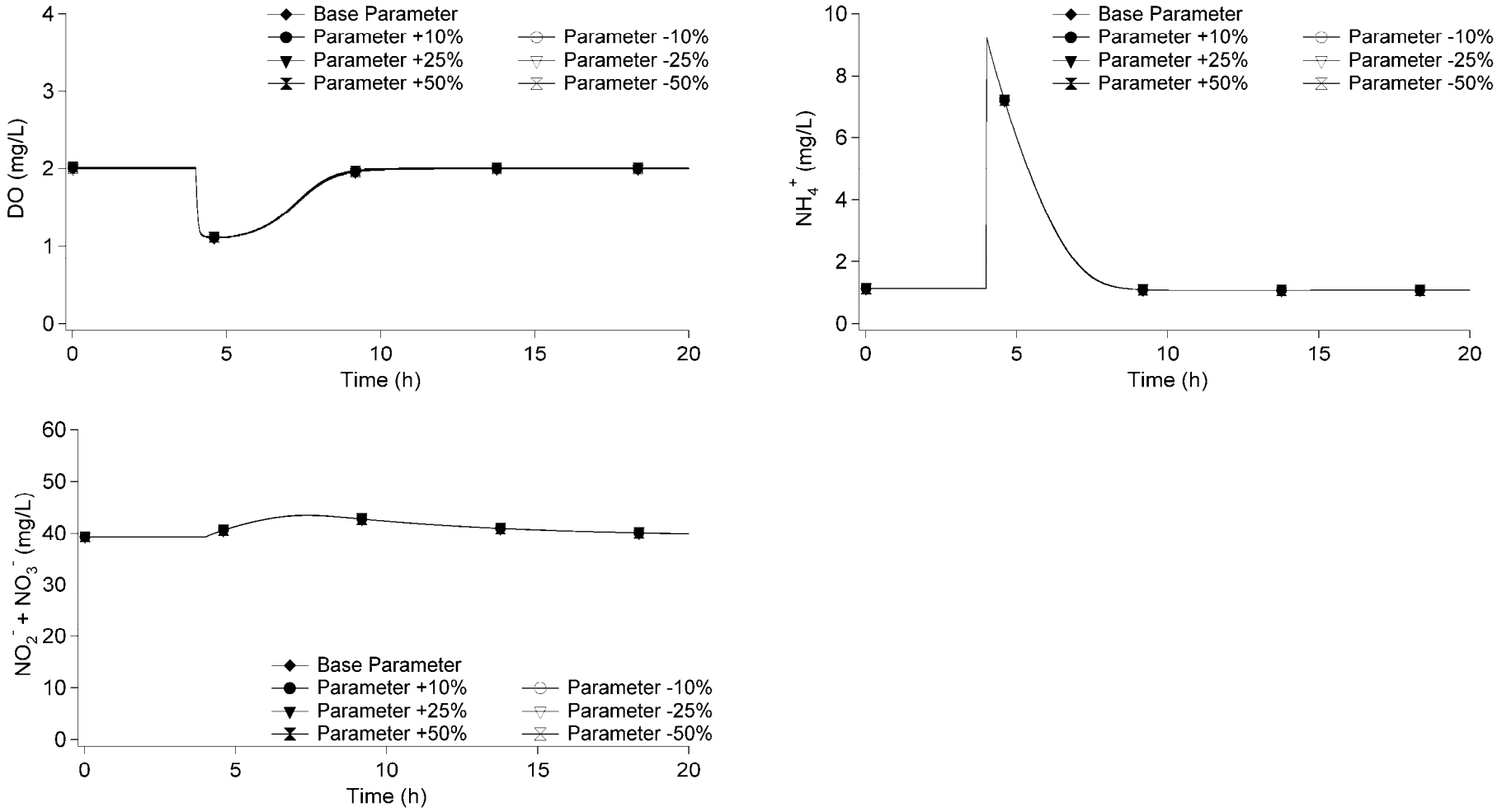

Figure A-28 Effect of heterotroph substrate inhibition coefficient (K_S) on dynamic response (ASM1 – Cranfield data).

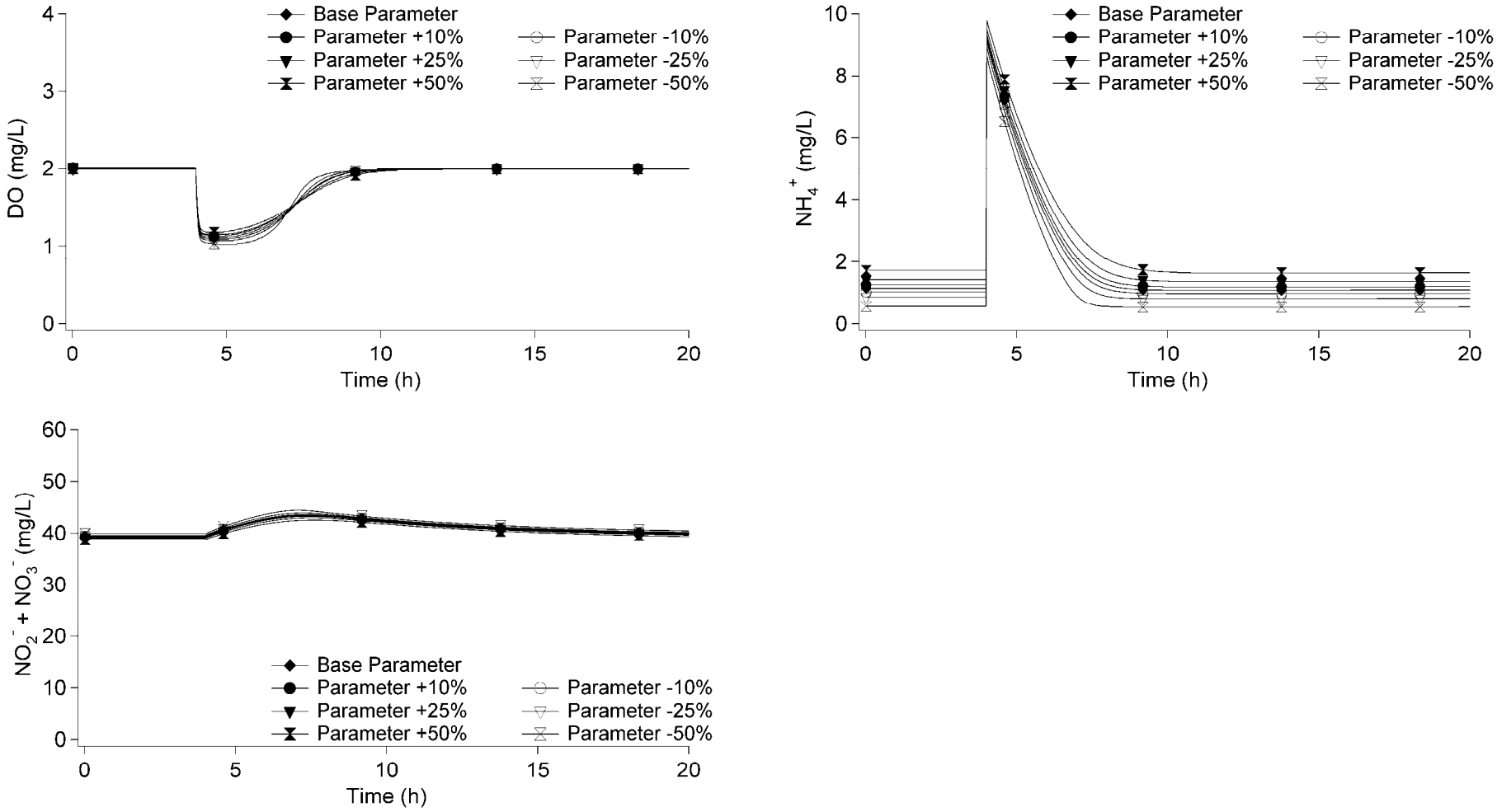

Figure A-29 Effect of autotroph ammonia inhibition coefficient (K_{NH}) on dynamic response (ASM1 – Cranfield data).

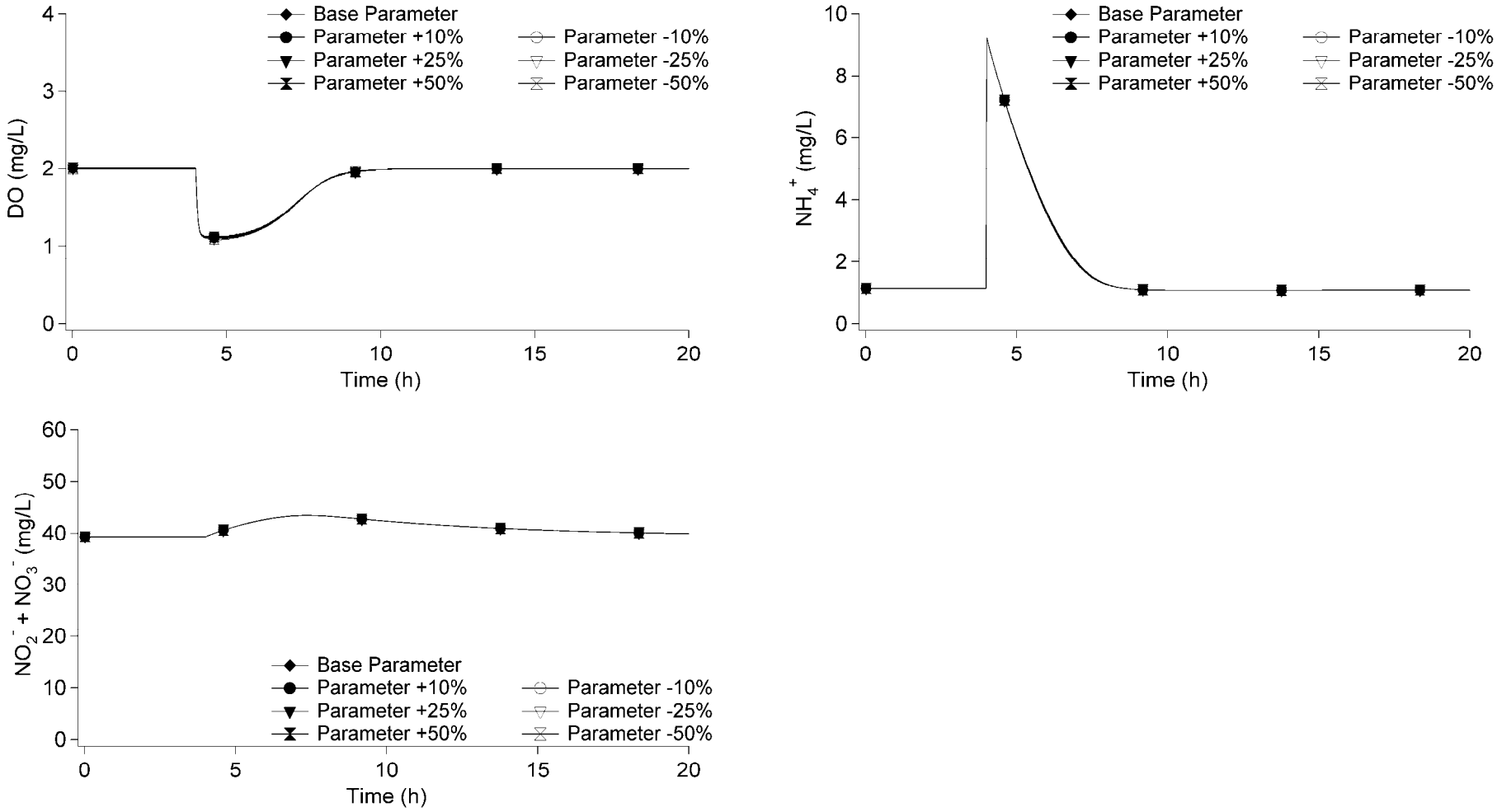

Figure A-30 Effect of hydrolysis half-saturation coefficient (K_X) on dynamic response (ASM1 – Cranfield data).

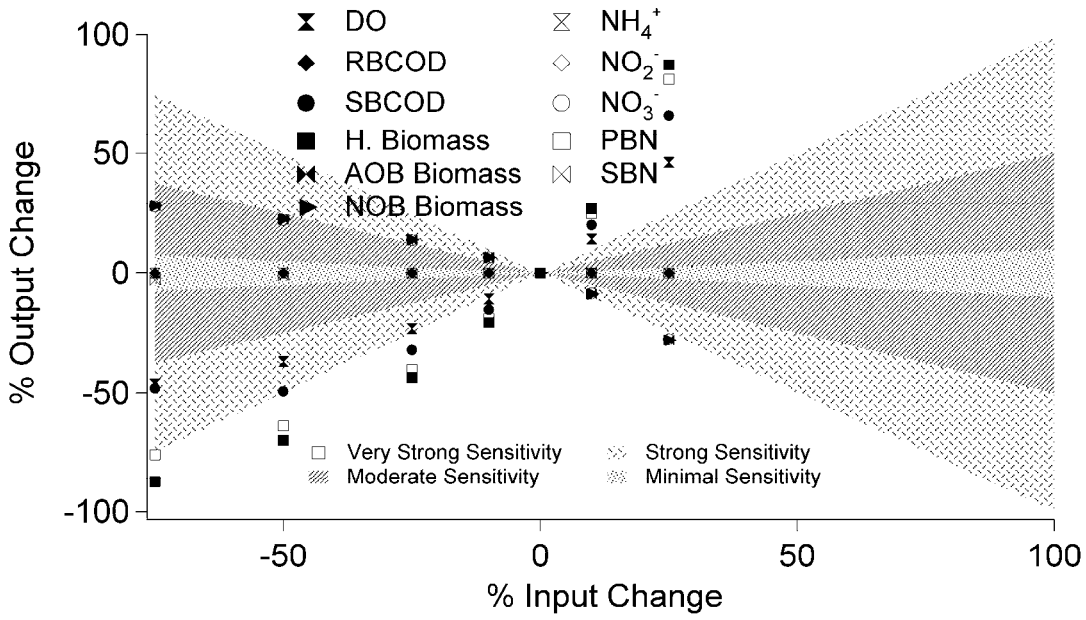

Figure A-31 Effect of heterotroph yield (Y_H) on system state variables (ASM1-Nowak – UNSW data).

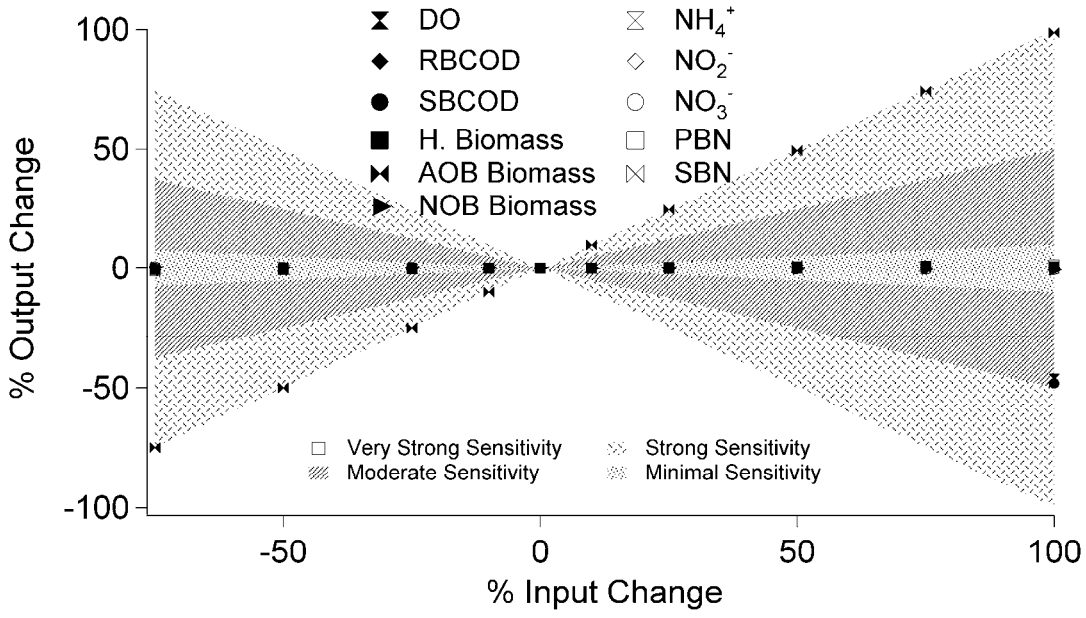

Figure A-32 Effect of AOB yield (Y_M) on system state variables (ASM1-Nowak – UNSW data).

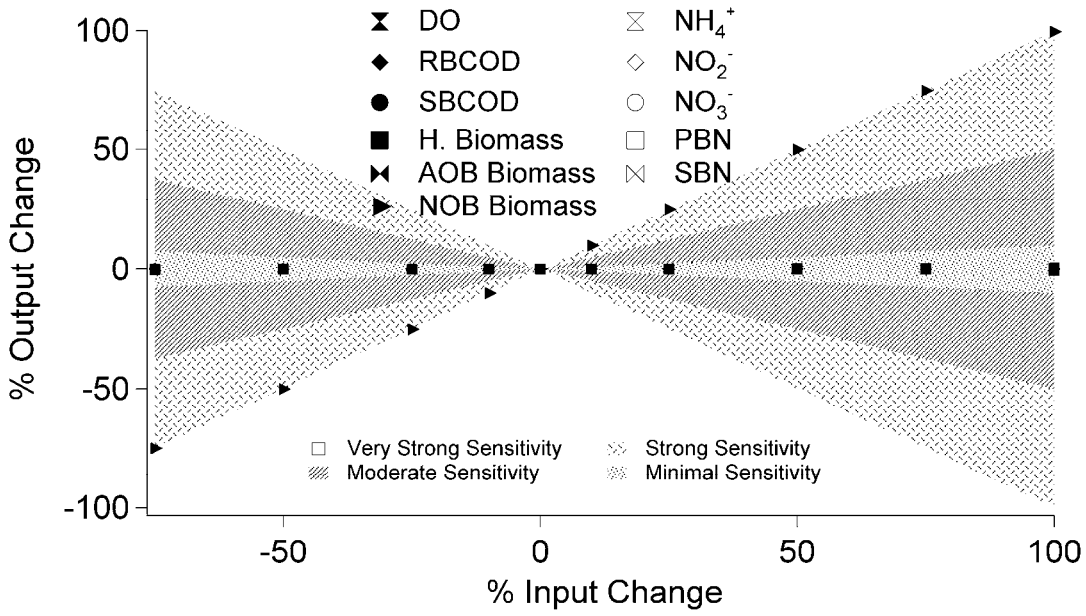

Figure A-33 Effect of NOB yield (Y_N) on system state variables (ASM1-Nowak – UNSW data).

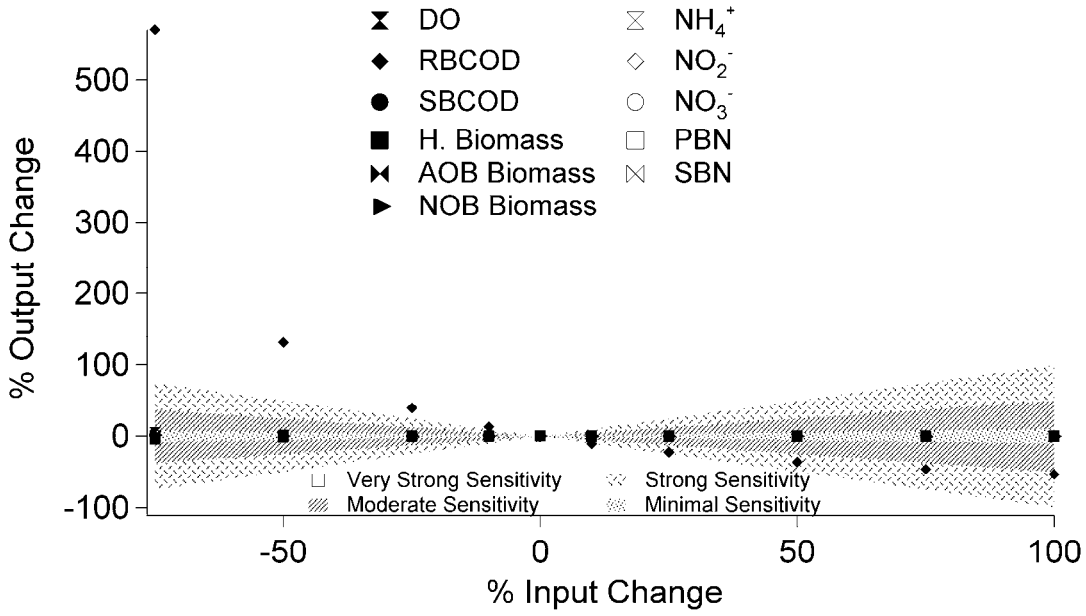

Figure A-34 Effect of heterotroph maximum specific growth rate (μ_H) on system state variables (ASM1-Nowak – UNSW data).

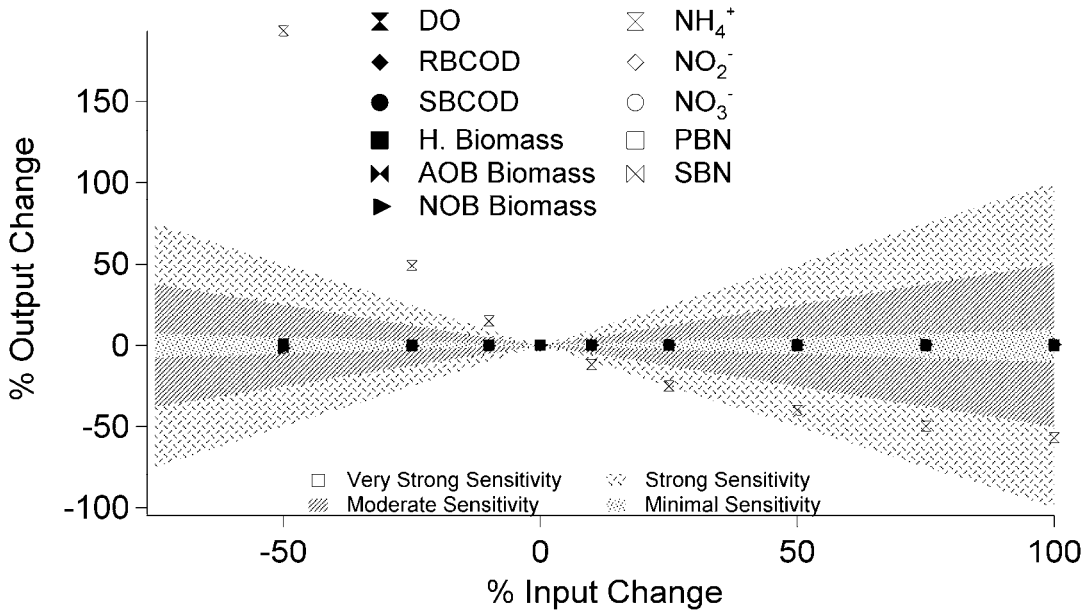

Figure A-35 Effect of AOB maximum specific growth rate (μ_M) on system state variables (ASM1-Nowak – UNSW data).

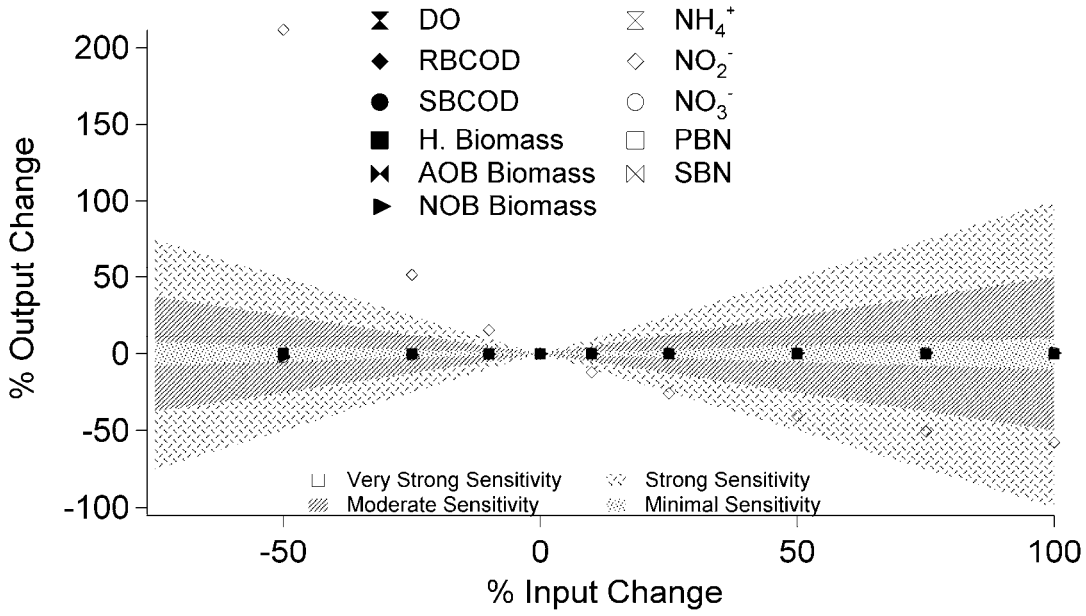

Figure A-36 Effect of NOB maximum specific growth rate (μ_N) on system state variables (ASM1-Nowak – UNSW data).

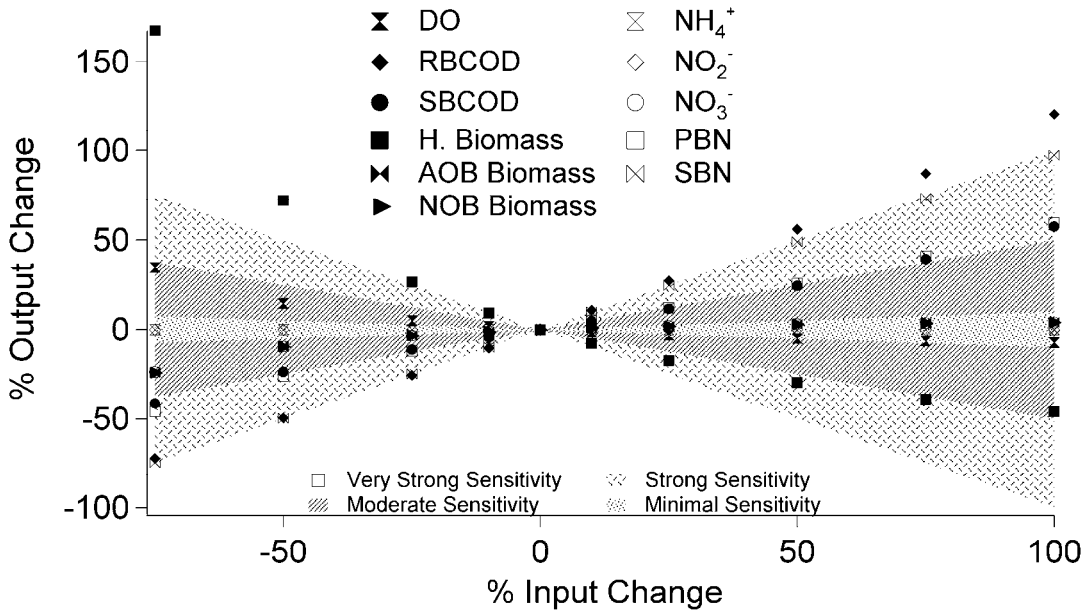

Figure A-37 Effect of heterotroph decay coefficient (b_H) on system state variables (ASM1-Nowak – UNSW data).

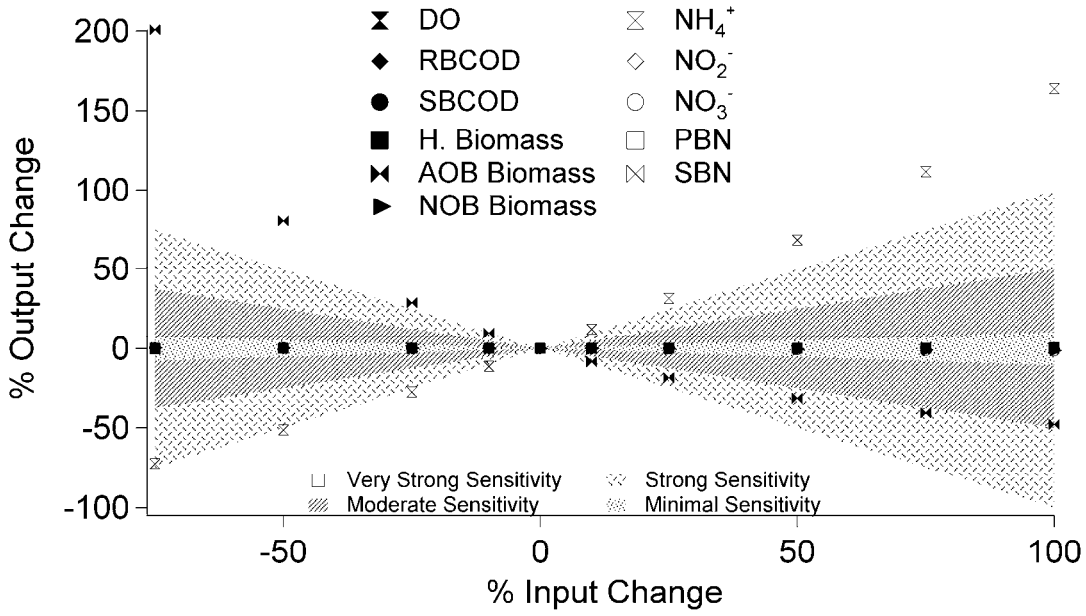

Figure A-38 Effect of AOB decay coefficient (b_M) on system state variables (ASM1-Nowak – UNSW data).

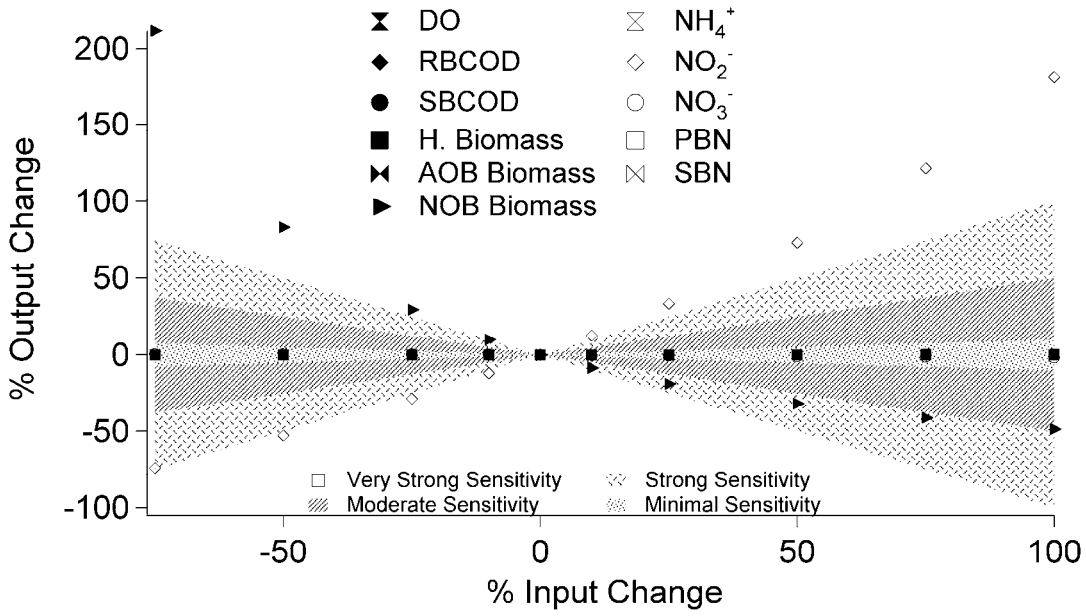

Figure A-39 Effect of NOB decay coefficient (b_N) on system state variables (ASM1-Nowak – UNSW data).

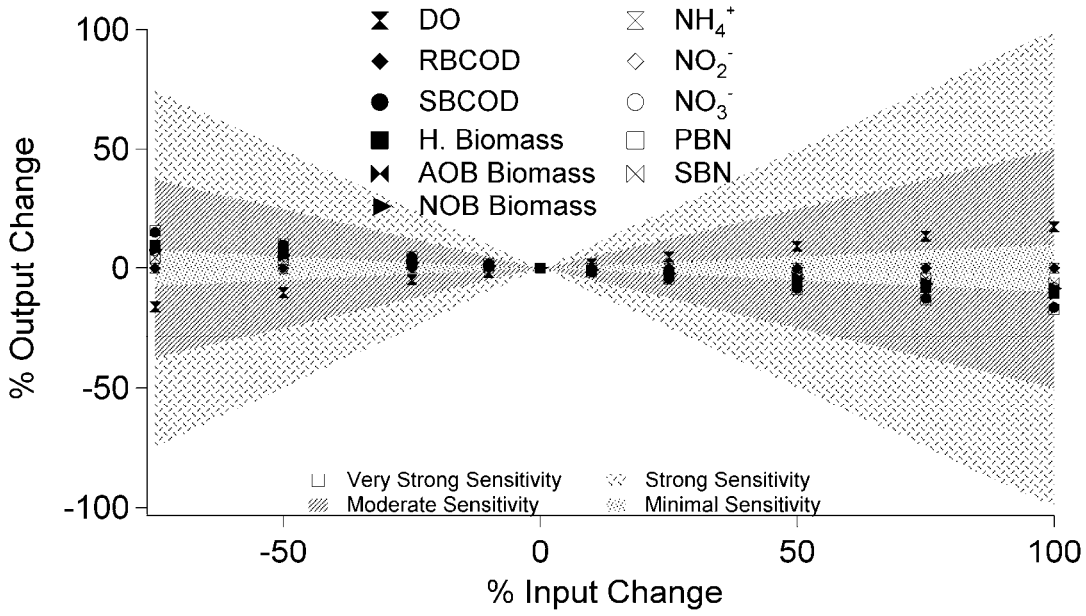

Figure A-40 Effect of biomass decay partitioning factor (f_p) on system state variables (ASM1-Nowak – UNSW data).

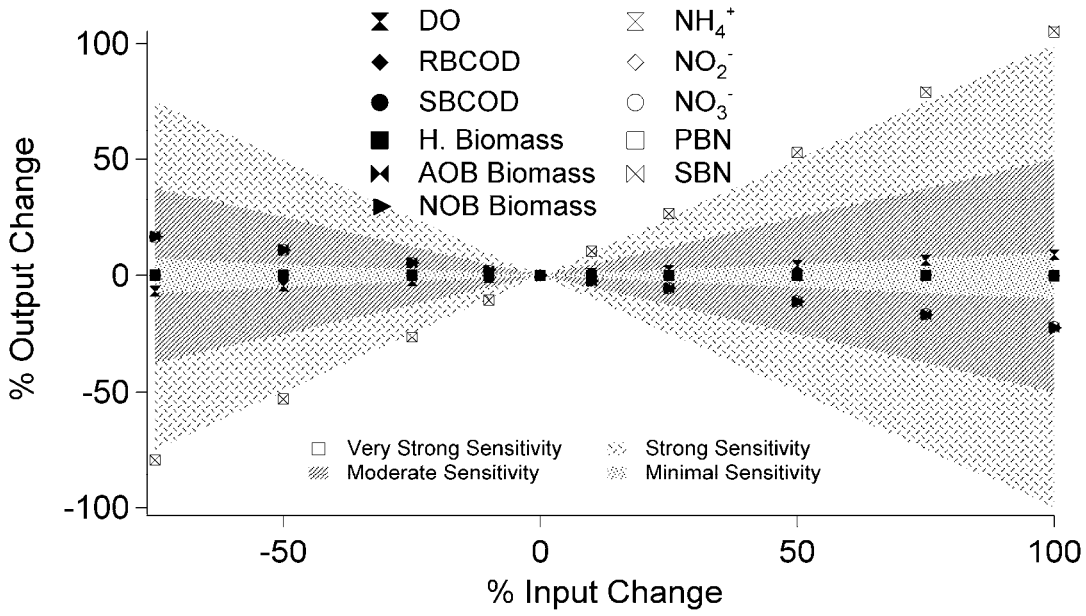

Figure A-41 Effect of biomass nitrogen fraction (i_{XB}) on system state variables (ASM1-Nowak – UNSW data).

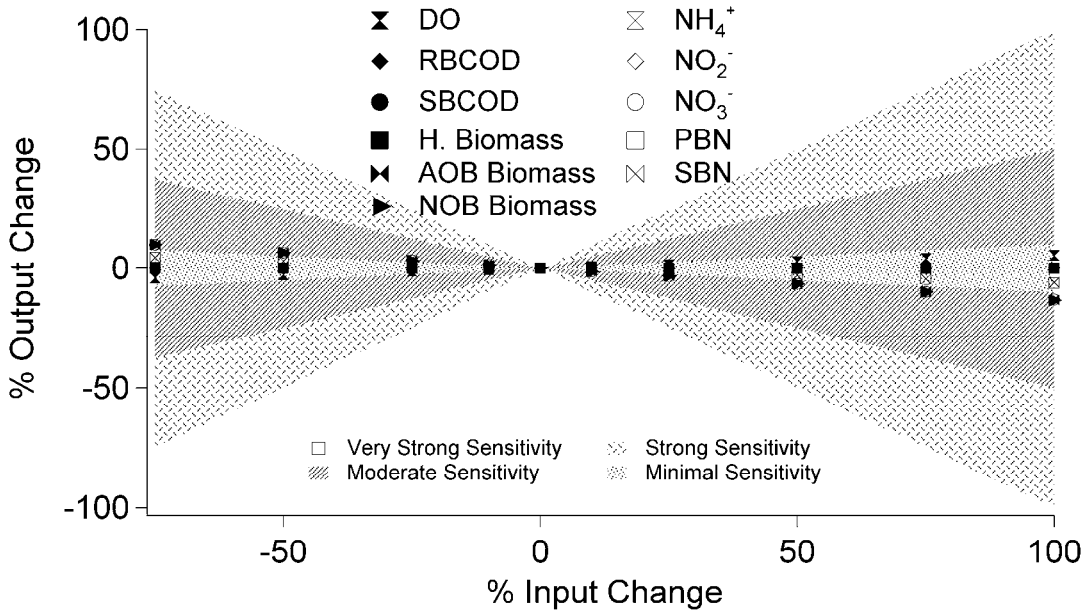

Figure A-42 Effect of particulate product nitrogen fraction (i_{XP}) on system state variables (ASM1-Nowak – UNSW data).

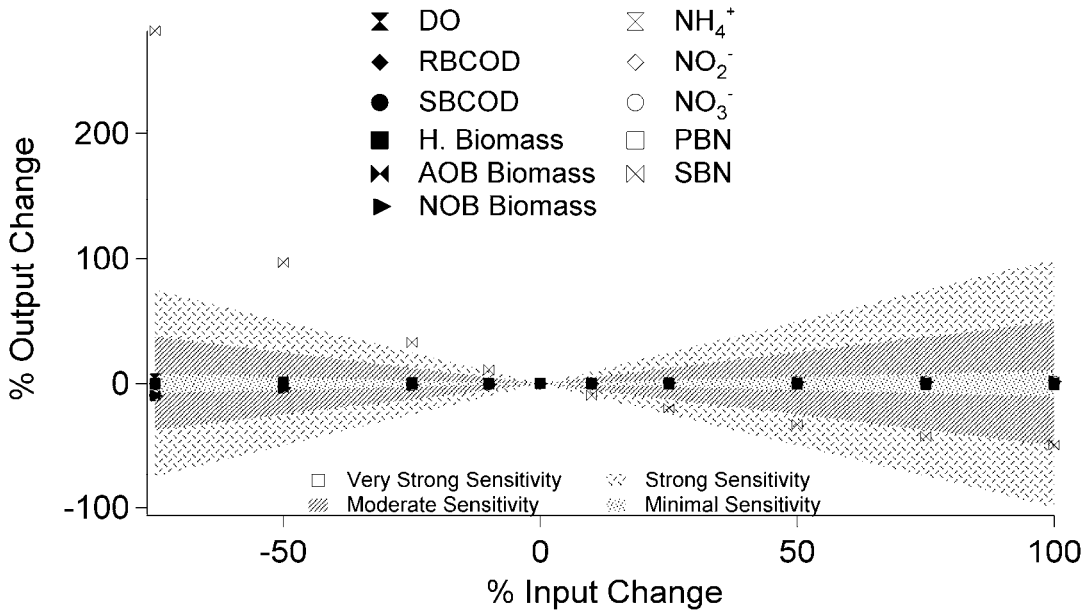

Figure A-43 Effect of ammonification rate (k_a) on system state variables (ASM1-Nowak – UNSW data).

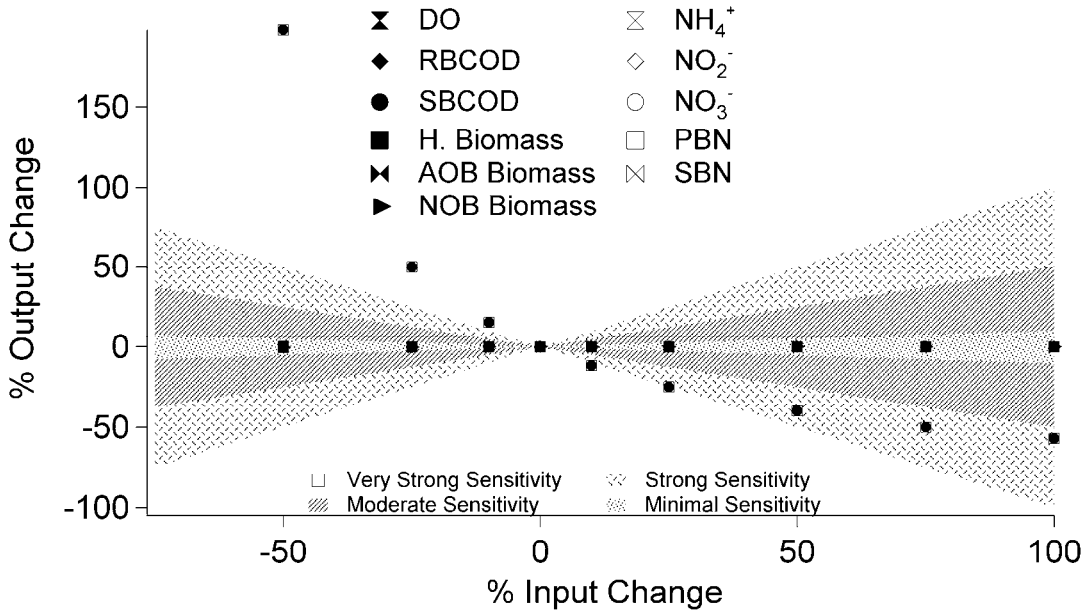

Figure A-44 Effect of maximum specific hydrolysis rate (k_H) on system state variables (ASM1-Nowak – UNSW data).

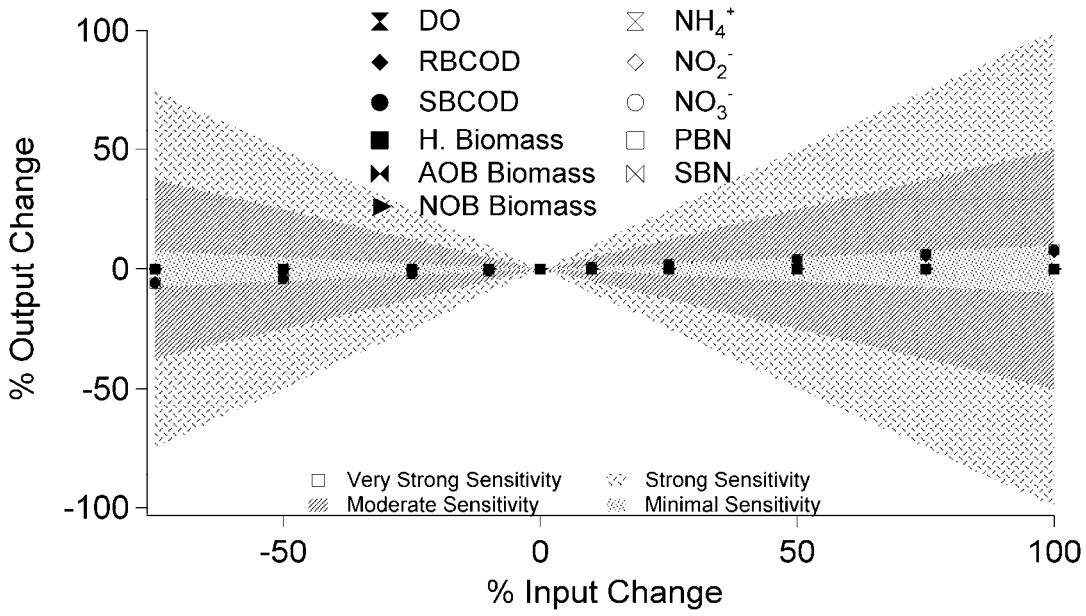

Figure A-45 Effect of heterotroph DO inhibition coefficient (K_{OH}) on system state variables (ASM1-Nowak – UNSW data).

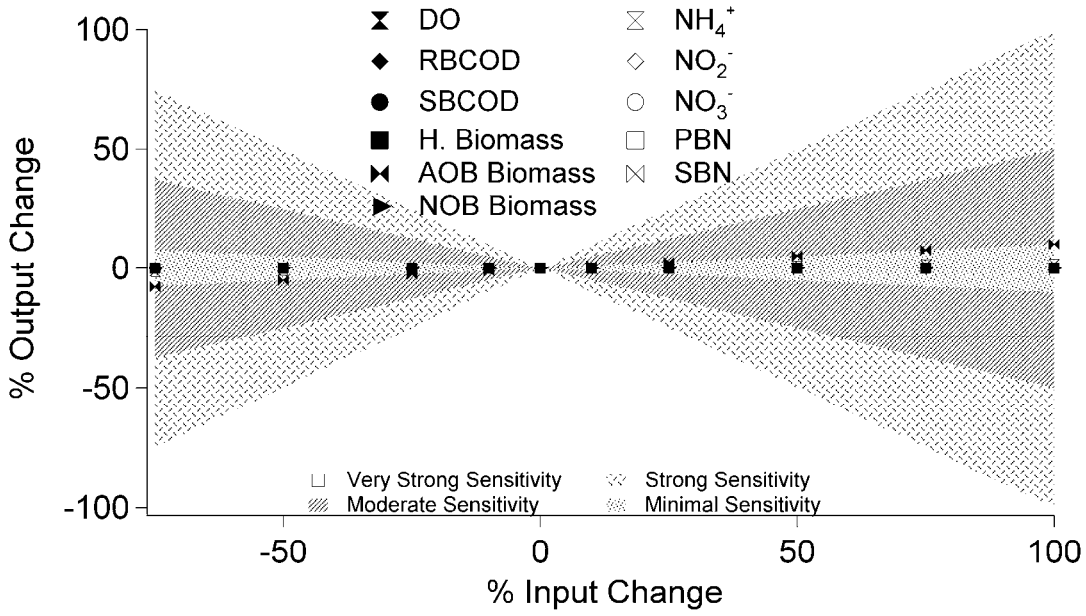

Figure A-46 Effect of AOB DO inhibition coefficient (K_{OM}) on system state variables (ASM1-Nowak – UNSW data).

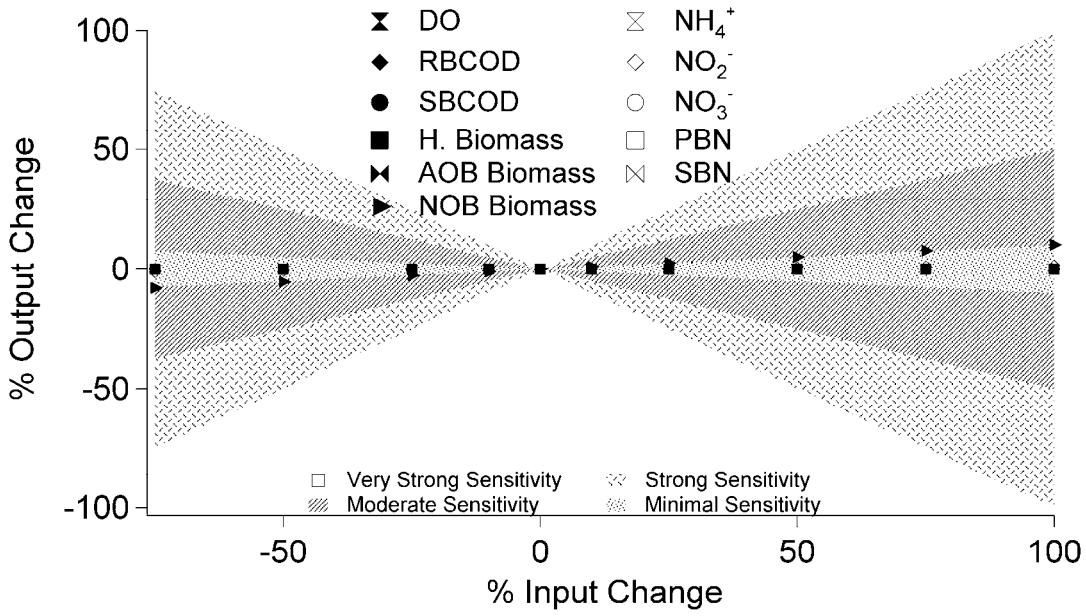

Figure A-47 Effect of NOB DO inhibition coefficient (K_{ON}) on system state variables (ASM1-Nowak – UNSW data).

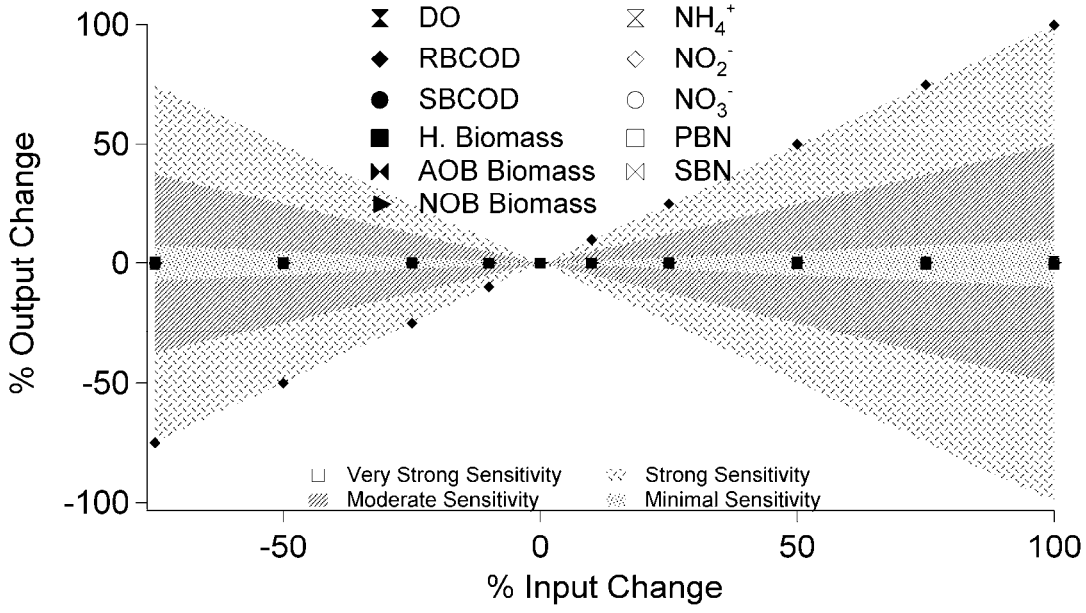

Figure A-48 Effect of heterotroph substrate inhibition coefficient (K_S) on system state variables (ASM1-Nowak – UNSW data).

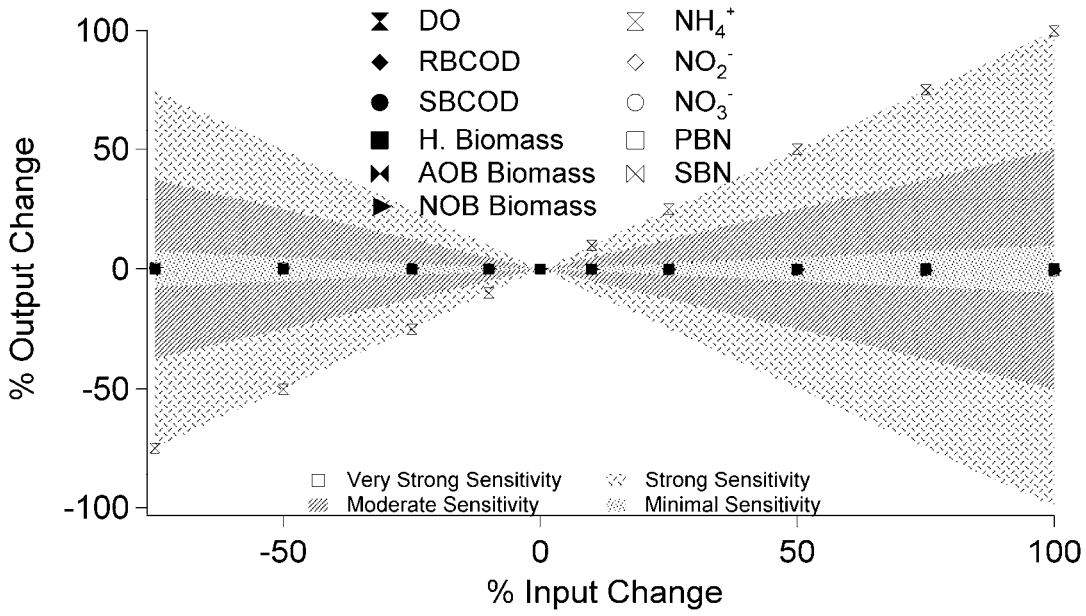

Figure A-49 Effect of ammonium inhibition coefficient (K_{NH}) on system state variables (ASM1-Nowak – UNSW data).

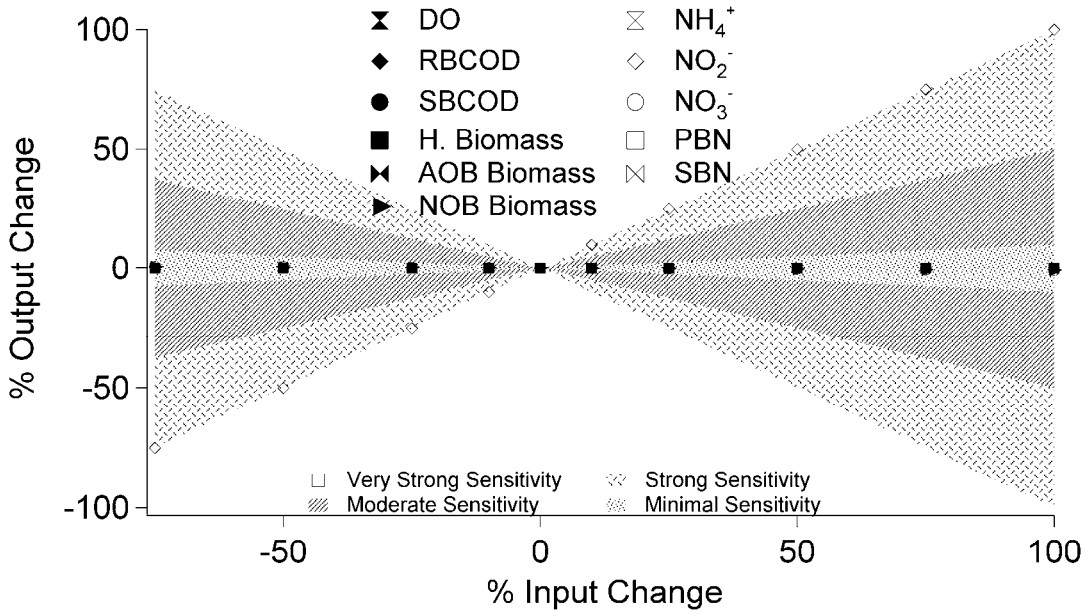

Figure A-50 Effect of nitrite inhibition coefficient (K_{NO2}) on system state variables (ASM1-Nowak – UNSW data).

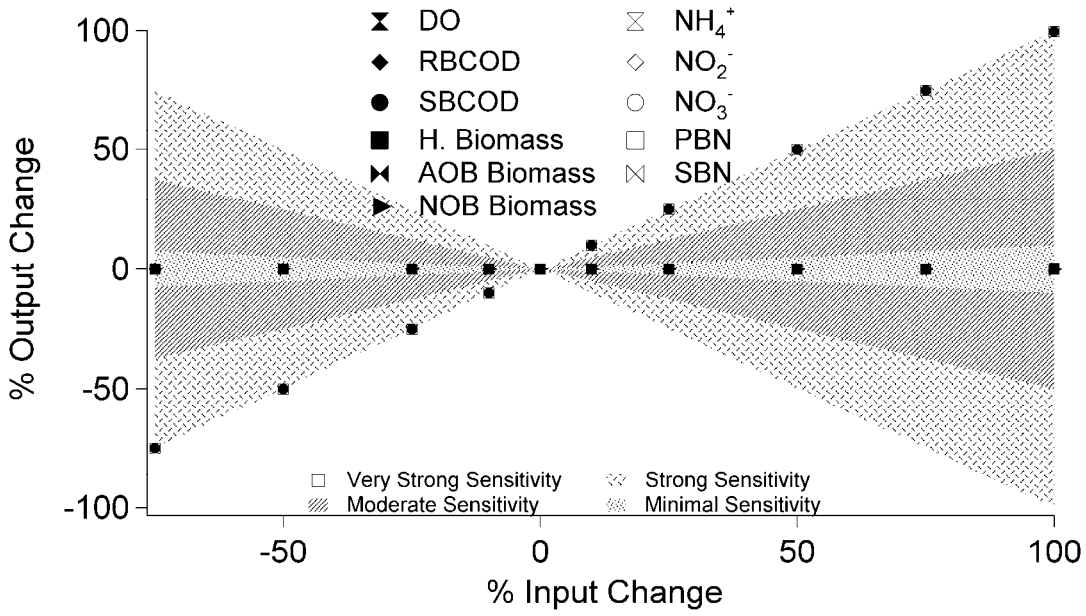

Figure A-51 Effect of hydrolysis half-saturation coefficient (K_X) on system state variables (ASM1-Nowak – UNSW data).

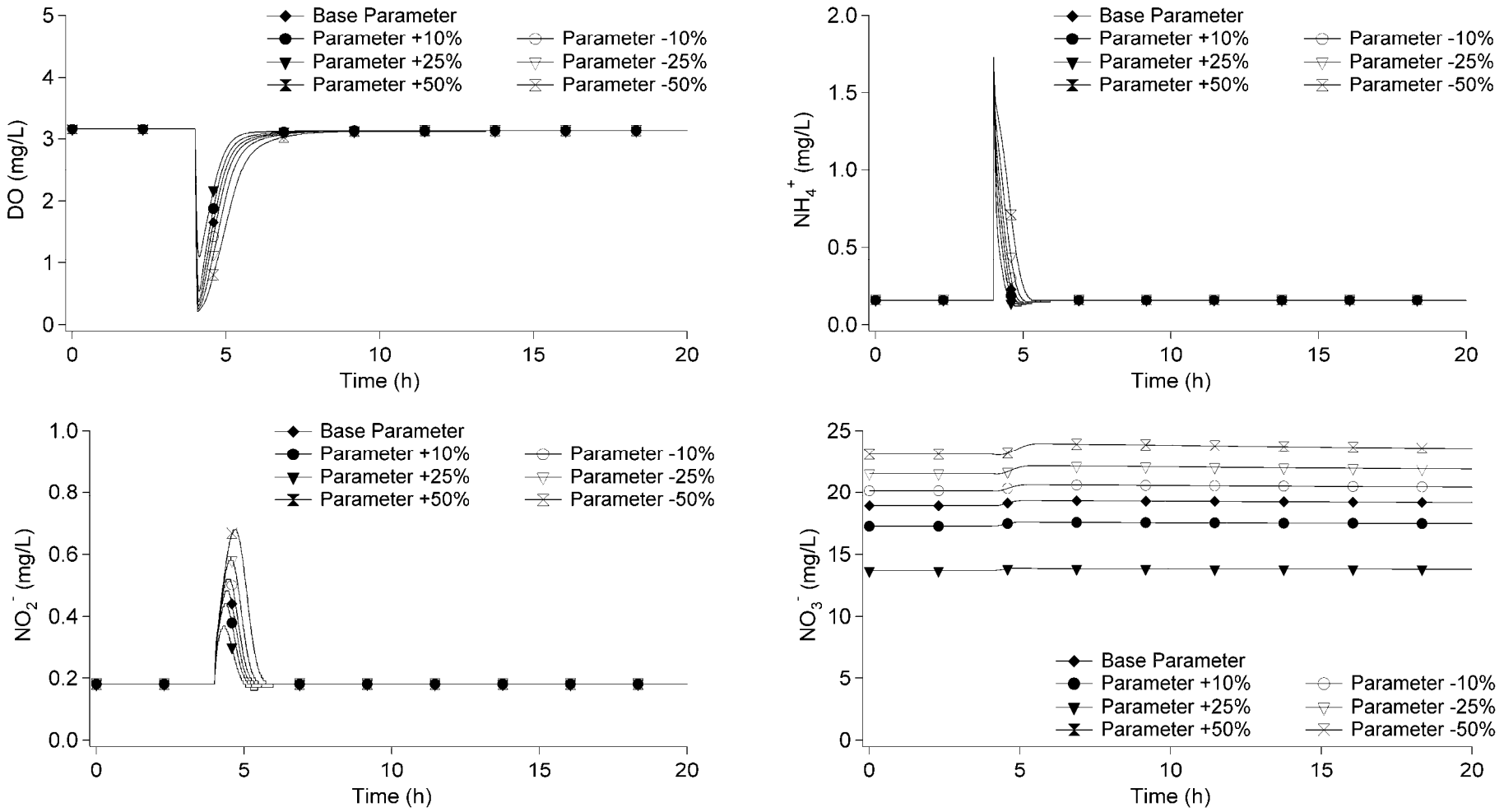

Figure A-52 Effect of heterotroph yield (Y_H) on dynamic response (ASM1-Nowak – UNSW data).

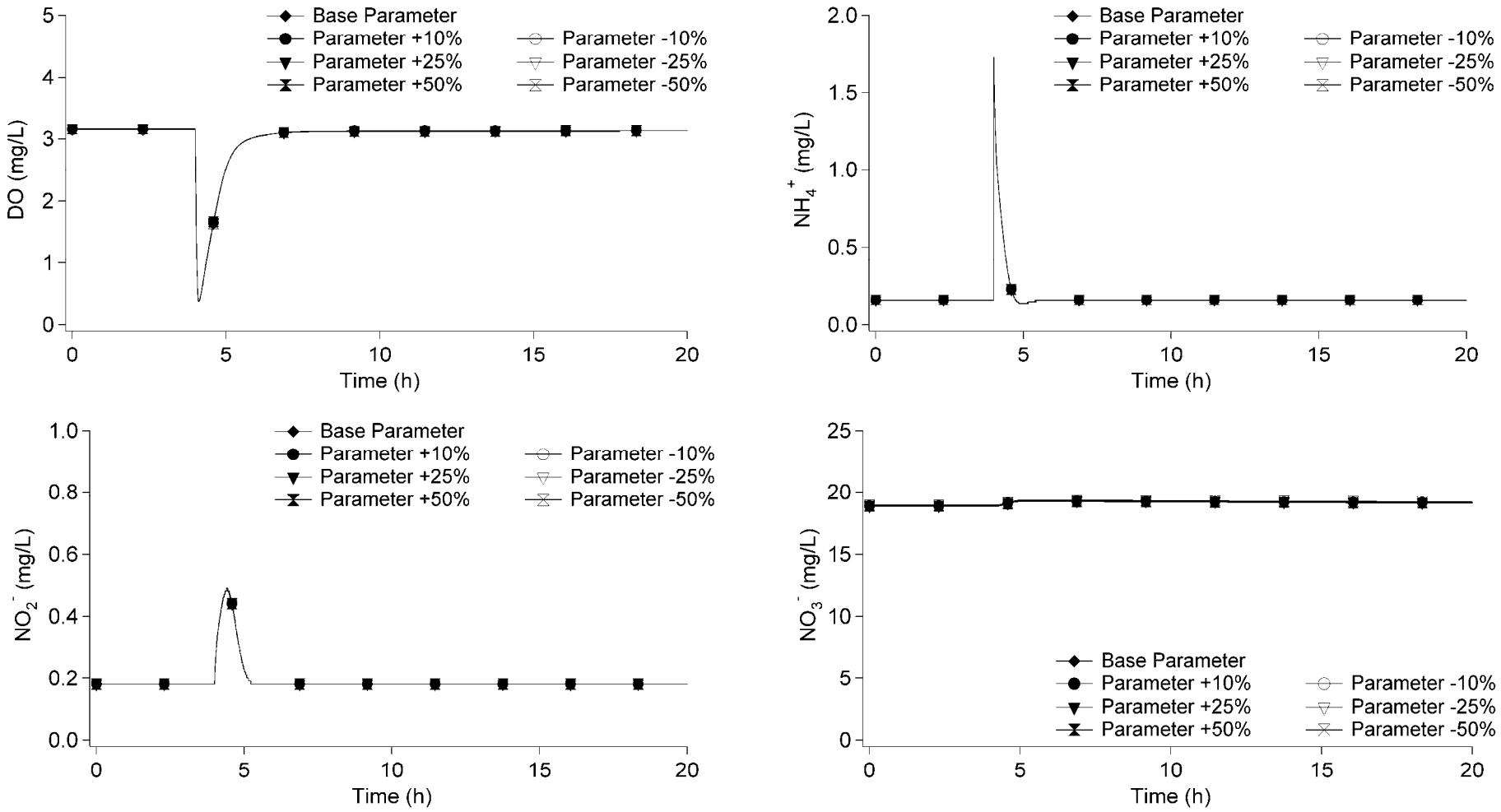

Figure A-53 Effect of AOB yield (Y_M) on dynamic response (ASM1-Nowak – UNSW data).

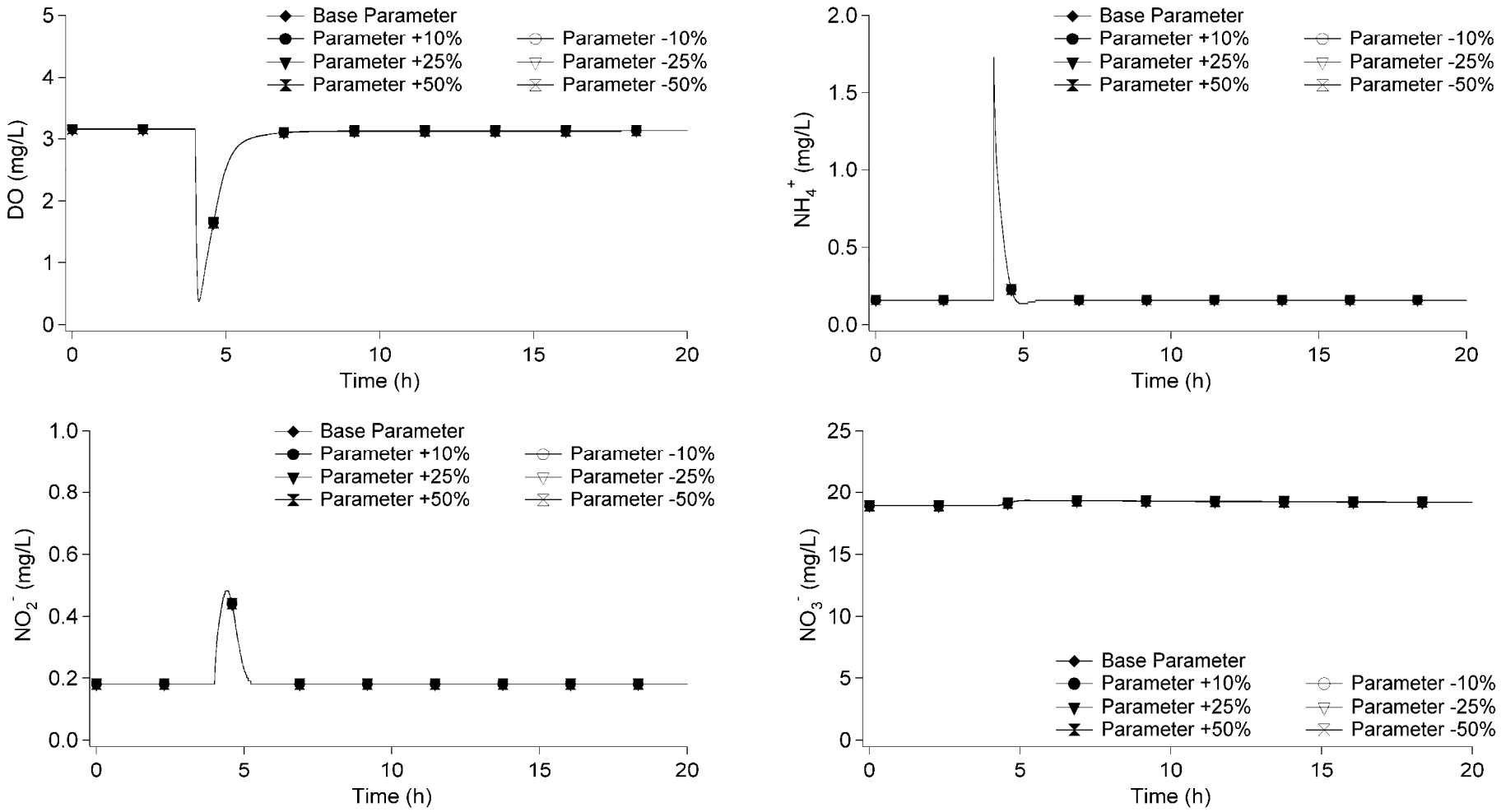

Figure A-54 Effect of NOB yield (Y_N) on dynamic response (ASM1-Nowak – UNSW data).

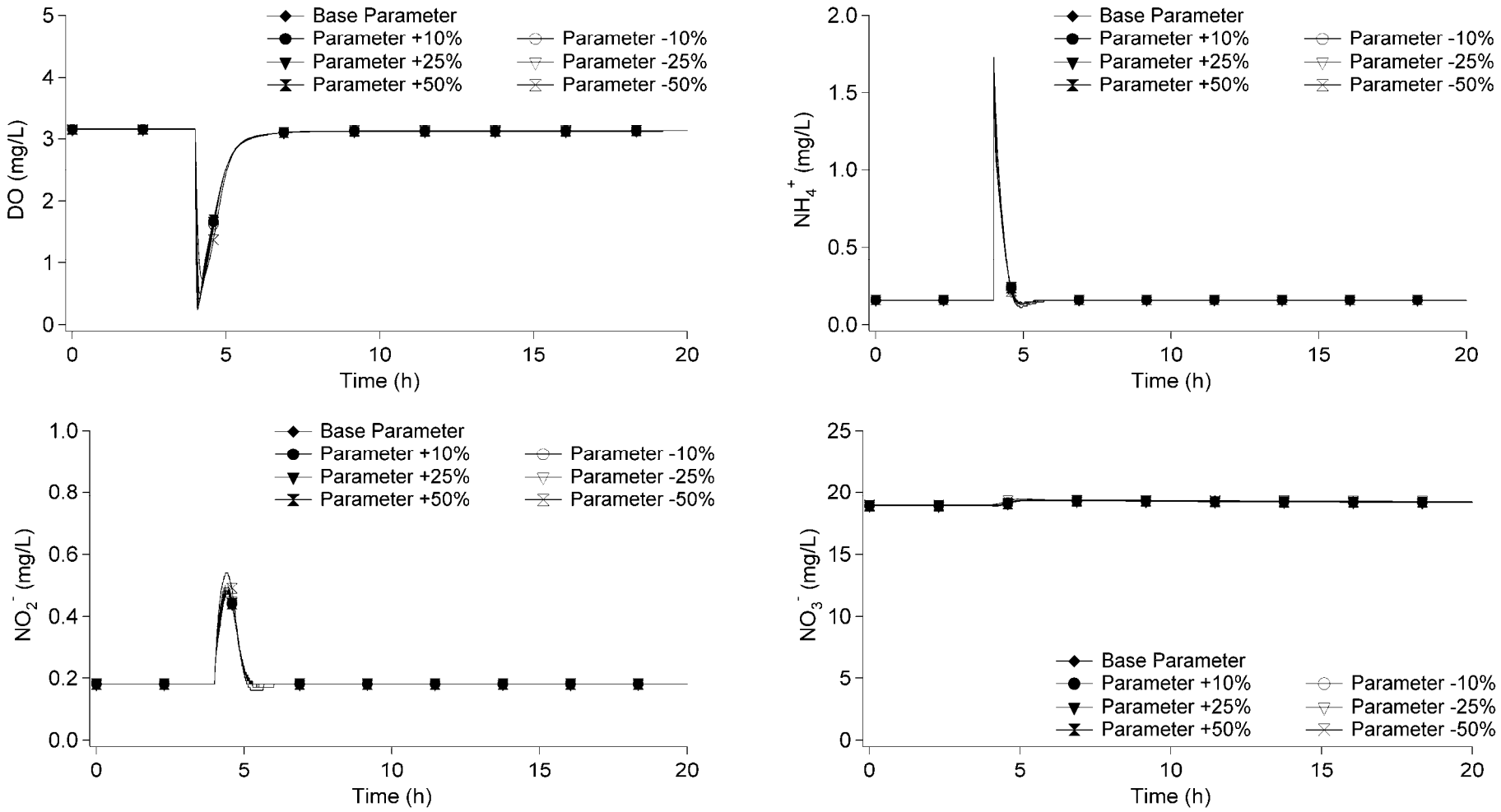

Figure A-55 Effect of heterotroph maximum specific growth rate (μ_H) on dynamic response (ASM1-Nowak – UNSW data).

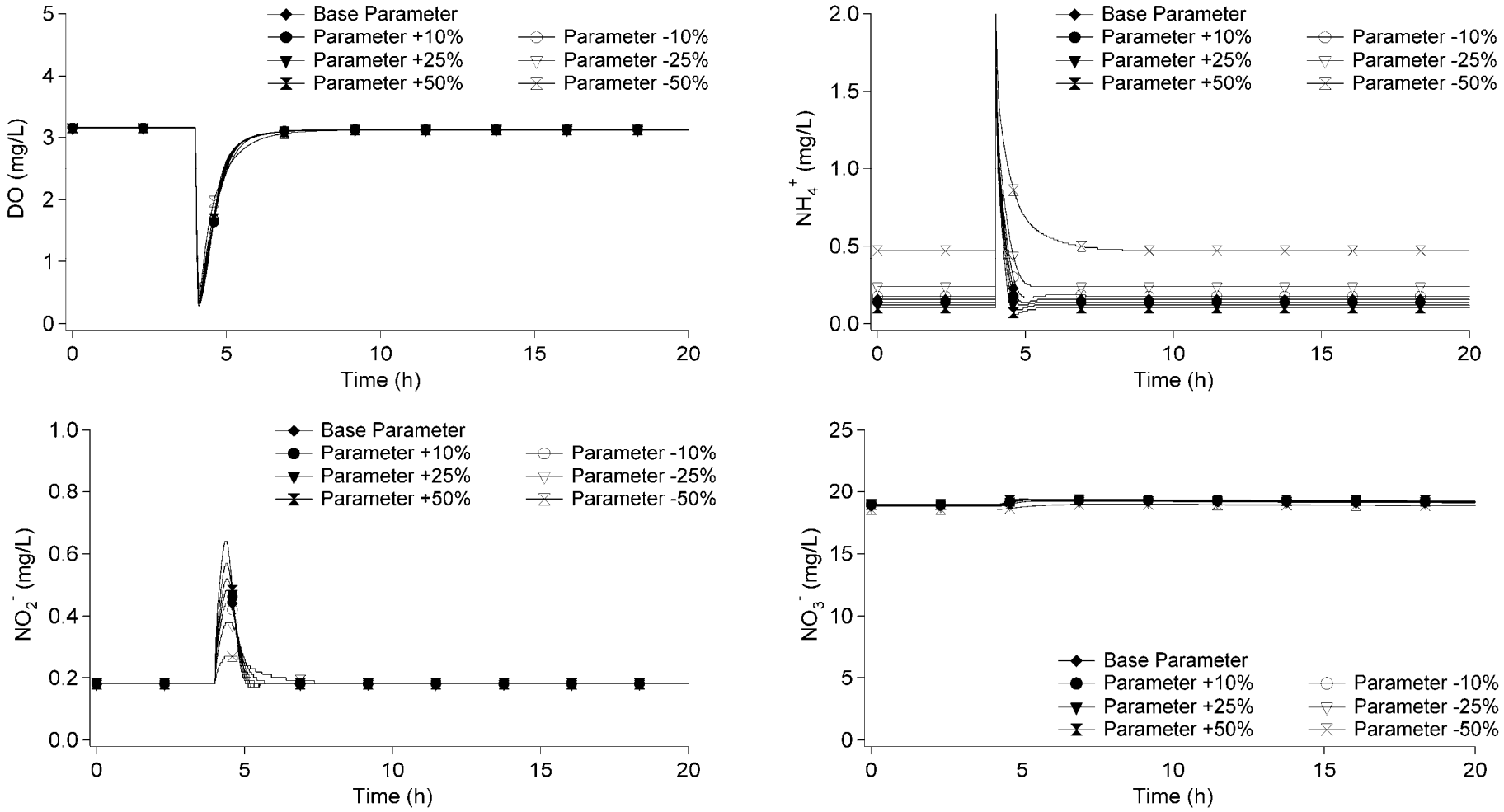

Figure A-56 Effect of AOB maximum specific growth rate (μ_M) on dynamic response (ASM1-Nowak – UNSW data).

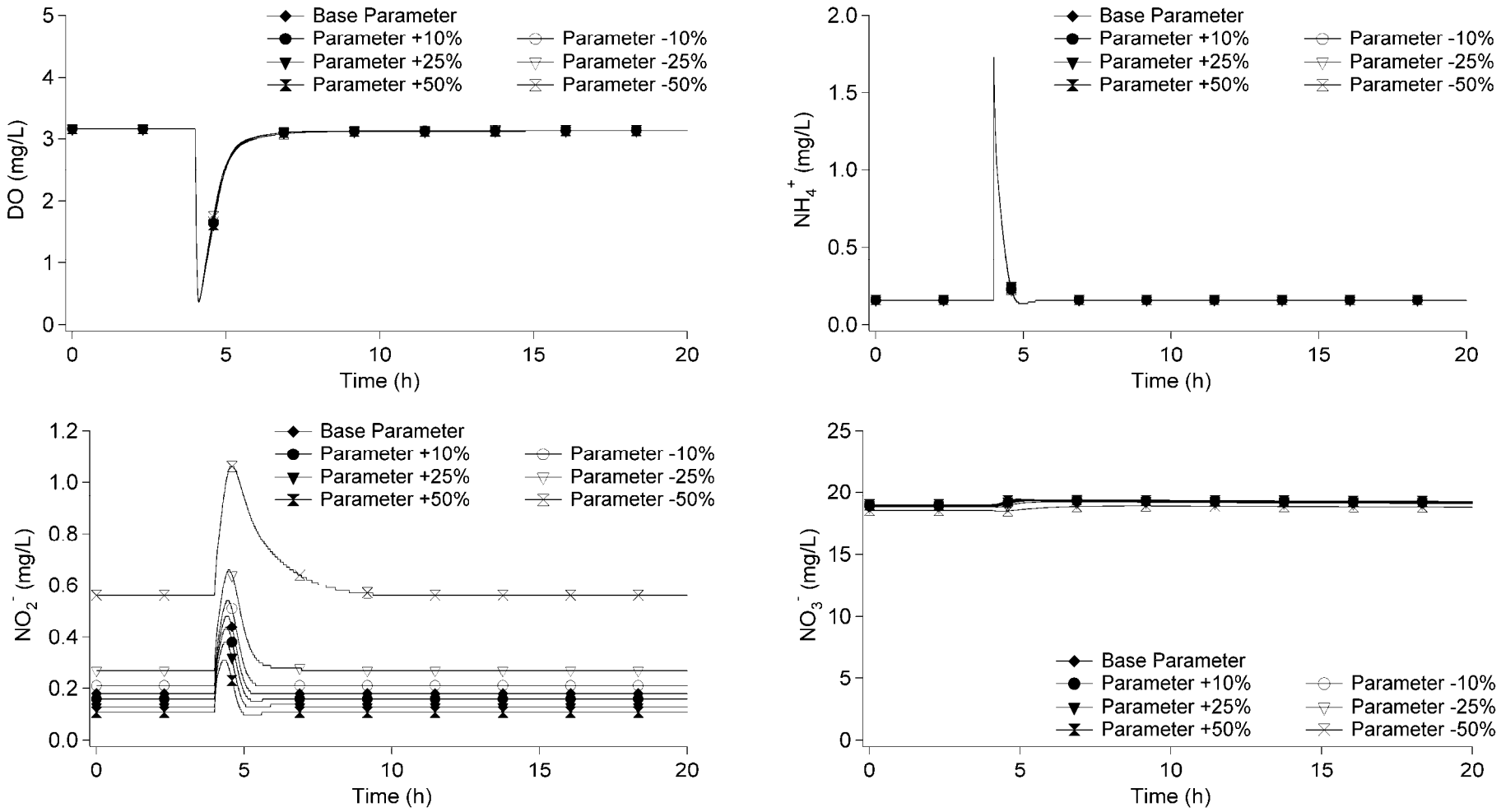

Figure A-57 Effect of NOB maximum specific growth rate (μ_N) on dynamic response (ASM1-Nowak – UNSW data).

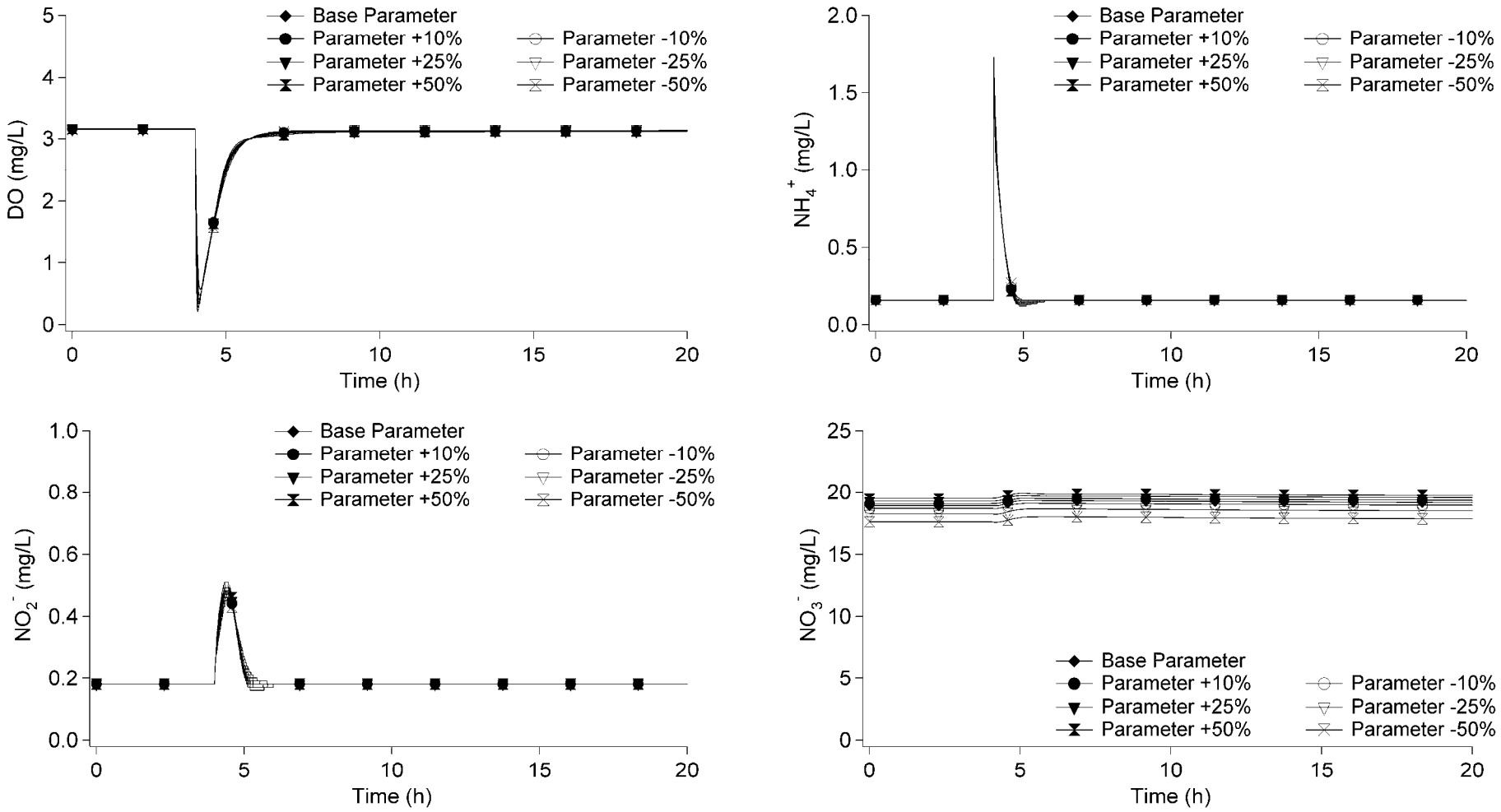

Figure A-58 Effect of heterotroph decay coefficient (b_H) on dynamic response (ASM1-Nowak – UNSW data).

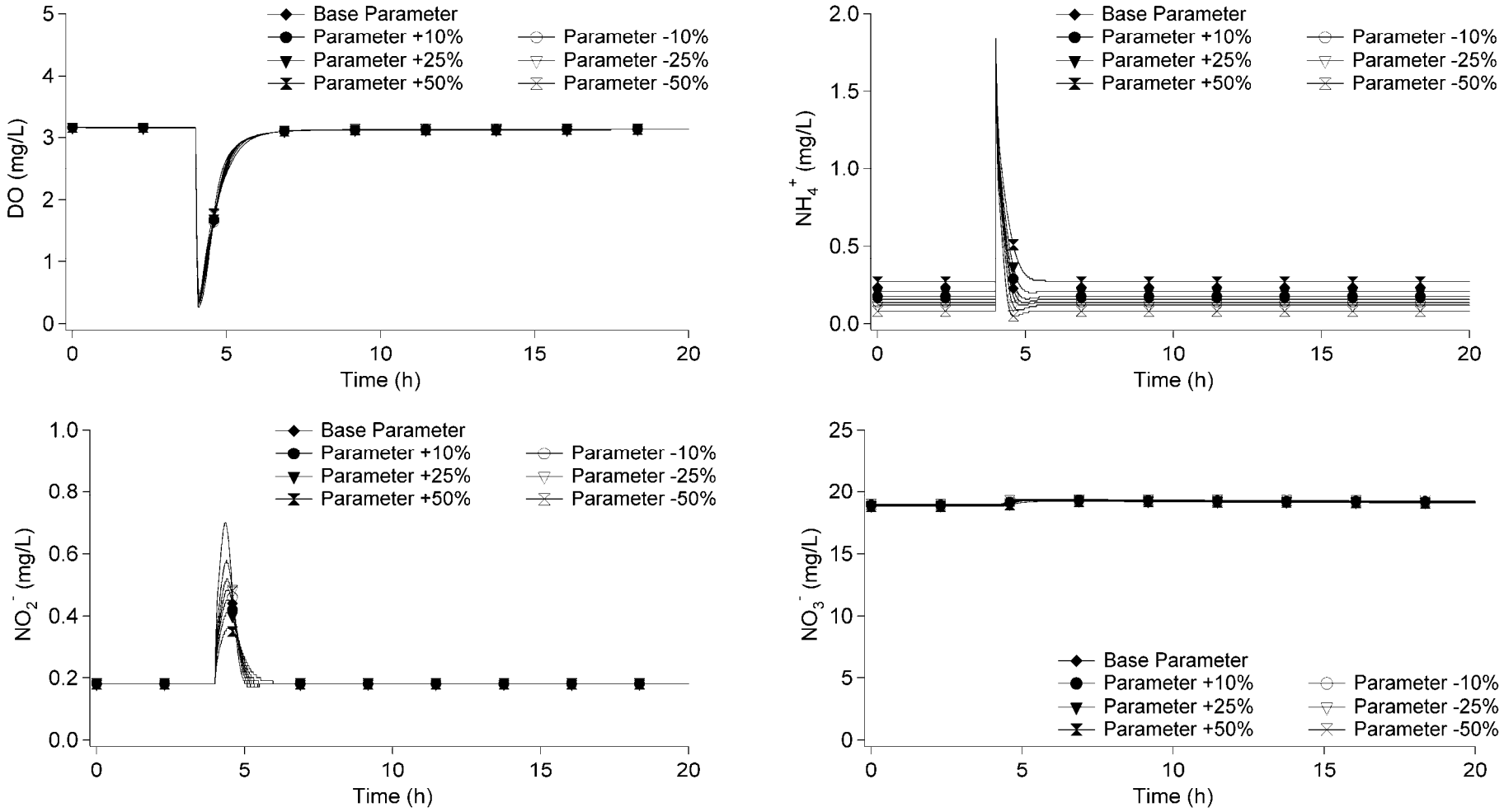

Figure A-59 Effect of AOB decay coefficient (b_M) on dynamic response (ASM1-Nowak – UNSW data).

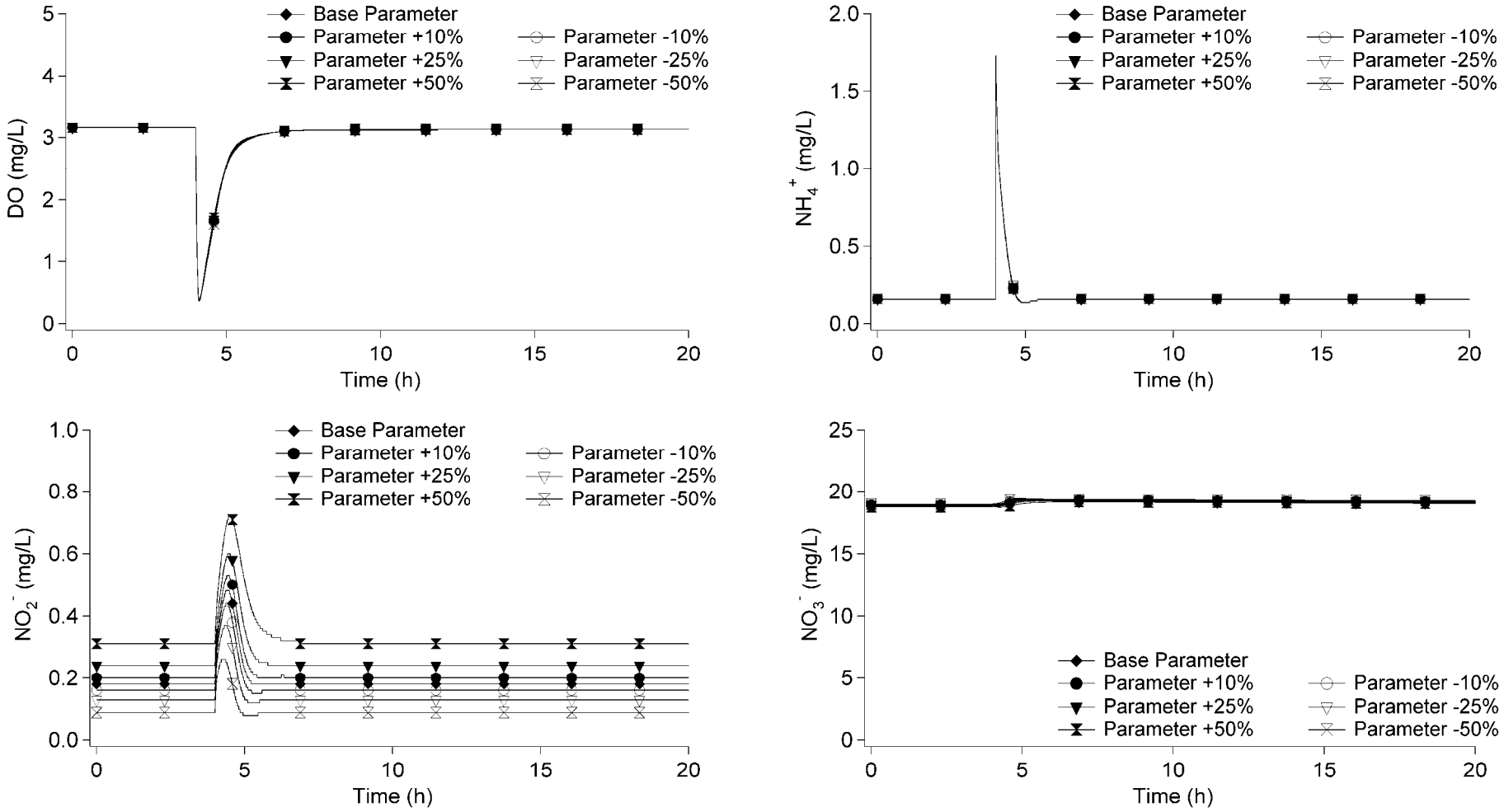

Figure A-60 Effect of NOB decay coefficient (b_N) on dynamic response (ASM1-Nowak – UNSW data).

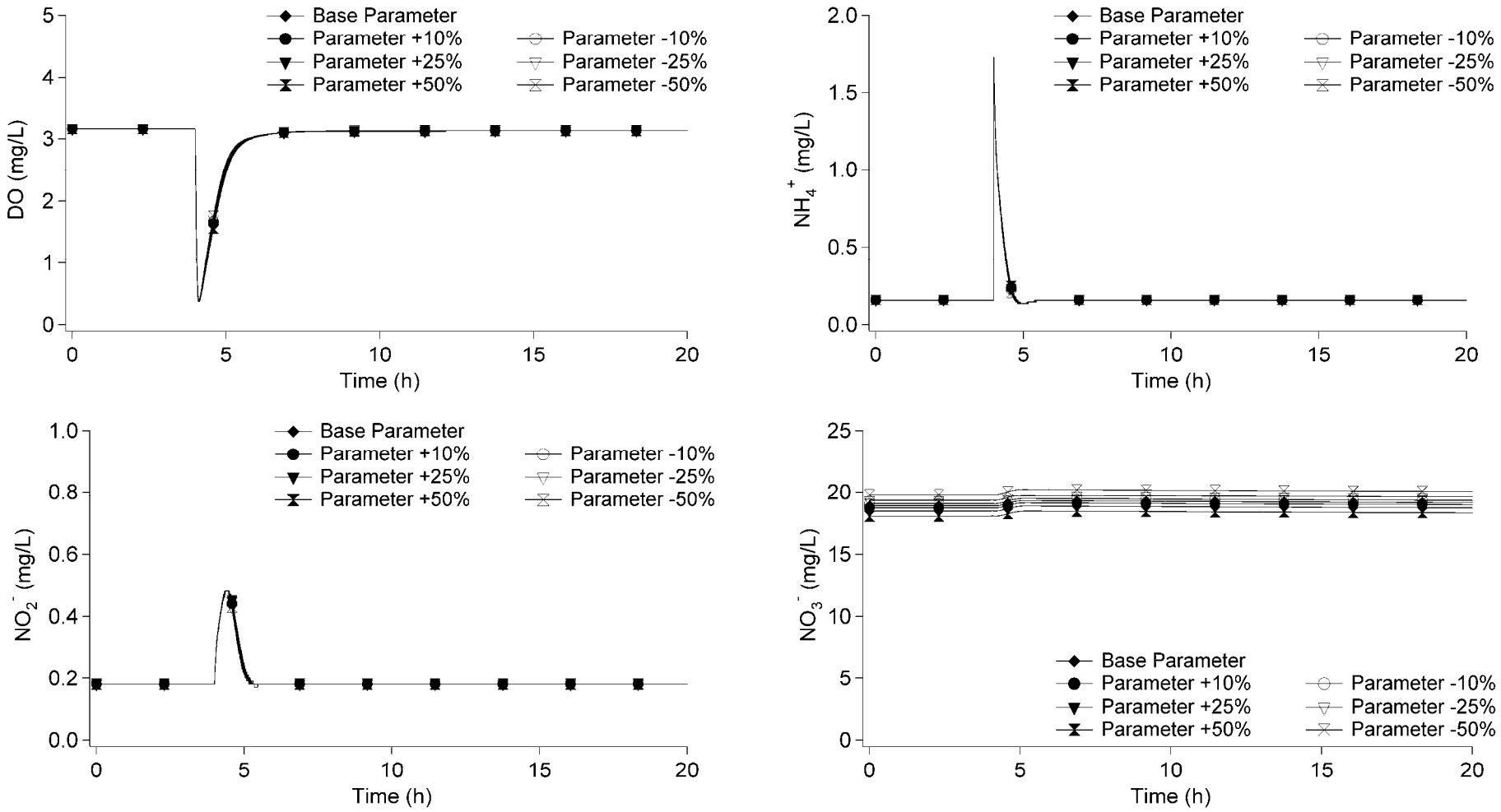

Figure A-61 Effect of biomass decay partitioning factor (f_p) on dynamic response (ASM1-Nowak – UNSW data).

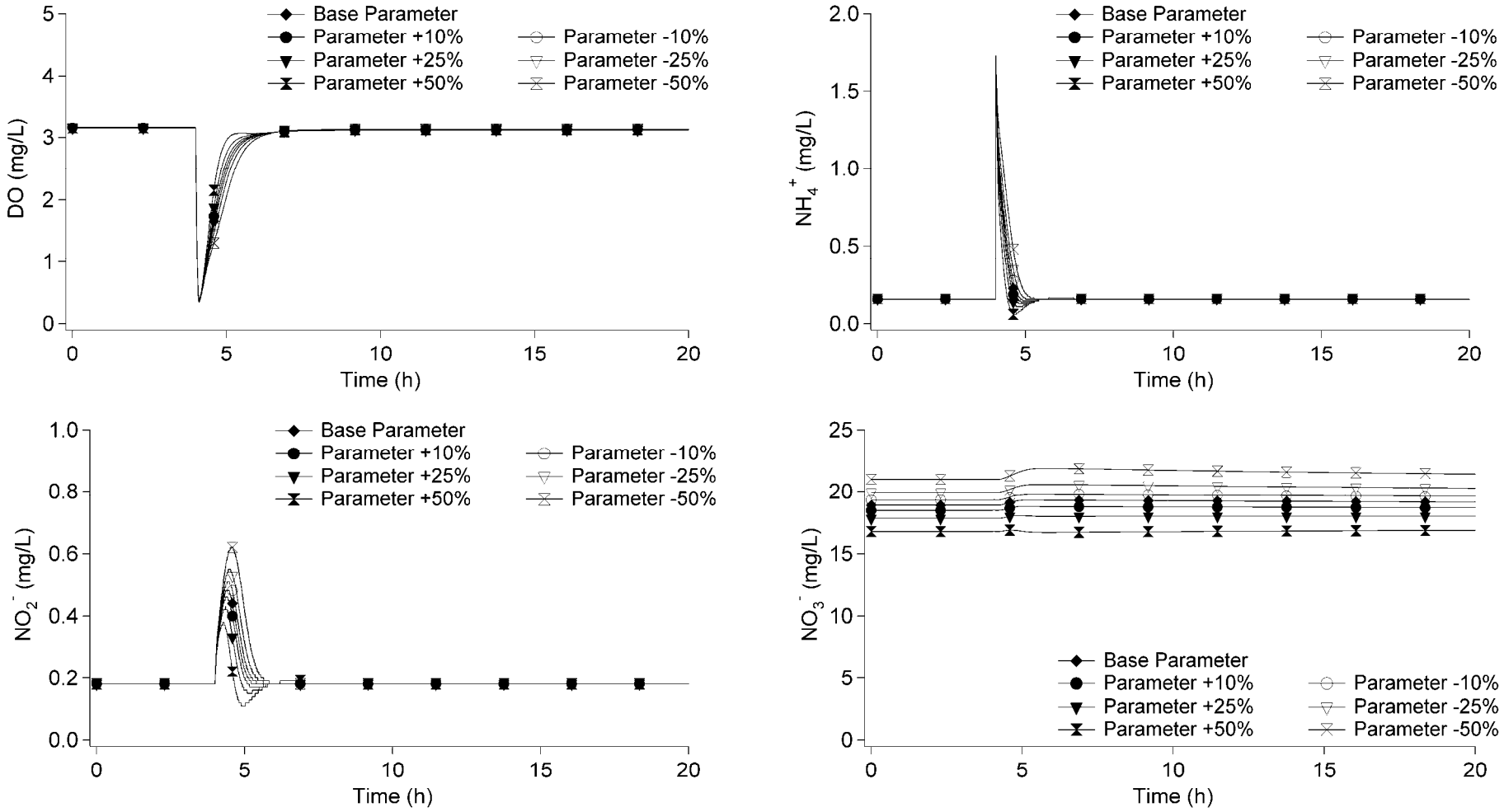

Figure A-62 Effect of biomass nitrogen fraction (i_{XB}) on dynamic response (ASM1-Nowak – UNSW data).

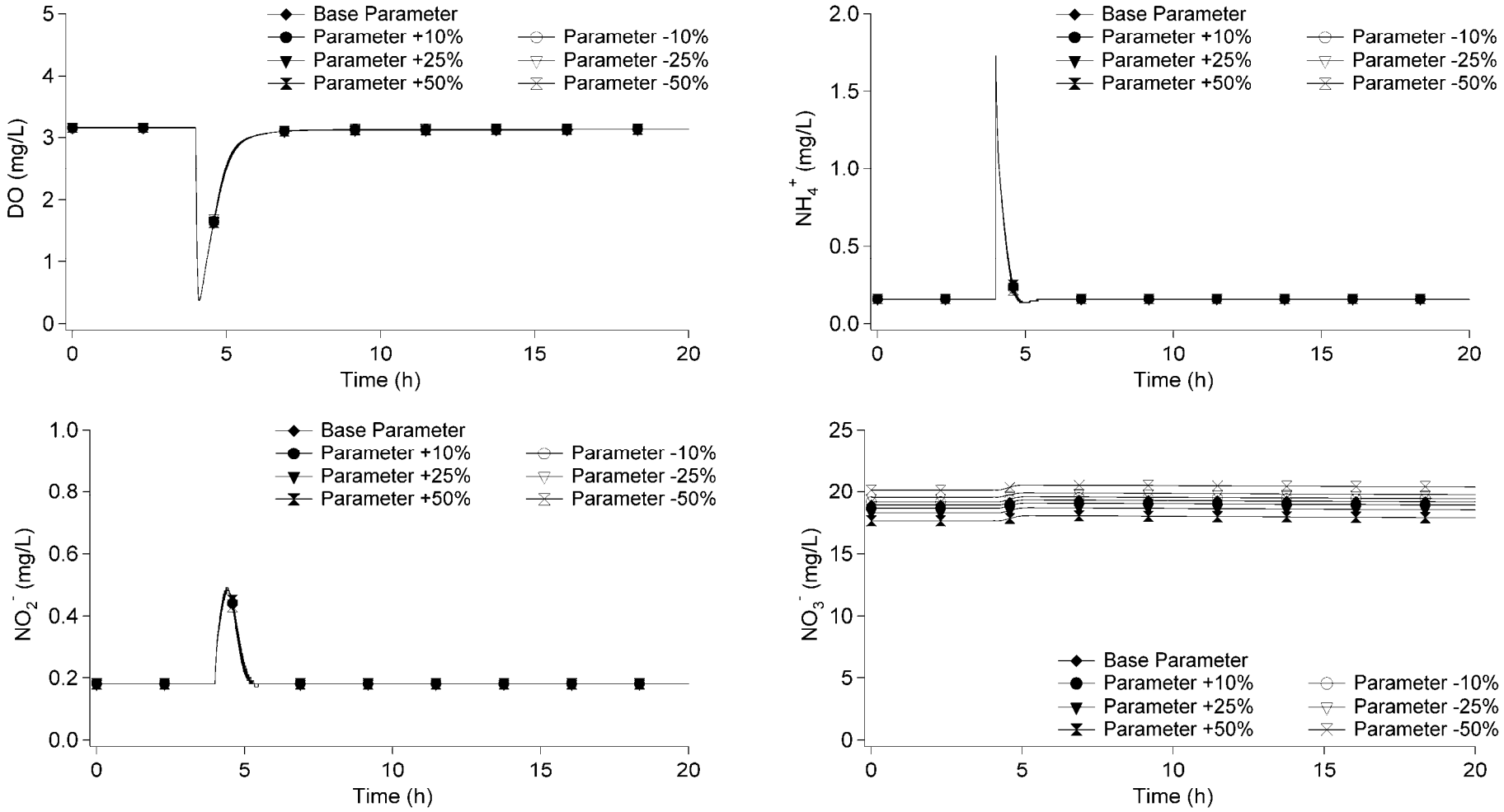

Figure A-63 Effect of particulate product nitrogen fraction (i_{XP}) on dynamic response (ASM1-Nowak – UNSW data).

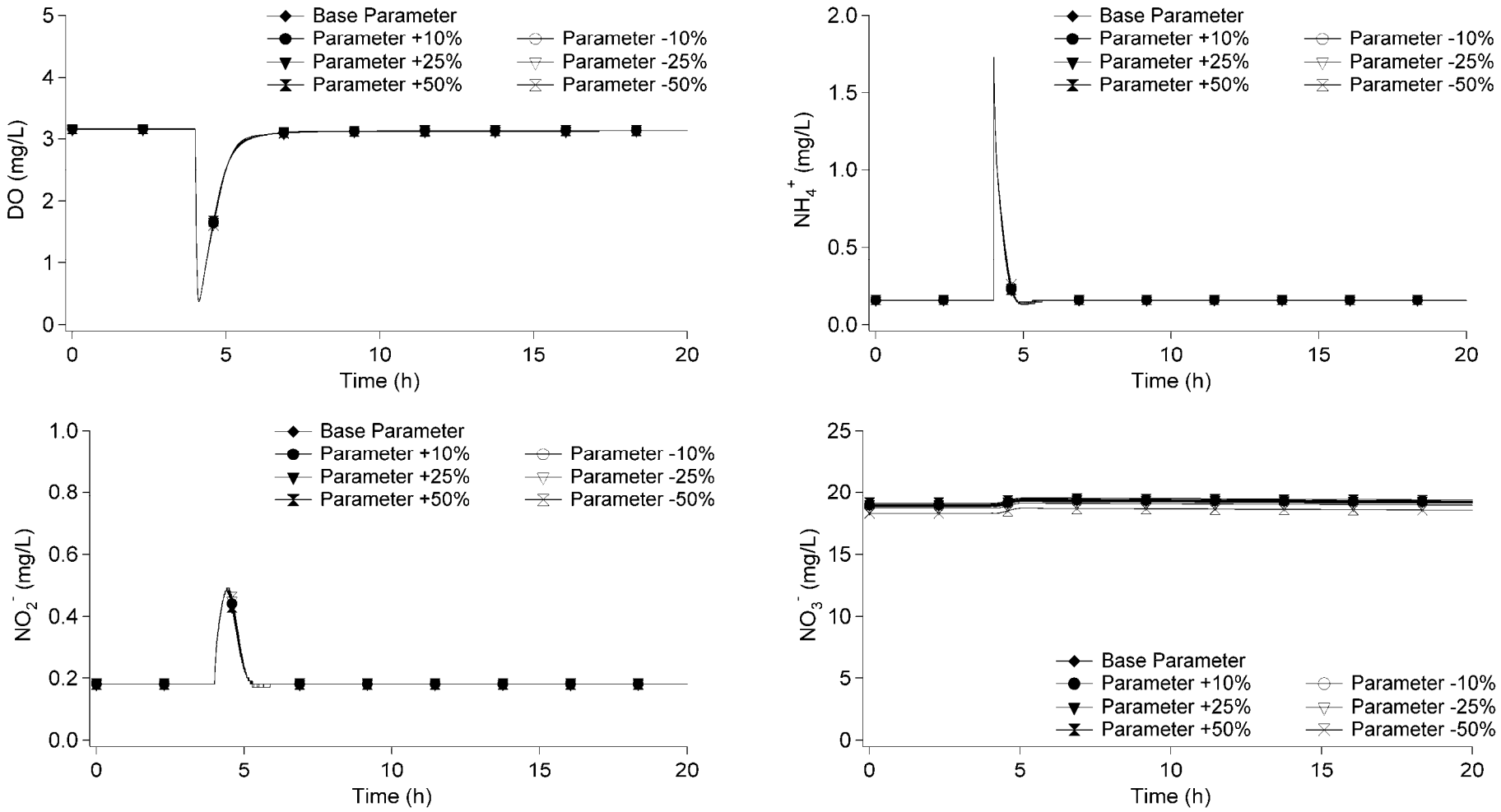

Figure A-64 Effect of ammonification rate (k_a) on dynamic response (ASM1-Nowak – UNSW data).

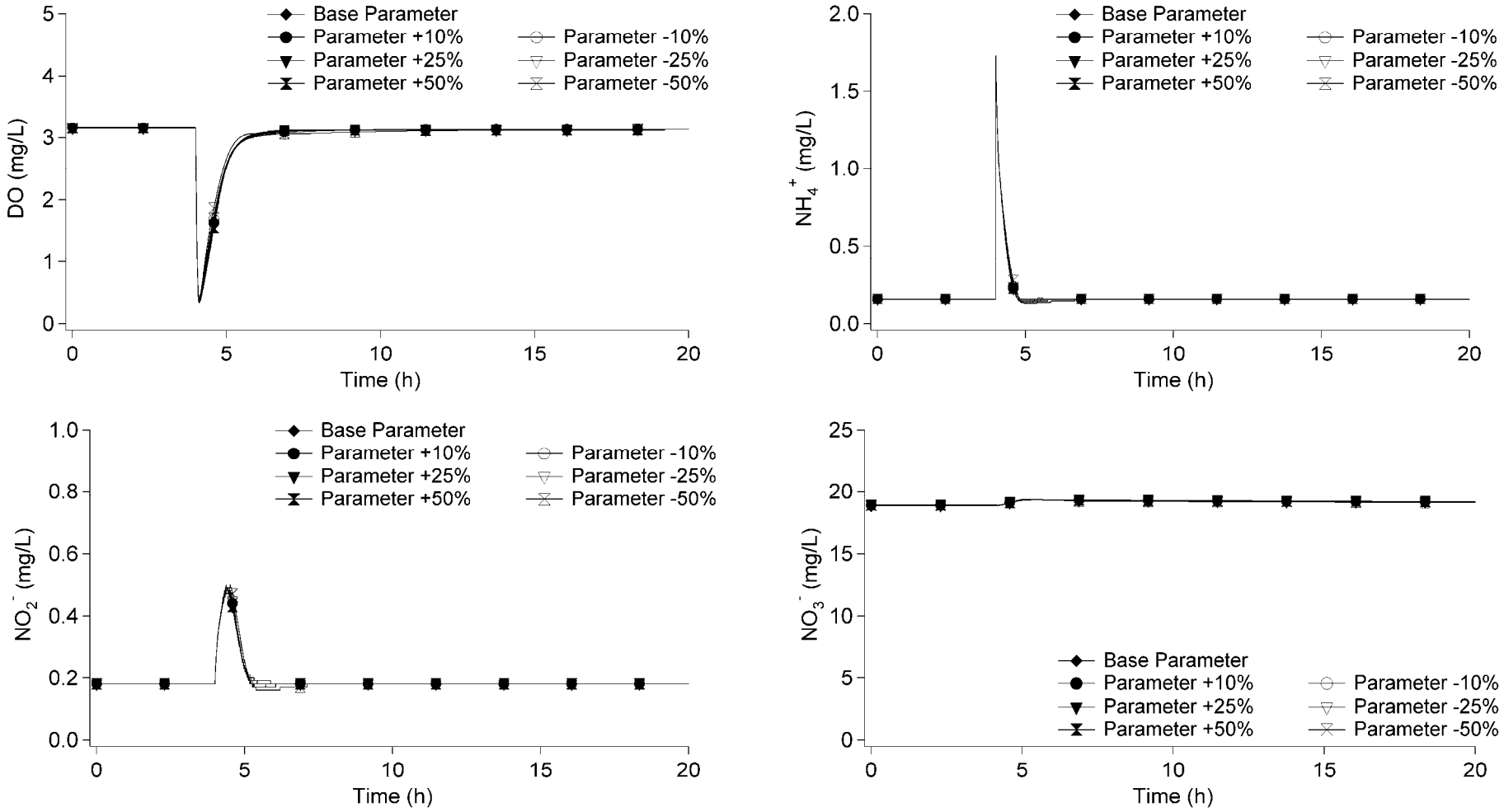

Figure A-65 Effect of maximum specific hydrolysis rate (k_H) on dynamic response (ASM1-Nowak – UNSW data).

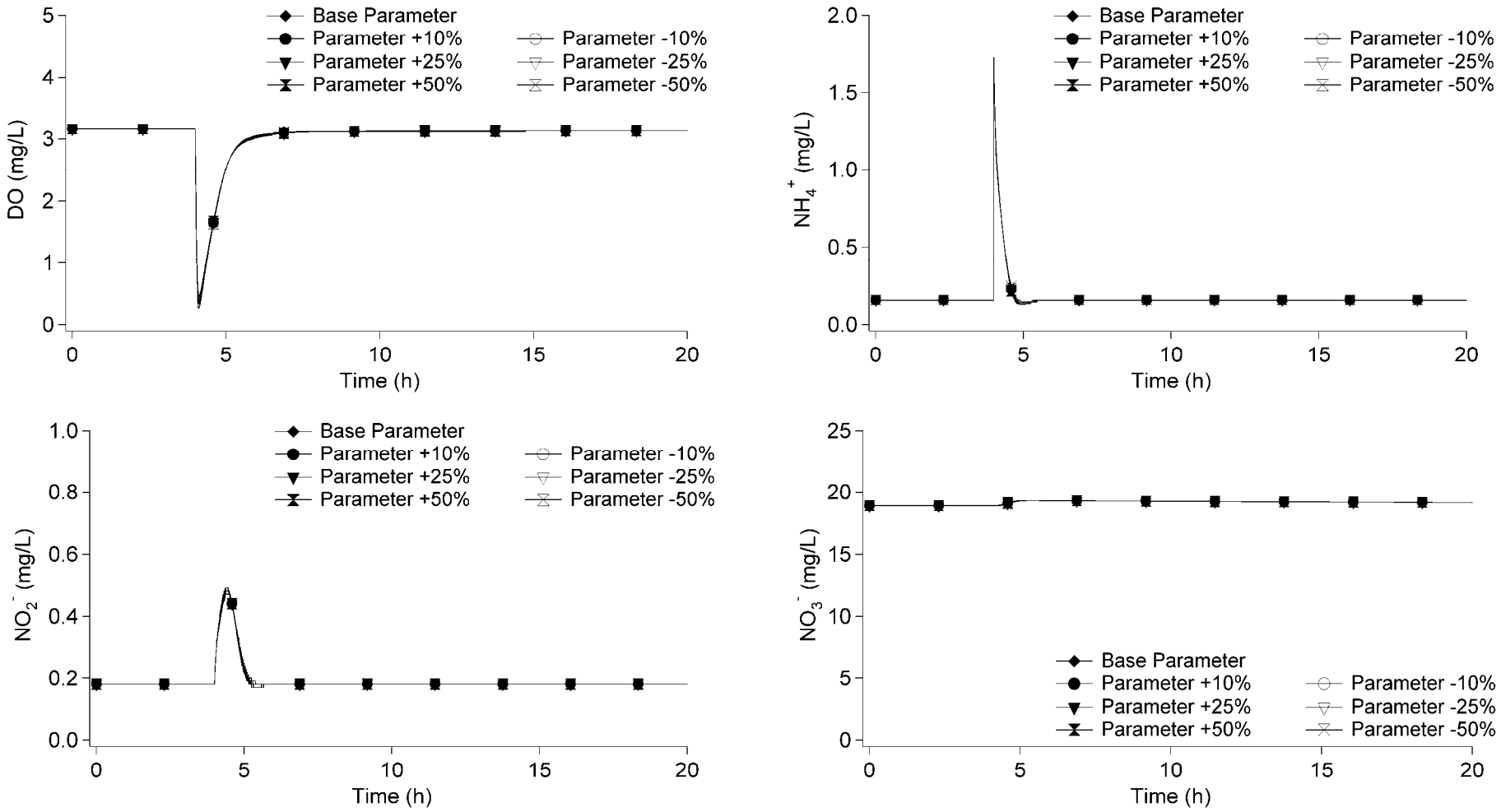

Figure A-66 Effect of heterotroph DO inhibition coefficient (K_{OH}) on dynamic response (ASM1-Nowak – UNSW data).

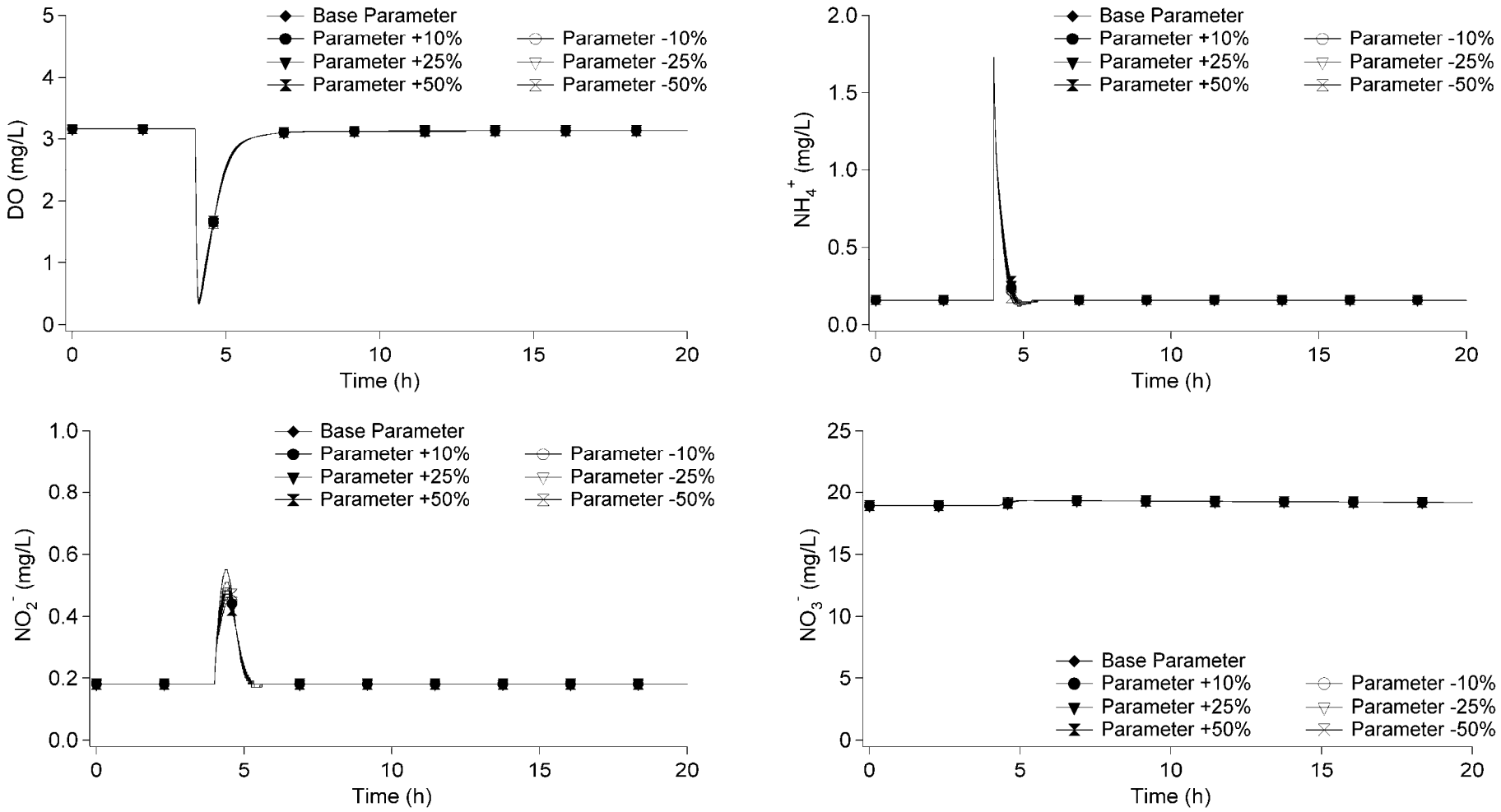

Figure A-67 Effect of AOB DO inhibition coefficient (K_{OM}) on dynamic response (ASM1-Nowak – UNSW data).

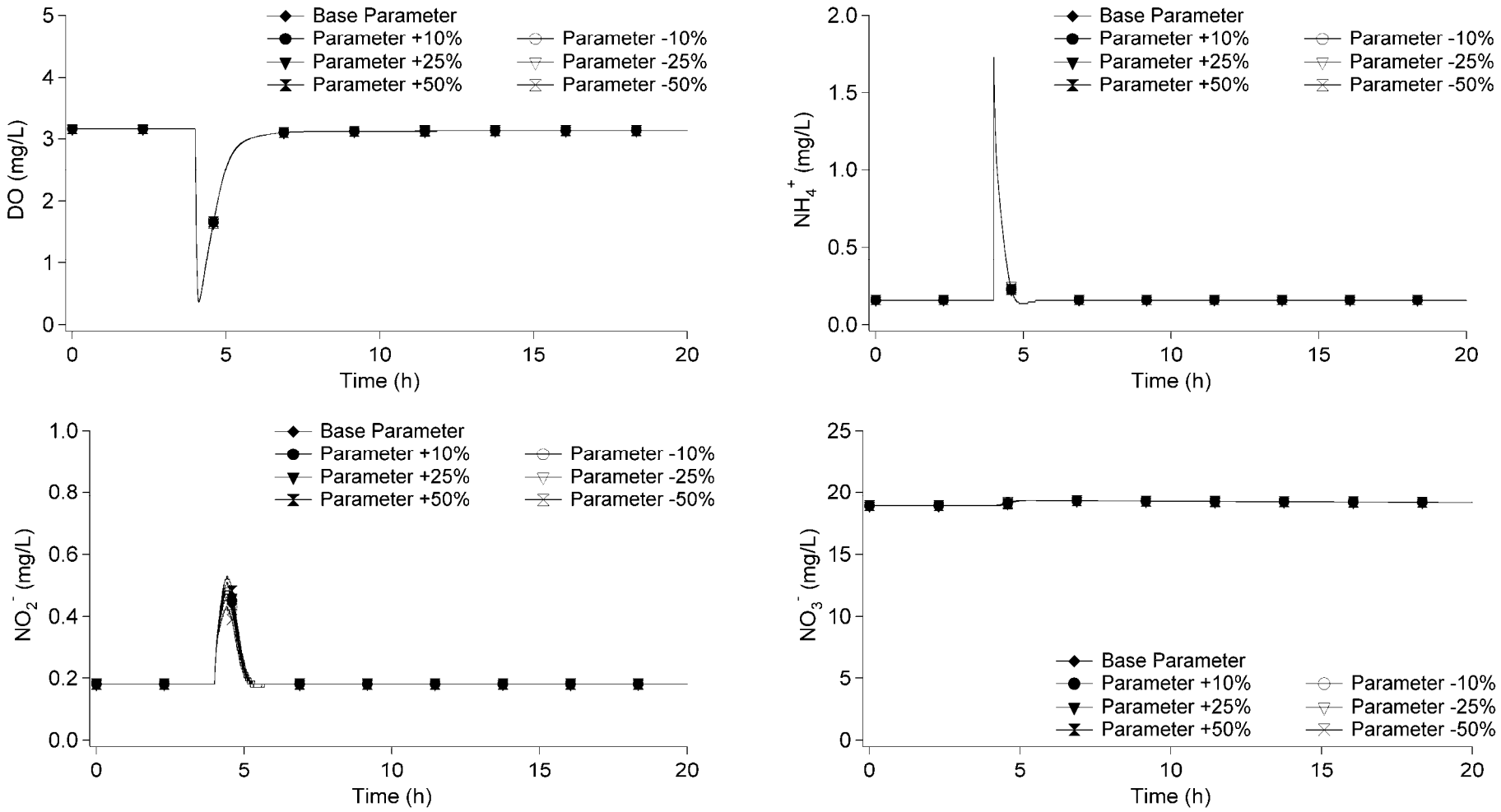

Figure A-68 Effect of NOB DO inhibition coefficient (K_{ON}) on dynamic response (ASM1-Nowak – UNSW data).

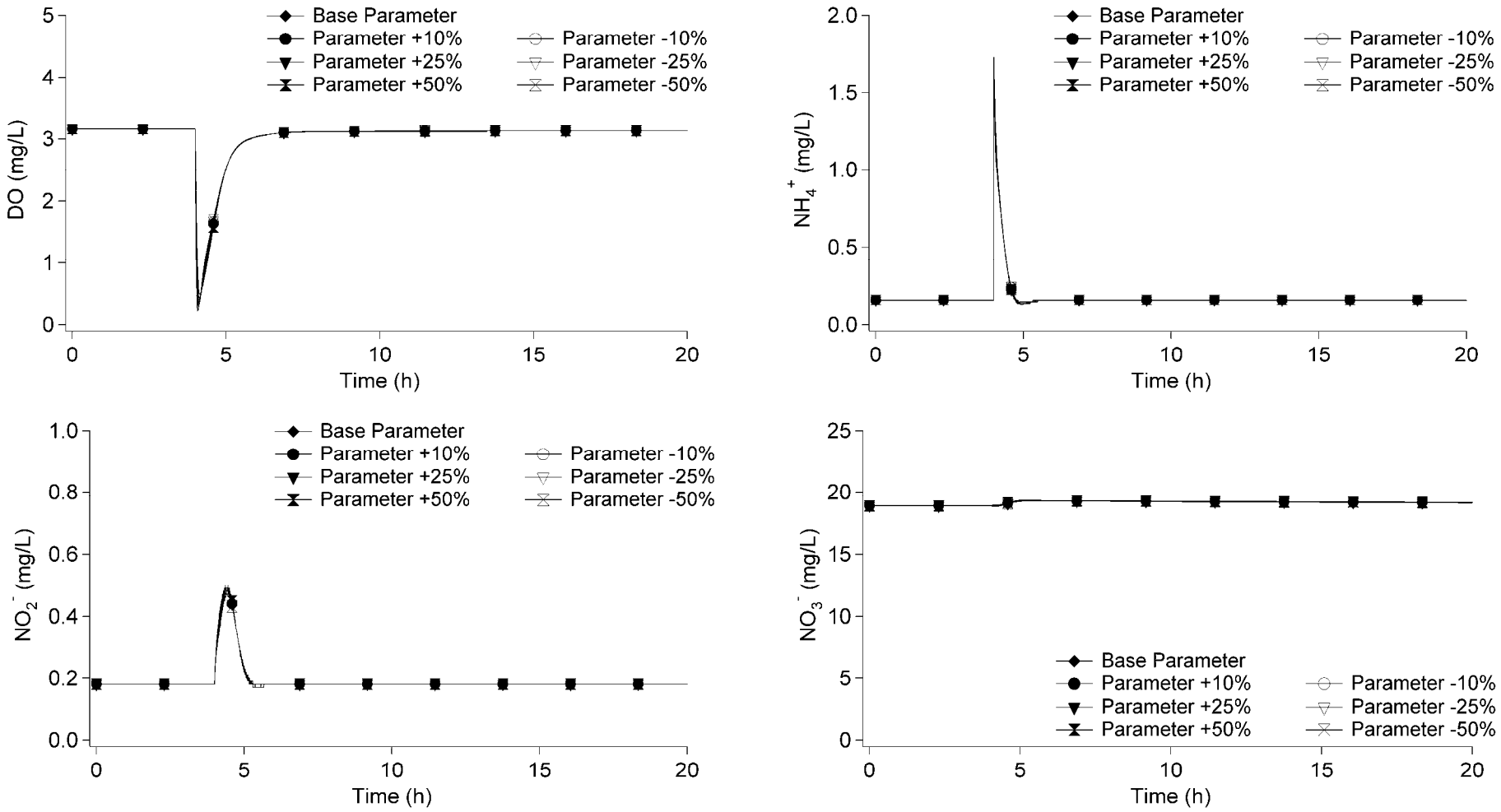

Figure A-69 Effect of heterotroph substrate inhibition coefficient (K_S) on dynamic response (ASM1-Nowak – UNSW data).

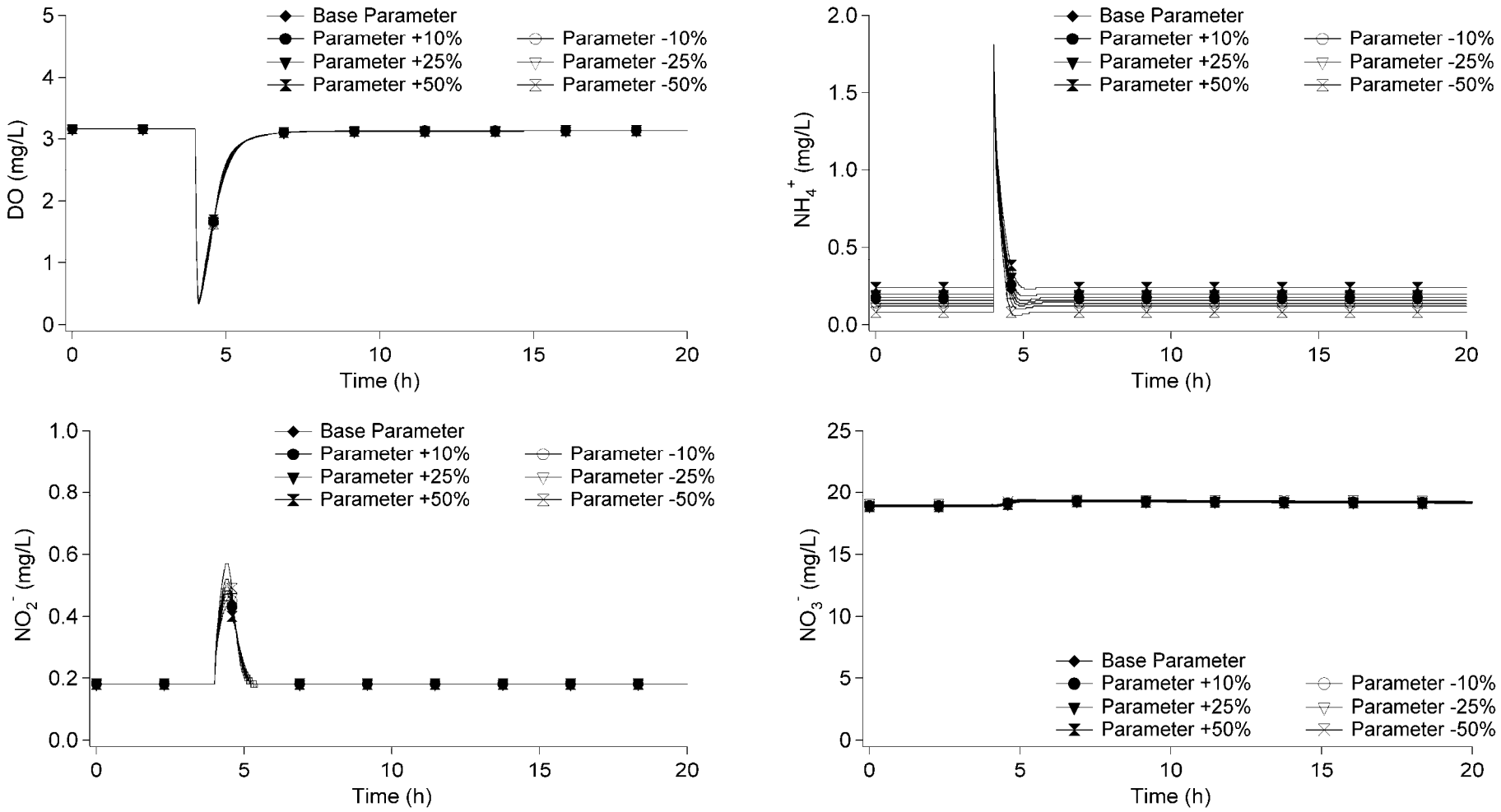

Figure A-70 Effect of ammonium inhibition coefficient (K_{NH}) on dynamic response (ASM1-Nowak – UNSW data).

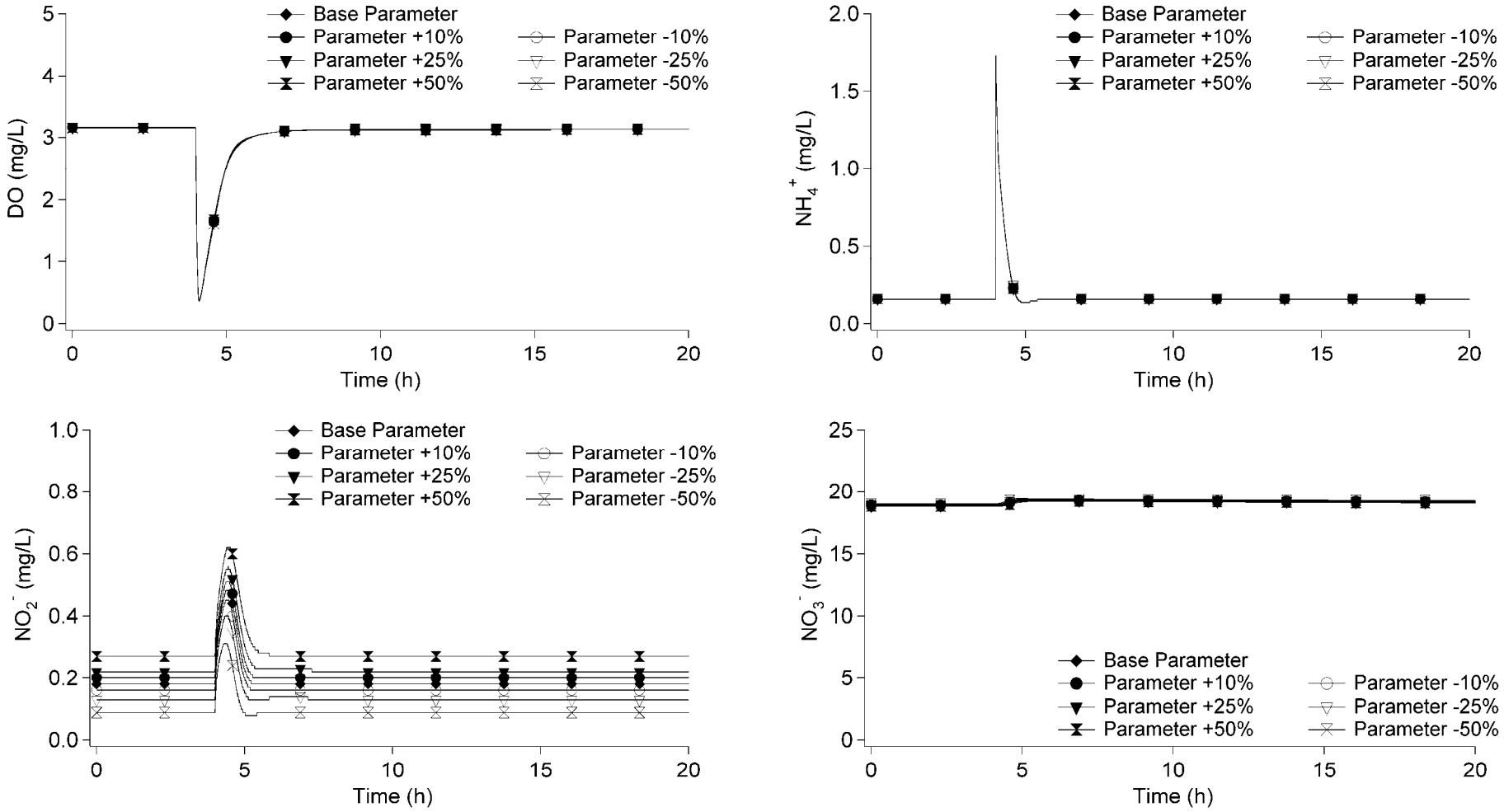

Figure A-71 Effect of nitrite inhibition coefficient (K_{NO2}) on dynamic response (ASM1-Nowak – UNSW data).

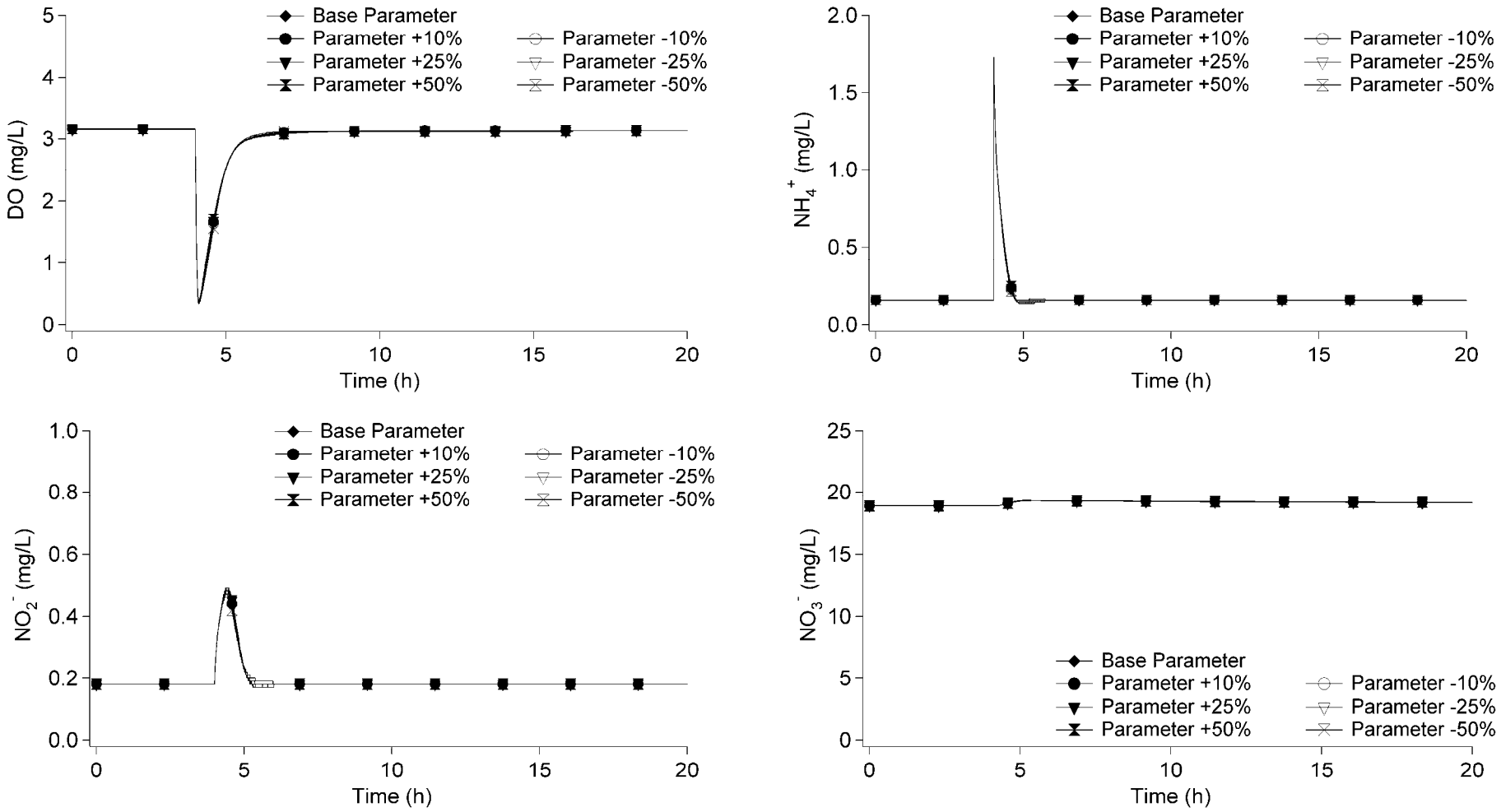

Figure A-72 Effect of hydrolysis half-saturation coefficient (K_X) on dynamic response (ASM1-Nowak – UNSW data).

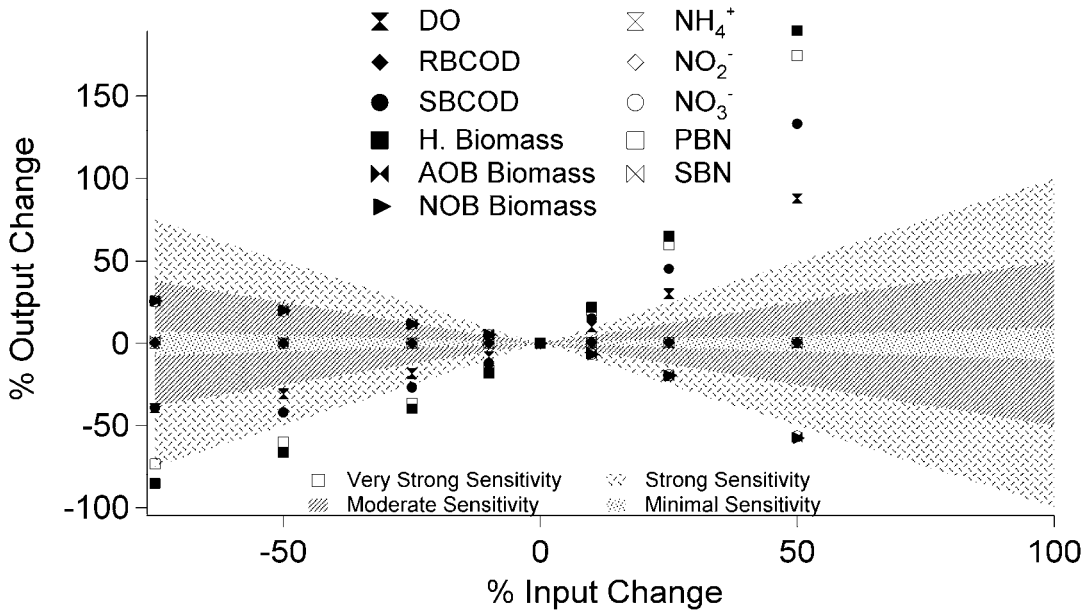

Figure A-73 Effect of heterotroph yield (Y_H) on system state variables (ASMN – UNSW data).

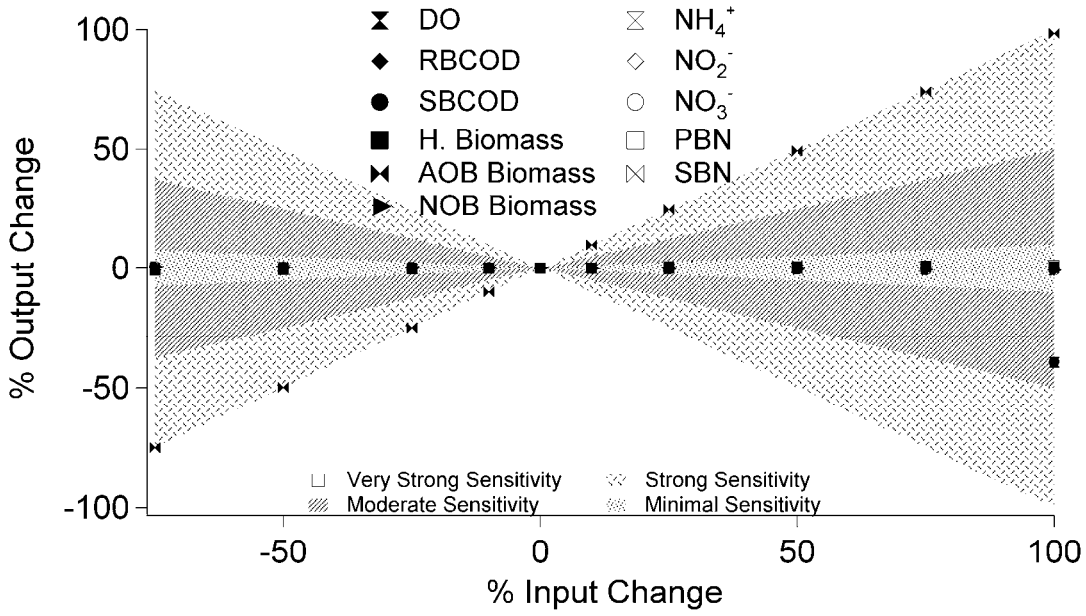

Figure A-74 Effect of AOB yield (Y_{A1}) on system state variables (ASMN – UNSW data).

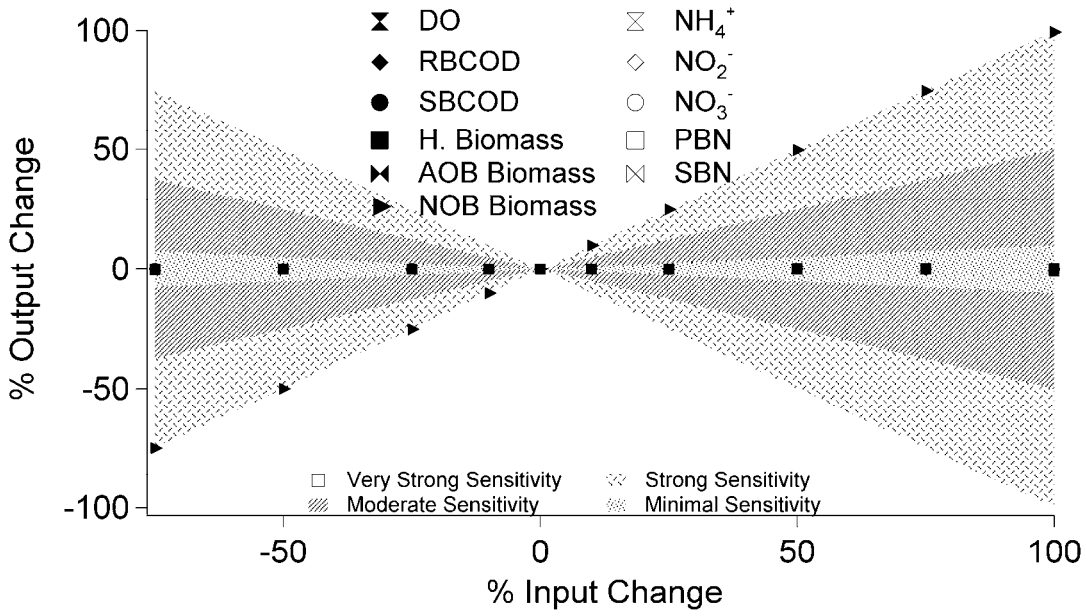

Figure A-75 Effect of NOB yield (Y_{A2}) on system state variables (ASMN – UNSW data).

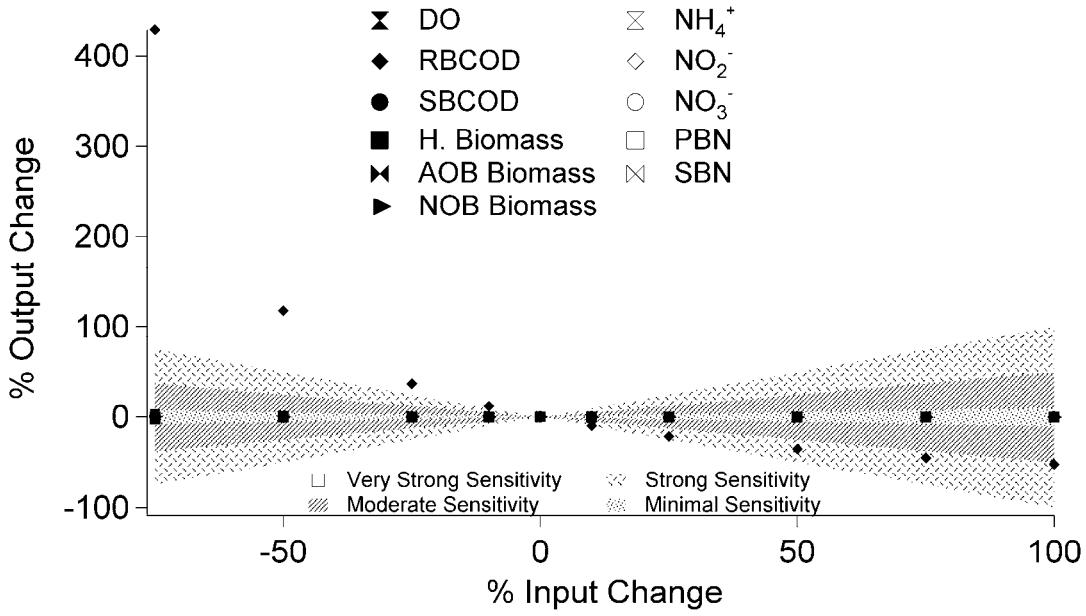

Figure A-76 Effect of heterotroph maximum specific growth rate (μ_H) on system state variables (ASMN – UNSW data).

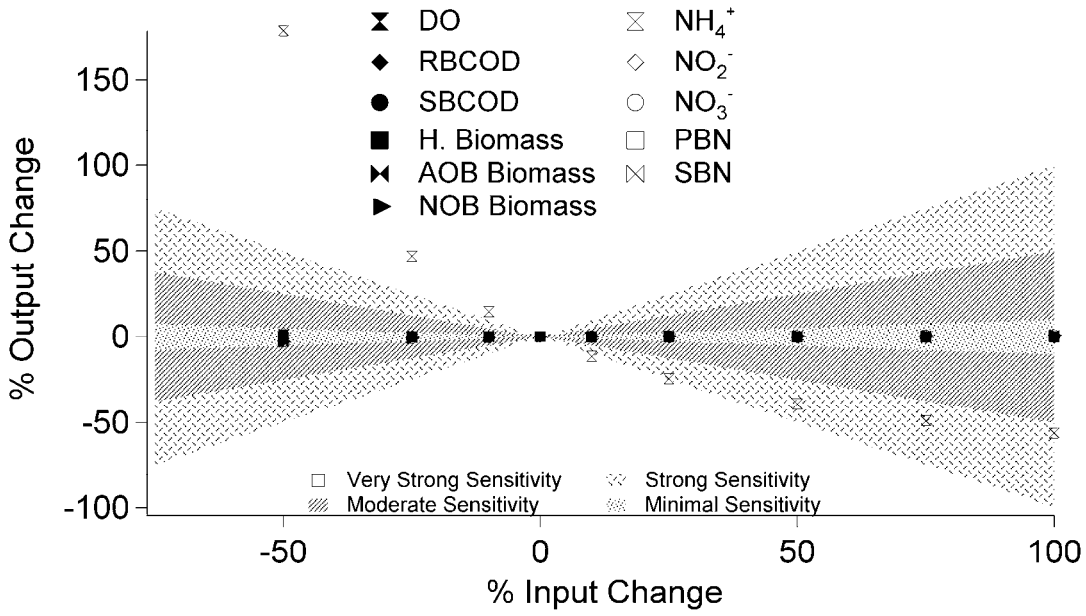

Figure A-77 Effect of AOB maximum specific growth rate (μ_{A1}) on system state variables (ASMN – UNSW data).

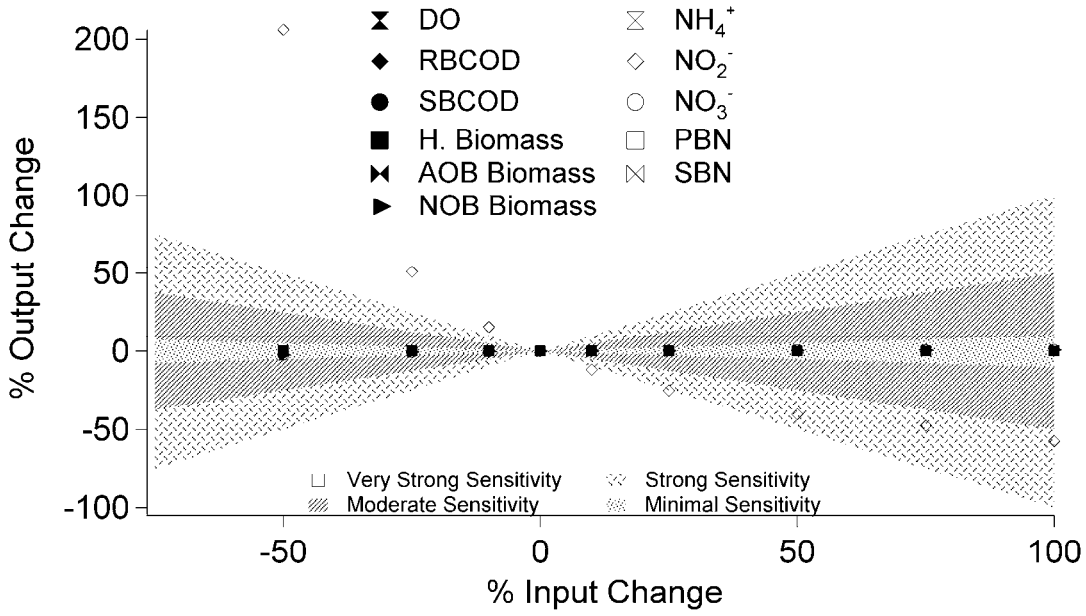

Figure A-78 Effect of NOB maximum specific growth rate (μ_{A2}) on system state variables (ASMN – UNSW data).

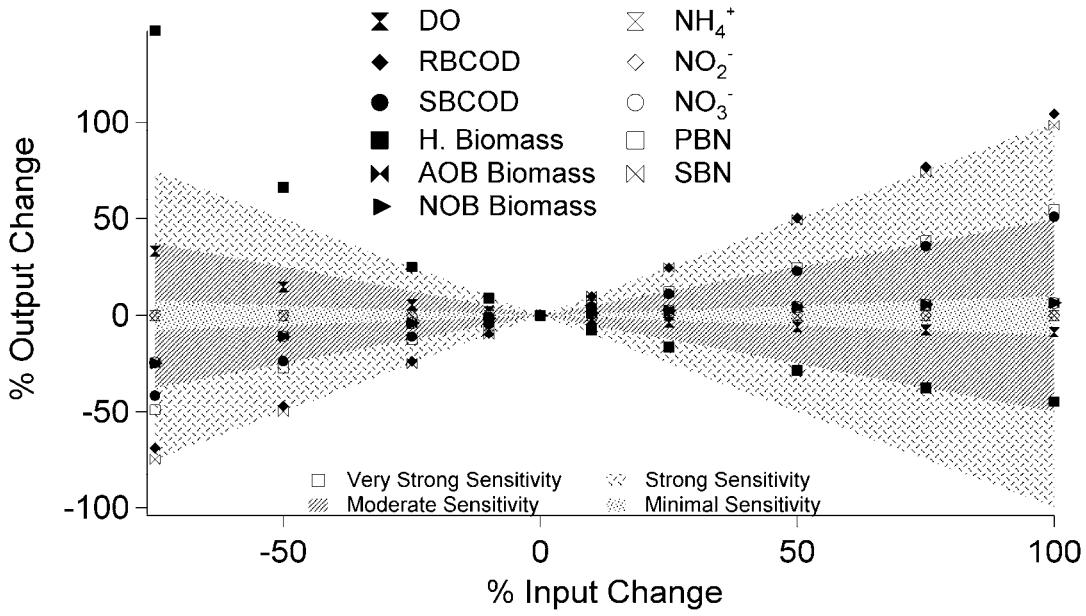

Figure A-79 Effect of heterotroph decay coefficient (b_H) on system state variables (ASMN – UNSW data).

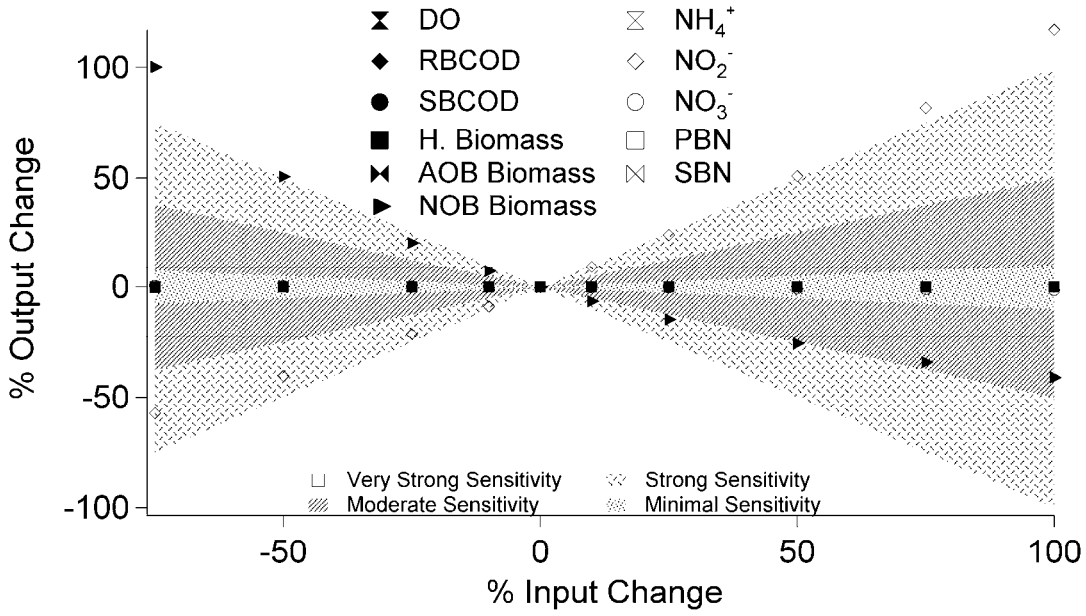

Figure A-80 Effect of AOB decay coefficient (b_{LA1}) on system state variables (ASMN – UNSW data).

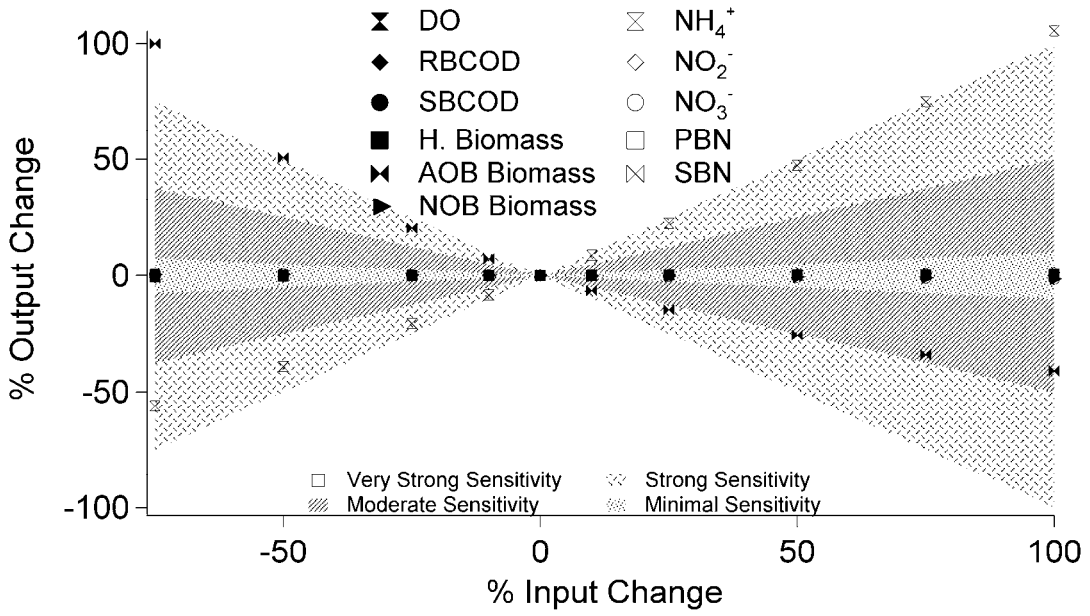

Figure A-81 Effect of NOB decay coefficient (b_{LA2}) on system state variables (ASMN – UNSW data).

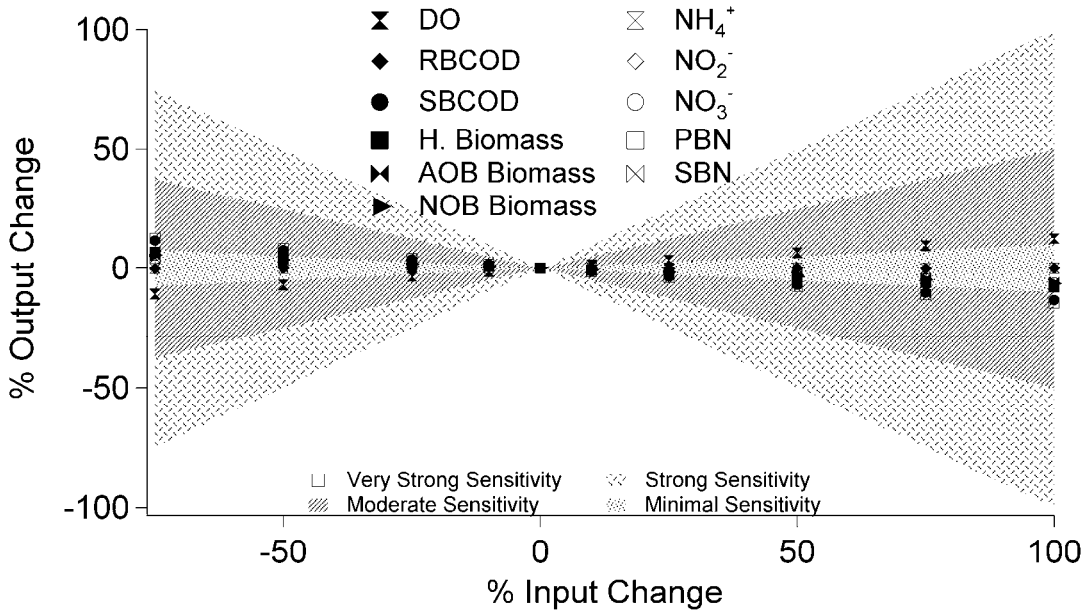

Figure A-82 Effect of biomass decay partitioning factor (f_d) on system state variables (ASMN – UNSW data).

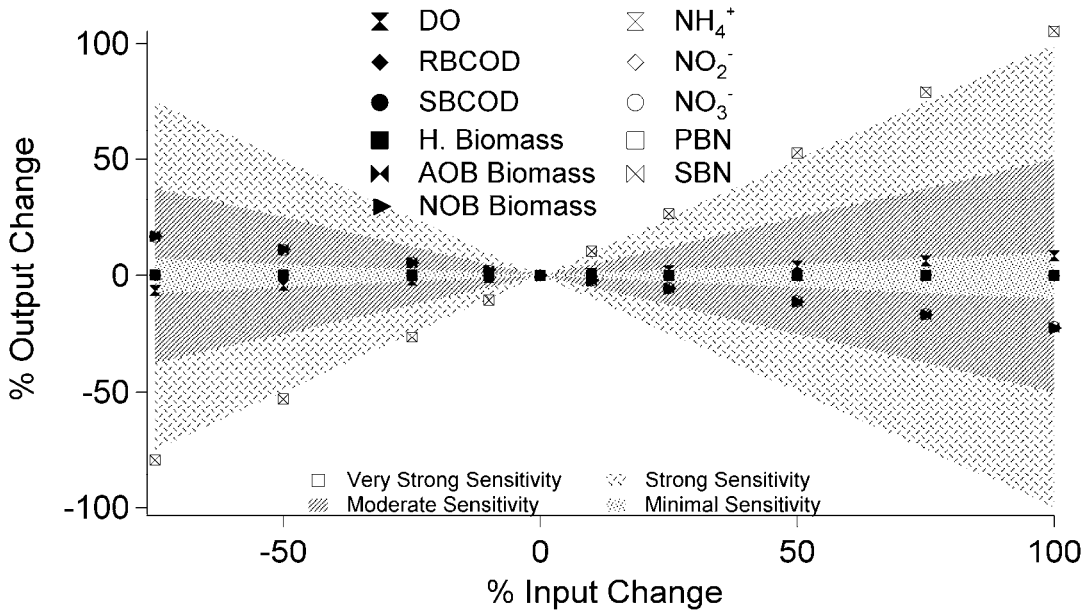

Figure A-83 Effect of biomass nitrogen fraction ($i_{N/XB}$) on system state variables (ASMN – UNSW data).

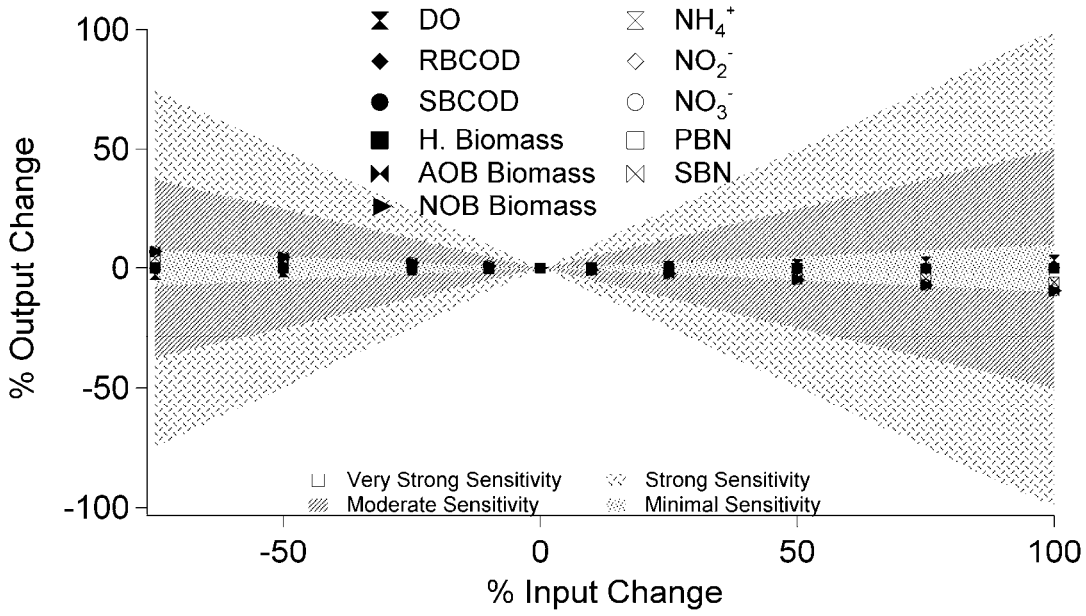

Figure A-84 Effect of particulate product nitrogen fraction ($i_{N/XP}$) on system state variables (ASMN – UNSW data).

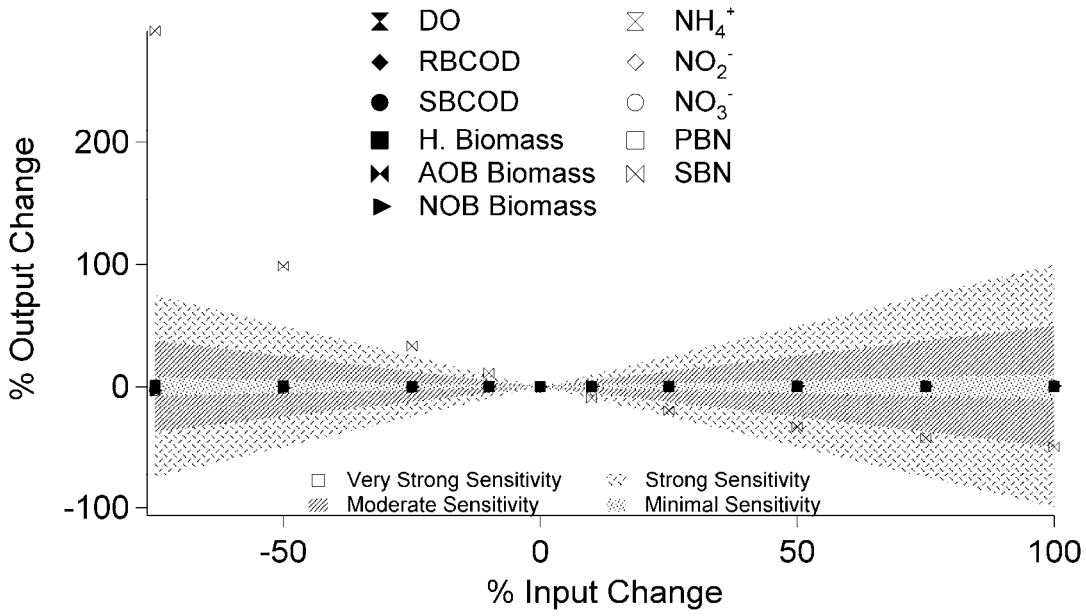

Figure A-85 Effect of ammonification rate (k_a) on system state variables (ASMN – UNSW data).

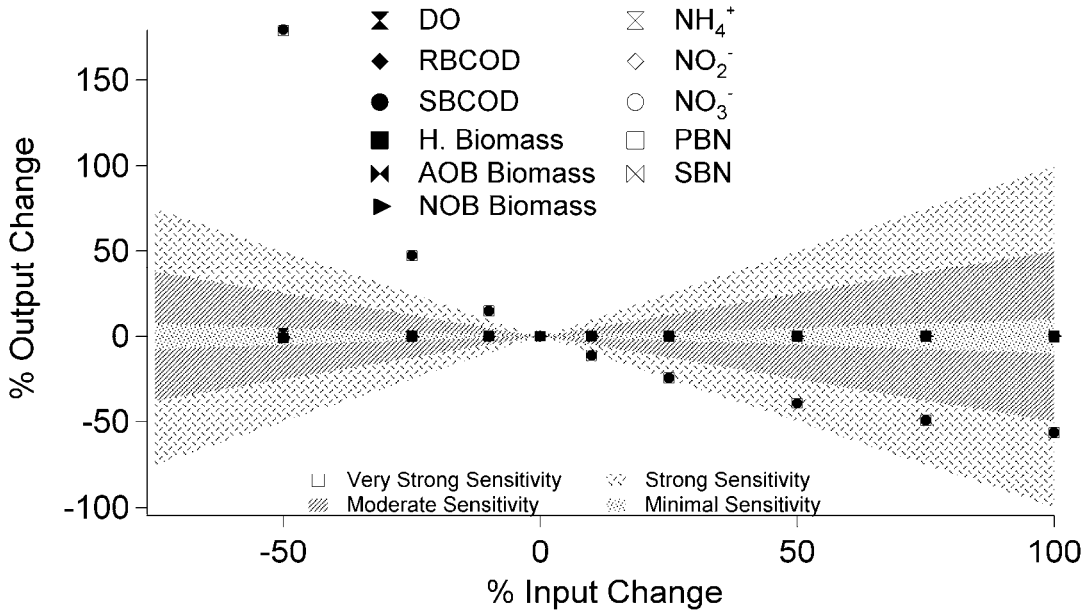

Figure A-86 Effect of maximum specific hydrolysis rate (k_H) on system state variables (ASMN – UNSW data).

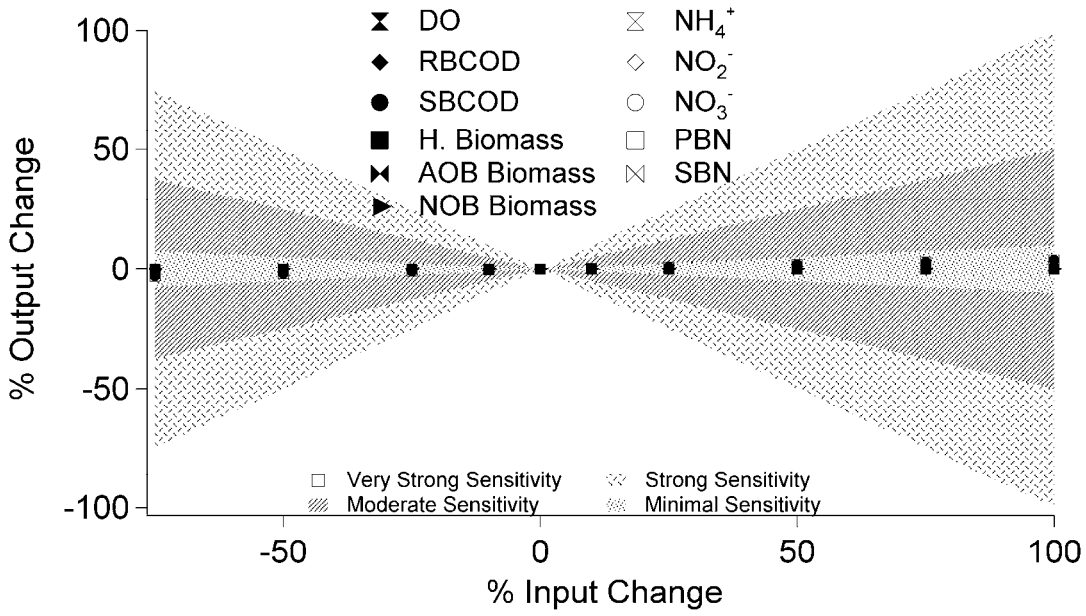

Figure A-87 Effect of heterotroph DO inhibition coefficient (K_{OH}) on system state variables (ASMN – UNSW data).

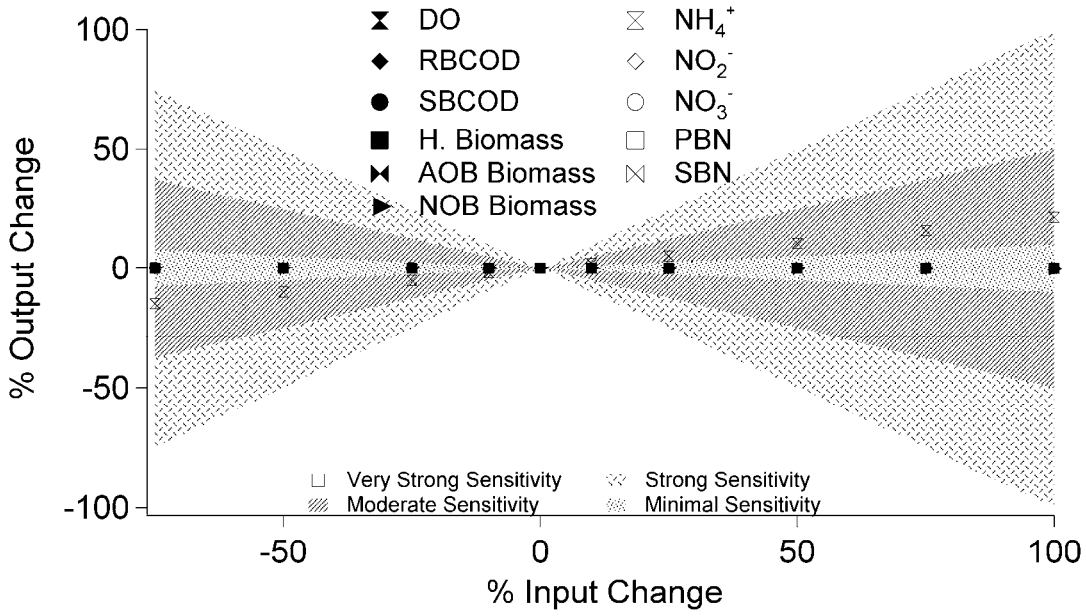

Figure A-88 Effect of AOB DO inhibition coefficient (K_{OA1}) on system state variables (ASMN – UNSW data).

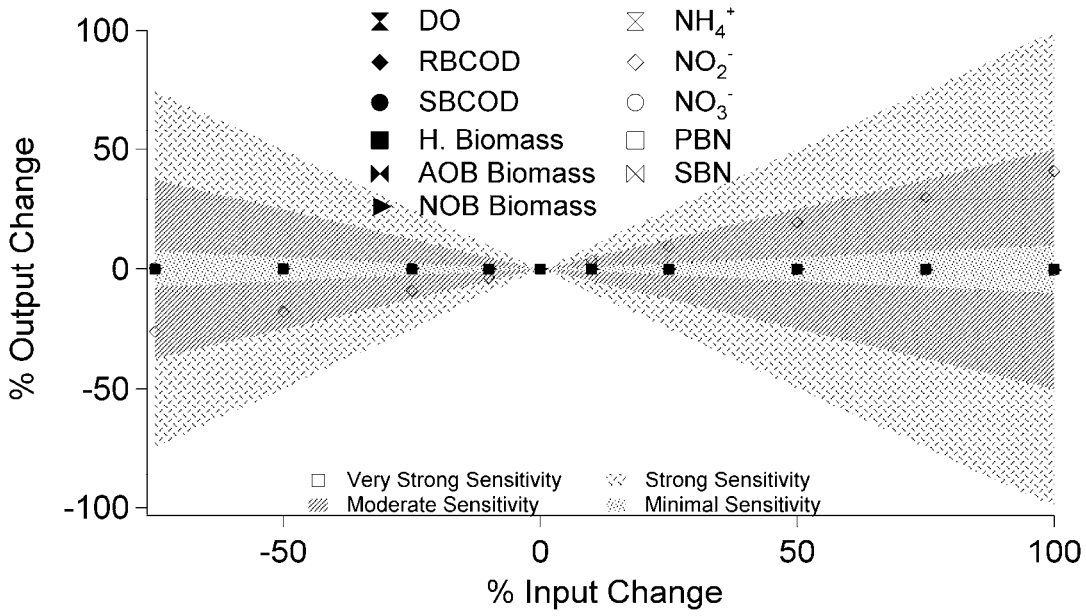

Figure A-89 Effect of NOB DO inhibition coefficient (K_{OA2}) on system state variables (ASMN – UNSW data).

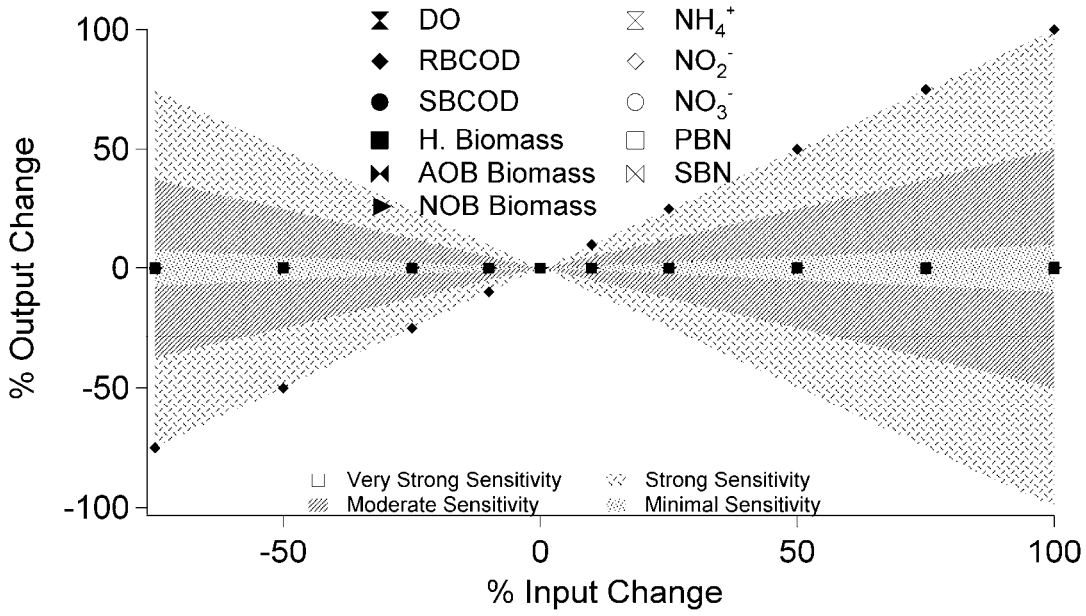

Figure A-90 Effect of heterotroph substrate inhibition coefficient (K_S) on system state variables (ASMN – UNSW data).

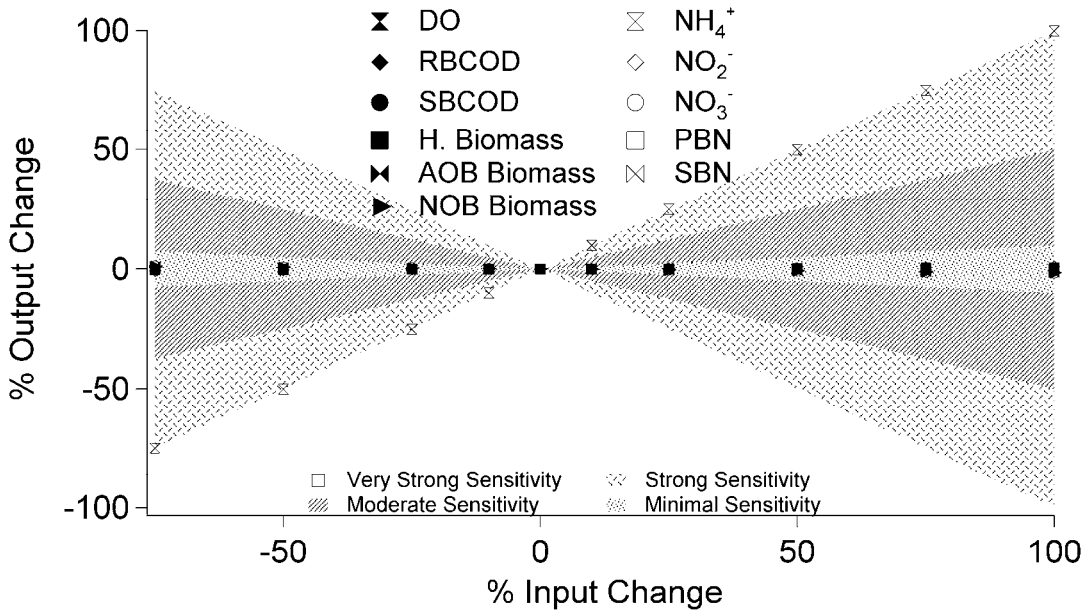

Figure A-91 Effect of free ammonia inhibition coefficient (K_{FA}) on system state variables (ASMN – UNSW data).

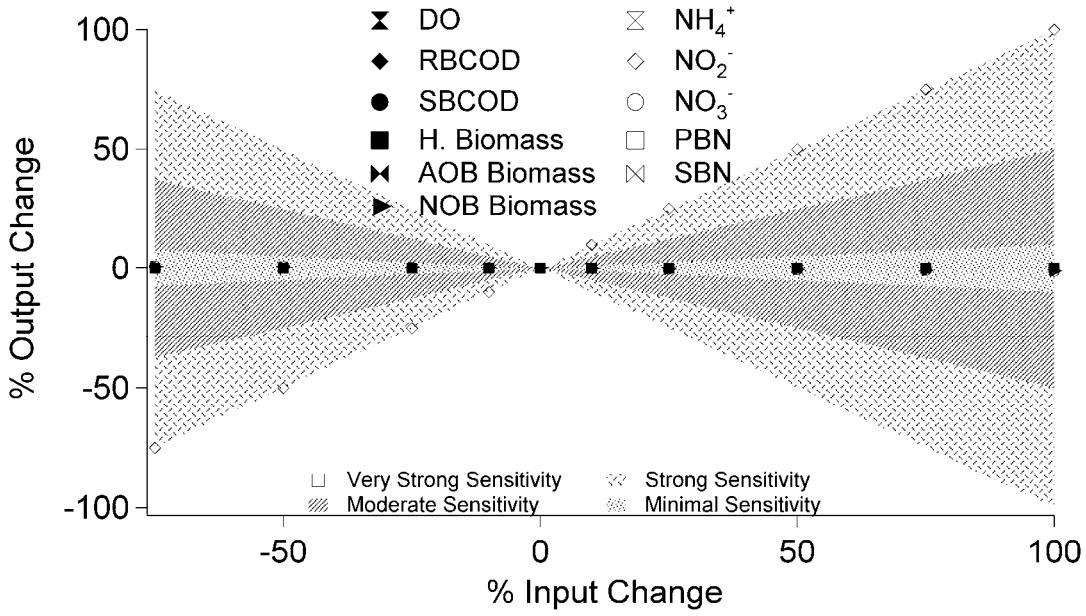

Figure A-92 Effect of free nitrous acid inhibition coefficient (K_{FNA}) on system state variables (ASMN – UNSW data).

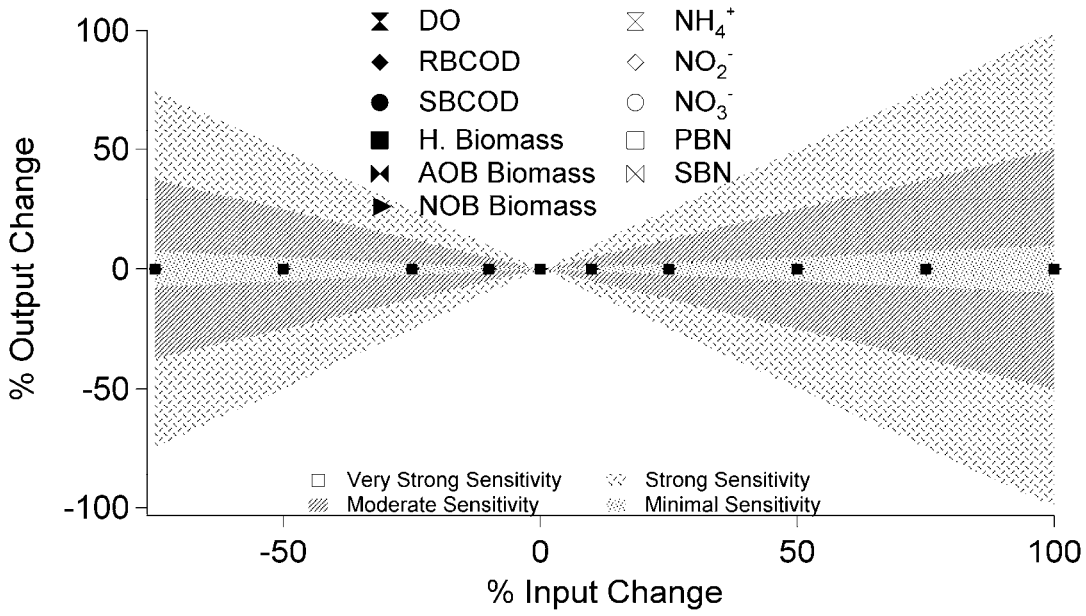

Figure A-93 Effect of AOB free ammonia inhibition coefficient (K_{I9FA}) on system state variables (ASMN – UNSW data).

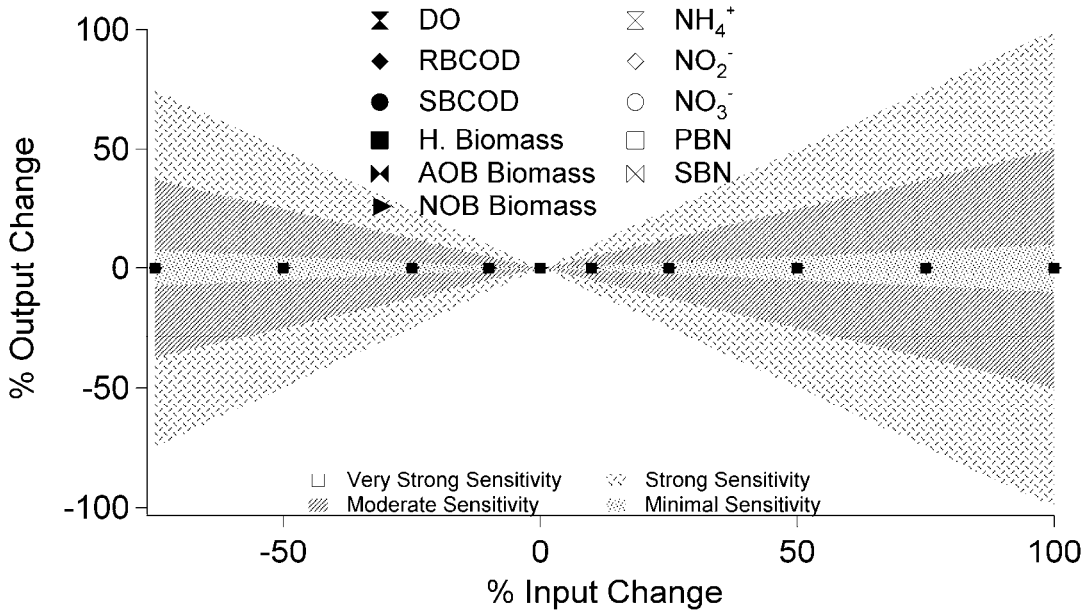

Figure A-94 Effect of AOB free nitrous acid inhibition coefficient (K_{I9FNA}) on system state variables (ASMN – UNSW data).

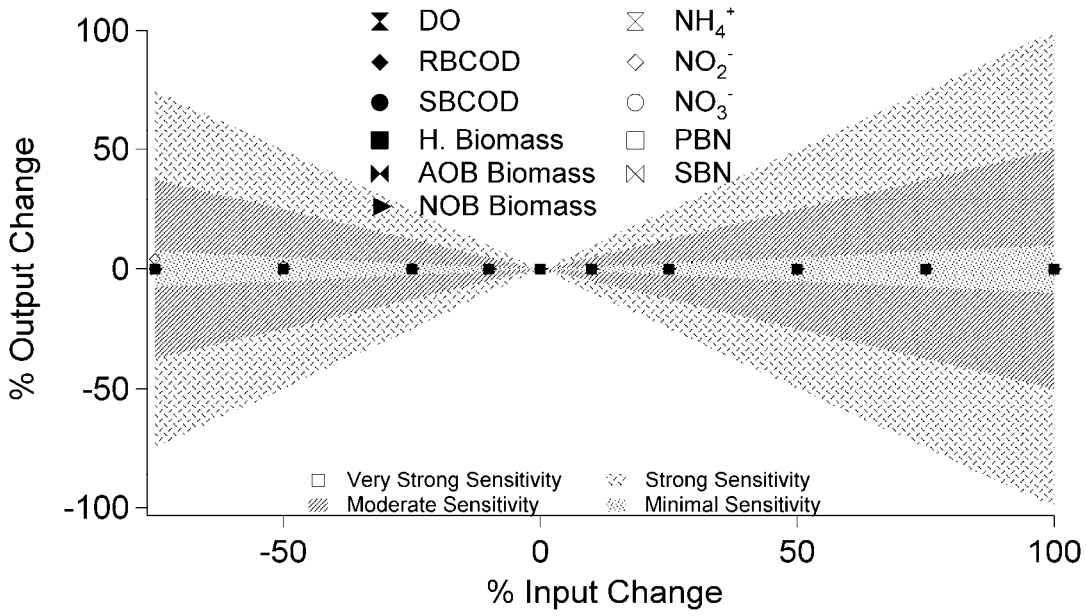

Figure A-95 Effect of NOB free ammonia inhibition coefficient (K_{I10FA}) on system state variables (ASMN – UNSW data).

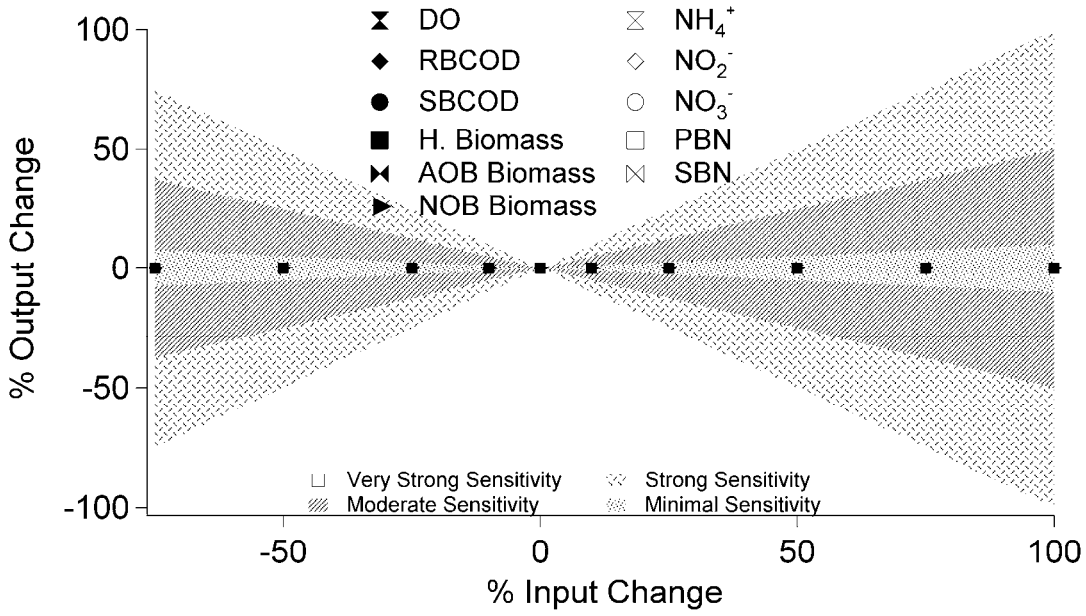

Figure A-96 Effect of NOB free nitrous acid inhibition coefficient (K_{I10FNA}) on system state variables (ASMN – UNSW data).

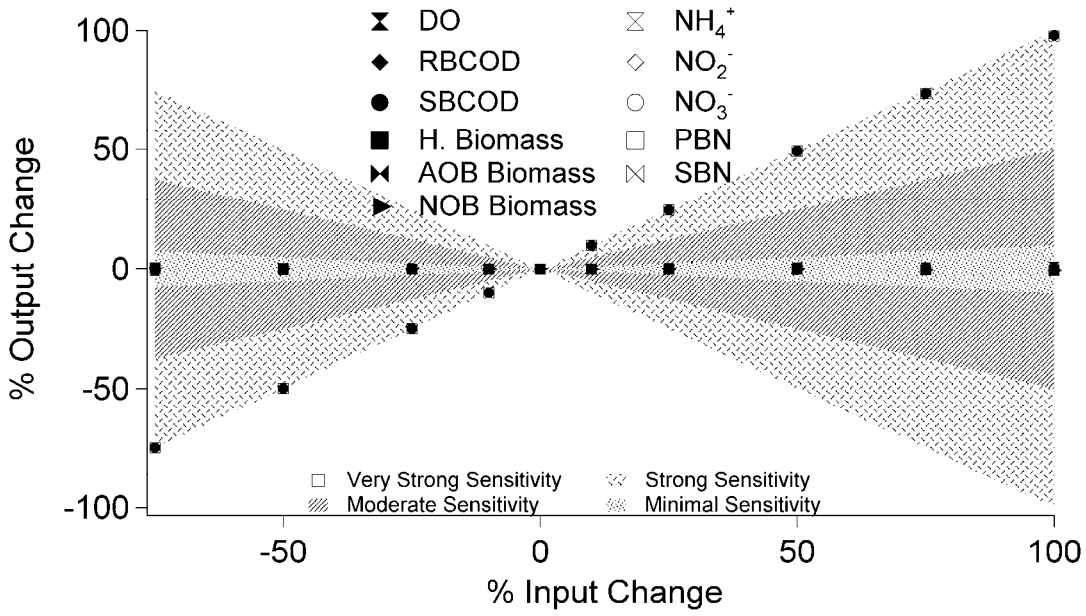

Figure A-97 Effect of hydrolysis half-saturation coefficient (K_X) on system state variables (ASMN – UNSW data).

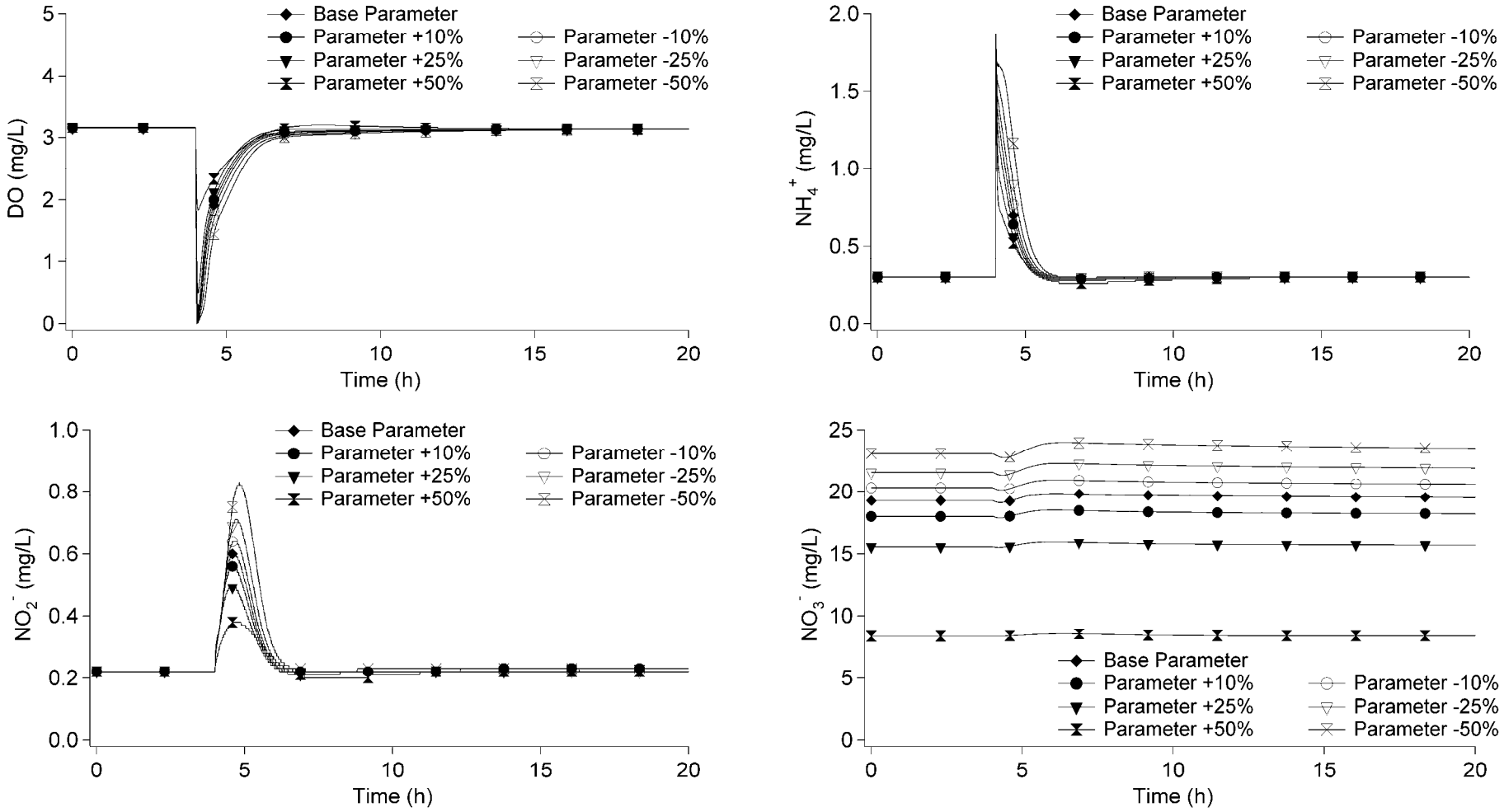

Figure A-98 Effect of heterotroph yield (Y_H) on dynamic response (ASMN – UNSW data).

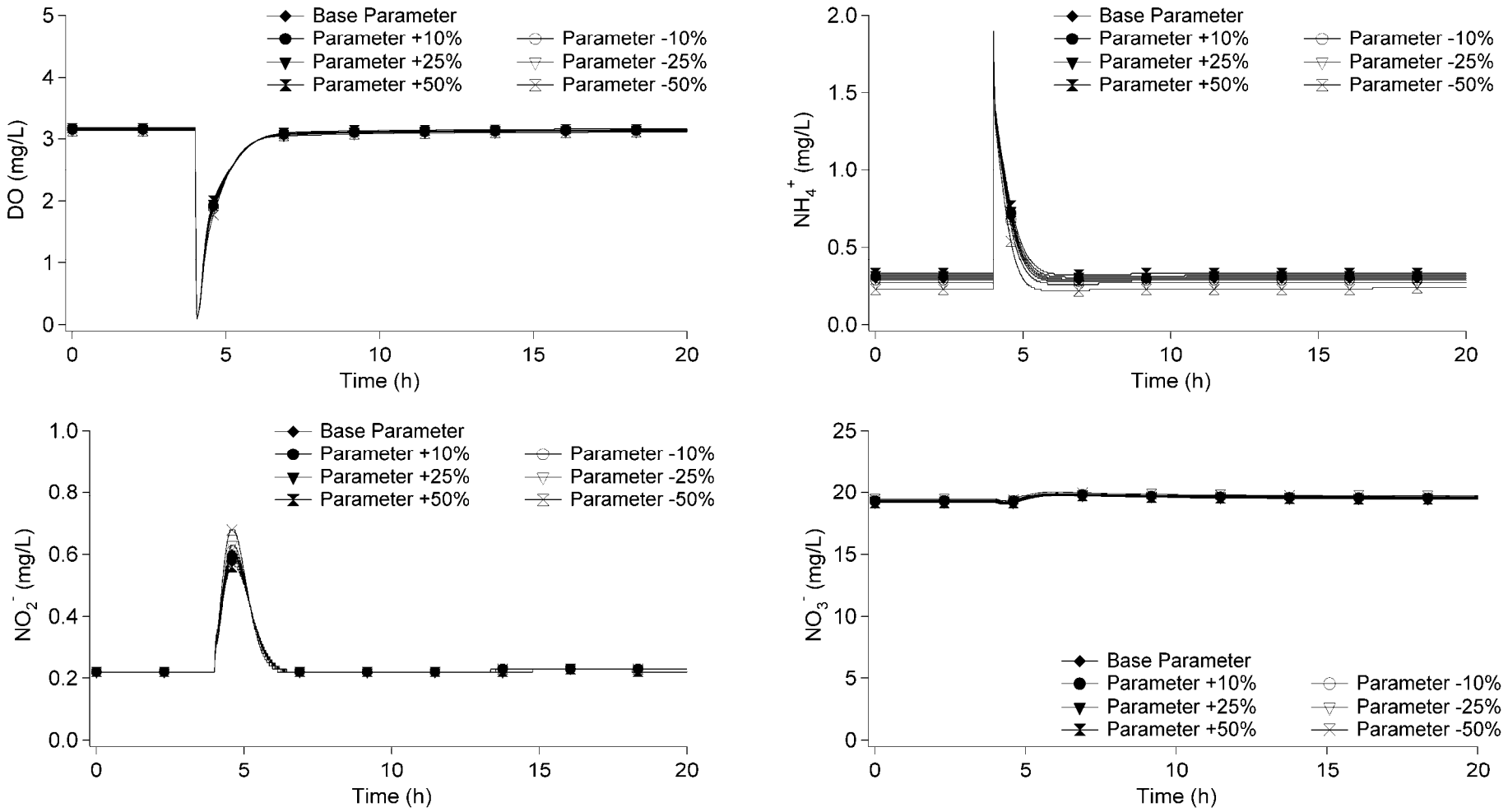

Figure A-99 Effect of AOB yield (Y_{A1}) on dynamic response (ASMN – UNSW data).

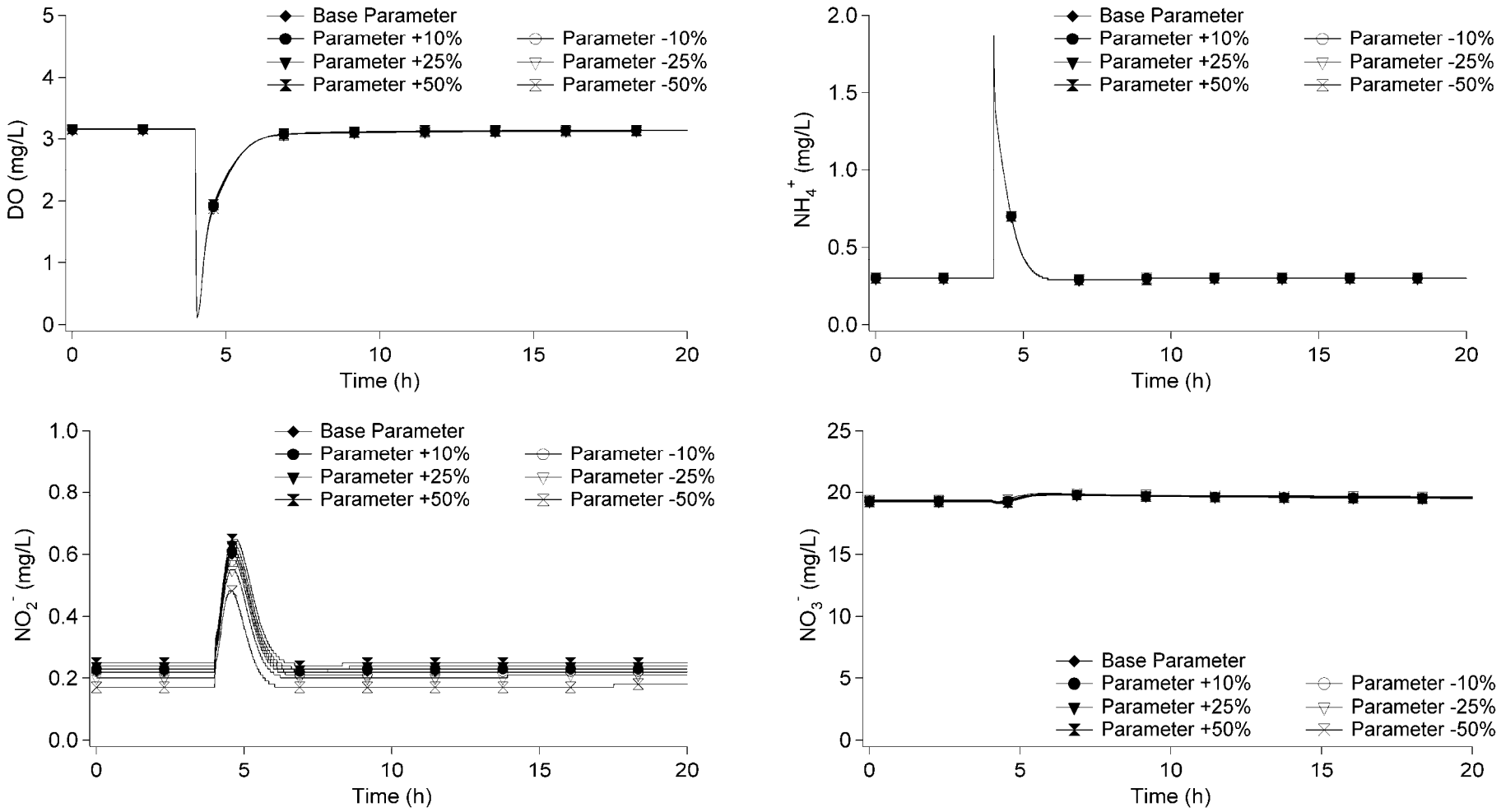

Figure A-100 Effect of NOB yield (Y_{A2}) on dynamic response (ASMN – UNSW data).

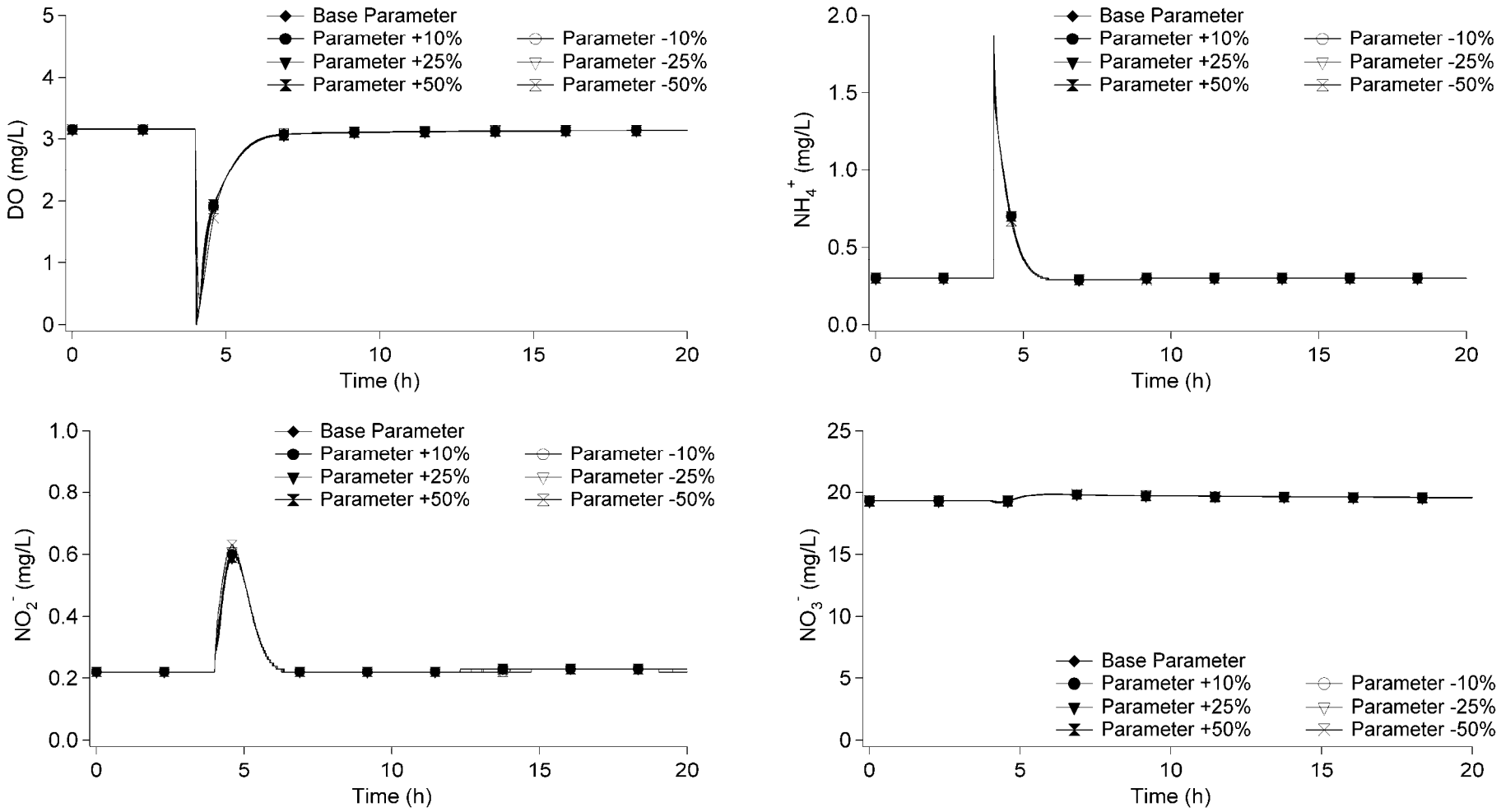

Figure A-101 Effect of heterotroph maximum specific growth rate (μ_H) on dynamic response (ASMN – UNSW data).

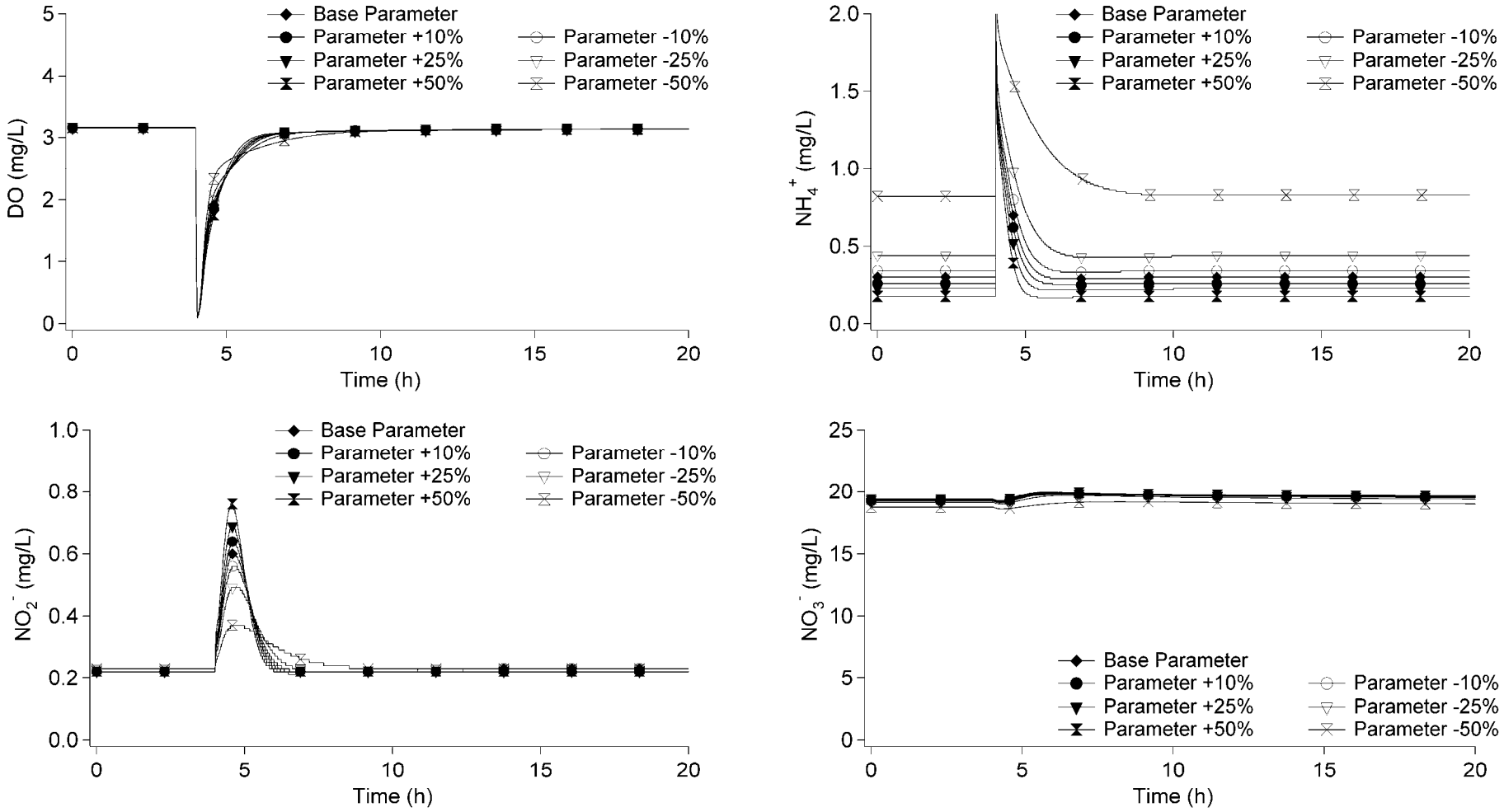

Figure A-102 Effect of AOB maximum specific growth rate (μ_{A1}) on dynamic response (ASMN – UNSW data).

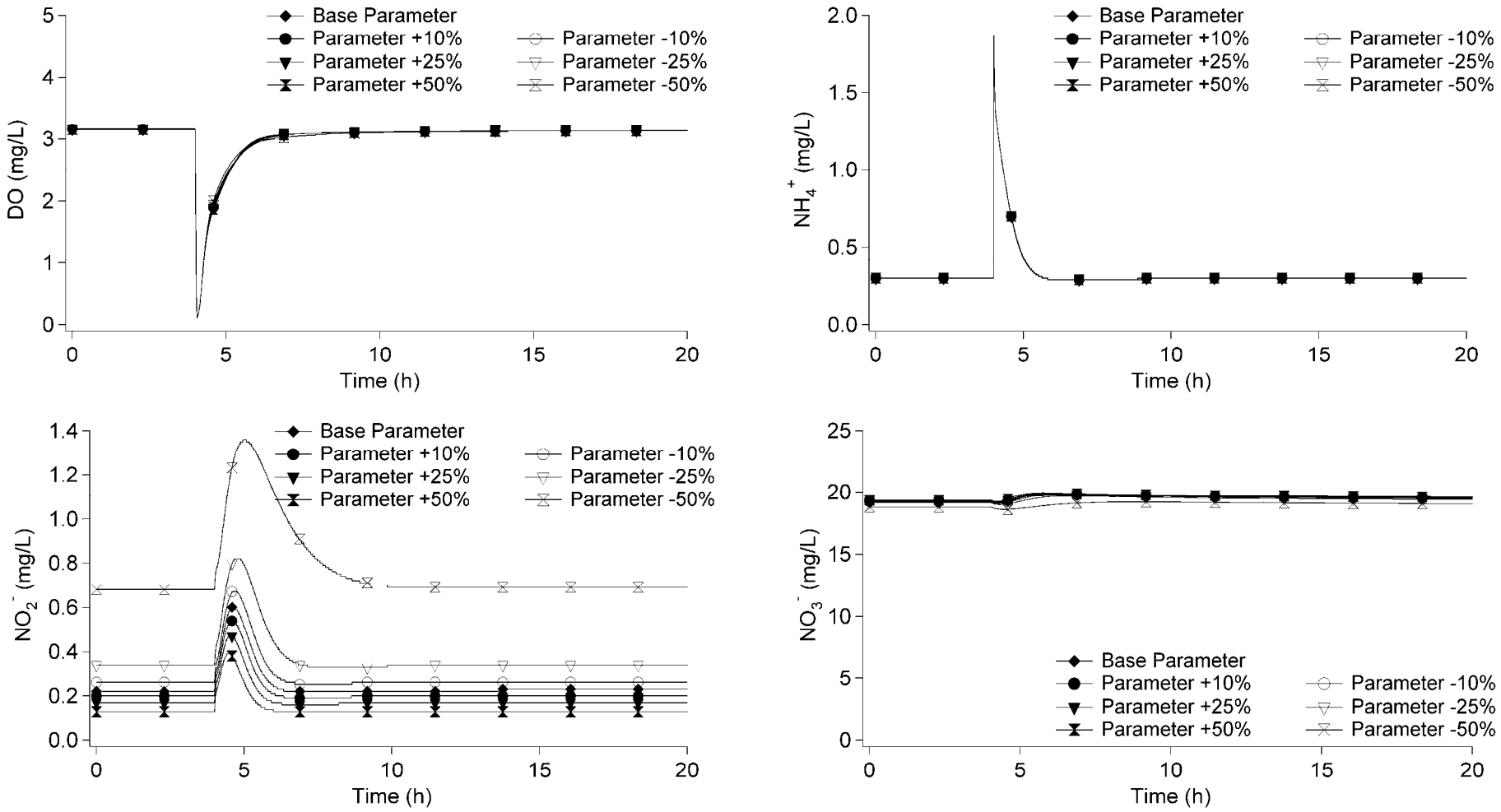

Figure A-103 Effect of NOB maximum specific growth rate (μ_{A2}) on dynamic response (ASMN – UNSW data).

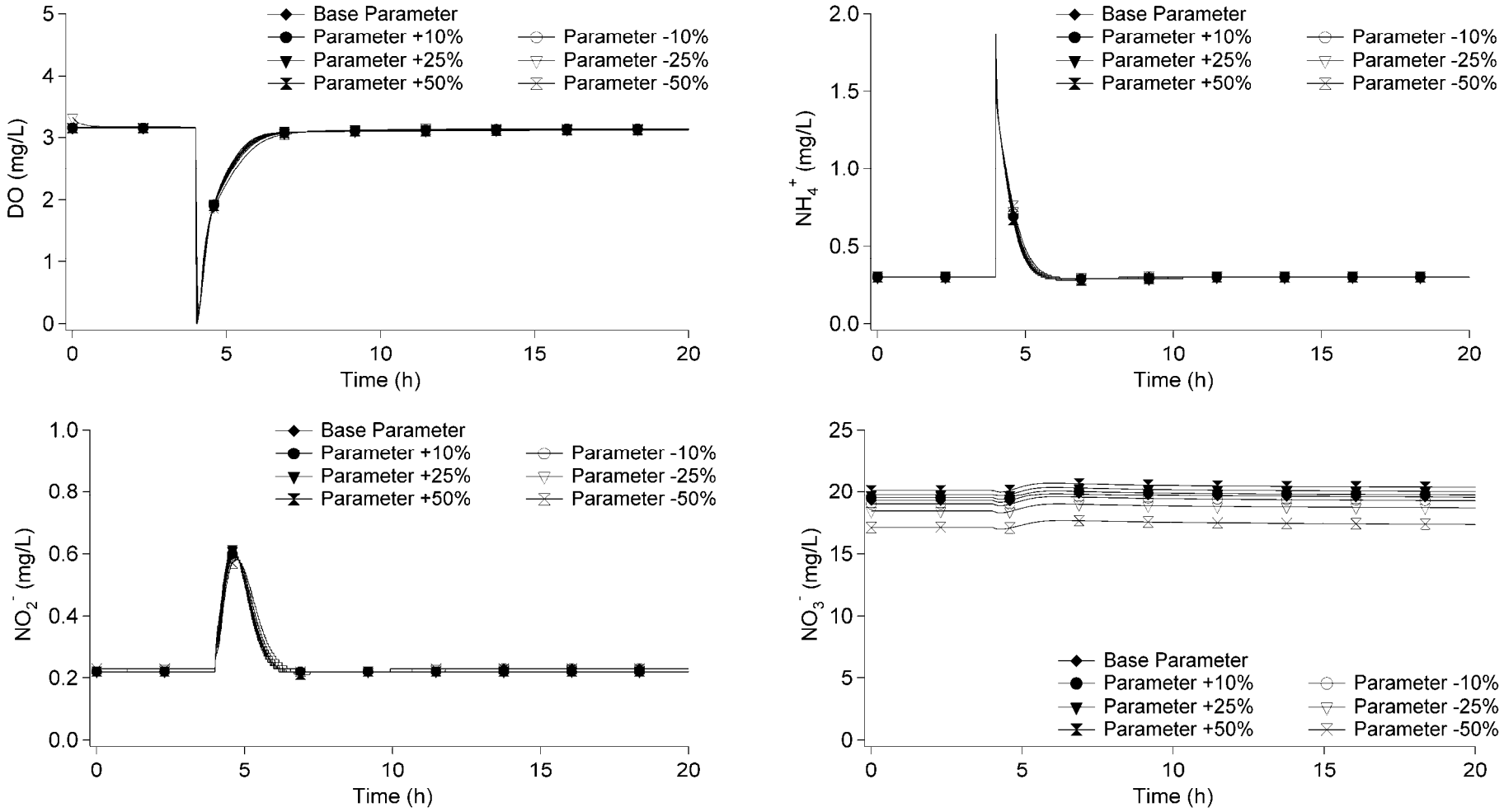

Figure A-104 Effect of heterotroph decay coefficient (b_H) on dynamic response (ASMN – UNSW data).

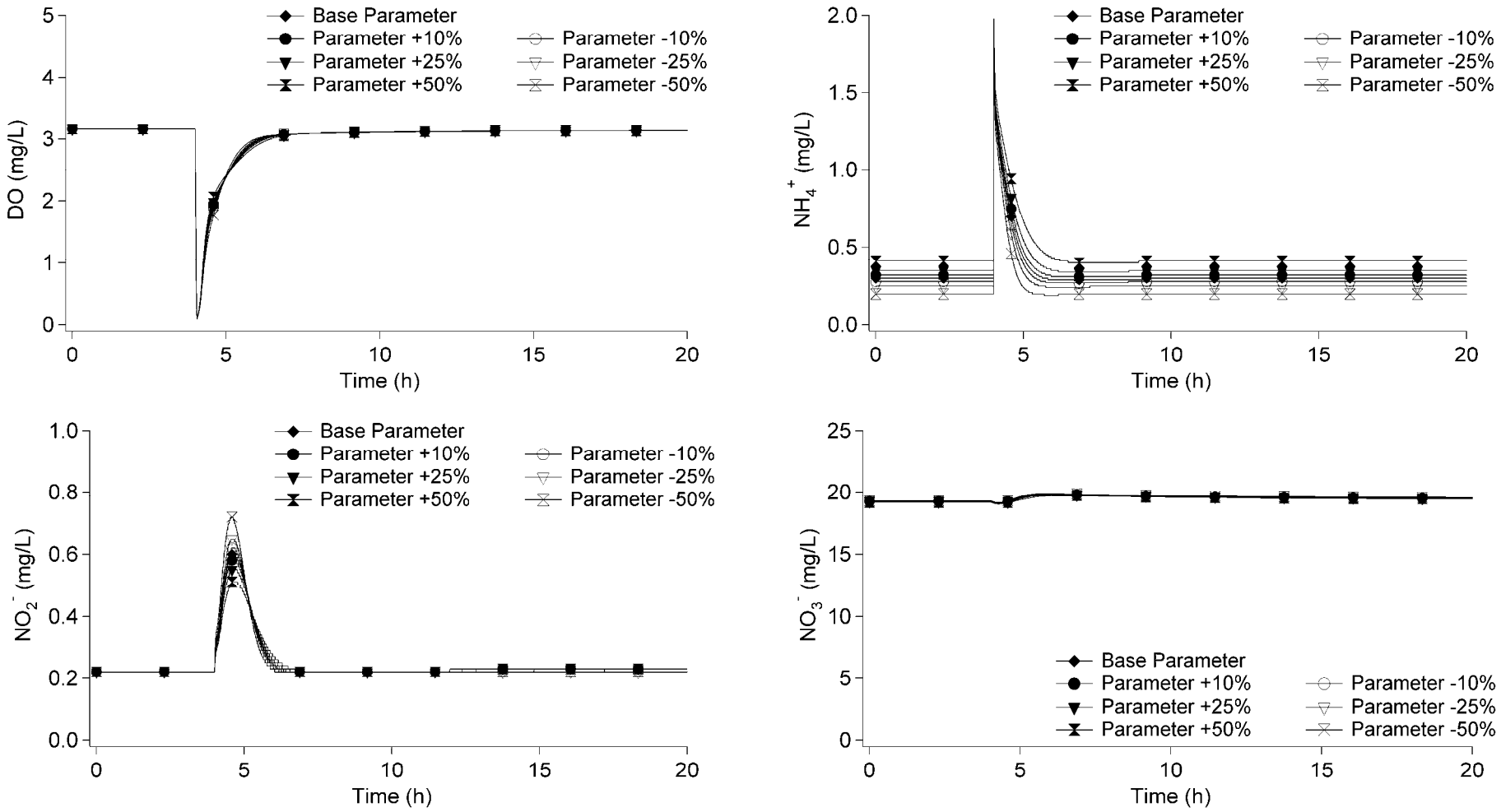

Figure A-105 Effect of AOB decay coefficient (b_{LA1}) on dynamic response (ASMN – UNSW data).

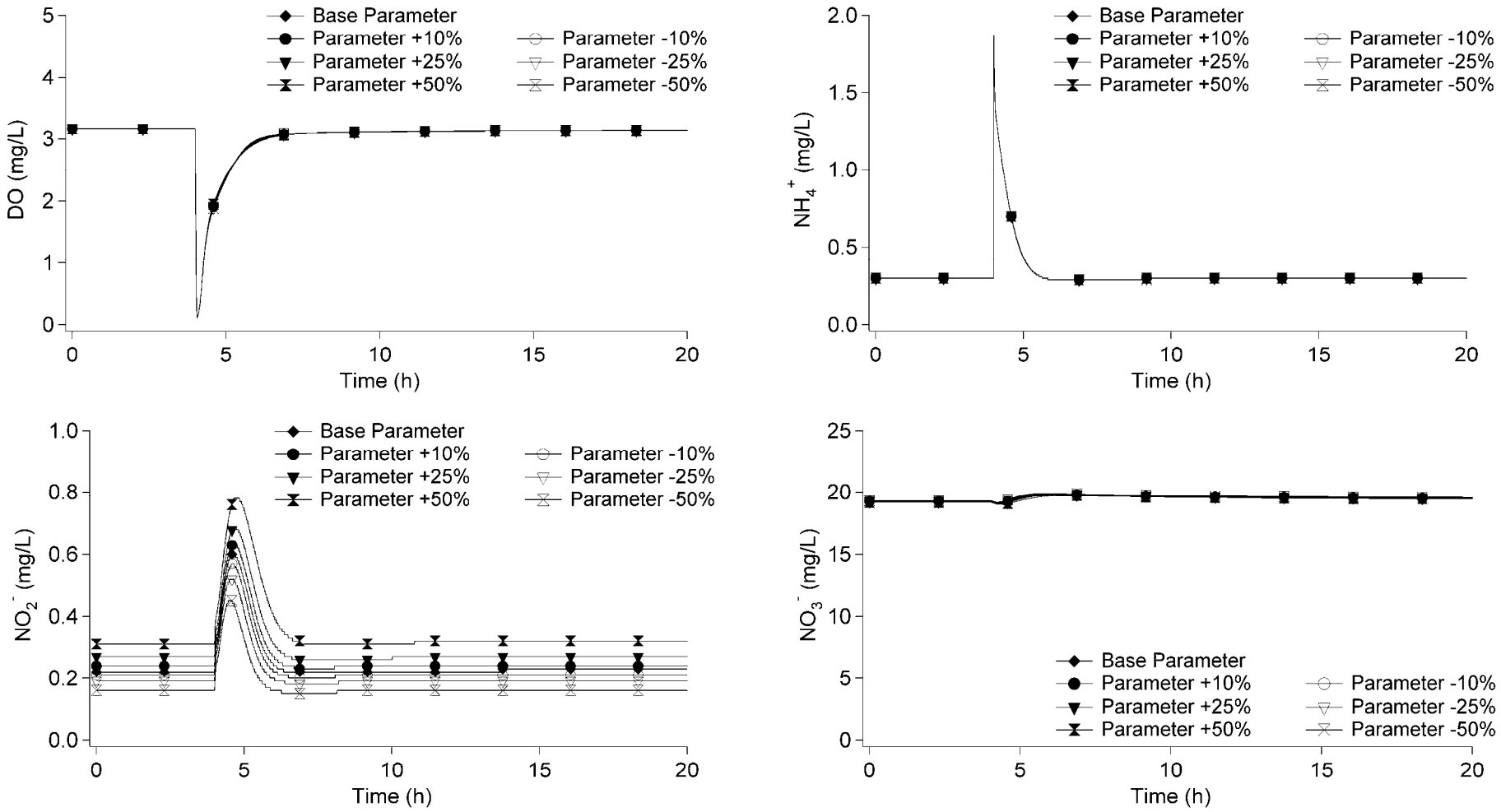

Figure A-106 Effect of NOB decay coefficient (b_{LA2}) on dynamic response (ASMN – UNSW data).

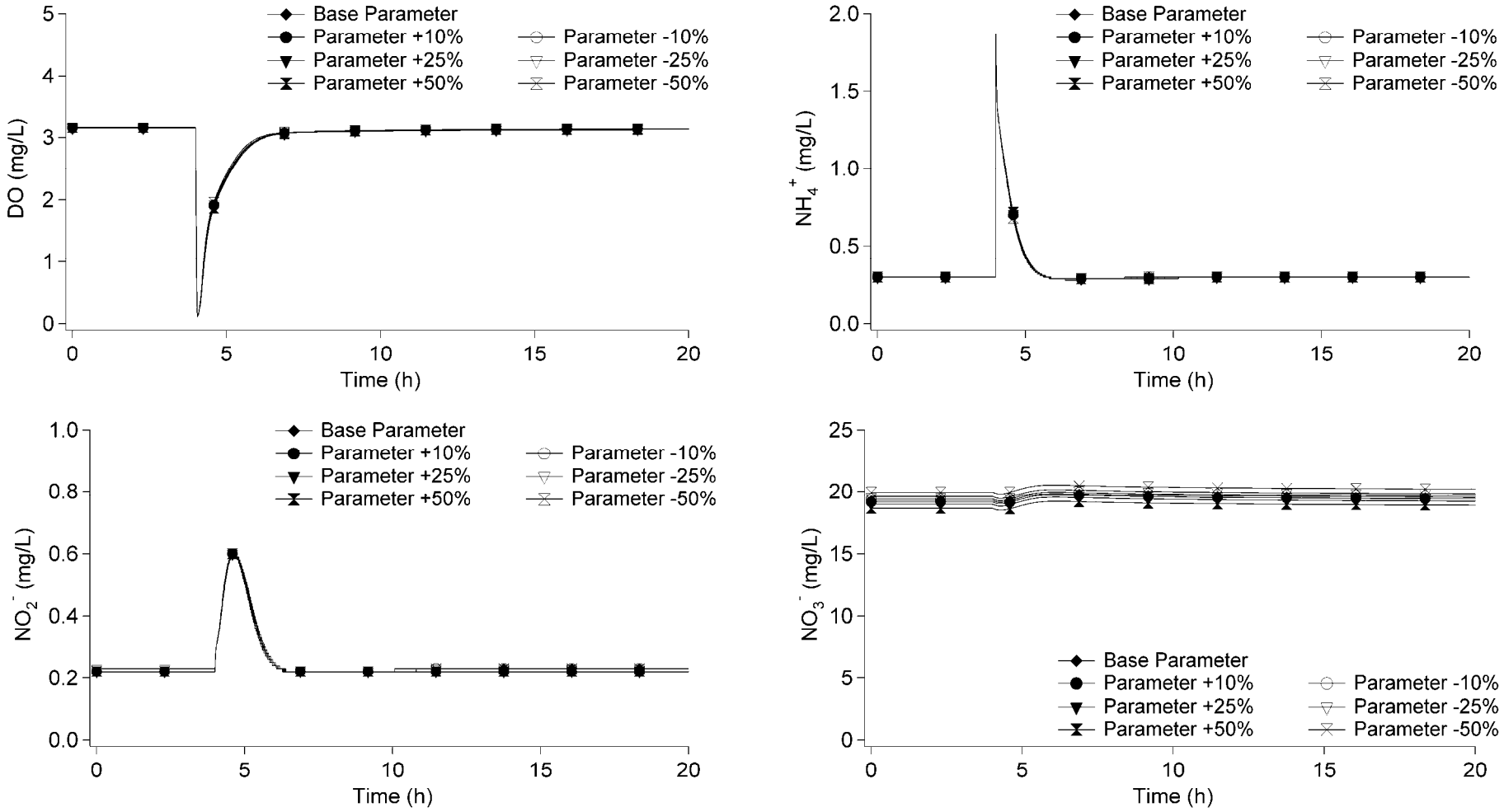

Figure A-107 Effect of biomass decay partitioning factor (f_d) on dynamic response (ASMN – UNSW data).

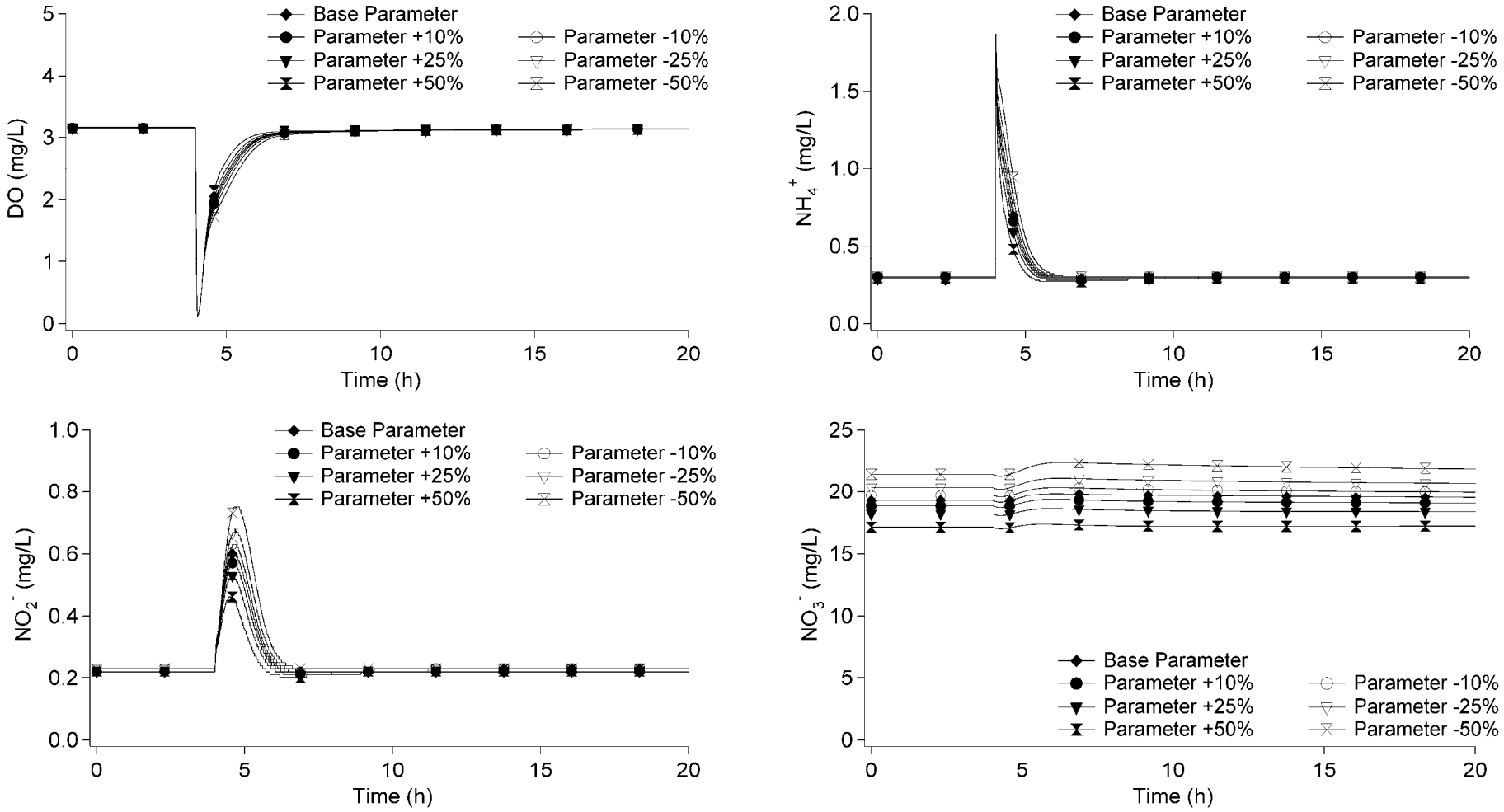

Figure A-108 Effect of biomass nitrogen fraction ($i_{N/XB}$) on dynamic response (ASMN – UNSW data).

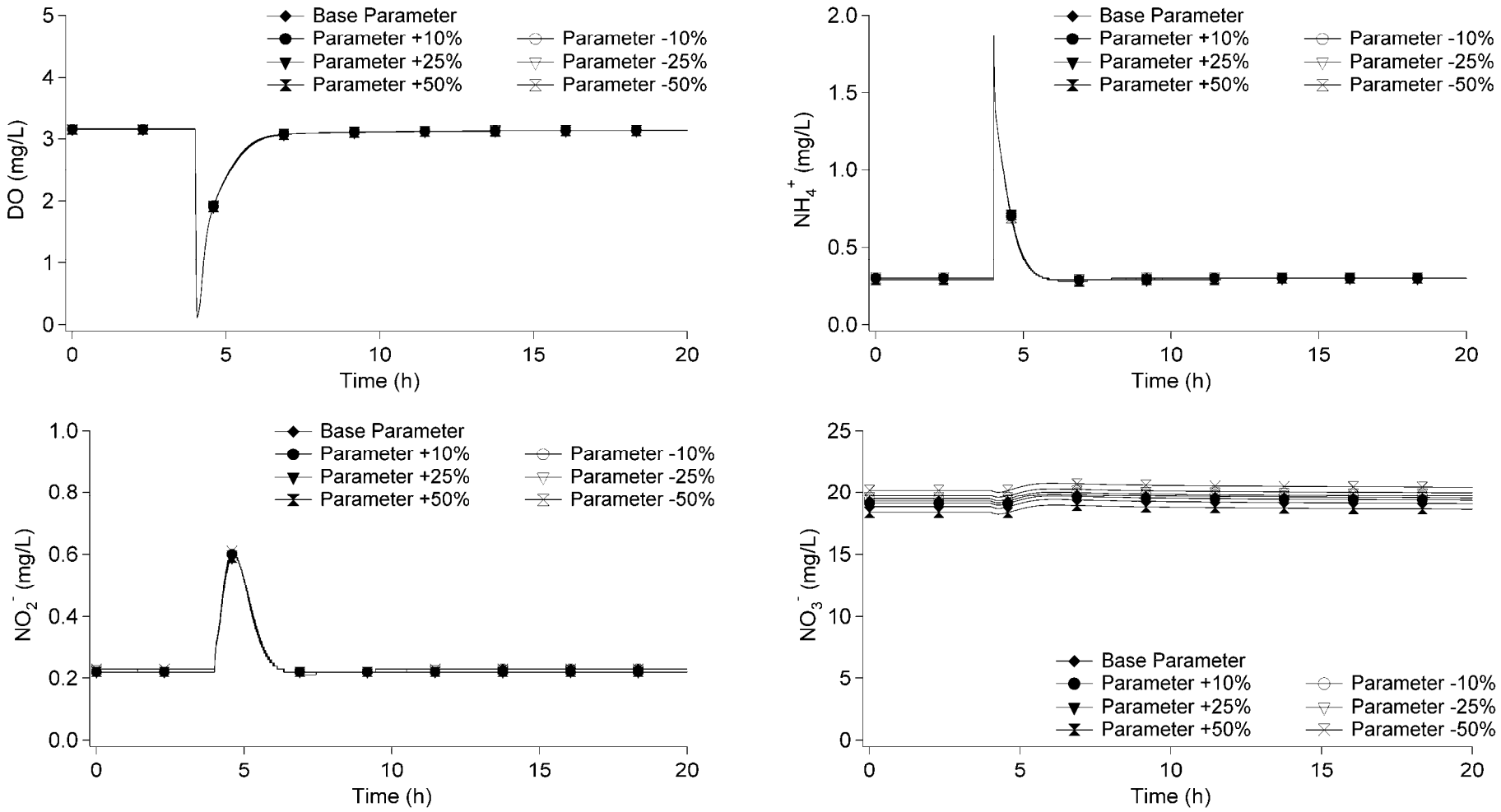

Figure A-109 Effect of particulate product nitrogen fraction ($i_{N/XP}$) on dynamic response (ASMN – UNSW data).

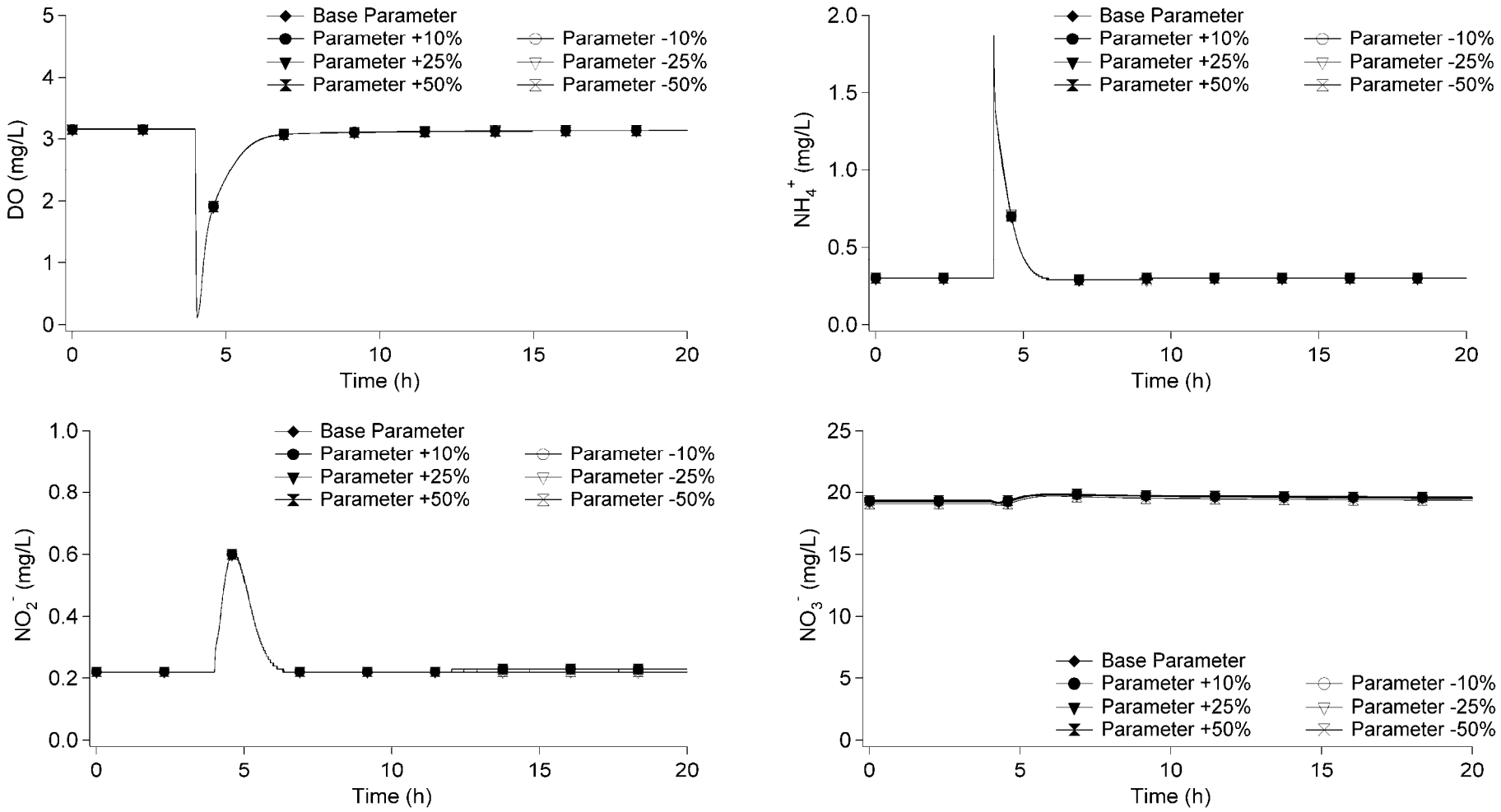

Figure A-110 Effect of ammonification rate (k_a) on dynamic response (ASMN – UNSW data).

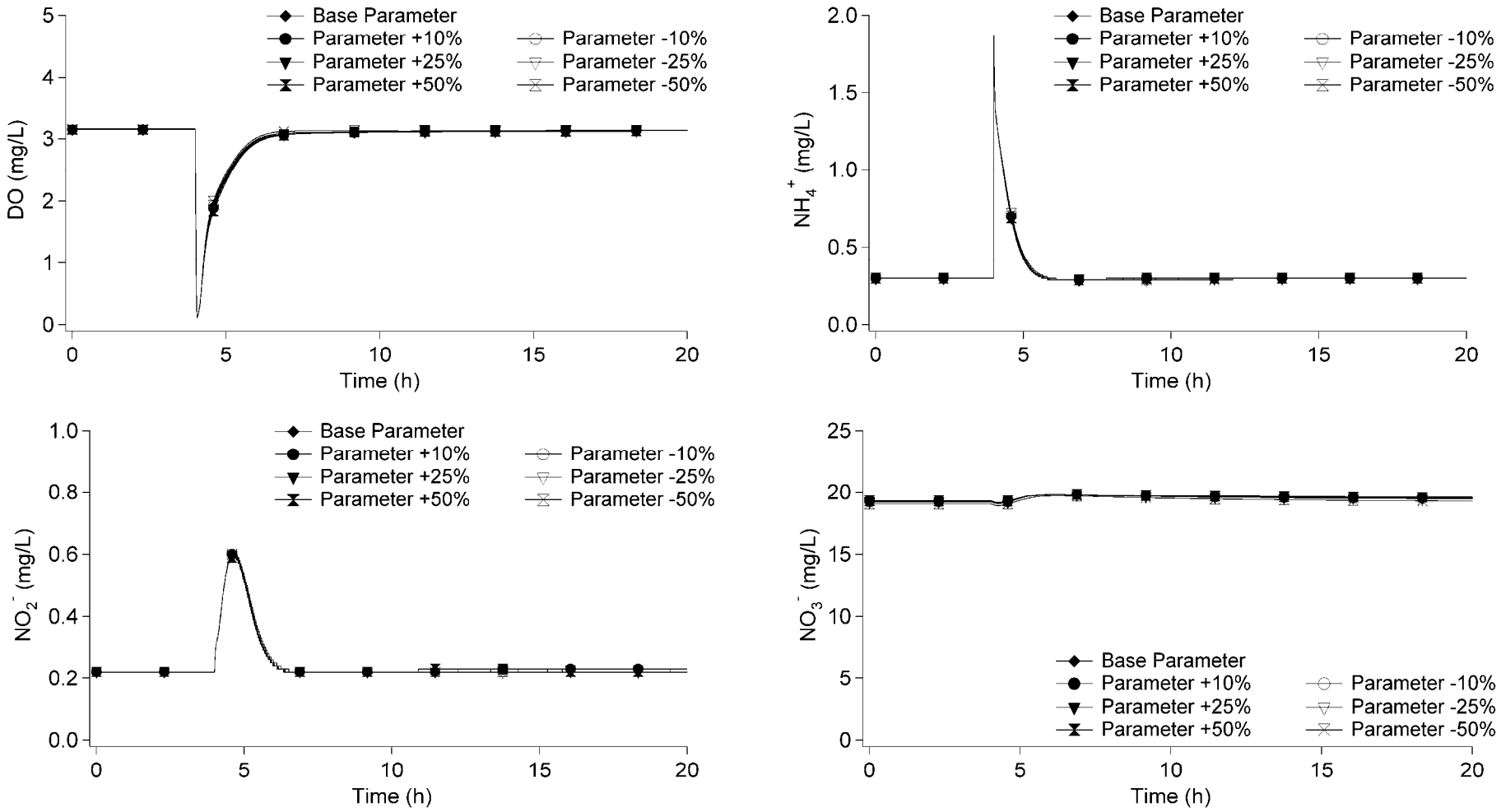

Figure A-111 Effect of maximum specific hydrolysis rate (k_H) on dynamic response (ASMN – UNSW data).

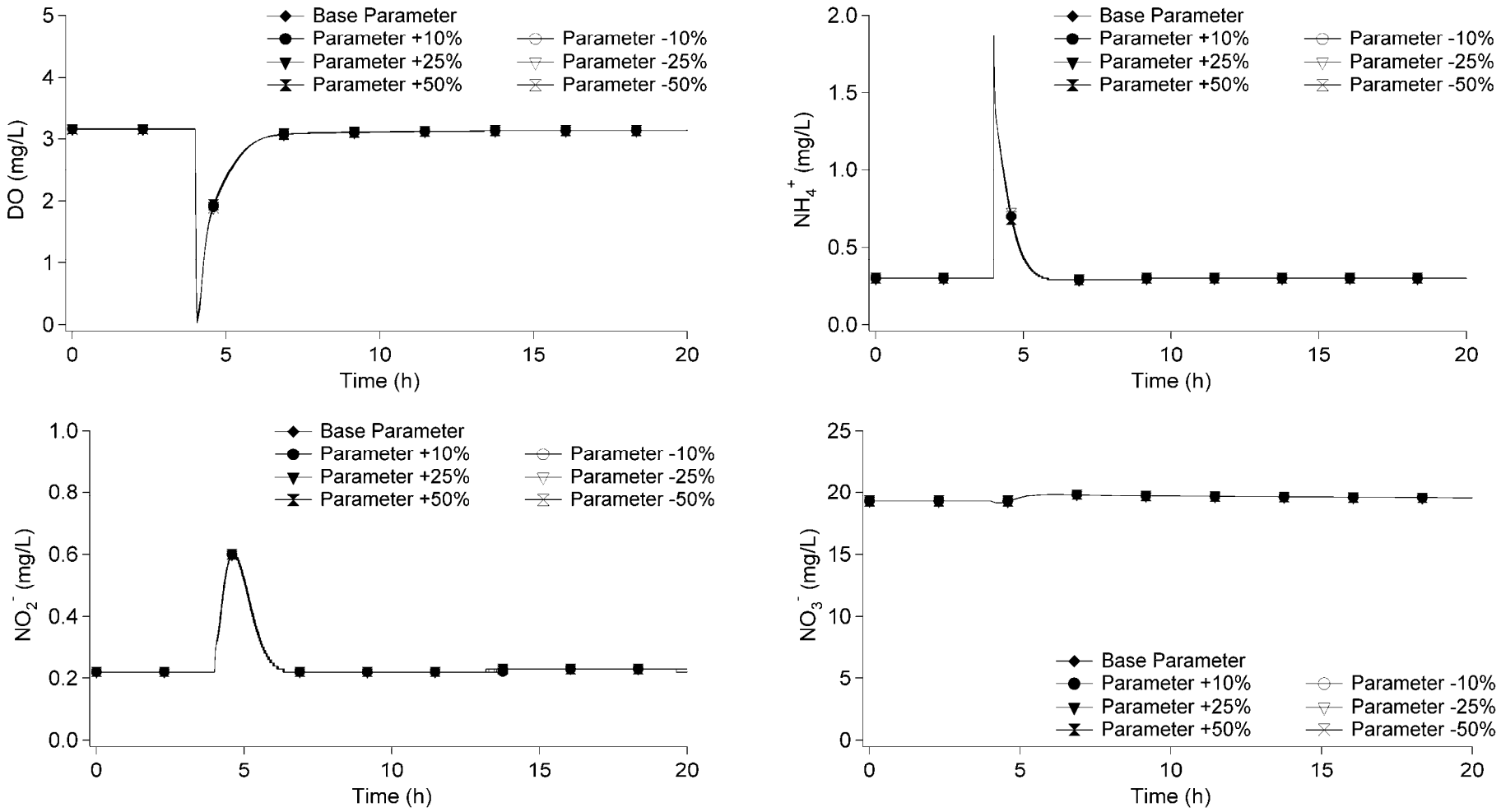

Figure A-112 Effect of heterotroph DO inhibition coefficient (K_{OH}) on dynamic response (ASMN – UNSW data).

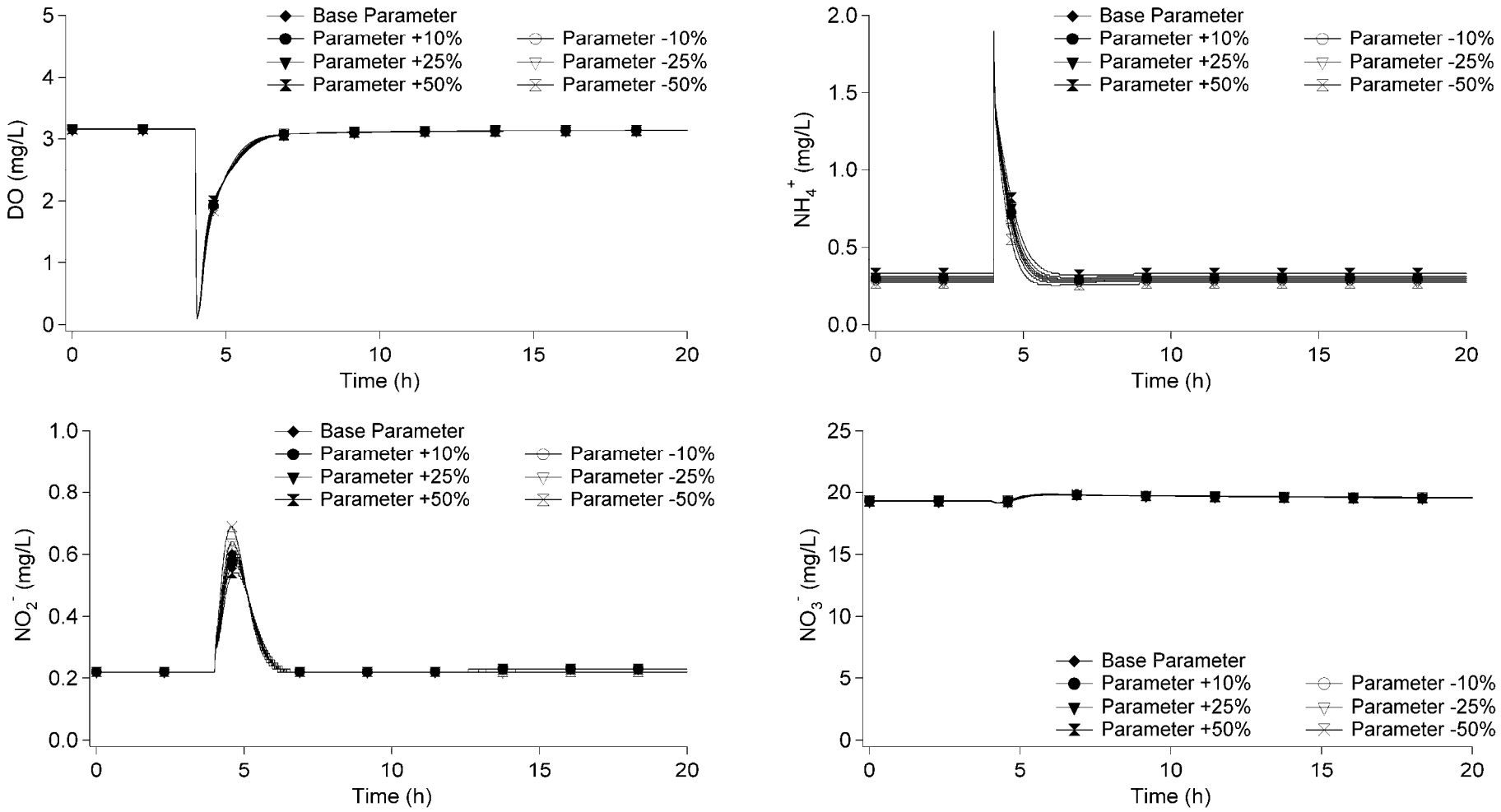

Figure A-113 Effect of AOB DO inhibition coefficient (K_{OA1}) on dynamic response (ASMN – UNSW data).

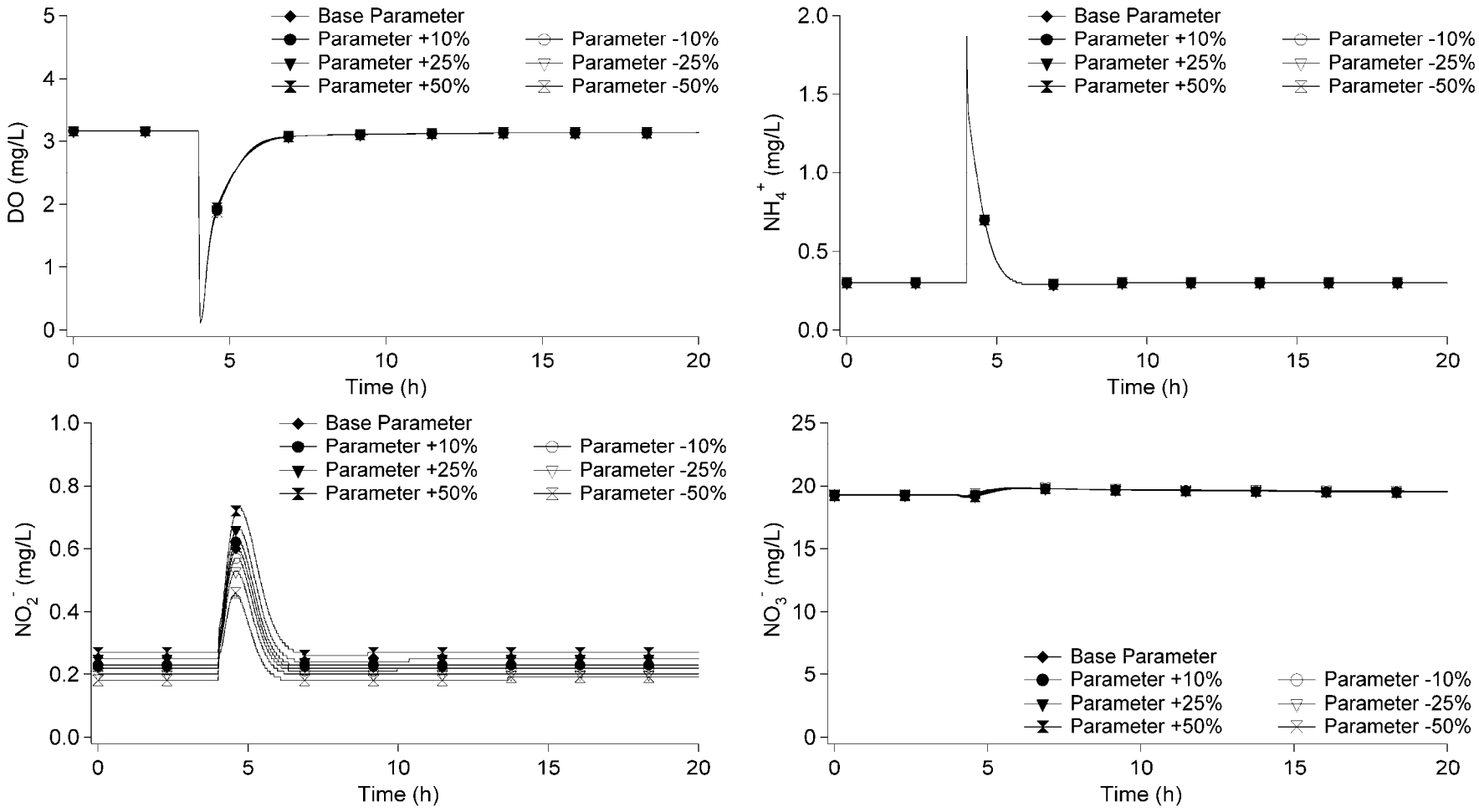

Figure A-114 Effect of NOB DO inhibition coefficient (K_{OA2}) on dynamic response (ASMN – UNSW data).

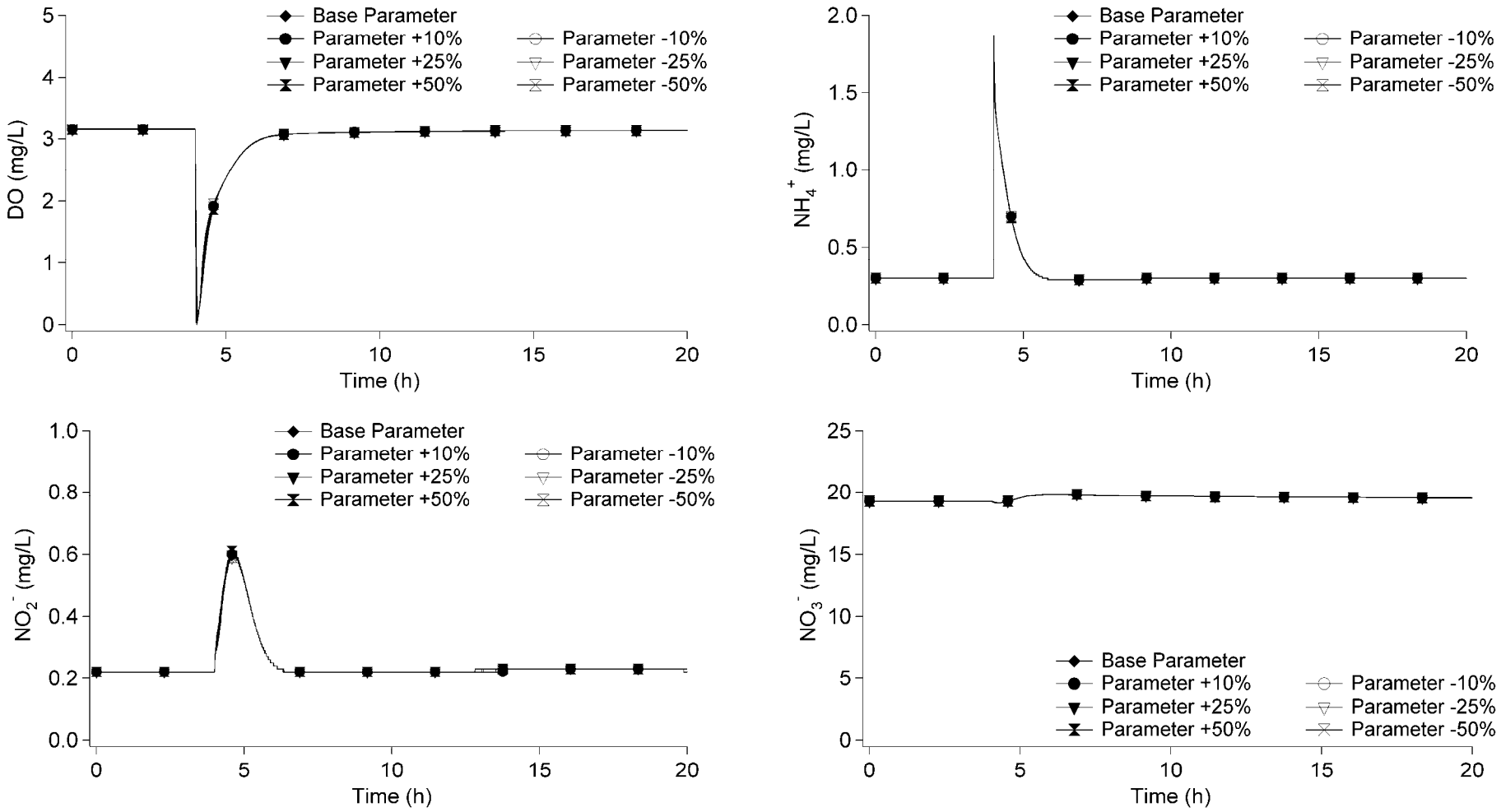

Figure A-115 Effect of heterotroph substrate inhibition coefficient (K_S) on dynamic response (ASMN – UNSW data).

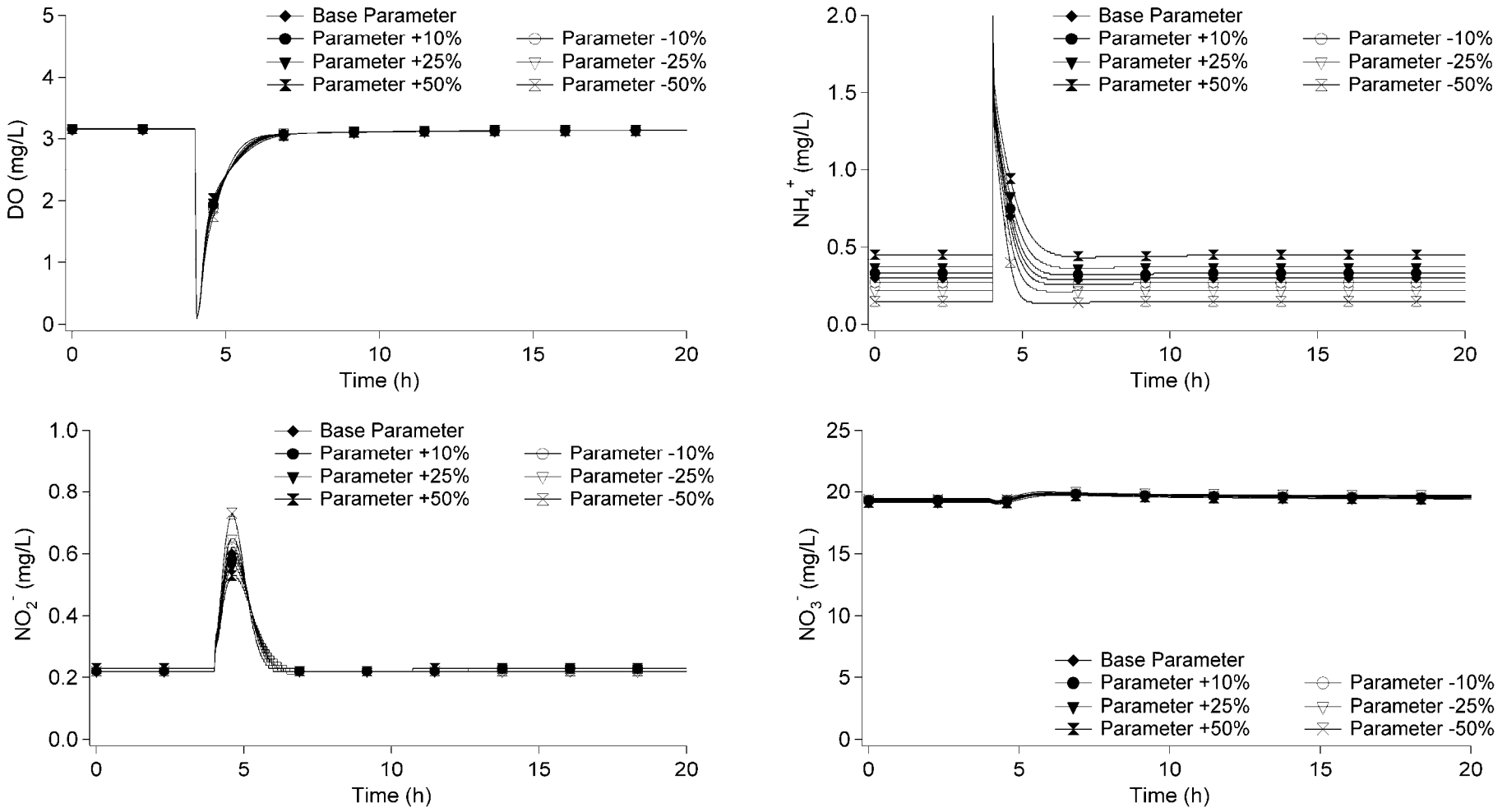

Figure A-116 Effect of free ammonia inhibition coefficient (K_{FA}) on dynamic response (ASMN – UNSW data).

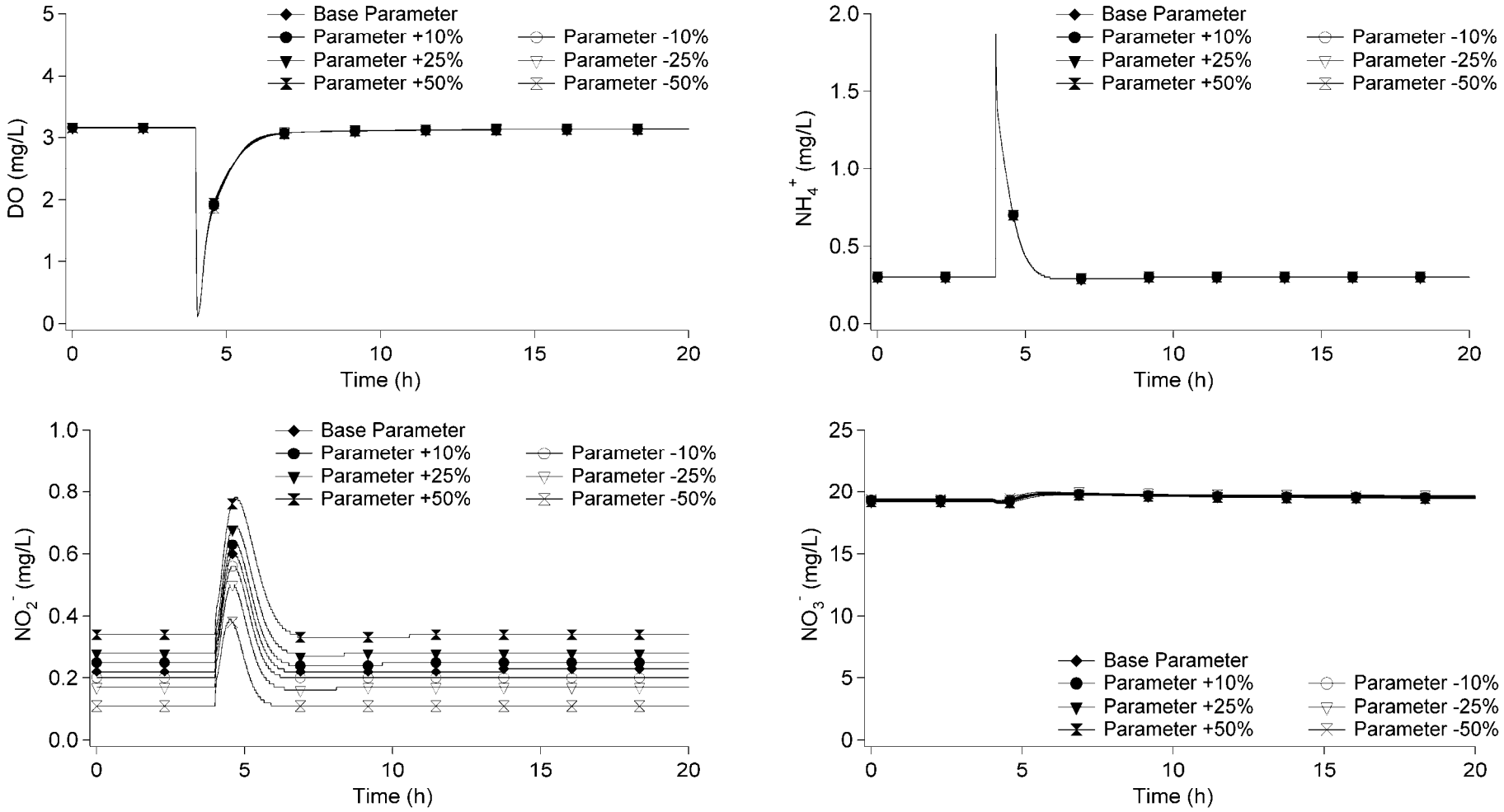

Figure A-117 Effect of free nitrous acid inhibition coefficient (K_{FNA}) on dynamic response (ASMN – UNSW data).

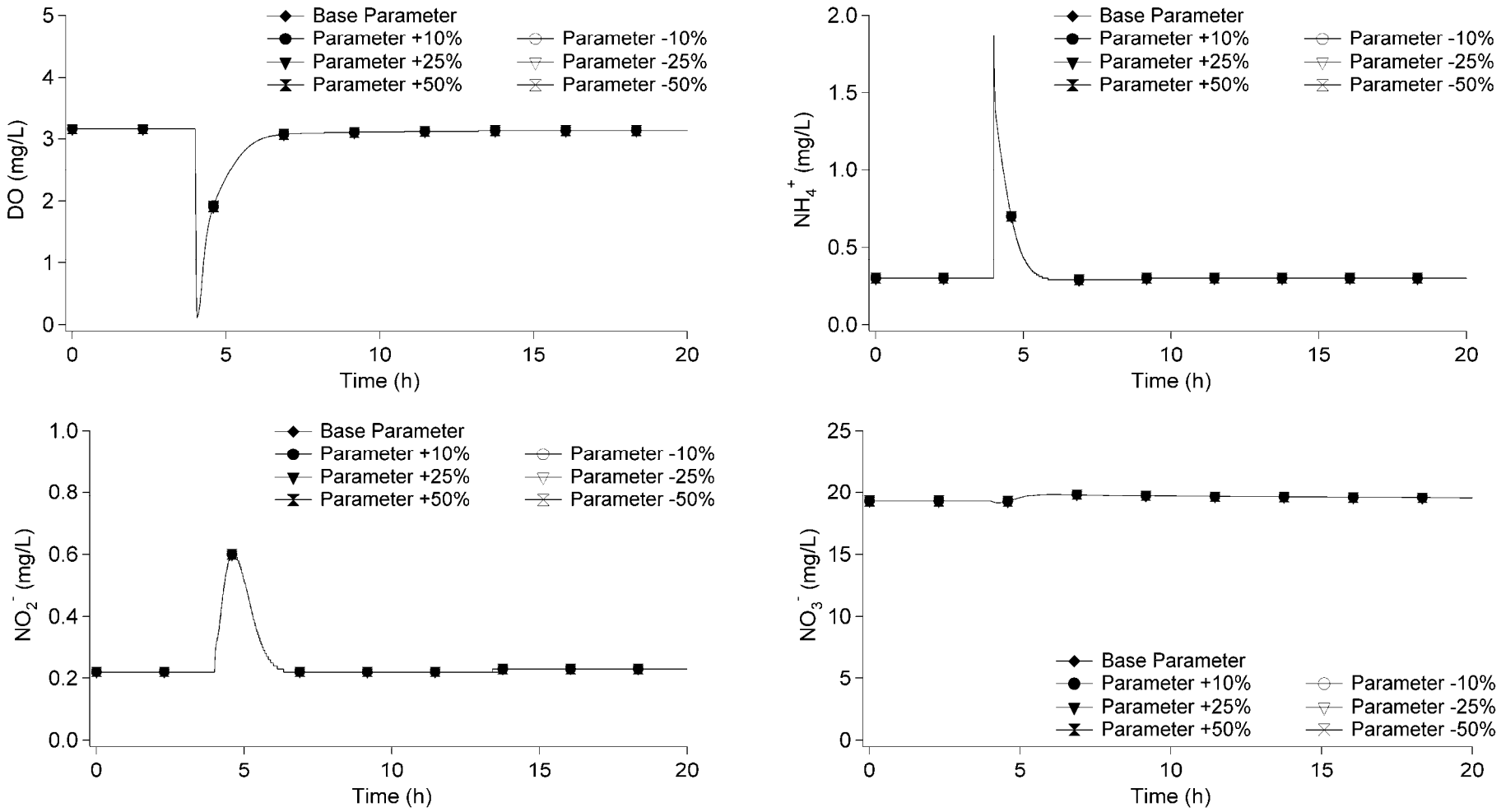

Figure A-118 Effect of AOB free ammonia inhibition coefficient (K_{I9FA}) on dynamic response (ASMN – UNSW data).

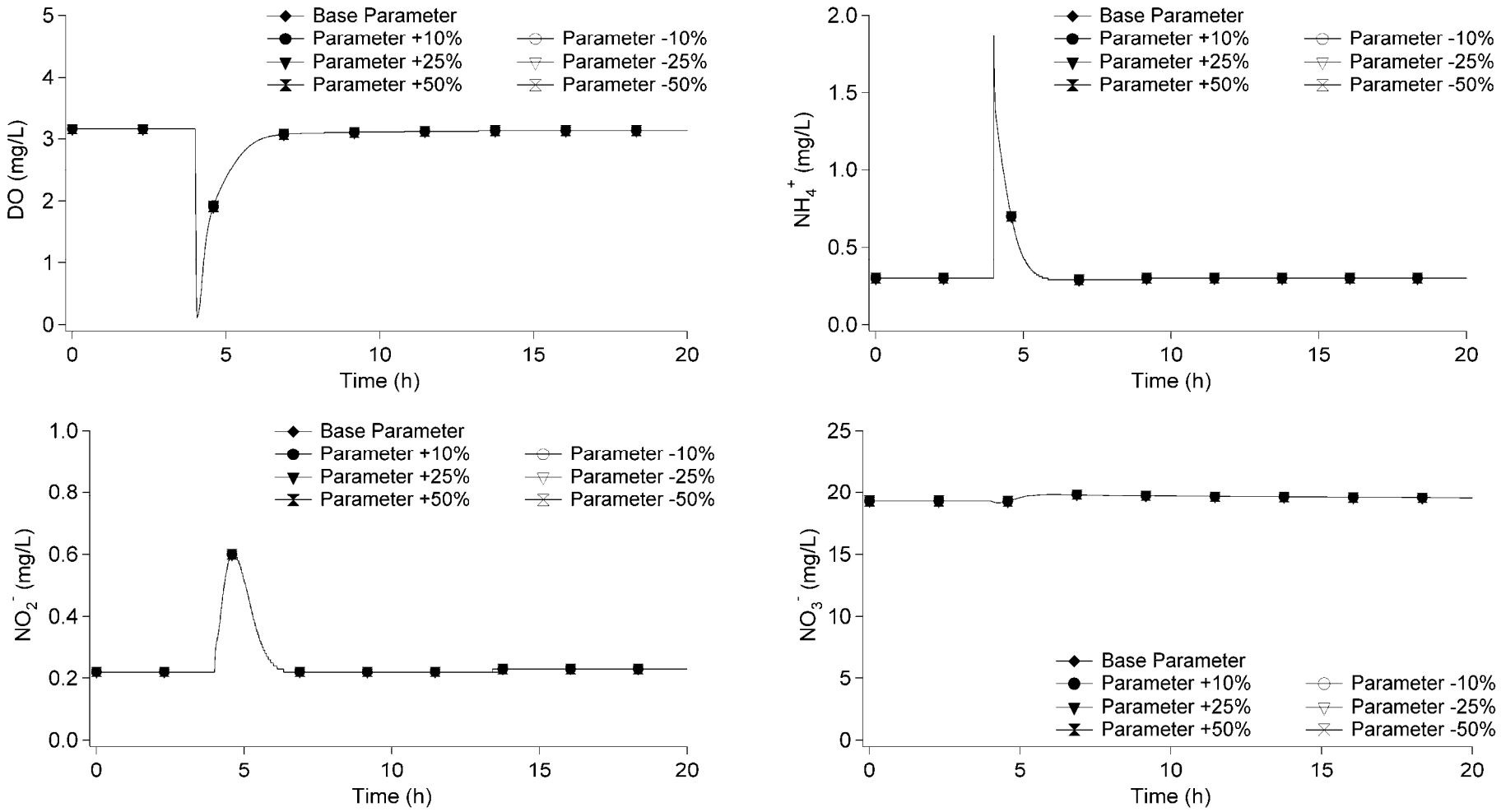

Figure A-119 Effect of AOB free nitrous acid inhibition coefficient (K_{I9FNA}) on dynamic response (ASMN – UNSW data).

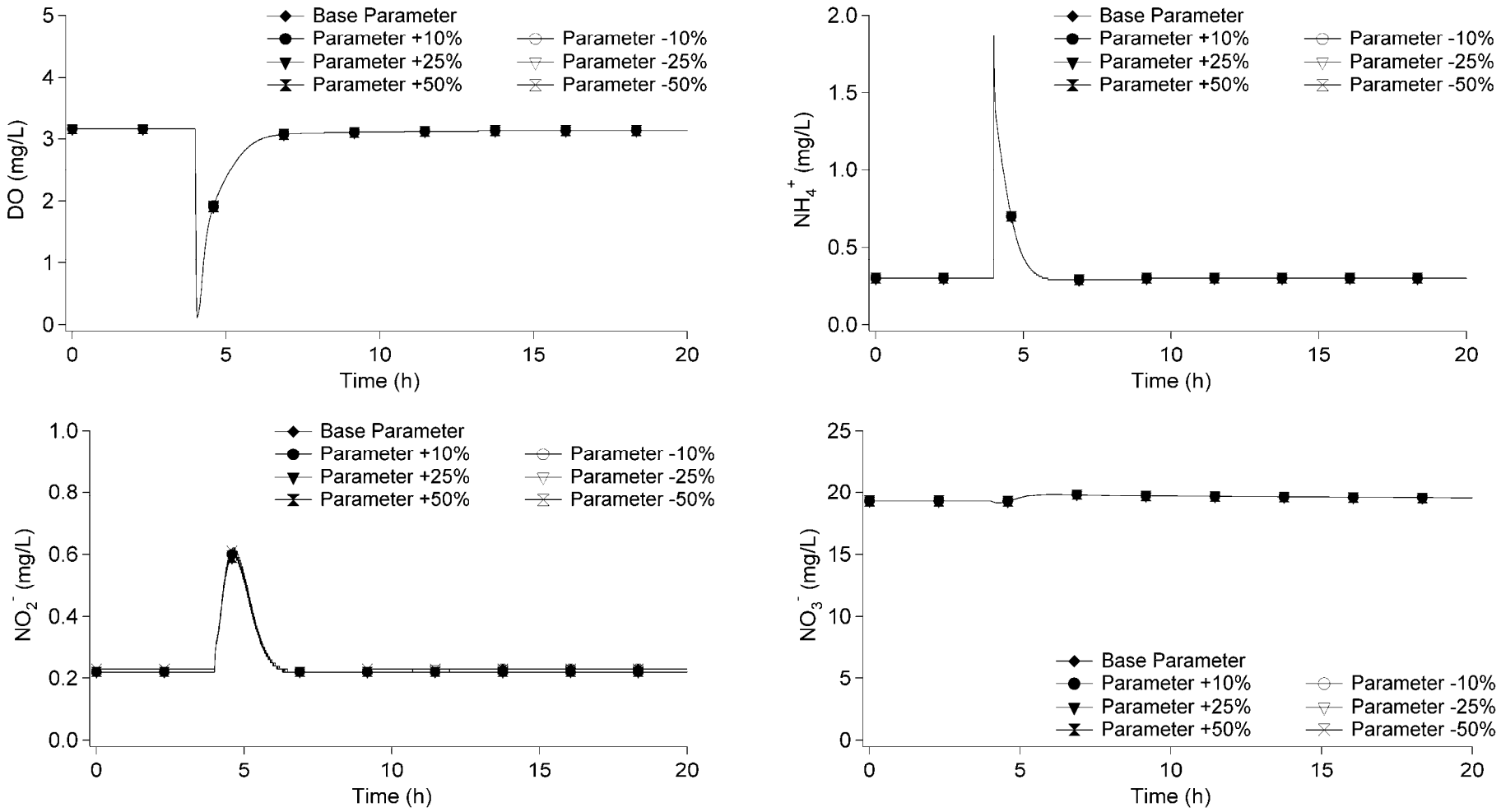

Figure A-120 Effect of NOB free ammonia inhibition coefficient (K_{I10FA}) on dynamic response (ASMN – UNSW data).

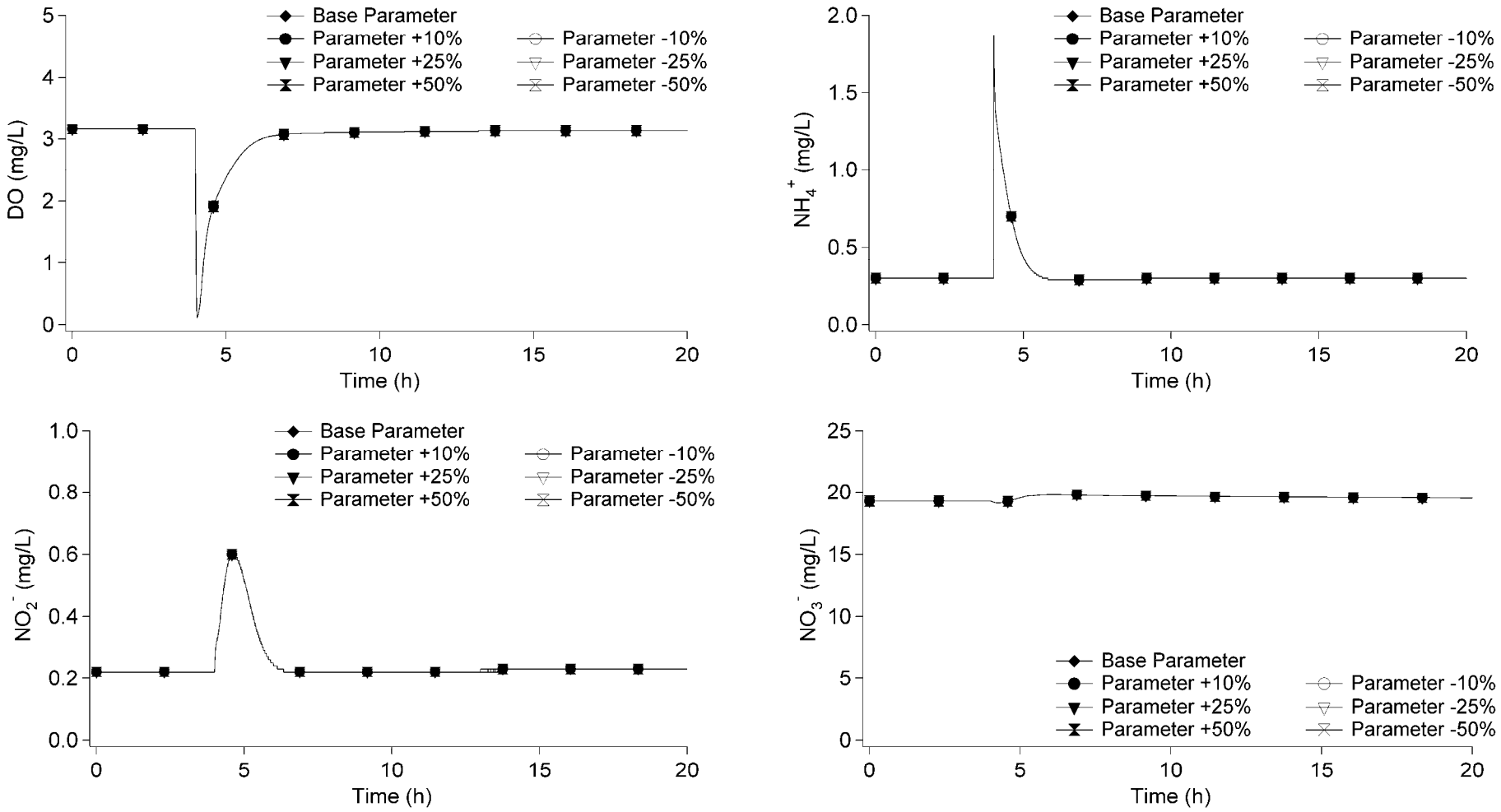

Figure A-121 Effect of NOB free nitrous acid inhibition coefficient (K_{I10FNA}) on dynamic response (ASMN – UNSW data).

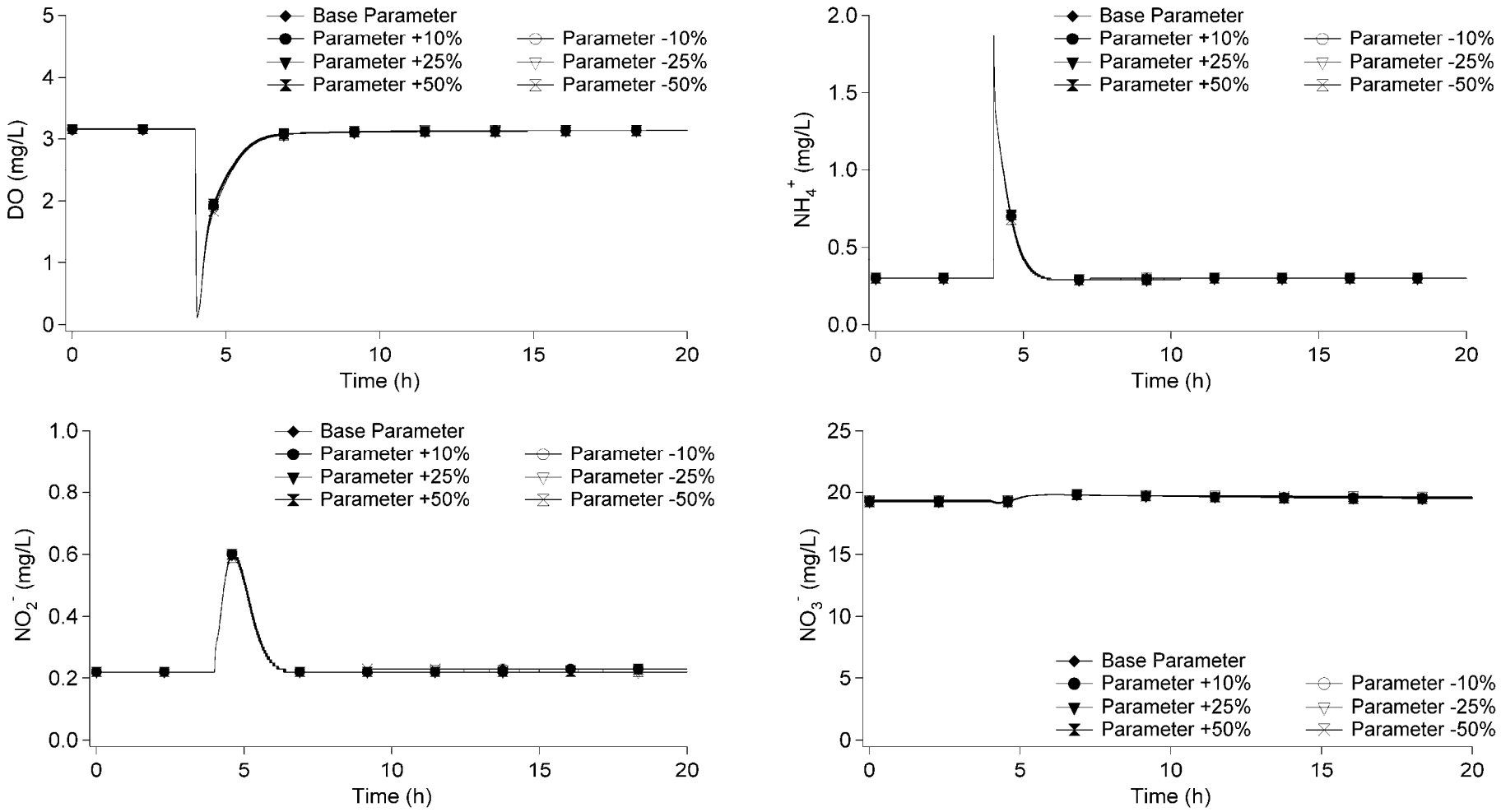

Figure A-122 Effect of hydrolysis half-saturation coefficient (K_X) on dynamic response (ASMN – UNSW data).