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Mital Pindoria-Nandha

Planning an Aquifer Storage and Recovery scheme in the Sherwood Sandstone aquifer

Cranfield Water Science Institute
Stream EngD

EngD
Academic Year: 2011 - 2015

Supervisor: Paul Jeffrey
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This thesis is submitted in partial fulfilment of the requirements for the degree of EngD

ABSTRACT

Aquifer Storage and Recovery (ASR) involves the injection of water into an aquifer for subsequent recovery from the same well. Whilst ASR provides a competitive alternative to reservoir storage, a lack of precedence of successful schemes and uncertainties with respect to regulatory requirements, and abstracted water quality and quantity have limited its implementation in the UK. The ambition of this research is to improve understanding of these impediments with particular reference to the Sherwood Sandstone aquifer. Drawing on existing project review and risk management approaches, a decision support tool to help scheme designers scope ASR scheme potential and challenges was developed and tested. The tool provides practitioners with a systematic method for early stage evaluation of ASR schemes with testing confirming broad value and alignment with business processes. Limitations on the recovery of recharged water was investigated through a critical literature review on clogging with geochemical, biological, physical and gaseous binding processes identified as the most likely mechanisms to impact an ASR scheme in this aquifer. Water quality changes during storage and the impact of storage period on recovered water quality were investigated in the laboratory using ASR simulating columns, with storage times of 15, 20, 30 and 60 days. Water quality improvements such as biodegradation of disinfection by-products, denitrification and sulphate reduction were observed. However recovered water quality deteriorated with respect to iron, arsenic, manganese, total organic carbon and nickel. These results, together with the review of regulations conducted as part of decision support tool development, suggest that the current interpretation of the Water Framework Directive requirements is overly restrictive and is deterring wider implementation of ASR in the UK. Conclusions focus on the need for a more appropriate approach to regulating ASR schemes, in particular, one which adopts a risk based approach to determining water quality standards.

Keywords: Aquifer Storage and Recovery, Planning, Column Tests, Clogging, Water Quality, Water Framework Directive

ACKNOWLEDGEMENTS

Undertaking an EngD is a long and difficult process which I could not have completed without the support I received. I would like to thank my primary academic supervisor, Professor Paul Jeffrey who was always happy to provide guidance and direction with the research as well as with the overall process of manging the project with all its challenges. I would also like to thank Dr Kristell Le Corre Pidou who joined the supervisory team late but made a great impact on the project. I could not have completed my experimental work without your guidance and support. Thank you also to Professor Bruce Jefferson for providing a unique perspective on the project as well as excellent experimental advice. A special thanks goes to Dr Marc Pidou, who not only provided me with advice, but also lent me essential equipment in my greatest hour of need. Thank you to the Lab Technicians at Cranfield. Completing the research would not have been possible without all the help and support I received from all of you.

Thank you to Anglian Water Services and EPSRC for funding the research. Within Anglian Water, I would like to thank Barrie Holden, my manager and supervisor, for always pushing me to be more confident in my work and providing me with guidance, support, and lots of laughs, especially towards the end of the project when you recognised that I was feeling overwhelmed. Thank you to Mark Berry for temporarily stepping in as my supervisor. You always believed in me and even though my research was not within your expertise, and you strived to challenge me and improve my work. Thank you to Mike Cook, Nick Walters and Steve Moncaster for all your advice and help with the project and always making time for me. I would also like to thank the Innovation team for making me feel like a part of the team, with a particular thanks to Fionn Boyle for helping me navigate the IT systems.

I would like to thank everyone in the STREAM programme for providing me with such an incredible and unique experience - I will always cherish the memories. In particular, I feel very lucky to have met my colleagues and friends in Cohort 3, who made the whole EngD so much more fun and exciting. Thank you Tania Rice and Paul Jeffrey for keeping STREAM running - it is definitely a worthy programme.

I would also like to thank my family and friends for their support and tolerating all the complaining and ranting when things got tough. Thank you to my sisters and brother in-laws who always supported me in every way they could, with a special thanks to Binita Khoda for her help with the thesis. A very special thanks goes out to my parents Kanti and Manju for always believing in me and pushing me to be the best version of myself. I would never have been able to complete this EngD without your support.

Last but definitely not least, I would like to thank my wonderful husband Mitess. The fact that my research is not in your field of expertise did not stop you from helping me wherever you could. You provided me with the motivation when I felt like I couldn't keep going and I can honestly say that without your help and support, I would not have finished my thesis.

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LIST OF ABBREVIATIONS

AOC	Assimilable Organic Carbon
ASR	Aquifer Storage and Recover
BDOC	Biodegradable Dissolved Organic Carbon
BGS	British Geological Society
DBP	Disinfection by-products
DOC	Dissolved Organic Carbon
DWI	Drinking Water Inspectorate
GWDD	Groundwater Daughter Directive
HAA	Haloacetic Acid
MAR	Managed Aquifer Recharge
MFI	Membrane Filtration Index
NAT	Natural Aquifer Treatment
NWI	National Water Initiative
PCV	Prescribed Concentration or Value
PFI	Parallel Filtration Index
SPT	Strategic Planning Tool
THM	Trihalomethane
TOC	Total Organic Carbon
TSS	Total Suspended Solids
WFD	Water Framework Directive

1 Introduction

1.1 Background

Storing water as a means to ensure security of water availability has a very long history. Historically, reservoirs have been favoured to provide this storage as they allow rapid filling and release of water, provide large storage potential, and are relatively easy to manage and monitor. However, the high financial, social and environmental costs of reservoirs, coupled with their vulnerability to contamination, high evaporation rates and the decreasing availability of land have driven investigations into alternate storage methods such as Aquifer Storage and Recovery (ASR). ASR is one of the techniques by which Managed Aquifer Recharge (MAR) can be implemented. MAR is the purposeful recharge of water to aquifers for subsequent recovery and includes a collection of techniques, defined by Dillon (2005) as:

- Infiltration basins: Ponds constructed and water is allowed to infiltrate to the underlying unconfined aquifer.
- River bank filtration: extraction of groundwater from a well near a river to induce infiltration from the river to the well thereby improving the quality of water recovered.
- Dune filtration: Infiltration of water from ponds constructed in dunes and extraction from wells at lower elevation.
- Aquifer Storage Transfer and Recovery (ASTR): Injection of water into a well for storage and recovery from a different well, i.e. separate injection and recovery wells
- Aquifer Storage and Recovery (ASR): Injection of water into a well for subsequent recovery from the same well as needed.

1.2 Project Development

Although infiltration techniques of MAR are more widely implemented than injection techniques (IGRAC and Acacia Institute, 2007), this research concentrates on ASR due to the higher level of interest in this technique from the UK water industry. ASR provides an unrivalled method of storing water since aquifers offer storage capacities of similar magnitude to reservoirs without much of the large capital investment and environmental and social impacts associated with above-ground storage. Furthermore, ASR supports staged development since additional wells can be added to increase storage capacity when needed, unlike with reservoirs which have to be sized to anticipate future demands. In the United States of America and Australia, using aquifers to store water from the engineered water cycle has become a common practice because of the cost effectiveness and operational flexibility of the technique (Pyne, 2005a; Dillon et al., 2009). There is a growing interest in ASR in the UK and several water utilities have included it in their water resource management plans (plans detailing how future water demand will be met) (Anglian Water, 2014; Severn Trent Water, 2014; South east water, 2014; Thames Water, 2015). Despite this interest, there are only three operational aquifer recharge schemes in the UK; the North London Aquifer Recharge Scheme operated by Thames Water in London, a scheme at Loftsome Bridge operated by Yorkshire Water in Yorkshire (Evans et al., 2008) and an agricultural scheme operated by farmers in Nottinghamshire (Gale et al., 2002). This disappointingly low level of implementation is driven by three principal considerations as identified by Rachwal, (2013), and are illustrated in Figure 1.1.

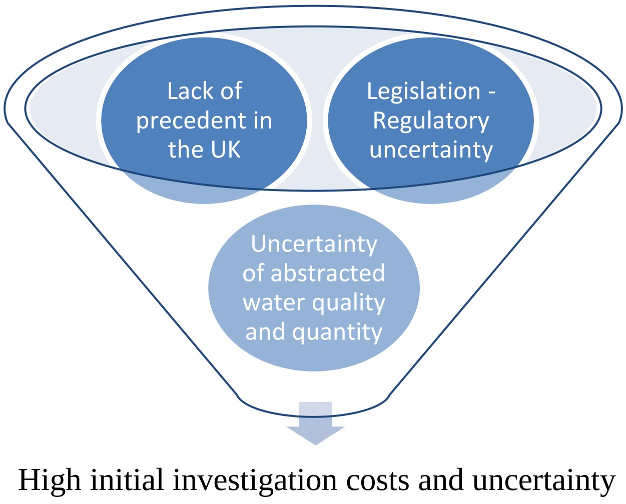


Figure 1.1: Barriers to wider implementation of ASR schemes in the UK

Firstly, a lack of precedent for ASR schemes in the UK concentrates interest in the associated risks and mitigation requirements at the expense of the potential benefits of such schemes. Reservoirs have been used for decades and the industry is comfortable with them. ASR in contrast is a relatively new technology therefore confidence in it is not as high. Secondly, legislative and regulatory uncertainty with respect to interpretation of the requirements of the Groundwater Daughter Directive (GWDD), which is the most important regulation in the context of injection water standards, has slowed progress. This is because water companies are not keen on implementing expensive desk studies and pilot schemes, when there is uncertainty as to the standards and procedures they are required to comply with. Furthermore, the absence of a specific ASR license means that several different licenses are required, making the process more difficult and time consuming. Finally, uncertainties associated with potential water quality changes in the aquifer and the quantity of recoverable water means that initial investigation costs are high. It is important to understand these potential changes as they influence the system design. There is additionally an uncertainty related to the quantity of water that will remain in storage as a result of potential losses due to dispersion, other abstractors etc., all of which reduce the quantity of recoverable water.

Aquifers are a natural environment rather than an engineered environment, therefore each scheme will differ in the benefits it can provide and may not always operate as expected. For this reason, the initial investigation costs are relatively high as pilot ASR sites are necessary to provide an accurate assessment of viability, and even then, the situation may change over time as the natural environment evolves. There is a need to reduce the uncertainties surrounding the design and operation of ASR schemes. This research was commissioned by Anglian Water with the support of Engineering and Physical Sciences Research Council (EPSRC) and Cranfield University, to address these barriers and promote wider implementation of ASR in the UK. The first step was to investigate whether existing risk assessment frameworks could be used to reduce uncertainties associated with ASR schemes. It was concluded that existing frameworks were not appropriate as none adequately addressed threats to all the components of an ASR scheme, therefore a new ASR specific framework (Strategic Planning Tool) was developed and tested in the context of the UKs regulatory environment.

During development and testing of the framework, it became clear that further investigations on the Hydrogeochemical Assessment would be beneficial. The main aspects of this assessment included the interrelationship between potential water quality changes that may occur during storage, clogging which may impact ASR operations and pre-treatment and post-treatment requirements. Anglian Water had a particular interest in commissioning an ASR scheme in the Sherwood Sandstone aquifer in the Newton on Trent area in Lincolnshire UK, thus further investigations focused on this aquifer. The influence of clogging was investigated via a literature review which provided sufficient insight, however there was a gap in knowledge with regards to the potential water quality changes that may occur when treated surface water was stored in this aquifer. Column investigations with respect to the fate of metals and disinfection by-products were implemented to address this gap, since these were identified as the key parameters of concern. Output from both of these were then used to form a discussion around the influence of clogging and water quality changes on each other and on pre/post treatment requirements, the role of regulations and the overall impact of all of these on the viability of the proposed ASR scheme. This is the first discussion of its kind and therefore a unique contribution to knowledge. The specific gaps in knowledge/practice addressed by this research are as follows:

1. Potential water quality changes that may occur when treated surface water is stored in a Sherwood Sandstone aquifer, and the influence of recharge water quality and storage time, on the recovered water quality
2. Influence of the regulatory agenda on wider implementation of ASR in regions where it is not yet established
3. Provision of a framework to improve the viability assessment process for ASR schemes in the UK.

The outputs of this research are pertinent in a variety of contexts; firstly, the experimental work improves the general understanding of the mechanisms responsible for changes in water quality during storage in an aquifer, and this information can be used to inform other ASR schemes. Secondly, the discussion around the role of regulations in ASR schemes can be used to help inform the regulatory agenda in other regions where ASR is not yet established. Finally, although the Strategic Planning Tool is specific to the UK, the benefit of the process oriented methodology is demonstrated, and can be adapted to suit other regions.

1.3 Aims and objectives

The main purpose of this research is to reduce the uncertainties surrounding the design and operation of ASR schemes in the UK and to inform the regulatory agenda, with a particular interest in the Sherwood Sandstone aquifer. This will be achieved by attaining the following objectives:

1. Develop a methodology to better characterise the threats to ASR schemes before commissioning a pilot plant (Chapter 2).
2. Understand the potential clogging mechanisms which may impact an ASR scheme and the influence on overall viability of the scheme (Chapter 3 and 5)
3. Investigate the potential changes in water quality with respect to metals and disinfection by-products when treated surface water is stored in the Sherwood Sandstone aquifer (Chapter 4)
4. Discuss the current state of regulations with respect to ASR in the UK and their influence on the viability of ASR schemes (Chapter 5)
5. Evaluate the relationships between water quality changes, clogging and pre/post treatment requirements with a view to informing the regulatory agenda and promoting a risk based approach to scheme approval (Chapter 5)

1.4 Thesis structure

The thesis is presented as a collection of chapters, all contributing to the research objectives as illustrated in Figure 1.2. Chapter 2 begins with an evaluation of the appropriateness of current methodologies available to assess the viability of ASR schemes in the UK. It determines that current methodologies do not meet the requirements for UK proponents, and a new tool (Strategic Planning Tool) is created to assess the viability of ASR schemes. The tool is unique as it provides a holistic methodology that enables a unified understanding of threats, requirements and opportunities of a potential ASR scheme, with guidance specific to UK regulatory and industrial structure. The value and usability of the tool is tested in a variety of ways.

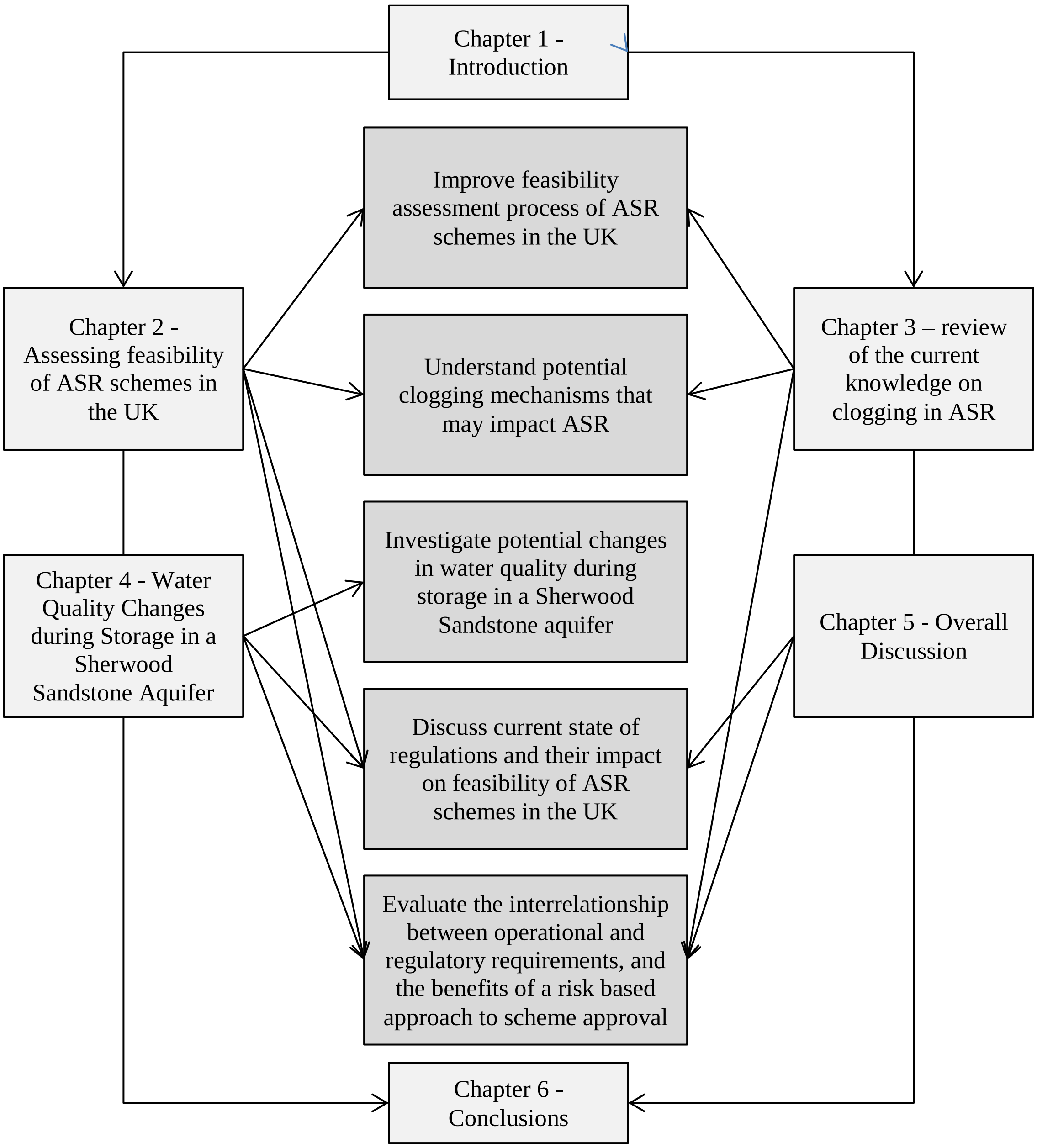


Figure 1.2: Thesis Plan. Dark Grey boxes represent the research objectives and lighter grey boxes represent the chapters of the thesis

Chapter 3 reviews current knowledge on clogging in ASR in order to identify the main clogging mechanisms experienced in various ASR schemes, and the mechanisms most prevalent at Sandstone ASR sites. The various parameters influencing these clogging mechanisms are discussed to understand how to best manage clogging. The most prevalent mechanisms were identified as physical and biological clogging. The information in this chapter provides a unique source of compiled information on the clogging experienced at ASR sites around the world.

Chapter 4 initially reviews the literature to determine the state of knowledge with respect to the fate of metals and disinfection by-products during storage in a Sherwood Sandstone aquifer. The required information was not available therefore column investigations were commissioned to investigate the changes in water quality during storage in a Sherwood Sandstone aquifer that may impact the quality of recovered water.

Chapter 5 consolidates the findings from previous chapters to evaluate the relationship between pre-treatment requirements set by the GWDD, potential improvements and deterioration in water quality during storage, clogging potential, post-treatment requirements and the overall impacts of these on the viability of an ASR scheme. This evaluation is used to provide a commentary on the influence of the regulatory agenda on the viability of ASR schemes, and the role of the Strategic Planning Tool in informing the implementation of the GWDD and promoting a risk based approach to scheme approval.

2 Assessing the Viability of ASR Schemes in the UK

2.1 Introduction

ASR provides an unrivalled method of storing water sustainably however each system differs in the benefits it can provide and does not always operate as expected because aquifers behave as biochemical reactors rather than as inert systems (P. Dillon et al., 2010). There is no set standard of operation or technology choices that would guarantee a successful outcome and some of the key challenges associated with ASR are illustrated in Figure 2.1.

Figure 2.1: Summary of the key challenges to ASR in the UK. The Dark blue bubbles represent the operational and hydrological challenges and pale blue bubbles represent the non-technical constraints

A key first step in promoting ASR in the UK would be to reduce the uncertainties surrounding their design and operation, particularly with respect to formulating an appropriate unified risk assessment and management framework which can provide confidence in the scheme design and technology choice. A methodology to better characterise and quantify the risks associated with ASR schemes before commissioning a pilot plant would be invaluable as it could reduce uncertainties and investigation costs.

Part of the ambition of this research was to assess the suitability of existing formed risk management frameworks for (a) the UK context and (b) the early stages of scheme planning. This chapter reports a critical review of risk management frameworks as a first step towards the development of a comprehensive assessment framework suitable for ASR schemes in the UK. It draws on several literature bases to collate, compare, contrast and critique the suitability of existing risk management frameworks to the UK context. In considering the strengths and weaknesses of existing frameworks, a commentary on their relative suitability for jurisdictions where ASR is not yet a well-established water resources development option is provided. It further presents an alternative approach to assessing ASR viability, with specific guidance to the UK regulatory and industrial environment. A detailed description of the formation of this approach is provided, along with the various methods used to assess its value and usability.

2.2 Literature Review

Research Approach

Procedure for analysing documents involves three main stages; an initial superficial examination of the literature followed by a more thorough reading and finally interpretation of the literature (Bowen 2009). In order to develop the analysis presented in this section, an initial content analysis was undertaken as suggested by Bowen (2009), to organise the research to meet the initial ambition of assessing the suitability of existing formed risk management frameworks for (a) the UK context and (b) the early stages of scheme planning. This was followed by a more thorough thematic analysis, whereby patterns within the research were identified and emerging themes were used as categories for analysis (Fereday and Muir-Cochrane, 2006). An overview of the research approach is illustrated in Figure 2.2.

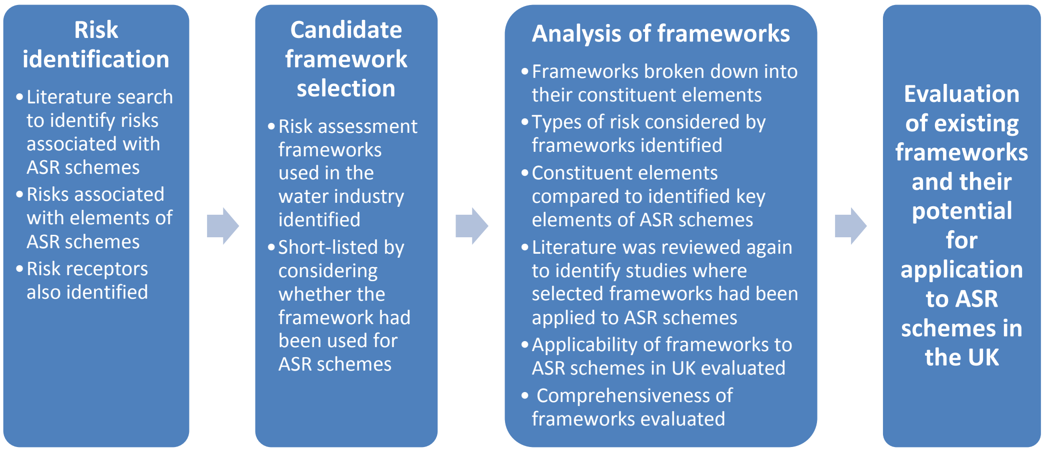


Figure 2.2: Procedures undertaken to develop the analysis

Both academic and grey literature databases were queried to identify the risks associated with ASR schemes and the regulatory requirements imposed on working schemes (initial examination). This analysis provided a foundation for identifying the elements of ASR projects that require consideration in a risk management strategy and further research was conducted to identify risk assessment/management frameworks that are currently used more broadly in the water industry (more thorough reading). These were broken down into their constituent elements and evaluated to assess their appropriateness for ASR schemes. Available case studies which reported use of these frameworks were then examined to produce a more comprehensive evaluation (interpretation of the literature).

2.2.1 Scoping the risks associated with ASR schemes

A holistic approach to risk management in an ASR scheme can be achieved by accounting for all the elements of an ASR scheme and considering the factors which contribute risks to each element. Such an overarching approach to ASR scheme risk assessment would cover strategic risk elements as well as process related elements such as pre-treatment, recharge, storage, recovery, and post treatment prior to final use. Each element presents a range of risks to different receptors (see Figure 2.3). The strategy element primarily considers business risk with the aim of strengthening the business case for the scheme. Due to the level of investment required to investigate the viability of ASR schemes, it is important to ensure from the outset that the strategic risk is minimised. Once this is achieved, the risk assessment for the rest of the elements can be tackled. The pre-treatment, recharge, storage and recovery stages contribute operational and environmental risks (which in turn poses regulatory risk). The post treatment stage carries an environmental, operational, human health and regulatory risk. Although it may be argued that all elements carry a risk to human health, the reasoning behind only evaluating it in the post treatment stage is that the water only poses a direct risk to human health once it is abstracted.

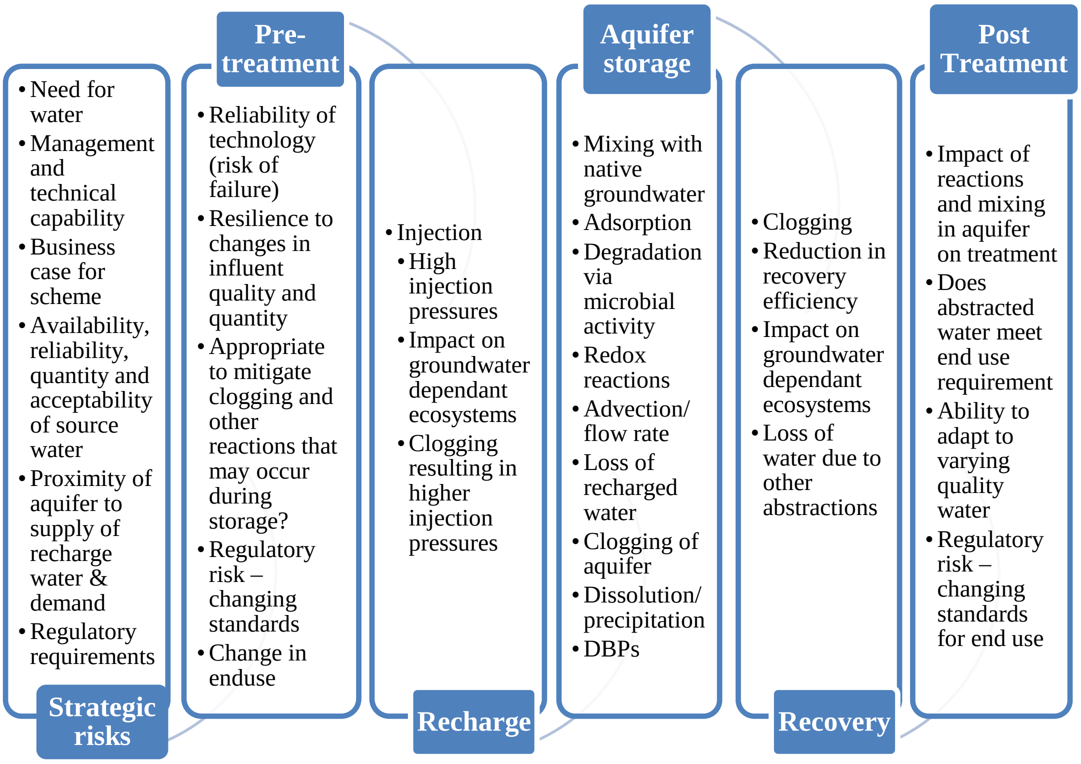


Figure 2.3: Proposed elements of an ASR risk assessment methodology and factors to consider in each element

Figure 2.3 provides a conceptual model of what an idealised holistic risk assessment/management framework for ASR schemes should include, and therefore constitutes a basis for comparison of candidate frameworks. It should be noted that many of the risk elements described in Figure 2.3 are interdependent and therefore cannot be considered in isolation. For example, introducing water containing oxygen into a reducing aquifer can result in mobilisation and precipitation of iron and manganese which could clog the wells and increase the recovery pressure (and energy) required. It can also result in the release of arsenic which would increase the post treatment requirements. The final assessment process therefore needs to be iterative to ensure the influences of the elements on each other have been accounted for once risk management strategies have been formulated.

2.2.2 Evaluation of risk management frameworks and their potential for application to ASR schemes in the UK

The UK has limited experience with ASR therefore it would be beneficial if the risk management framework used considers risks associated with ASR specifically, to ensure that the risks associated with all the elements of a scheme (as mentioned in Figure 2.3) are addressed. It should be clarified that this chapter is concerned with both risk management and risk assessment. Risk assessment is a process to evaluate the presence and severity of a risk, whilst risk management incorporates understanding, evaluating and prioritising the risk and putting in place appropriate strategies to reduce risk (Deere et al. 2001). The risk management frameworks are evaluated in terms of their potential to assess and manage the risks associated with ASR.

The review of risk management frameworks uncovered eleven candidate approaches (Table 2.1). From this list, a set of three frameworks (Hazard and Critical Control Point analysis (HACCP), Water Safety Plans, and the Australian guidelines for Managed Aquifer Recharge (MAR)) were selected for detailed analysis. HACCP and the Australian guidelines for MAR have both been applied to ASR sites which provide an opportunity to evaluate their appropriateness for use in ASR schemes in the UK. The Water Safety Plan approach was also evaluated as the regulator for drinking water quality in the UK (Drinking Water Inspectorate) has stated that drinking water improvement programmes must be identified using the Water Safety Plan approach (DWI, 2010b). The other frameworks identified in Table 2.1 were researched but were not evaluated further. The principles of the Australian drinking water guidelines (NHMRC-NRMMC, 2011) are incorporated in the more relevant Australian guidelines for MAR, and therefore were not evaluated separately. The South African Guidelines for planning and authorising artificial recharge schemes (Ravenscroft and Murray 2010), HAZOP (British Standard Institute 2002), the Methodology for Managing Microbial and Chemical Hazards in Water, Dutch Guidelines (Stuyfzand and Doomen, 2004), Pyne Guidelines (Pyne, 2005b), Brown Decision Support Tool (C. J. Brown, 2005) and Kazner Decision Support Tool (Kazner, Wintgens and Dillon, 2012) were not evaluated further as there were no published application of these to ASR schemes. Some of these will be evaluated further in Section 2.6.3

Table 2.1: Risk management frameworks used in the water industry and references detailing guidance for application and case studies where frameworks were used

Frameworks	Core References
Hazard and Critical Control Point (HACCP) analysis	Codex Alimentarius Commission 1997 – Guidance for Application Martel et al. 2006 – HACCP for Distribution Protection Havelar 1994 – HACCP for Drinking Water Supply Hellier 2000 – HACCP for Water Supplies Bryan 1993 – HACCP Application to Water Treatment Process Swierc et al. 2005 – Application of HACCP to MAR Melin 2009 - Application of HACCP to MAR
WHO Water safety plans (WSP)	Bartam et al. 2009 – WSP Manual Davison et al. 2005 – Managing Drinking Water Quality Dominguez-chicas 2010 – WSP in Indirect Potable Re-use Schemes
Australian guidelines for MAR	NRMMC-EPHC–NHMRC 2009 – Guidance for Application Page et al. 2009 – Application to ASR Page et al. 2010 - Application to ASR
Australian drinking water guidelines	NHMRC-NRMMC 2011 – Guidance for Application
South African guidelines	Ravenscroft and Murray 2010 - Planning and Authorizing Artificial Recharge Schemes
The Hazard and Operability analysis (HAZOP)	British Standard Institute 2002 Lihou, M Hokstad et al. 2009 Khan and Abbasi 1997
Methodology for Managing microbial & chemical hazards in water	UKWIR 2003 – Guidance for Application
Dutch Guidelines	Stuyfzand and Doomen 2004 - The Dutch experience with Managed Aquifer Recharge and Storage
Pyne Guidelines	Pyne, 2005 - Aquifer Storage and Recovery: A Guide to Groundwater Recharge Through Wells
Brown Decision Support Tool	Brown 2005 - Planning Decision Framework For Brackish Water Aquifer Storage and Recovery Projects
Kazner Decision Support Tool	Kazner et al. 2012 - Advances in Water Reclamation Technologies for Safe Managed Aquifer Recharge: Reclaim Water

In the following paragraphs the HACCP, WSP and Australian guidelines for MAR approaches are evaluated in terms of their appropriateness for ASR in the UK by considering; (i) the type of risks considered (i.e. strategic, operational, environmental, regulatory and human health), (ii) their ability to assess the elements listed in Figure 2.3, and (iii) their suitability to provide specific guidance on risks associated with ASR. It should be noted that the intention here is not to identify the closest match to an idealised framework but rather to select a starting point that provides enough structure and functionality to allow development of a bespoke framework for UK purposes.

2.2.3 Hazard and Critical Control Points

Introduction

An HACCP analysis provides an organised structured approach to assess risk and has been used in the food manufacturing industry for several decades. It encourages proactive management of hazards and hazardous situations by identifying CCPs, and implementing procedures at these points to minimise impact. The analysis has been tailored for use in the water industry (Havelaar 1994; Barry et al. 1998; Deere et al. 2001), and has become an important risk management framework in the sector.

Limitations

Although HACCP provides a solid generic structure for risk management, there are some important differences between the context within which its protocols were originally developed (the food industry) and the water industry. These disparities limit the potential application of HACCP to ASR schemes. For example, there are limited opportunities within an ASR system to implement the key strategic tools of an HACCP - the assignation of Critical Control Points (CCPs) and associated critical limits. CCPs are stages at which control can be implemented to minimise risk to an acceptable level. Such controls are only really viable during treatment processes, a constraint noted by authors of previous studies (e.g. Hellier 2000), and one which presents a danger that undue emphasis is placed on this aspect of operations.

A further limitation of the HACCP approach is the tendency for the analysis to focus in on a single point of control. In ASR schemes there are several sources of hazards and several stages in the process at which a hazard may be introduced into the system, thus a single barrier approach is not appropriate. For example, although the potential formation of DBPs during storage in an aquifer is a significant hazard, there is no single step that would eliminate this hazard. Chlorine dosage, pH, temperature and total organic carbon contribute to DBP formation above ground whereas adsorption, mixing and redox conditions in the aquifer influence the presence of DBPs in the aquifer (Pavelic et al. 2005). A focus on identifying a single CCP at the expense of a range of preventative measures can produce a risk management plan that undervalues alternative control measures. This can ultimately inhibit the multi-barrier approach that is essential in ASR systems. Swierc et al. (2005) demonstrated how HACCP could successfully be applied to an ASR scheme. Components of the scheme which required control measures but could not be classified as CCPs were instead classified as Quality Control Points (QCP). At these points, preventative measures could be implemented and monitored, enabling a multi-barrier approach. It should be noted though, that there is no specific guidance to assist new/less experienced operators in deciding what should be assigned as a QCP.

An additional weakness of an HACCP approach is its focus on hazards as opposed to risk. An assessment of likelihood and severity of the hazard can be incorporated in the hazard analysis stage of the process to provide a measure of the potential risk which allows for prioritisation during investigation - a procedure followed by Swierc et al. (2005). Although the authors provided a comprehensive risk assessment, it demonstrated the distinct difference between hazard management and risk management as the latter requires a more comprehensive understanding of the technical, managerial and human systems (Pollard et al. 2005). These are vital components of a risk management framework and can be used in the initial stages to assess strategic risk (the cost of attaining the required management and technical capability). Once a scheme is implemented, these features can be used to promote the on-going success of the scheme.

Application

HACCP has been applied to several ASR schemes in different countries. Melin (2009) conducted a study to assess and manage risk at four case study sites by employing a microbial and chemical risk assessment using deterministic quantitative methods and the HACCP framework. These studies along with that of Swierc et al. (2005) demonstrate that the approach can provide a comprehensive risk management framework, provided the assessor is familiar with the likelihood and severity of the hazards in the context of MAR. However, because of its focus on risk to human health, none of the case studies considered operational risks such as pressure and flow rates, stability of the well, clogging and aquifer dissolution, recovery efficiency etc., and therefore offered little insight into risk from an operational, environmental and strategic point of view.

2.2.4 Water Safety Plans

Introduction

Unlike HACCP guidelines which were initially developed for the food industry and adapted for the water industry, the WSP was developed specifically for the water sector and therefore provides guidance on risks specific to the industry. Although the WSP approach is based on HACCP, it acknowledges the limitations of the HACCP framework and therefore promotes a consideration of a wider range of preventative/control measures from catchment to tap, as opposed to isolated critical control points. It also considers risk rather than hazard from the outset and thus incorporates supporting features into the risk management framework (Bartam et al., 2009).

Limitations

The WSP provides a systematic and effective management and monitoring framework, however in systems where the uncertainties surrounding the hazards occurrence and removal are high, the precautionary approach required by the guidelines can result in a large proportion of hazards being apportioned as high risk, thereby assigning the scheme as high risk (Dominguez-Chicas and Scrimshaw, 2010). As explained in Section 1.1, scientific, regulatory and operational uncertainties surrounding ASR are higher than other water provision schemes in the UK (Rachwal, 2013) and therefore adopting a WSP based approach may provide an overly cautious and complicated risk assessment.

Like the HACCP framework, the WSP approach only considers the risk to human health (water quality) – operational, environmental and strategic risks are not explicitly considered. Although the Drinking Water Inspectorate (DWI) require a WSP to support a water provision scheme (DWI, 2010b), they are not the sole regulatory stakeholder. Approval is also required from the Environment Agency, who are concerned with the impact on the environment and OFWAT (economic regulator for water and sewerage sector in the UK), who require DWI and Environment Agency support, as well as an economically feasible scheme. A WSP would therefore not be sufficient as a stand-alone risk management framework for ASR schemes in the UK.

Application

The WSP was used to assess the risk to MAR schemes in India, however it was realised that the absence of necessary data during an initial risk assessment was a deterrent in its implementation (Dillon et al., 2010). Application of this methodology in areas where MAR is not yet established is hindered because identifying the likelihood and severity of hazards is difficult without prior field or laboratory investigations. Furthermore, it was noted that the WSP would need to be extended to provide protection to the aquifer and connected ecosystems, as the WSP was only concerned with risks to human health (Dillon et al., 2013). Strategic and operational risks were not considered.

2.2.5 The Australian guidelines for MAR

Introduction

The Australian guidelines for MAR were developed from the principles of the Australian Drinking Water Guidelines (NHMRC 2011) and address the need for a risk management methodology specifically formed for MAR. These guidelines provide a methodology that enables an assessment of the risks during storage in an aquifer with a level of detail similar to that applied to engineered treatment trains using approaches such as the HACCP (Page et al., 2010). The Australian guidelines for MAR are structured around the potential formation of twelve identified hazards in MAR schemes and provide advice on how to prevent or minimise their occurrence to an acceptable level.

The guidelines provide scientific direction for the development of ASR projects, and provide stakeholders with an insight into the extent of work required for the scheme to be successful. They help ensure that decisions on where to invest effort are based on an informed understanding of the next required level of investigation, since the cost increases as the stages of investigation progress. The guidelines include an entry level assessment, where the type and extent of the scheme, existence of a source of water and suitable aquifer, potential end use, environmental values, management capability and compatibility with groundwater management plans are all assessed. This stage is unique to this framework and provides important information on the likely level of complexity of a project before more detailed work is commissioned. This is important as it enables staged development and separates these guidelines from more general frameworks, since it allows the project to be abandoned (if necessary) at an early stage thereby saving costs and resources.

Limitations

Whilst the Australian guidelines offer a useful basis for risk management, it was noted that its focus on potential hazards can become a distraction from more process oriented considerations. This means that the risks associated with the processes in an ASR scheme may not be considered which could significantly impact the integrity of a scheme. For example, pre-treatment is an important barrier in ASR as it can protect the aquifer and operations against contamination and clogging, yet the risk to successful pre-treatment such as the reliability of the process to produce the quantity and quality of water required, and its resilience to changes in quality and quantity of influent, would not necessarily be considered. The framework does mention that the effectiveness of water treatment options should be addressed during its second stage but it implies that the treatment should be evaluated solely in terms of the quality of water it would produce, i.e. whether the concentration of the hazard of concern is reduced sufficiently. Although this is important, the risk to the pre-treatment process itself is also important. This is because it is usually possible to produce the required quality of water, however the reliability of the technology (maintenance costs, resilience etc.) will impact the viability of the pre-treatment process.

The drawback of forming a risk management plan around hazards is further demonstrated when considering reactions that take place in the aquifer, as each hazard identified can result in several different outcomes. For example, dissolution reactions can increase the diameter of the well, resulting in increases in yield and reduced clogging. It can also result in the collapse of uncased wells, undermining and collapse of the overlying aquitard, production of turbid water and development of preferential flow paths which affect the residence time and storage in the aquifer (Page et al. 2009, 2010).

Finally, societal norms, regulatory standards and views on acceptability all provide a reference to the significance of a hazard in a risk assessment, all of which vary in different countries. For example, when determining the risk posed by pathogens in the recharge water, the Australian guidelines take into account the aquifers treatment capacity (NRMMC-EPHC–NHMRC, 2009). This would not be the case in the UK since the Environment Agency is currently not concerned with potential improvements in water quality during storage when determining the recharge water quality (see Section 2.5.1). As the Australian guidelines are hazard oriented, their application may be limited in regions with different views on the risks posed by these hazards.

Application

They have been applied to several sites in Australia to identify the highest priority hazards and assess the risk posed by the twelve hazard types as prescribed in the guidelines (Page et al., 2010). The source of water, pre-treatment, potential changes during subsurface storage and post treatment stages are all considered during the risk assessment and the framework was used successfully to provide a staged approach to assess risk. However, application of the guidelines to projects in India, China, Mexico, South Africa and Jordan revealed that while the entry level assessment provided a useful method by which issues may be identified (Dillon et al., 2010), the quantitative, hazard oriented assessment was difficult to complete as the water quality data necessary to complete the assessment was not available (Dillon et al., 2014).

2.2.6 Comparison of the HACCP, WSP and Australian Guidelines for MAR

The HACCP and WSP approaches provide a staged approach to effectively manage risks in water recycling schemes. Their main constraint in the context of application to ASR, is that they are primarily concerned with risk to human health and do not explicitly incorporate risk to business, operations and the environment. This is because the HACCP was developed to identify and minimise microbial contamination (HDR Inc. & Cadmus Group 2006), and the WSP was developed to minimise microbial and chemical contamination (Hamilton et al. 2006) in drinking water. These frameworks work for conventional water supply options, as in these cases, the environmental risk is mitigated by regulatory standards such as the standards for releasing wastewater into the environment. When assessing risk associated with ASR schemes, there are added sources of risk related to storage in the aquifer and the impact of recharge and recovery pressures on the aquifer and other connected environments (Dillon et al., 2010) as illustrated in Figure 2.3. These are unique to ASR schemes and environmental and operational risks need to be included if these elements are to be properly considered, as required by the UK regulatory bodies.

Storage in the aquifer is a major source of risk in ASR schemes due to the potential changes in water quality that may occur (Pyne, 2005b; Stuyfzand et al., 2005; Vanderzalm et al., 2009; Maliva and Missimer, 2010; Rachwal, 2013), yet it is not adequately addressed in the HACCP and WSP approaches. Mixing with native groundwater can change the quality of recharged water and redox reactions can mobilize metals and increase concentrations of arsenic, iron, manganese and hydrogen sulphide (Page et al. 2008). Furthermore, aquifer dissolution can increase the concentration of certain minerals such as calcium in recovered water. Water quality can also improve during storage due to adsorption and biodegradation within the aquifer matrix which can reduce turbidity, organic carbon, organic compounds, inorganic compounds and pathogens. Conversely, adsorption and biological growth can clog the aquifer matrix which reduces the hydraulic conductivity and effective porosity, ultimately decreasing the recharge rates. This demonstrates how some processes can have a positive impact on the water quality while having a detrimental impact elsewhere. It also illustrates the complexity of the reactions and the risks associated with them.

The impact of recharge and recovery pressures on the aquifer and other connected environments are also neglected by the HACCP and WSP approaches since they do not present a risk to human health, even though they would be assessed by the Environment Agency before a scheme is permitted (see Section 2.5.1). Recharge and recovery pressures are initially dependant on the hydraulic properties of the aquifer (see Section 2.5.2) however during operation, clogging can increase these pressures (see Chapter 3). Clogging is a major operational risk (Martin, 2013b), for example where injection wells are used, clogging increases the pressure in the injection/recovery well and reduces the rate of recharge/recovery (Rinck-Pfeiffer et al. 2000). High injection pressures increase the energy requirements, and can rupture the aquitard. The assumption that adequate pre-treatment would mitigate clogging does not always hold true, as changes in water quality during storage may result in clogging during recovery (See Chapter 3). This is therefore an important operational risk to consider as it can result in high maintenance costs. Recharge and recovery not only pose a risk to operation, they can also affect ecosystems that are dependent on the groundwater system as the water table is raised and lowered. This impact increases with higher injection/recovery pressures.

ASR schemes are complex as they have several sources of risk that uniquely interact with each other according to site conditions. Without guidance on the assessment and management of all the risk elements, a risk assessment could result in a significant proportion of high risk parameters being identified. This may give a false impression of the complexity of such schemes and prevent further investigations. It would also unnecessarily increase the time and effort spent on the risk assessment. General risk management frameworks leave the possibility for potentially critical risks to be overlooked simply due to unfamiliarity with ASR schemes. Although work reported by Havelaar (1994), Martel et al. (2006), Bartam et al. (2009) and NHMRC (2011) all provide examples of hazards to consider in water provision schemes, they do not provide guidance on the specific risks of different provision systems, and thus do not provide guidance specific to ASR schemes.

The Australian guidelines provide the only framework considered in this research that includes risk to the environment, human health as well as risk to the business (operational risk). It should be noted that these guidelines were developed specifically for MAR in Australia and as such are tailored to Australian regulatory requirements. The structure of the UK's regulatory environment differs to Australia since in Australia groundwater replenishment is managed from both a quantity and quality perspective as it is seen as an environmentally advantageous solution (Parsons et al., 2012), while in the UK it is governed under groundwater pollution regulations (see Chapter 5). This is an important distinction since governing aquifer recharge activities under groundwater pollution regulations prevents recognition that recharge is necessary to secure the supply of water therefore the proponent has a vested interest in protecting the water quality in the aquifer (Dillon et al., 2013). It is for this reason that the Environment agency in the UK is currently not interested in the potential improvements in water quality that may occur during storage, while the Australian guidelines account for these.

The hazard oriented methodology of the Australian guidelines is also restrictive in the UK context, since as explained in Section 2.2.5, risks to the elements of an ASR scheme such as pre-treatment are not considered, interactions between different hazards/processes are more difficult to assess and the risk associated with the hazards will vary in different regions depending on the societal norms, regulatory standards and views on acceptability of different hazards.

Finally while the Australian guidelines cover the water quality and protection of human health and environment aspects required for effective ASR, they do not consider the allocation of water resources, availability of suitable aquifer for recharge or other water governance issues (NRMMC-EPHC–NHMRC, 2009). These are important considerations when determining the feasibility of a proposed scheme, however they cannot be classified as hazards and therefore are not included in the guidelines.

What is clear from the foregoing discussion comparing these three approaches is that a process oriented methodology is better able to encourage the sort of iterative approach to risk identification, characterisation and management which ensures that interdependencies between hazards are taken into account. This is especially important due to the site specific nature of ASR schemes and the associated risks. The HACCP framework encourages an iterative approach, though it requires operational monitoring of the effectiveness of preventative measures to enable this. WSPs differ because they require that risks are reassessed and prioritised once preventative measures are established before operational monitoring. The Australian guidelines for MAR encourage modelling to be carried out before commissioning to verify the effectiveness of the preventative measures identified. These results are then validated during operation (Page et al. 2008). Encouraging this iterative approach before a pilot site is constructed is important as a more thorough risk assessment/management study can be undertaken during the desktop investigation stage. This can then be validated during a pilot study. A summary of the strengths and weaknesses of all three frameworks is provided in Table 2.2.

Table 2.2: Benefits and limitations of the HACCP, WSP and Australian guidelines for ASR approaches

Risk Framework	Strength	Weakness
Hazard and Critical Control Point analysis (HACCP)	Encourages proactive management of hazards by identifying critical control points (CCP) & mitigation measures Encourages iterative risk assessment before operation begins	Focuses on hazard to human health Considers hazard rather than risk No supporting programmes Focus on CCP
WHO Water Safety Plans (WSP)	Provide a structured approach to identify, prioritize & manage hazards, assess the risk & implement appropriate mitigation measures at each step in the water supply chain Based on HACCP but Tailored for the water industry	Focuses on reducing risk to human health Precautionary approach coupled with high uncertainties in ASR results in over-cautious assessment
Australian MAR Guidelines	Designed to identify risk to business, environment & human health Identifies mitigation measures MAR specific guideline thus focused on hazards & mitigation measures associated with MAR	Based on the potential formation of hazards. Focus on potential hazards can be a possible distraction from more process oriented considerations Tailored to Australian regulations

2.3 Gap in Knowledge/practice

Risk assessment frameworks currently used in the water industry such as the HACCP and WSP do not provide an appropriate methodology to assess the feasibility of ASR schemes in the UK as they are only concerned with risk to human health, and do not appropriately account for operational, strategic and environmental risks associated with ASR schemes. The Australian guidelines for MAR provide a useful basis for a feasibility assessment, however the hazard oriented methodology is deemed to be restrictive, especially for proponents unfamiliar with ASR investigations. Furthermore, they are based on Australian regulations which differ to the current state of UK regulations.

A process oriented methodology to assess the viability of ASR schemes by evaluating potential threats to the business, environment, human health and operations in the context of UK regulations is therefore required. Since risk assessments tend to work around hazards, the aim was to create a decision support tool rather than a risk assessment framework, as this would allow for a process oriented methodology. In order to address this, the following research questions were set:

1. What are the threats that require consideration when planning an ASR scheme in the UK?
2. How do these threats influence the feasibility of an ASR scheme?
3. What are the conditions that may present these threats?
4. How are these threats/conditions presenting the threats influenced by varying operating and environmental conditions?

2.4 Forming the Strategic Planning Tool

As mentioned in Chapter 1, the lack of precedent for ASR schemes in the UK concentrates interest in the associated risks and mitigation requirements at the expense of the potential benefits of such schemes. An appropriate feasibility assessment can promote ASR by improving the understanding of both the opportunities and threats offered by ASR (Pirnie and Jackson, 2011).

The Australian guidelines provide an excellent baseline upon which a framework appropriate for the UK can be built. Due to the lower level of experience with ASR in the UK, a process oriented approach is more useful as forming a feasibility assessment around the processes involved rather than the potential hazards encourages a wider range of potential threats to be considered, interactions to become more apparent and pre-treatment to be treated as a separate element rather than just a preventative measure. A process oriented approach binds the problem, allowing the whole process to be conceptualised. This makes it easier to follow for new proponents and can provide a better understanding of the threats to successful implementation. The framework should also consider the context of UK regulations and industrial structure and address the barriers to ASR in the UK thereby encouraging its implementation.

The Strategic Planning Tool (SPT) was developed to provide a unified, process oriented methodology to integrate all the elements of an ASR scheme when assessing its viability. It breaks down the complexities of the viability assessment processes so that businesses unfamiliar with such schemes can understand the key threats, requirements and opportunities of a potential ASR scheme.

a. The SPT provides a scope for investigation during the pilot phase and can contribute to better investment decisions.
b. The process oriented methodology makes it easier to use across different sites and allows hazards specific to the site conditions to be assessed rather than investigating all possible hazards.
c. The SPT is specific to the UK context, as it considers the regulations and industry structure in the UK and therefore can be used as a guide to what regulators and other stakeholders would require of the scheme

The first step in forming the SPT was establishing a scope to prevent an overly ambitious assessment. If the whole water cycle were to be considered then the assessment would become extremely complicated, making it difficult to implement. As shown in Figure 2.3, pre-treatment, recharge, subsurface storage, recovery and post treatment are the main elements that need to be considered, therefore this is the boundary proposed for the SPT. The influence of the catchment is a consideration within pre-treatment rather than an element in itself. The strategic element is also included due to the high initial investigation cost associated with ASR schemes. There is little point in spending time and money investigating other risks if the risk to business is not acceptable. Furthermore the concept of "acceptable risk" is variable. For example, if there is a desperate need for water then higher costs are acceptable. Defining the strategic risk from the beginning gives a better indication of the "acceptable risk" to the proponent for the rest of the assessment.

Assessing the viability of ASR is complicated because the natural environment (i.e. an aquifer) is used to provide storage. This means that no two projects are alike, as the environmental conditions for storage are highly variable. There are however common issues/constraints that sites may share, which can be identified via a review of relevant ASR literature and reports from ASR operations. A thorough review of the available literature (Gale et al., 2002; Brown, 2005; Pyne, 2005a; NRMMC-EPHC–NHMRC, 2009; Maliva and Missimer, 2010; Ravenscroft and Murray, 2010) revealed several factors that required consideration when determining the viability of a project, and these have been summarised in Table 2.3. These factors were organised and grouped into two main sections – strategic factors (which included regulatory, environmental and human wellbeing) and operational/technical factors.

Table 2.3: Key Strategic and operational factors to consider when planning and designing ASR schemes

Strategic risk factors	Operational/procedural risk factors
• Is there a demand for the water and what will be the end-use of the water? • The availability, reliability, quality, quantity and acceptability of the source water • Availability of a suitable aquifer o Ability to receive and store water o Storage capacity o Hydraulics o Native groundwater quality • Proximity of supply and demand • Regulatory requirements o License requirements o Water rights and nearby wells o Environmental impacts o Environmental values of the aquifer • Management capability and competency • Planning requirements • Supporting programs • Benefits of scheme – does the scheme meet the Anglian Water key strategic priorities • Compatibility with groundwater management plans • Risk of things going wrong • Pre-treatment, and post treatment requirements • Reliability and continuity of supply – clogging and recovery efficiencies plus climate change, population growth etc – resilience is one of the Anglian Water key priorities • Cost	• Source water quality (hazards & pre-treatment) and ambient groundwater quality • Products of reactions between source water, aquifer material and native groundwater • Potential for clogging • By-products of water treatment and ASR maintenance operations • Residence time – mixing, attenuation, migration • Water treatment options resilience, reliability, cost and effectiveness • Fate of contaminants in the recharge water during storage - Biodegradation, inactivation or accumulation and uncertainties regarding the fate. • Effectiveness of preventative measures and operational controls • Suitability of abstracted water for end use • Recovery efficiency • Type of aquifer (mineralogy, confinement, depth etc.) • Hydrogeological considerations: o K, T, fracture zones o volumes of recharge and recovery o storage capacity o water quality changes due to geochemical processes. • Hydrological model: o hydraulic head changes (gradients) o hydraulic interactions o local and regional groundwater flow and quality o migration of recharged water o extent of attenuation zone o aquifer response to recharge and recovery

The final stage of re-organisation involved grouping these factors into suitable titles which could be used to structure the viability assessment, as illustrated in Figure 2.4.

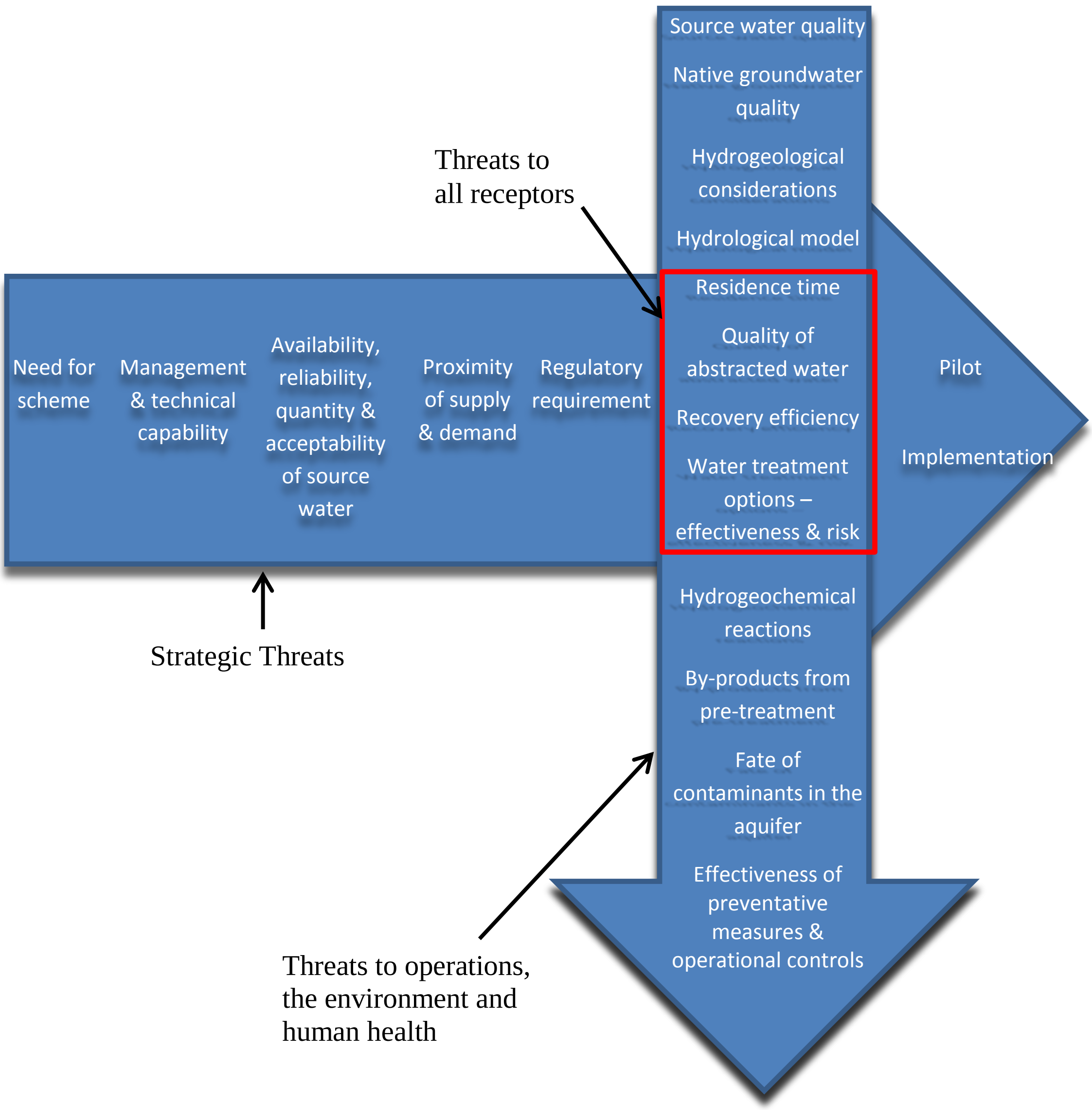


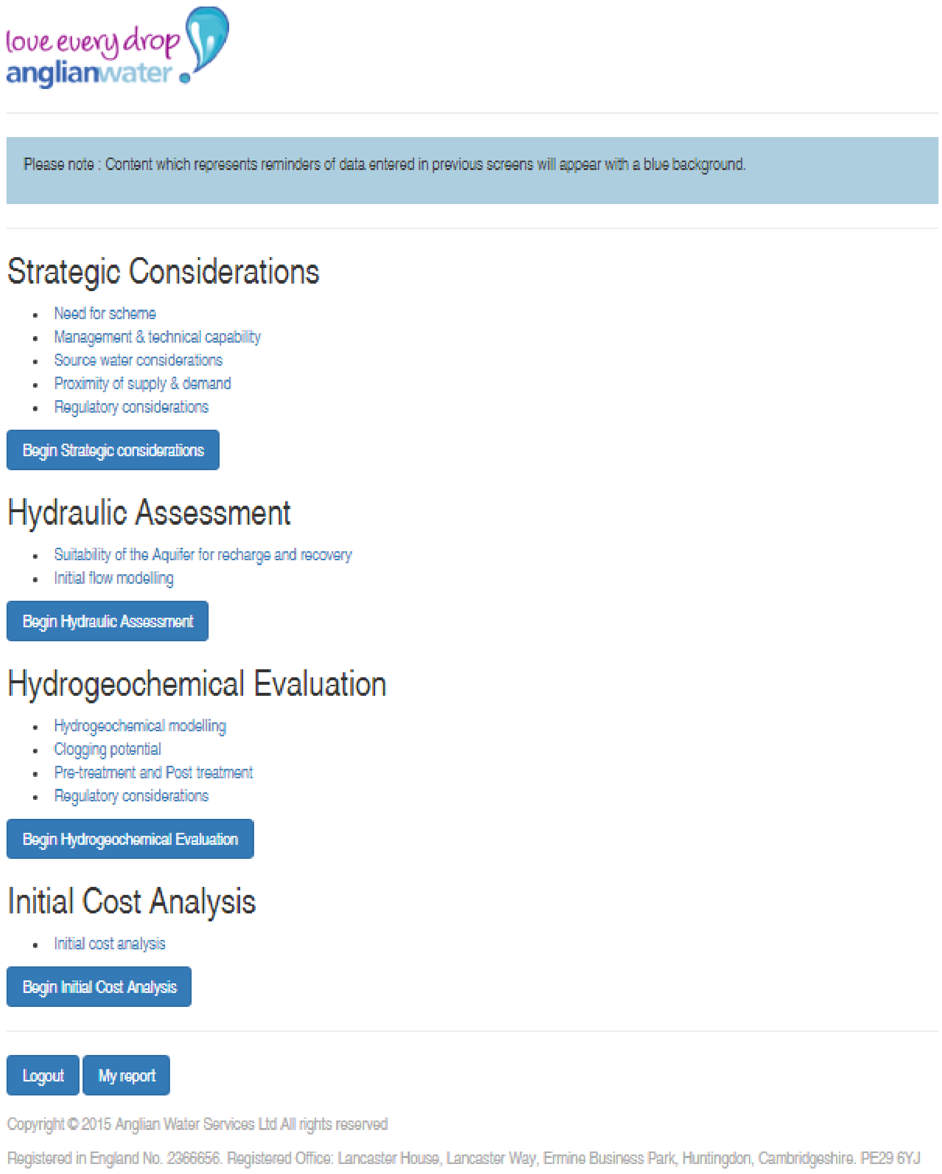
Figure 2.4: Factors to consider in a viability assessment for ASR schemes.

The threats to operations, the environment and human health shown in the vertical could broadly be grouped into hydraulic considerations (hydrological model, hydrogeological considerations, residence time and recovery efficiency) and hydrogeochemical considerations (source water quality, native groundwater quality, quality of abstracted water, water treatment options, hydrogeochemical reactions, by-products from pre-treatment, fate of contaminants in the aquifer and effectiveness of preventative measures and operational controls). The main sections of the viability investigation would therefore be (i) Strategic Assessment, (ii) Hydraulic Assessment, (iii) Hydrogeochemical Assessment and additionally a section for (iv) Initial Cost Assessment was added to provide the proponent with a rough estimation of the potential costs for the scheme. These sections will form the overall structure of the SPT, and the elements that require consideration within each of these sections will be explored (see Figure 2.7).

2.5 Strategic Planning Tool (SPT) Description

The SPT provides step by step guidance on assessing the viability of ASR schemes by calling attention to the variety of processes that may result in threats to the scheme and the conditions that would promote these threats. The value of framing the analysis in this way is that it breaks down the complexities of the processes involved so that businesses unfamiliar with such schemes can understand the threats to a scheme. It would also provide a scope for investigation during a pilot investigation and contribute to better investment decisions. The process oriented methodology improves its applicability across different sites, as it allows hazards specific to the site conditions to be assessed rather than investigating all possible hazards (as would be the case in a hazard oriented methodology such as the Australian Guidelines for MAR – see section 2.2.6). Furthermore, the SPT is specific to the UK context and considers the regulations and industry structure in the UK.

The logic and structure of the SPT is illustrated in the process diagrams in Appendix A, and these were used to create the web-app which formed the SPT as shown in Figure 2.5. The SPT was split into four sections, each consisting of a logical assessment of the threats and opportunities to the area. The SPT features a reporting function which allows the user to save/print the viability assessment, thereby allowing the user to write a detailed investigation document, using the report produced by the tool as a skeleton.



Please note : Content which represents reminders of data entered in previous screens will appear with a blue background.

Strategic Considerations

- Need for scheme
- Management & technical capability
- Source water considerations
- Proximity of supply & demand
- Regulatory considerations

Hydraulic Assessment

- Suitability of the Aquifer for recharge and recovery
- Initial flow modelling

Hydrogeochemical Evaluation

- Hydrogeochemical modelling
- Clogging potential
- Pre-treatment and Post treatment
- Regulatory considerations

Initial Cost Analysis

- Initial cost analysis

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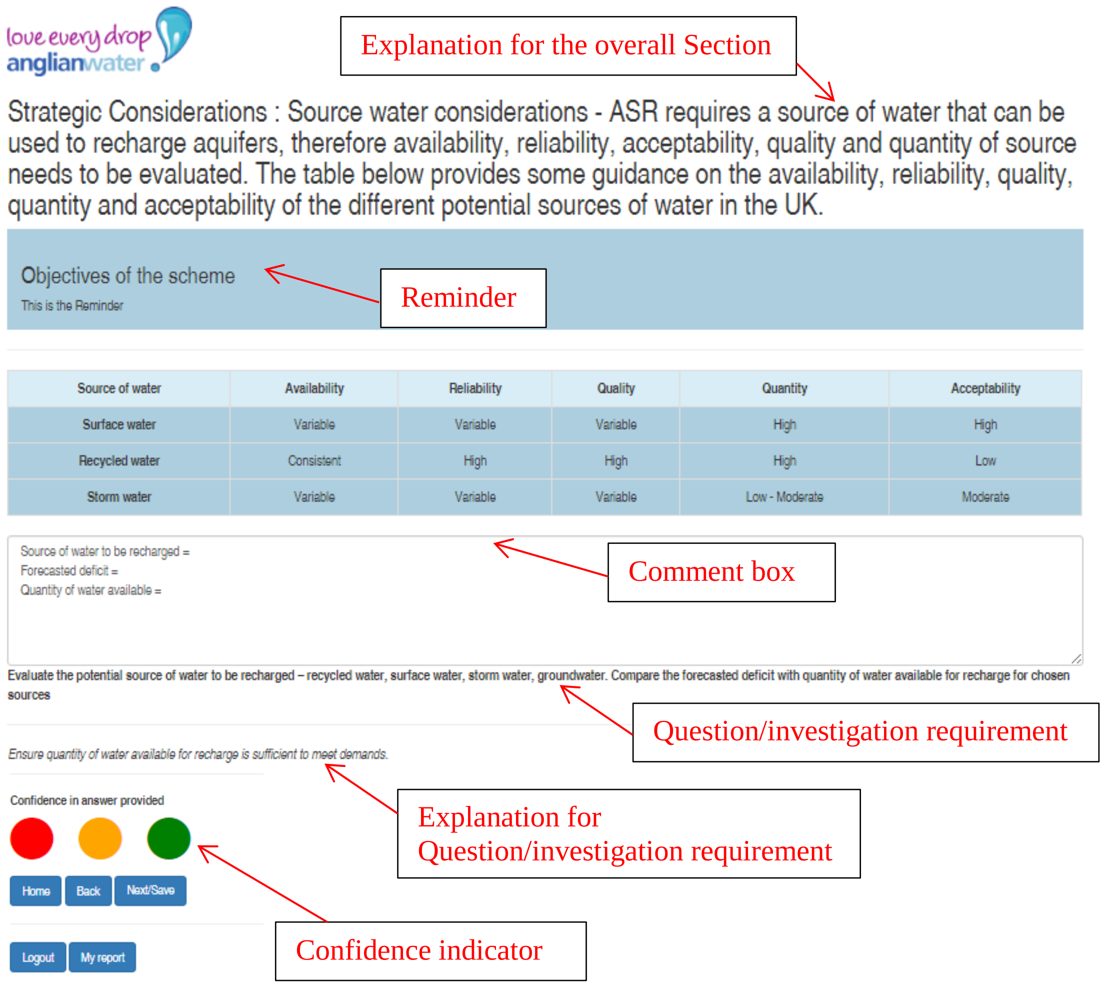
Figure 2.5: Web-app home screen

One of the main advantages of the process oriented methodology was that a more unified approach to evaluating the threats could be taken, and the knowledge/outputs generated from one section of the SPT could be used to inform other sections. This was implemented by providing information ("reminders") from previous relevant sections that would enable a more informed decision to be made. This is illustrated in Figure 2.6 which provides an example of the format of the user interface. In the 'source water considerations' section of the strategic assessment, there is a requirement to evaluate the potential source of recharge water. This evaluation would vary depending on the objectives of the scheme as defined in the 'need for scheme' section, therefore the entry from the "objective of the scheme" is shown as a "reminder" in a blue box at the top. The use of reminders in this way allows the user to understand how different aspects of the viability assessment impact each other. Comment boxes are provided to complete the evaluation/input any necessary information.



Strategic Considerations : Source water considerations - ASR requires a source of water that can be used to recharge aquifers, therefore availability, reliability, acceptability, quality and quantity of source needs to be evaluated. The table below provides some guidance on the availability, reliability, quality, quantity and acceptability of the different potential sources of water in the UK.

Objectives of the scheme

This is the Reminder

Source of water	Availability	Reliability	Quality	Quantity	Acceptability
Surface water	Variable	Variable	Variable	High	High
Recycled water	Consistent	High	High	High	Low
Storm water	Variable	Variable	Variable	Low - Moderate	Moderate

Source of water to be recharged =
Forecasted deficit =
Quantity of water available =

Evaluate the potential source of water to be recharged – recycled water, surface water, storm water, groundwater. Compare the forecasted deficit with quantity of water available for recharge for chosen sources

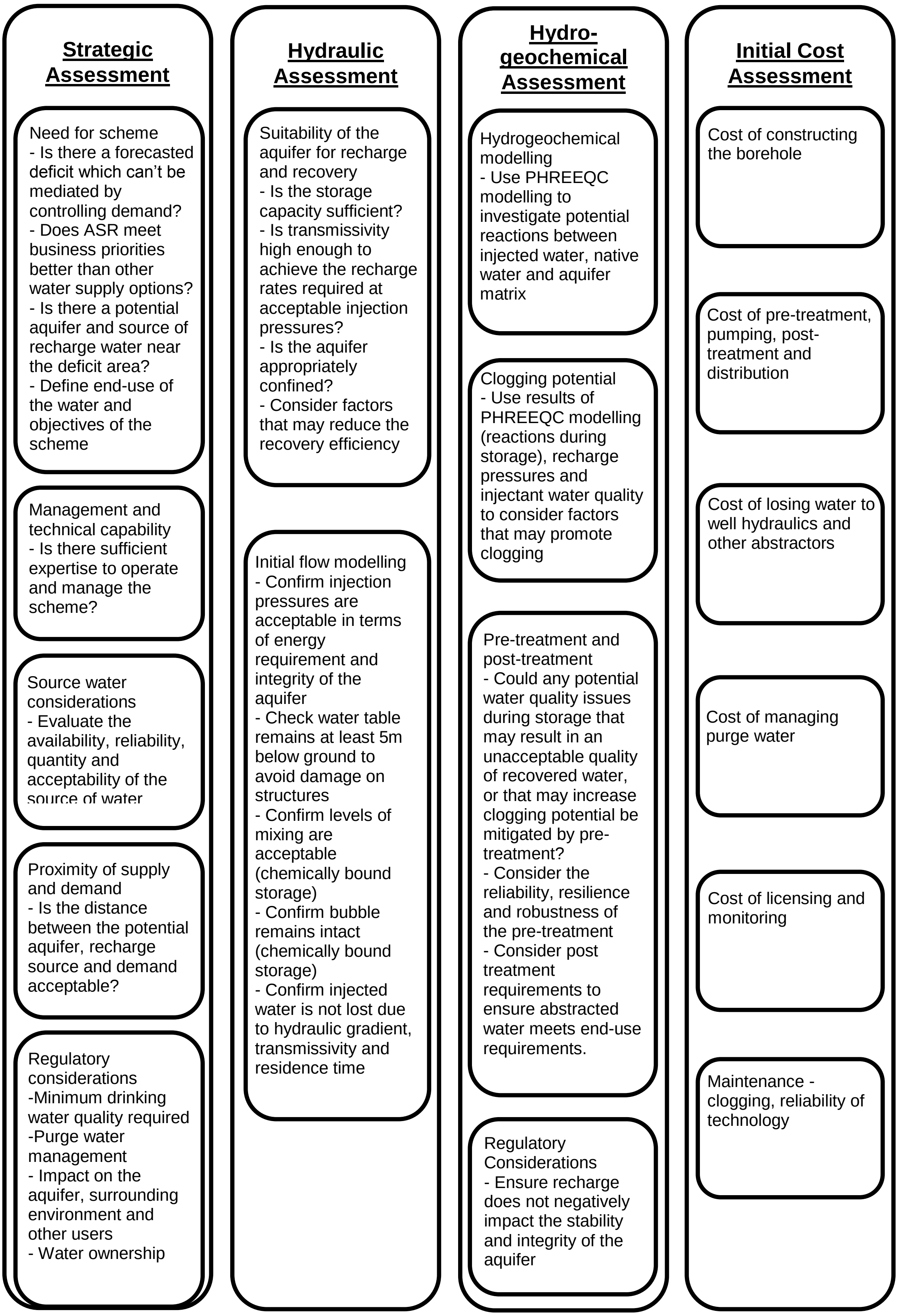
Ensure quantity of water available for recharge is sufficient to meet demands.

Confidence in answer provided

🟥 🟧 🟩

Figure 2.6: Web-app interface - sample question

It can be noticed from Figure 2.6, that explanations were added to the logic to provide further detail and guidance to the user, and clarify the requirements of each page to ensure the user understood how to populate the SPT. These explanations are detailed in Appendix B. Additionally, confidence indicators on each page allow the user to flag up any areas of uncertainty that can be followed up at a later stage. Figure 2.7 below provides an overview of the key areas of assessment in the SPT.



Strategic Assessment

Need for scheme
- Is there a forecasted deficit which can't be mediated by controlling demand?
- Does ASR meet business priorities better than other water supply options?
- Is there a potential aquifer and source of recharge water near the deficit area?
- Define end-use of the water and objectives of the scheme

Management and technical capability
- Is there sufficient expertise to operate and manage the scheme?

Source water considerations
- Evaluate the availability, reliability, quantity and acceptability of the source of water

Proximity of supply and demand
- Is the distance between the potential aquifer, recharge source and demand acceptable?

Regulatory considerations
-Minimum drinking water quality required
-Purge water management
- Impact on the aquifer, surrounding environment and other users
- Water ownership

Hydraulic Assessment

Suitability of the aquifer for recharge and recovery
- Is the storage capacity sufficient?
- Is transmissivity high enough to achieve the recharge rates required at acceptable injection pressures?
- Is the aquifer appropriately confined?
- Consider factors that may reduce the recovery efficiency

Initial flow modelling
- Confirm injection pressures are acceptable in terms of energy requirement and integrity of the aquifer
- Check water table remains at least 5m below ground to avoid damage on structures
- Confirm levels of mixing are acceptable (chemically bound storage)
- Confirm bubble remains intact (chemically bound storage)
- Confirm injected water is not lost due to hydraulic gradient, transmissivity and residence time

Hydro-geochemical Assessment

Hydrogeochemical modelling
- Use PHREEQC modelling to investigate potential reactions between injected water, native water and aquifer matrix

Clogging potential
- Use results of PHREEQC modelling (reactions during storage), recharge pressures and injectant water quality to consider factors that may promote clogging

Pre-treatment and post-treatment
- Could any potential water quality issues during storage that may result in an unacceptable quality of recovered water, or that may increase clogging potential be mitigated by pre-treatment?
- Consider the reliability, resilience and robustness of the pre-treatment
- Consider post treatment requirements to ensure abstracted water meets end-use requirements.

Regulatory Considerations
- Ensure recharge does not negatively impact the stability and integrity of the aquifer

Initial Cost Assessment

Cost of constructing the borehole

Cost of pre-treatment, pumping, post-treatment and distribution

Cost of losing water to well hydraulics and other abstractors

Cost of managing purge water

Cost of licensing and monitoring

Maintenance - clogging, reliability of technology

Figure 2.7: Summary of the structure of the Strategic Planning Tool

It was recognised that a variety of skills and data would be required to successfully use the tool therefore a data and skills requirement sheet is included at the start of the tool (Appendix C). This highlights the requirements of each section in terms of data and expertise. Although the explanations in the tool provide guidance with regards to the level of detail that should be considered, the final decision on the level of detail to input is the users. It is therefore important that the users have an appropriate level of expertise. This open ended approach was specifically chosen over a data driven approach as it provides flexibility to the application of the SPT, allowing it to be used in various stages of the ASR planning and development phases. For example, it can be used in the initial desktop investigation (pre-feasibility) stage where little detail is available, to provide a high level evaluation of the potential for ASR at different sites. It can also be used in the more detailed investigation stage to evaluate the technical (including the hydraulic and hydrogeochemical investigations), strategic and financial feasibility of an ASR scheme at a chosen site in order to provide a more focused scope for pilot investigations.

The following sections provide justifications and reasoning for inclusion of the various elements in the SPT. This information differs to that presented in Appendix B, which provides the actual explanations as seen in the web-app.

2.5.1 Strategic Assessment

The strategy element primarily considers business risk and has the aim of strengthening the business case for such schemes. Due to the level of investment required to investigate the viability of ASR schemes, it is important to ensure from the outset that the strategic risk is minimised and is acceptable. The data and skills required to complete this section is highlighted in Appendix C.

Need for the scheme

Areas with a forecasted deficit need to be identified and the ability of demand control measures to reduce this deficit considered. If it is expected that demand control will not be enough, then other water supply options need to be explored, including ASR. If ASR meets the business's priorities better than the alternatives, then the availability of a potential aquifer and source of water for recharge should be considered.

The objectives of the scheme and the end-use of the recovered water need to be decided and prioritised at this stage. Objectives are based on the purpose of the scheme, for example provision of long term storage, seasonal storage, groundwater management, scheme etc. The End-use of water is defined by the proposed user of the recovered water, for example municipal, agricultural, industrial and potable use. These are often overlooked as they are not considered a priority, however failure to define appropriate objectives and end-use can lead to the project being designed incorrectly and underperforming, since each objective and end-use would have different storage and water quality requirements. The objectives and end-use would therefore have implications on the source water considerations and suitability of the aquifer for recharge and recovery. These are discussed further in the following sections.

Management and technical capability

An ASR scheme can evolve over time since storage is in a natural environment, therefore the management and technical capability within the business to design and operate the scheme should be evaluated to ensure the business has, or can economically acquire the capability to implement, operate and maintain the scheme.

Source water considerations

Availability, reliability, quantity and acceptability of source water needs to be considered at an early stage. ASR does not provide a new source of water, instead it provides an option to store water thereby regulating the availability of water in the same way a reservoir does. It therefore requires a source of water that can be used for recharge. Table 2.4 below provides some guidance on the availability, quality, quantity and acceptability of the different potential sources of water in the UK. It should be noted that this is a general guidance and will differ in different regions of the UK.

Table 2.4: Guidance on the availability, quality, quantity and acceptability of the different potential sources of water in the UK

Source of water	Availability	Quality	Quantity	Acceptability
Surface water	Variable	Variable	High	High
Recycled water	Consistent	High	High	Low
Storm water	Variable	Variable	Low - Moderate	Moderate

Potential sources should be evaluated to ensure there is a source of water available for recharge that is reliable enough to achieve the systems objectives. For example, surface water and storm water rely on rainfall which is increasingly less reliable as the climate changes, whereas recycled water is very reliable since wastewater will be produced as long as water is consumed. If the objective of the scheme is to provide seasonal storage, that is the water would be recovered annually, then the source of water needs to be more reliable, as the aquifer will need to be recharged annually. If long-term storage is needed then reliability of water is less important as the water is banked over a longer period of time, therefore recharge over the course of one year is not as vital as in seasonal storage.

The quantity of water available for recharge needs to be sufficient to meet demands, and the regulatory and public acceptance of using the source of water should be considered. For example using recycled water as a source of water would provide a reliable source in terms of quantity and quality of water however public and regulatory acceptance may be problematic. Alternatively, surface water/storm water are more acceptable however they are also less reliable in terms of availability and quality. All these factors need to be evaluated in the context of the systems objectives and end-use.

Proximity of supply & demand

The potential ASR site should be close to the demand for water as well to the source of recharge water to minimise transport and infrastructure costs. The acceptable costs in this respect will depend on the need for the scheme, as if the scheme is essential to securing water provision, then higher costs are likely to be acceptable.

Regulatory requirements

Regulatory requirements of the scheme must be established as these will impact the requirements of the system. The Environment Agency has stated that it will take a risk based approach to permitting and that the recharge water will need to meet at least drinking water standards at the point of injection regardless the quality of native groundwater (Page, 2013)(the implications of this is discussed further in Chapter 5). It is worth noting that if a potable aquifer is recharged then it is possible that a "better than drinking water" standard is enforced. Potable/near potable aquifers would likely have more onerous treatment and monitoring requirements than brackish aquifers.

Purge water which is produced during well construction and rehabilitation needs to be disposed of appropriately. The method of disposal will depend on both the quality of the purge water and the regulatory requirements for disposal. Potential disposal methods include discharge to a storm water system, sewers or a nearby river. Alternatively, there may be a potential to distribute it to nearby industry/farmers both of whom could use the water without significant treatment, depending on its quality. Purge water can contain suspended solids, pathogens, metals, nutrients and organics, therefore the requirements for potential methods of disposal need to be considered (Pyne, 2005b).

Any potential improvements or degradation in recharge water quality during storage will not be considered by the Environment Agency, except in circumstances where it negatively impacts the stability/integrity of the aquifer e.g. excessive dissolution which can destabilise the well and aquifer (Page, 2013). There is also a general requirement of minimal impact on the surrounding environment/users, e.g. dehydration/flooding of nearby wells or the environment during recovery/recharge (Page, 2013). The hydraulic connection to the environment and other users should therefore be assessed as ASR can affect ecosystems, rivers and wetlands that are dependent on the groundwater system as the water table is raised and lowered.

With regards to water ownership and protection from unauthorised abstractors, once an ASR scheme is set up, it would be protected from large abstractions. However the Water Act 2003 allows abstractions up to 20 m^3/d without a licence, or a requirement to inform nearby scheme operators. An inventory of existing wells/ potential users should therefore be conducted to understand the potential loss in stored water quantity.

2.5.2 Hydraulic Assessment

This is an essential part of the assessment as it addresses the storage capacity of the aquifer as well as highlight potential concerns associated with the recharge and recovery elements of the ASR scheme, in terms of the pressures required their associated impacts, and the potential recovery efficiency of the scheme. The data and skills required to complete this section is highlighted in Appendix C.

Suitability of the aquifer for recharge and recovery

The three main considerations when choosing an aquifer for an ASR scheme are the storage capacity, the hydraulic properties of the aquifer and whether the aquifer can achieve useful storage (Maliva and Missimer, 2010). The storage capacity of the aquifer is a product of the effective porosity, length and width of the formation. Effective Porosity is the pore space in a unit volume of rock in which the water can move freely. It differs from void porosity which also considers the water that is bound e.g. by absorption, therefore is not able to move freely. The effective porosity is often lower than the void porosity therefore it is imperative that effective porosity is used (Hofkes 1986). Historical water levels and abstraction data should be taken into account since this provides a more realistic idea of available storage capacity. A comparison between the storage capacity available and the amount of storage required will determine if the aquifer is capable of storing the required quantity of water.

Injection pressures and their impact on the aquifer, operational cost and the surrounding environment contribute the main risk to injection. It is therefore important to select an aquifer with favourable hydraulics to achieve the required recharge rate at the lowest possible injection pressures. A high injection pressure not only increases the energy requirements and impact on connected environments, it also increases drawdown and can result in mechanical compaction of the aquifer matrix which further increases the injection pressures (Pyne, 2005b). Injection pressures should not exceed the maximum allowable limit if over pressurisation of the aquifer and potential rupture of the aquifer is to be avoided (Martin, 2013b). The injection pressure is primarily determined by the aquifer transmissivity which is the ability of an aquifer to transmit water, i.e. it is the rate of flow of water through a defined thickness (Maliva and Missimer, 2010). A higher transmissivity would result in lower injection pressures however it would increase the potential for mixing and migration of the stored water. The ideal transmissivity would therefore be strongly influenced by the objectives of the scheme, for example, if the objective is long term storage, then a high transmissivity increases the potential for the recharge water to be lost due to dispersion. If recharged water is to be stored in an aquifer with poor native groundwater quality, then high transmissivity would promote mixing between the waters, thereby reducing the quality of the stored water.

A balance needs to be found between the transmissivity and injection pressures/recharge rates. The minimum transmissivity required of an aquifer would largely depend on the target recharge rate which is dependent on the period of time the source of water used for recharge is available (Horvath et al., 1997). A high recharge rate would require a high transmissivity and vice versa. The maximum transmissivity would be determined by potential mixing or movement of water away from the site as explained above. It should be mentioned that if transmissivity is not sufficient to achieve the required recharge rates then multiple wells can be used to allow injection of the required volume at lower pressures. Alternatively, detention basins can be used to increase the period of availability thus accommodate a lower rate of recharge.

There are two main methods to achieve useful storage as explained by Maliva and Missimer (2010), namely chemically bounded storage and physical storage. Chemically bounded storage is where fresh water is stored in an aquifer of lesser water quality. The injected water displaces the native water and forms a “bubble” of water which is chemically bounded such that the walls of the “tank” are the boundary between the injected and native water, i.e. the mixing zone. This type of storage works best in confined aquifers to maintain a “bubble” of water. The aerial extent, thickness and depth of the confining layer need to be considered. If the confining layer is thin and the aquifer is relatively shallow then there is a risk of ground movement during injection and recovery, especially if injection pressures are high. The depth of the aquifer and the thickness of the confining layer will also influence the cost of drilling a borehole.

Physical storage is where the introduction of water into an aquifer causes an increase in the water level (pressure head), which persists until recovery of the water (Maliva and

Missimer, 2010). Unlike in chemically bounded storage, the recharge water in the aquifer does not need to form a bubble, however it does need to remain within the aquifer and not "leak out". If the aquifer is large then there will not be an increase in head simply because the water spreads throughout the aquifer. Thus small area aquifers that are confined at their base and laterally (bounded on all sides) to limit leakage are ideal for this type of storage.

The key objective of an ASR system is to recover a high percentage of recharged water at a quality that is ready to be put to beneficial use. The performance of an ASR system is expressed in terms of its recovery efficiency, which is the volume of water recovered relative to the volume of water injected for an operational cycle. A final consideration in the *hydraulic assessment* is therefore the factors that may reduce the recovery efficiency of the scheme. These are summarised in Table 2.5, which also illustrates how these factors vary depending on the type of storage used.

Table 2.5: Factors that influence recovery efficiency in both chemically bounded and physical storage systems

Factors that may reduce recovery efficiency	How factors impact recovery efficiency	Type of system
Native water TDS > 5000mg/l	5000mg/l is used as a guideline value above which density stratification would contribute significantly to mixing between the native water and stored "bubble" (Pyne, 2005b).	Chemically bounded storage
High dispersivity	Dispersivity determines how the "bubble" of water moves in the aquifer and will impact the mixing between the native and injected water. It can be evaluated by considering the aquifers heterogeneity & hydraulic conductivity (Maliva and Missimer, 2010).	Chemically bounded storage
High transmissivity (hydraulic conductivity x aquifer thickness)	High transmissivity promotes migration of the stored water, and this is exacerbated if the aquifer is at a high hydraulic head or with long residence times (however it can still have a significant impact on its own). The highest acceptable transmissivity can be defined by the degree of migration of the recharged water, and where chemically bounded storage is used, the mixing between native and recharge water that would be acceptable.	Chemically bounded storage & Physical Storage

High hydraulic gradient (groundwater flow models)	If aquifer is at a high hydraulic gradient relative to its surroundings then water will move from the high hydraulic gradient (the aquifer) to a low gradient and the water will be lost. It is more relevant where it is coupled with a high transmissivity or a long residence time.	Chemically bounded storage & Physical Storage
Long Residence time (objectives of the scheme)	Where chemically bounded storage is used, long residence times impact the levels of mixing due to hydraulic gradient, transmissivity and dispersivity. Duration of storage is more important in more saline aquifers because of potential mixing due to density stratification. Long residence times, coupled with either a high transmissivity or a high hydraulic gradient can promote migration of the stored water. It is less relevant where transmissivity and hydraulic gradients are low.	Chemically bounded storage & Physical Storage

Initial flow modelling

The final stage of the *hydraulic assessment* is to carry out groundwater flow modelling to predict the suitability of the aquifer for recharge and recovery. The main purpose of this modelling is to determine the impact of hydraulic parameters (hydraulic conductivity, transmissivity, dispersion etc.) on operations, predict system performance (i.e. recovery efficiency), perform mounding analysis (effect of injection on groundwater levels/pressure) and drawdown analysis (effect on abstraction on ground water level/pressure). It should be noted that this modelling would be based on assumptions/predicted data and not actual data therefore results provide an indication rather than conclusive evidence.

The modelling provides a better indication of the injection and recovery pressures required, the acceptability of which can evaluated in terms of the energy requirements and maintaining the integrity of the aquifer (i.e. the aquifer should not be over-pressurised). The system performance is also assessed. If chemically bounded storage is used, then the levels of mixing expected need to be acceptable (as summarised in Table 2.5 above) and the bubble of stored water should remain intact. If physical storage is used then the main considerations relate to ensuring that the injected water is not lost due to a hydraulic gradient, high transmissivity and long residence time. Finally the effects of mounding during recharge and drawdown during recovery need to be analysed to ensure there is no negative impact on the surrounding environment as explained in Section 2.5.1.

2.5.3 Hydrogeochemical Assessment

The main purpose of this analysis is to incorporate the storage element of the ASR scheme into the viability assessment. It therefore includes an initial assessment of the potential water quality changes that may occur during storage (which present a large proportion of the uncertainties associated with ASR schemes), pre and post treatment requirements bearing in mind the potential changes highlighted, as well as the potential for clogging, all of which influence the viability of an ASR scheme. The data and skills required to complete this section is highlighted in Appendix C.

Hydrogeochemical Modelling

The first step is to carry out hydrogeochemical modelling to predict the potential changes in water quality that may occur during storage. As in the case of hydraulic modelling, this would be based on assumptions/predicted data and not actual data. A hydrogeochemical model such as PHREEQC (Parkhurst and Appelo, 1999) should be used to investigate potential reactions between injected water, native water and aquifer matrix. PHREEQC is most commonly used as it can model potential geochemical reactions including dissolution/ precipitation, ion exchange, ion adsorption and redox reactions among others (Gaus *et al.*, 2000; Gale *et al.*, 2002; Anderson *et al.*, 2004; Riches *et al.*, 2007; Vanderzalm *et al.*, 2013; Willis-Jones and Brandes de Roos, 2013). Nearby boreholes can be used to measure quality of native water. Since a minimum of drinking water quality is required, this can be assumed to be the injectant water quality (unless the injectant quality is otherwise known). The mineralogy of the aquifer can be estimated by considering the geological composition of the aquifer.

Clogging Potential

Clogging is a major operational risk associated with aquifer recharge. It reduces the recovery efficiency and increases the injection/recovery pressures required, which in turn increases the energy requirements, reduces the recharge rates and increases the drawdown during recovery (NRMMC-EPHC–NHMRC, 2009). Despite this, there are currently no models available to predict the potential for clogging. The potential for clogging in ASR schemes was therefore examined in detail (Chapter 3), the results of which informed this decision support tool. Table 2.6 below provides a summary of the clogging mechanisms which may impact an ASR scheme and the parameters influencing these mechanisms. The results of the PHREEQC modelling (reactions during storage), recharge pressures required and injectant water quality can be used to identify the factors that may promote clogging, as shown in Table 2.6. It should be noted that the more factors that apply to the scheme, the higher the potential for clogging due to different mechanisms. This table is simply a starting point to understand the potential for clogging and is by no means a comprehensive assessment. A more detailed review of the potential clogging mechanisms and their influences can be found in Chapter 3.

Table 2.6: Points vulnerable to clogging during ASR and the main mechanisms of clogging responsible (adapted from Bloetscher et al., 2004; Pyne, 2005)

Types of clogging	Causes of clogging
Clogging of injection wells (that injection wells are vulnerable to clogging)	Where the injectant water has a level above 3NTU (and >3mg/l Total suspended solids), clogging of injection wells is more likely (Pavelic et al. 2007). Does injectant contain suspended solids?
	If the injectant contains biodegradable dissolved organic carbon then microbial clogging (biofouling) is likely. Does injectant contain biodegradable dissolved organic carbon?
Clogging of aquifer matrix	Air entrained in the recharge water enters the aquifer formation and lodges into the pore spaces, increasing resistance to flow. There is also an associated change in the redox potential in the area which can influence the geochemical reactions and microbial activity in the area, further exacerbating clogging. Does the injectant contain air?
	Gaseous binding from gasses coming out of solution can also block the

	pores of the aquifer e.g. the release of nitrogen gas due to denitrification of nitrates in the injected water. Will reactions during storage release gases?
	High injection pressures can result in mechanical compaction of the aquifer matrix. High injection pressures required?
Clogging of aquifer matrix and/or recovery wells (recovery wells are less vulnerable to clogging)	Dispersal of clay particles/swelling of clay colloid – may occur due to ion exchange between the recharged water and aquifer material. Is dispersal of clay particles/ swelling of clay colloids likely?
	Geochemical reactions (e.g. precipitation of minerals such as iron and manganese) can clog the recovery well and the aquifer matrix. Geochemical reactions likely?

Pre-treatment and Post treatment

The initial level of pre-treatment is defined by the regulatory requirements however at this stage the operational requirements need to be considered. The pre-treatment requirements are therefore adjusted to minimise any potential water quality issues that may arise during storage, which would result in an unacceptable quality of recovered water, or increase clogging potential as identified earlier. Water quality issues include release of inorganic minerals (such as arsenic, iron, manganese, trace species or hydrogen sulphide), formation/persistence of organic compounds (such as disinfection by-products), radionuclides (such as radium, radon and uranium), and an increase in turbidity due to dissolution and precipitation reactions (Maliva and Missimer, 2010). The acceptable quality for the recovered water depends on strategic considerations such as the end-use of the water, the acceptable cost for post-treatment and operational considerations such as potential for clogging. If necessary, the pre-treatment process should be adjusted to improve the abstracted water quality. This can be done in the PHREEQC model which allows the quality of injected water to be adjusted to produce the required abstracted water quality. The pre-treatment requirements to produce the modelled injected water quality can then be determined.

Although it is important to evaluate the pre-treatment in terms of the quality of water it would produce, pre-treatment is a vital barrier therefore it is also important to consider the risk to the pre-treatment process itself. This is because it is usually possible to produce the required quality of water however the reliability, resilience and robustness of the technology will impact the viability of the pre-treatment process and the overall integrity of a scheme. Reliability of the technology to produce the quantity and quality of water required is important to consider. If the technology selected is not reliable then there is a higher risk of failure, an increase in the maintenance and monitoring requirements etc. An unreliable process will increase the risks and the costs associated with the scheme.

Resilience of the technology to changes in quality and quantity of the influent should also be considered, as if the technology chosen is too sensitive and can't adapt to changes, then the risk of failure increases. It should be noted that the quality and quantity of influent is likely to be variable (depending on the source of water used) therefore the pre-treatment process chosen should offer some flexibility and resilience.

The technology should also be robust since the required quality of the injectant may change for example due to a change in the regulatory standards or end-use of water. Changing regulatory standards are a significant risk to pre-treatment and to the whole project, as it could require additional or even completely different pre-treatment methods. Similarly, a change in end-use can mean a different pre-treatment is required and can impact the viability of the scheme. If a higher quality of water is required then additional treatment will be required, if a lower quality water is required then the current level of treatment may not be economical thus different treatment may be required. This should be considered when designing the pre-treatment to ensure the process is flexible enough to accommodate changing requirements.

Finally the post treatment requirements need to be evaluated to ensure the abstracted water can meet end-use requirements. The technology chosen should have the ability to adapt to varying quality of water in order to accommodate potential changes in water quality during storage. It is also advantageous to have a robust process, which can accommodate changes in future requirements of the final water e.g. in case of a change to the end-use.

2.5.4 Initial Cost Assessment

This section provides an initial assessment of the potential costs associated with the ASR scheme. It should be noted that this section only provides the user with the factors that need to be taken into consideration when trying to estimate an initial cost, rather than actual detailed costing of the different aspects of the scheme. The data and skills required to complete this section is highlighted in Appendix C.

When assessing the initial cost of the scheme, the first factor to consider is the cost of constructing the borehole, which needs to take into account the number of boreholes (and size of the detention basin if required) as determined in the *hydraulic assessment*.

The costs associated with pre-treatment, pumping, post-treatment and distribution are also important (Ravenscroft and Murray 2010). The cost of treatment can be estimated using the pre-treatment and post treatment requirements determined. Cost of pumping during injection and recovery can be estimated by considering the required injection pressures and recharge rates as found in the initial flow modelling. Distribution cost can be estimated by considering the distance between the source of water and the aquifer, and the aquifer to demand area.

Cost of losing water due to well hydraulics or other abstractors should also be considered. This cost can be estimated by determining the number of wells in the storage area and the quantity of water abstracted by these wells. The water lost due to hydraulics can be estimated using information from the initial flow modelling.

Purge water, which is produced when ASR wells are flushed during testing and as a part of clogging management, needs to be disposed of, therefore the infrastructure requirements for this disposal needs to be accounted for. This is often neglected in the initial planning stages, and can become an expensive problem if the infrastructure to appropriately dispose of the purge water is not readily available.

Cost of licensing and monitoring should include an estimated cost for abstraction licenses for the source of water and recovering the water after storage, a license to inject the water in the aquifer, and a license for disposing purge water during flushing. On-going monitoring will likely be required therefore the cost of this should also be accounted for. This should include drilling and maintaining monitoring boreholes, water quality testing, frequency of testing and reporting etc.

Finally, the maintenance requirements of the scheme should be estimated by considering the potential clogging mechanisms that may impact the scheme, and the potential mitigation requirements. The potential cost of maintaining the technology in the treatment train and boreholes should also be factored in.

Once the initial cost has been estimated, the final step in this decision support tool is to reconsider all the water supply options and re-evaluate if ASR is still the best water supply option. The minimum recharge to make the project worthwhile should also be considered and a decision made as to whether the scheme should proceed to pilot investigations.

2.6 Assessing the value and usability of the Strategic Planning Tool

In order to evaluate the value and usability of the SPT, it’s logic, coherence and completeness needs to be tested (verification) and its ability to address its intended purpose (validation) also needs to be examined (Sojda, 2007). Additionally, considering user satisfaction with the system can promote successful implementation of the SPT. Verification of a decision support tool is usually completed via intense personal checks to ensure that the decision making logic (Appendix A) has been accurately translated into computer code (Rykiel, 1996), and this was the method used to verify the SPT. There are several methodologies to evaluate the validity of a decision support tool including testing against a pre-selected gold standard, comparing real time and historic data sets for comparison, using Delphi groups and comparison to other models/decision support tools (Rykiel, 1996; Sojda, 2007).

The SPT is a not a data driven tool therefore testing against a pre-selected gold standard or comparing real time and historic data sets for comparison is not possible. Instead, the fitness for purpose/validity of the SPT, i.e. confidence in the tools ability to deliver what it claims, was tested using a four tier method; (1) expert knowledge in the form of

Delphi groups were used to test the logic and usability of the SPT, (2) a survey of existing ASR sites helped identify the most prevalent threats, and these were checked against the SPT to ensure it was capable of prompting consideration of the major threats as identified in the survey, (3) a comparison of the SPT with other guidelines and decision support tools available helped to identify the relative advantages/shortfalls of the SPT and (4) the value and usability of the SPT as a whole was tested during deployment to assess viability of a potential ASR project in the Anglian region.

2.6.1 Key outputs from Delphi groups

Two Delphi groups were convened, the first at Cranfield University and the second at Anglian Water Services, details of which can be found in Table 2.7. Each group systematically went through the SPT and any suggestions/comments were recorded.

Table 2.7: Details of the Delphi groups and the points of discussion at each group

Members	Roles	Reason for selection	Points of discussion
Delphi Group 1 – Cranfield University (27/01/2014)			
Paul Jeffrey	Professor of Water Management	Active researcher in the field of MAR	1. Overall format and clarity of the SPT 2. Validity of the content of the SPT 3. Identification of missing elements 4. Level of detail of the SPT
Bruce Jefferson	Professor of Water Engineering	Active researcher in the field of MAR	
Delphi Group 2 – Anglian Water Services (24/02/2014)			
Barrie Holden	Innovation Clean Water Programme manager	Main stakeholder for research output – business direction	1. Overall format and clarity of the SPT 2. Validity of the content of the SPT 3. Identification of missing elements 4. Level of detail of the SPT 5. Applicability of the SPT within the business 6. Does the SPT meet the requirements?
Nick Walters	Water Resources Groundwater Manager	Leading current ASR scheme feasibility investigation	
Mike Cook	Water Resources Manager	Experience in planning two previous ASR schemes	

The following recommendations were made by the Delphi groups, and were incorporated into the SPT.

1. A data and skills requirement sheet needs to be added at the front of the SPT to give the proponent an idea of the data, type of people and skills required to effectively go through the SPT (Appendix C). This requirement sheet will clarify the type of skills and data required in each part.
2. Some of the questions need to be rephrased to be clearer. It needs to be clear that the SPT does not provide a risk assessment methodology, it only provides prompts to the requirements of an ASR scheme so that potential threats may be identified.
3. Clearer objectives for the SPT and an explanation of where it lies within the Anglian Water decision gates. This will clarify the level of detail required, the work already conducted in the stages prior to implementing the SPT, data available to use in the tool and data that will be provided by the tool. It needs to be clear that the aim of the SPT is to expose the strengths and weaknesses in the scheme rather than provide a business case.
4. Guidance is needed to explain the level of detail/data required when implementing the SPT. This can be achieved by providing sample answers or more detail in the explanations.
5. Use of a traffic light system to provide an indication on the level of confidence in the answer given and flag up areas of uncertainties that need to be addressed/revisited with more data
6. Minor formatting changes including the layout of some sections, the way data is presented in some sections and the use of colours.

2.6.2 Survey of existing sites

A Substantial quantity of literature is available on the operation of ASR schemes, issues encountered and measures taken to mitigate them, however most of these studies concentrate on one part of a scheme, for example water quality changes, site evaluation etc. There have been some multidisciplinary studies such as that reported by Dillon et al., (2006), Vanderzalm et al., (2009) and the RECLAIM WATER project (Kazner et al., 2012) which have considered a wider range of risks across different schemes. Although these provide significant detail of the schemes, they do not consider both strategic and operational threats and neither do they consider risk from conception to operation.

The International Groundwater Resource Assessment Centre (IGRAC) commissioned a survey of 449 MAR scheme entries in 60 countries around the world, of which 139 were classified as recharge using boreholes, wells and shafts (IGRAC and Acacia Institute, 2007). This study provided an inventory of MAR schemes with information on the source of water used, the group of users profiting from the MAR technique, the purpose of the MAR technique from a water management perspective, the average scale of schemes of a MAR technique, the geological composition of the aquifer being recharged, the number of schemes of each MAR technique and the total capacity of all schemes of a MAR technique. Although it provides valuable information on a very large scale, this is an inventory and does not provide information on the most prevalent threats to ASR schemes, which is the main requirement of this investigation.

Pirnie and Jackson (2011) developed a survey which was sent to 22 utilities in Texas to understand the potential for ASR to provide additional storage and the key barriers to widespread implementation of this technology. The survey was concerned with the utilities understanding of ASR, whether the utility had previously considered ASR to meet storage or water supply needs, and to identify any concerns that may have limited evaluation/implementation of ASR. It was therefore mostly concerned with the business and strategic drivers/constraints of ASR such as familiarity and experience of using the technology. This report was very useful as it provided information on perceived and actual threats to ASR schemes however it was only based on utilities in Texas, and as previously discussed, the experience level and regulatory structure for ASR in the UK differs from that in Texas. Furthermore, this survey did not provide information on the type of viability assessment conducted or how the threats were assessed by the utilities, and therefore a relationship between the level of assessment and the success/failure of the scheme cannot be established using this information.

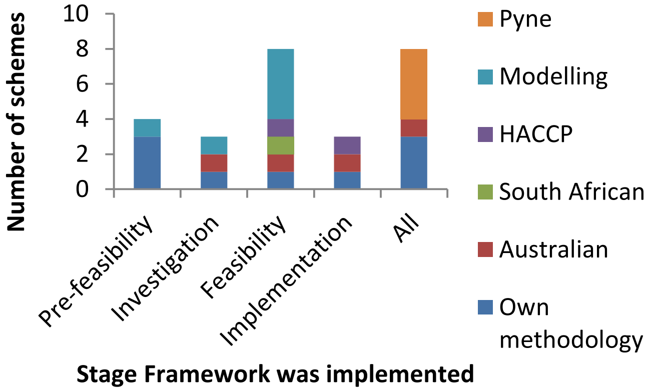
Since the required information was not readily available, a survey (Appendix D) was formulated to determine the value of the SPT in terms of its ability to identify potential threats (strategic, operational, environmental and threats to human health) to an ASR scheme and identify the threats that would increase the complexity of the scheme. This was sent out to UK water companies investigating ASR and other international ASR operators. The aim of this survey was to characterise the key threats associated with ASR schemes, how these threats were assessed, causes, indicators and mitigation measures for these risks. The response to the survey provides a useful indication of the risk frameworks/viability assessment methods that were used in the schemes and the operators experience of using them, recalcitrant risks associated with schemes and indicators that may be used to identify high risk schemes.

The information acquired from the survey was organised in a spreadsheet as shown in Appendices E and F. This allowed all the responses to be viewed in one format, which facilitated analysis of the responses. The results were analysed in two batches – the first batch (Appendix E) included the risk assessment framework/methodology implemented, the stage of investigation at which it was implemented and whether the respondent felt it identified all the risks. The information was then grouped and summarised to show the number of schemes that used each framework and the stage at which the framework was implemented in each case.

The second batch (Appendix F) considered the threats identified after the scheme was commissioned, causes, potential indicators and mitigation measures for these threats, and the effectiveness of the mitigation measures. This provided some data on the most prevalent threats and how they may be avoided. Respondents had the freedom to identify any threats they felt were appropriate, therefore some formatting was necessary. The threats identified fell into one of seven tittles namely hydrological limitations, water quality issues (source/recovered water), clogging, source water availability (quantity), regulatory approval/water rights, maintenance (current/future) and economics/funding, therefore these were established as the main categories of threats. Categorising the threats in this way allowed the number of schemes reporting threats under these tittles to be identified, which in turn provided information on the category of threats reported as most prevalent. The respondents were also asked whether the threats could have been identified in earlier investigation stages, whether a more comprehensive risk assessment could have benefited the scheme and what that they would do differently if they could re-design the scheme. The responses to these questions provided further insight on the effectiveness of their risk assessment methods.

Results of the survey: Frameworks used to assess viability of ASR schemes

A total of nineteen surveys were completed, seven of which were UK schemes (all trialled/implemented ASR schemes) and twelve international schemes (nine used injection & three used recharge basins). Respondents originated from Australia, America, Spain, Belgium and UK. Figure 2.8 below, depicts the variety of risk assessment frameworks used by different schemes and the stages at which the framework was implemented. The risk assessment frameworks used included guidelines developed by Pyne, (2005), Modelling (hydraulic/hydrogeochemical modelling), Hazard and Critical Control Point analysis, South African guidelines for Aquifer Recharge (Ravenscroft and Murray, 2010), Australian guidelines for Aquifer Recharge (NRMMC-EPHC–NHMRC, 2009) and in-house internal frameworks. The frameworks were implemented at various stages of the schemes life-cycle - Pre-feasibility (initial desktop investigations), Investigation (more detailed analysis which include hydraulic and hydrogeochemical studies), Feasibility (pilot scale testing) and Implementation (full scale operation).



Framework used	No. of schemes
Own methodology	6
Modelling	5
Pyne	4
None	4
Australian	3
South African	1
HACCP	1

Figure 2.8: Risk assessment methodologies used and stages of implementation (Left) and breakdown of number of schemes reported to have used each framework (right)

The number of schemes shown to have implemented the different frameworks in the graph differs from the numbers shown in the table because some schemes used more than one framework, while others applied the same framework at more than one stage. For example a scheme in Spain used the Australian guidelines at the investigation stage, South African guidelines at the feasibility stage and their own methodology at all stages to assess potential threats. It is interesting to note that most schemes used their own methodology to investigate the viability of the scheme, and these were used at different stages, with the majority using it in both the pre-feasibility and all the stages. The second most common methodology used was modelling (one scheme used it in the investigation and feasibility stages, one scheme used it in the pre-feasibility stage while the remaining three used it only in the feasibility stage). This was followed by the Pyne methodology which was used in all stages and None (i.e. no risk assessment was implemented), both of which were used in four schemes. The Australian guidelines were used in three schemes, one of which used them in all stages of investigations, the other used it in the feasibility and implementation stages while the final scheme used it only in the investigations stage. Finally the South African guidelines and HACCP which were only used in one scheme with the former used in the feasibility stage and the latter in both feasibility and implementation stages.

These results were further broken down to compare the type of investigation carried out in the UK with that carried out in international schemes (Table 2.8). International scheme investigations involved a variety of frameworks, however a trend was noticed whereby local guidelines were generally used, i.e. Australian schemes favoured Australian guidelines and American Schemes favoured Pyne guidelines.

Table 2.8: Summary of the frameworks used to investigate the viability of surveyed ASR schemes, in order of most to least implemented

Method of investigation used	UK	International
Own	4	2
Modelling	5	0
Pyne	0	4
None	2	2
Australian	0	3
South African	0	1
HACCP	0	1

The Pyne methodology was implemented in four schemes in America, however it should be mentioned that there is some bias to this result as all four schemes were investigated by David Pyne, who also filled out four surveys. The Australian guidelines were used in the Australian schemes as well as one Spanish scheme which additionally used the South African guidelines and their own methodology to assess viability. Although other guidelines may be used, local guidelines are preferable as they take into account the local conditions for planning and designing ASR schemes. Two schemes, both of which were in America, did not implement a detailed viability assessment, one of which (Mesa northwest water reclamation plant) did not experience any threats that could have been mitigated by a more detailed viability assessment, while the other (Sand Hollow reservoir spreading basin) found that in hindsight, a better viability assessment may have been able to mitigate some of the threats.

The most common method employed to assess viability of ASR in the UK was modelling, followed by own internal methods. In two cases, a combination of both were used, while the two other schemes did not conduct a viability assessment and only expert judgement was used. Modelling is not a viability assessment framework in itself, it is one of the tools that should be used to perform the assessment (see Chapter 4). Three schemes used only modelling as their main method of viability assessment, while two schemes used modelling and their own internal methodology. All the UK schemes used either their own methodology only, modelling, only or a combination of the two.

It can be inferred that the quality of investigation programmes for ASR schemes in the UK are not appropriate, and could be a reason for the low rate of implementation despite several pilot investigations. Of the seven UK respondents, only two schemes proceeded to full scale implementation, five of the seven respondents stated that a more comprehensive risk assessment would have benefited the schemes. These results therefore provide some evidence pertaining to the value of the SPT and its role in improving the viability assessment process, thereby promoting wider implementation of ASR in the UK.

Results of the survey: key threats to ASR schemes

The second part of the survey attempted to identify the key threats to ASR schemes and whether these could be characterised by a comprehensive risk assessment. The data from this section was compared to the SPT to ensure the most prevalent threats as identified in the survey and the conditions presenting these threats were included in the SPT.

Figure 2.9 below shows the results of the threats to the schemes as identified in the surveys. Respondents were asked to include up to four threats to the successful operation or further development of a scheme. An important finding of the survey was that water quality issues were identified as the most common threat for both international and UK ASR schemes. The second most common threat according to UK respondents was hydrological limitations while international respondents identified all other threats with the exception of source water availability as equal second. These findings therefore support the structure of the SPT, which has dedicated *hydrogeochemical* and *hydraulic assessments*, which promote more detailed investigations into water quality issues and hydrological limitations respectively – the two threats most prevalent to UK schemes. It should be noted that the other groups of threats are also included in the SPT.

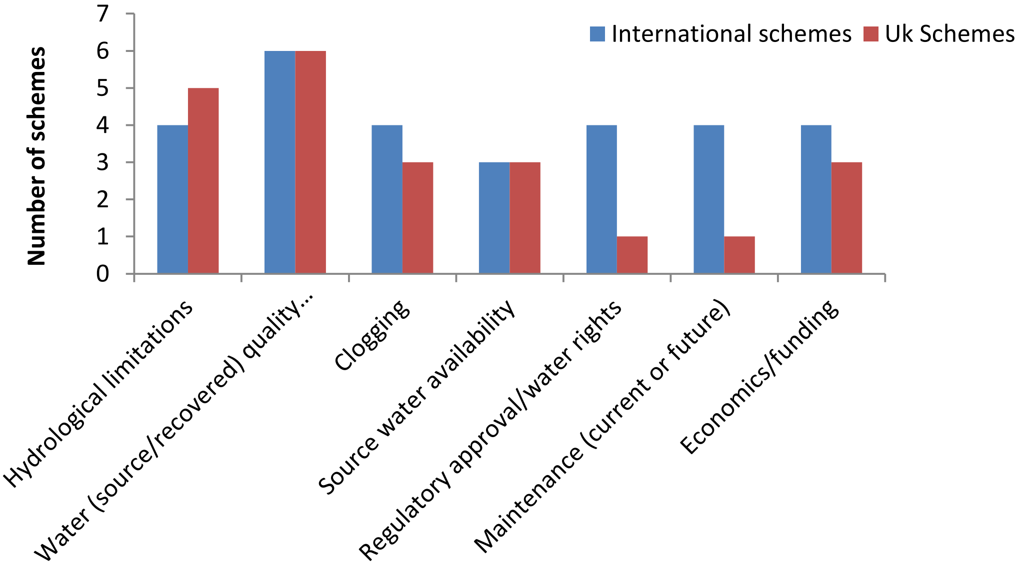


Figure 2.9: Threats to the successful implementation of ASR schemes

Regulatory approval/water rights and maintenance (current or future) showed the biggest variation in the difference between the results from UK and international schemes, with international schemes identifying them as threats more often than UK schemes. A reason for this could be that all but two of the UK schemes are pilot schemes that did not proceed to implementation and these threats are realised in the longer term, while technical threats such as hydrological limitations and water quality issues are usually realised in the initial testing phase.

There are useful potential lessons that can be learnt using the experience from past failed schemes in the UK and the international experience. Where more thorough assessments were conducted using ASR specific guidelines such as the Australian guidelines and Pyne guidelines, technical threats such as hydrological limitations and water quality issues were avoided, however strategic threats such as maintenance, source water availability and funding remain. These need to be quantified in more detail in the initial stages of assessment, taking into account the local conditions and requirements. These insights provide some evidence of the importance of *strategic assessment*, which many viability investigations overlook. This is therefore considered a further strength of the value of the SPT. Finally, it should be noted that all of the threats to ASR schemes identified in the survey were already addressed in the SPT. The causes and indicators of these threats as identified in the survey were cross checked with the SPT to ensure that the SPT promoted early detection of these threats where possible. The mitigation measures identified in the survey were also used to provide some context/guidance on the complexity of a scheme if these threats were likely.

2.6.3 Comparison with other guidelines

Guidelines currently available to assist proponents in identifying threats and assessing the viability of ASR schemes were evaluated against each other and the SPT. The guidelines used in the comparison included South African Guidelines (Ravenscroft and Murray, 2010), Dutch Guidelines (Stuyfzand and Doomen, 2004), Pyne Guidelines (Pyne, 2005b), Australian Guidelines (NRMMC-EPHC–NHMRC, 2009), a decision support tool (DST) developed by Brown (2005) (henceforth termed Brown DST) and another decision support tool developed by Kazner et al., (2012) (henceforth termed Kazner DST). The results of the first stage of analysis can be found in Figure 2.10 below.

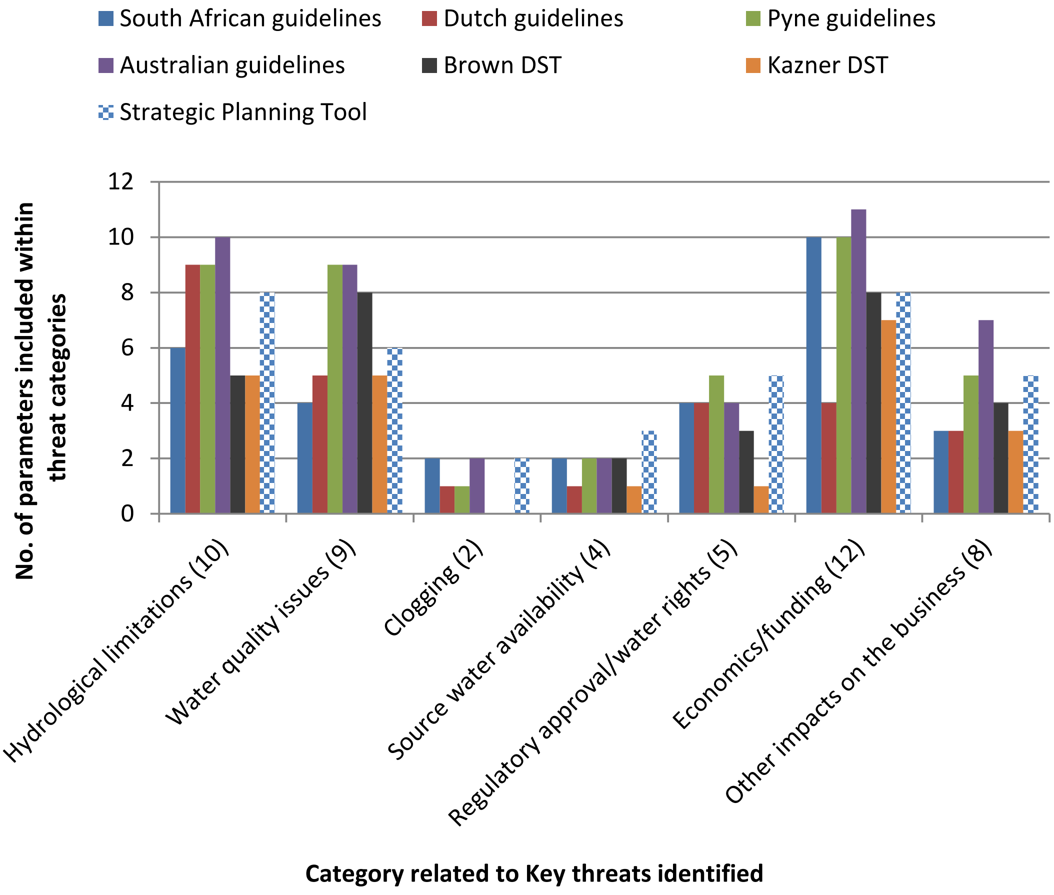


Figure 2.10: Initial comparison of ASR guidelines and decision support tools (DST) currently available, with the proposed Strategic Planning Tool

The four guidelines and two DST's were compared against the proposed SPT, by first identifying and comparing the parameters considered by each guideline/DST. The parameters were then grouped into the categories identified in the survey as generating the key threats to ASR, i.e. Hydrological limitations, Water quality issues, Clogging, Source water availability, Regulatory approval/water rights, Economics/funding and Other impacts on the business was also included. Each category contains various parameters, for example the Water quality issues category included parameters such as source water quality, native water quality, pre-treatment/post-treatment requirements, etc. Further details on this can be found in Appendix G. The total number of parameters in each category, as identified by analysing the guidelines/DST's, are indicated in brackets next to each category shown in the graphs. Each guideline/DST is represented in Figure 2.10 by considering the number of parameters met within each category of threats. Details on this comparison can be found in Appendix G.

It can be noted that the Australian and Pyne guidelines are the most inclusive, with the Australian guidelines including the most parameters in all but the "Regulatory approval/water rights" categories, where the Pyne guidelines and the SPT are more inclusive. It should also be noted that when considering just the decision support tools currently available, the SPT is the most inclusive in all categories except the "Water quality issues" category, where the Brown DST out-performs the SPT, and in the "Economics/funding" category where its performance is equal to the Brown DST. These results however are based on a general evaluation which doesn't take the UK context or the objectives of the SPT into consideration.

The results were adjusted to reflect the aim of the SPT, which is to simplify the process of assessing the viability of the scheme and to provide a methodology that enables a unified, holistic understanding of threats, requirements and opportunities of a potential ASR scheme before implementation of detailed investigations and a pilot scheme. The adjustments made to the evaluation and the reasoning for these changes can be found in Appendix G. Figure 2.11 illustrates the results of the evaluation once the UK context and the objectives of the SPT have been considered.

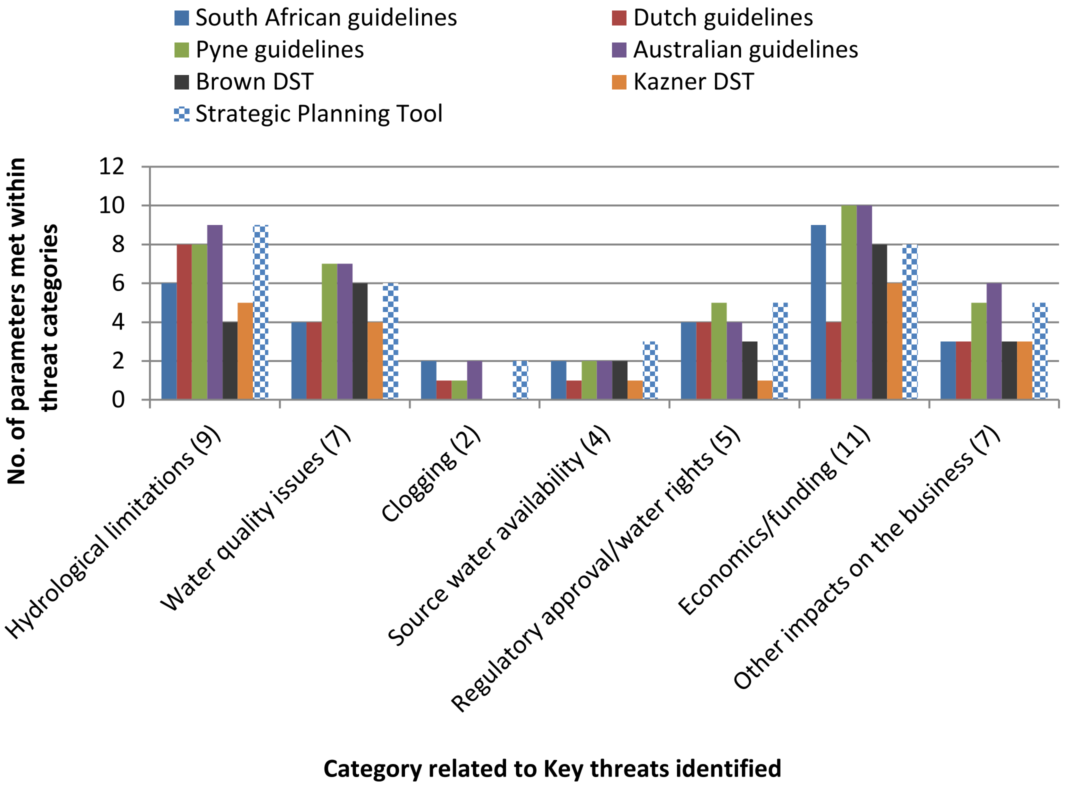


Figure 2.11: Comparison of ASR guidelines and decision support tools (DST) currently available, adjusted for the UK context and objectives of the proposed Strategic Planning Tool

The SPT was still out performed by other guidelines in some categories, therefore outputs of this evaluation were incorporated in the SPT by including parameters identified in other guidelines that would improve the tools ability to achieve its aim. Details on these parameters can be found in Appendix G. The final results of the comparison of all the guidelines in the context of UK and the objectives of the SPT, after the missing elements identified from the other guidelines were incorporated, can be seen in Figure 2.12. These results show that the SPT performs as well or better than the other guidelines in assessing threats in all categories.

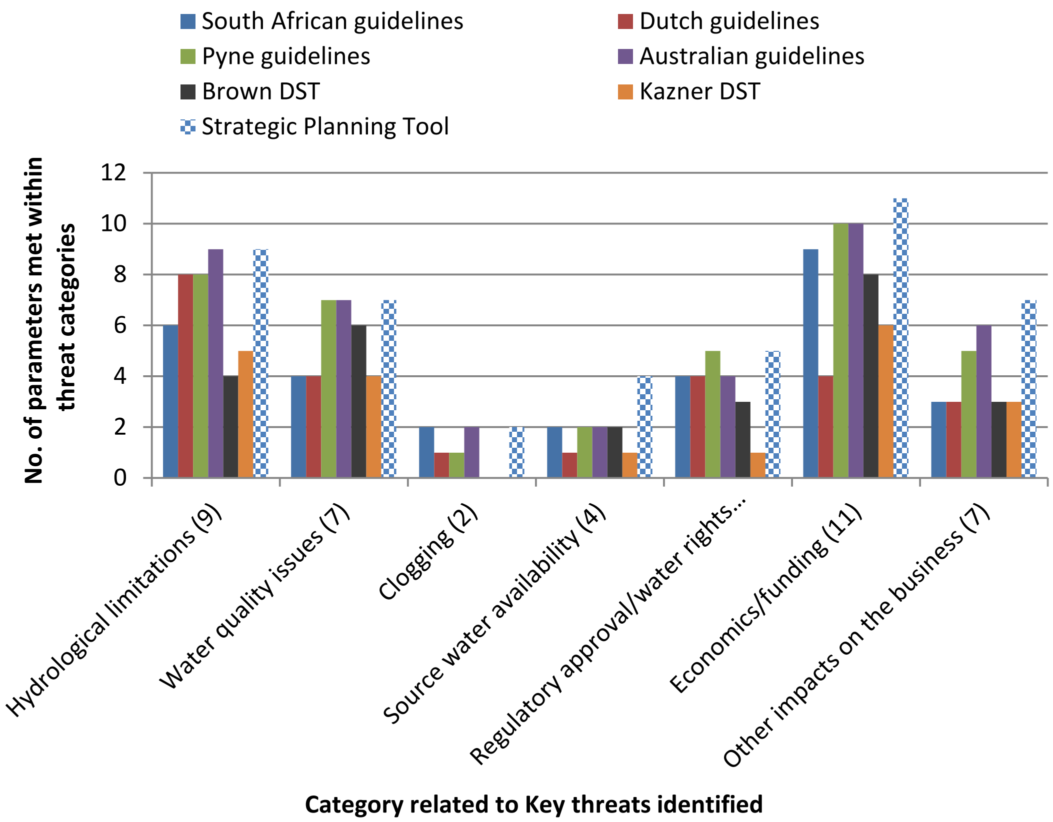


Figure 2.12: Comparison of ASR guidelines and decision support tools (DST) currently available after adjustments and missing parameters identified in other guidelines were included in the Strategic Planning Tool

It is important to mention that the SPT is not a simple compilation of guidelines currently available to assess the viability of ASR schemes. It is unique as it provides a step by step approach to identify the threats and processes that need to be considered to successfully operate an ASR scheme. The comparison with the other guidelines was used only to ensure that all relevant threats and indicators to these threats were considered for the SPT to be effective in achieving its aim.

The main strength of the developed tool is that it is a process oriented methodology which provides a clear step by step framework to assessing viability. As explained in Section 2.2.6, process orientation ensures that the risks associated with processes (e.g. pre-treatment) such as reliability, robustness and resilience of the technology are also included, which is important when assessing scheme viability, as it impacts costs. The process oriented methodology also allows the SPT to be iterative to an extent, which sets it apart from the other available frameworks. For example, initial pre-treatment requirements are determined by regulatory considerations. However, at a later stage, technical considerations such as potential for clogging and deterioration in water quality during storage are considered by using the results from PHREEQC modelling, to determine if adjusting the pre-treatment could mitigate these issues. The SPT provides a process by which the user can adjust the pre-treatment and then use PHREEQC to determine whether the new injectant quality would mitigate any of the identified issues with respect to the potential for clogging and water quality changes. It therefore provides an iterative process by which a balance between pre and post treatment requirements can be realised.

A further strength of this SPT is that it is formed in the context of UK regulatory and sector structure. The water industry in England and Wales has a unique structure in that although the utilities have a monopoly, they are tightly regulated by OFWAT, the economic regulator for the water sector in England and Wales. OFWAT promotes economy and efficiencies whilst protecting the interests of consumers. Companies must comply with OFWAT requirements as well as those of the Environment Agency and shareholders. This structure shapes the way the industry assesses water supply options.

It is important to note that ASR is relatively well established in the USA, Australia and some countries in the EU such as the Netherlands (IGRAC and Acacia Institute, 2007), and each of these countries have established their own criteria/framework for assessing the viability of ASR. In the USA the Pyne and Brown guidelines were formed, Australia formed the Australian guidelines for MAR and the Netherlands also have their own guidelines. The SPT is the first published framework for assessing viability of ASR schemes in the UK.

2.6.4 Testing during deployment of the Tool

A hydrogeological and hydro-geochemical assessment was commissioned by Anglian Water Services to identify suitable areas of the Sherwood Sandstone aquifer for ASR and identify the potential sites for pilot well construction (Diamanti and Hardisty, 2015). The SPT was utilised by two hydrogeologists from Mott Macdonald (who were contracted to complete the assessment) to guide this investigation through the issues that require consideration when assessing the viability of potential ASR sites.

The implementation of the SPT was evaluated using two techniques; observation of the users during deployment and a debriefing after completion. Templates were created to ensure a structured evaluation was conducted. Two aspects of the tool were evaluated; (a) the tool as an artefact, i.e. the reliability and clarity of the Tool, and (b) the tool as a function, i.e. the tools ability to achieve the intended outcomes. Each of these aspects were broken down into performance attributes and the method of evaluation (observation/debriefing) to form a suitable evaluation programme. Debriefing was utilised to evaluate both the tool as an artefact and the tool as a function, and observation was used to evaluate only the tool as an artefact. As can be seen in Appendix H, the user's views on the SPT's ability to achieve the performance attributes were ascertained by asking pre-determined questions during the debriefing, and looking for pre-determined behaviours/situations during observation.

It should be noted that the SPT is intended to provide an initial assessment of the viability of a potential ASR scheme. During testing however, the SPT was used as part of an investigation to identify one or more sites for the drilling and testing of a pilot ASR well in the Sherwood Sandstone aquifer. This therefore narrowed the scope of the investigation significantly with most of the Strategic Assessment not being relevant to the scope of work. Furthermore PHREEQC modelling was not completed and therefore there was minimal input of detail in this section, which meant there was limited detail on the *hydrogeochemical assessment* in the report produced by the web-app. The implementation of the SPT was therefore not in the intended manner, as only the technical viability was of concern in this investigation, however some valuable insights were still provided by its deployment.

Evaluation of results from the templates

Overall the SPT performed well in its first application. A summary of the user's responses to the debriefing and the observations made are shown in Appendix I, along with a brief commentary on the validity of these responses and observations. Overall the function of the tool was determined to be suitable as it was found to achieve the intended outcomes which were:

1. Provide a unified, holistic methodology to assess viability of ASR in the UK
2. Provide a methodology that would allow businesses unfamiliar with ASR to assess the viability of such schemes
3. Provide a process oriented methodology that promotes the SPT's use across different sites
4. Provide a cost effective methodology to assess the viability of such schemes
5. Provide guidance specific to the UK context by considering the regulations in the UK
6. Provide some indication of the complexity and cost of the scheme as well as provide a scope for investigation during a pilot

The users felt that the SPT adequately integrated and consolidated all the elements of ASR thereby providing a unified, holistic methodology that could be used by businesses unfamiliar with ASR to understand the potential threats involved, and the factors that need to be considered when planning and designing an ASR scheme. The advantage of the process oriented methodology was also recognised as it was used to compare three different potential sites during deployment. It is therefore justifiable to claim that the SPT is versatile enough to use across different sites within a UK context.

Cost effectiveness of the SPT was measured by considering whether the outputs of the tool met the desired outcome (effectiveness), if the outputs measured up to the resources spent to produce them (efficiency) and if the time invested was seen as appropriate considering the outputs provided (economy). These form the 3E's of measuring cost effectiveness as defined by the National Audit Office. The users felt that the tool did not meet the desired outcome as a "tick box" exercise. This expectation was likely a result of a miscommunication in the briefing provided to them by Anglian Water, as the tool was never meant to provide such an output. No comment was offered on the efficiency of the tool as the users were contracted to complete the investigation and the resources spent were Anglian Water's. Following up on this comment, Anglian Water was approached, and they felt that this condition was fulfilled. Finally, the time invested was seen as appropriate considering the outputs provided. It can therefore be concluded that the tool was cost-effective.

Understanding the regulatory requirements was not in the scope of the contracted work and the users were not confident in their expertise in this aspect, however they felt that most regulatory requirements with regards to ASR in the UK were covered by the SPT. Similarly, the users were only concerned with specific aspects of a viability study therefore although they felt the SPT provided an adequate indication of the complexity of a scheme, they were not confident in their assessment.

The final objective of the SPT was to provide an indication of the complexity of the scheme, the ability to roughly estimate the cost of the scheme as well as provide a scope for further investigations during a pilot. The users agreed that the tool does provide an indication of the complexity of the scheme however the users were mostly concerned with specific aspects and therefore were not able to answer with confidence. In terms of the ability to roughly estimate the cost of the scheme, the users felt this was provided but suggested the presentation of the costing section could have been improved upon, by adding an ability to sum up the costs and being more explicit that only actual costs should be entered. The lack of these explicit instructions were however intentional as it is not always possible to get costs at such an early stage of scheme development, therefore this format allows the user to make notes on factors that would influence costs, which could be taken further at the next stage of investigation. Finally, the users felt that the SPT did provide a scope for further investigations during a pilot however they identified some factors which should be included in the tool to improve its functionality in this aspect. These included identifying faults and fractures in the geology, potential sources of contamination around the borehole, size of distribution pipes and existing infrastructure e.g. roads. These could all be included in the logic of the SPT.

The tool as an artefact was tested by considering the connectivity between relevant sections of the SPT, ease of use, clarity and the format of the report. Connectivity of the knowledge between relevant sections of the tool was assessed during debriefing by asking the users if they had an improved understanding of the interconnections in the tool (e.g. how ‘availability of water’ in the *strategic assessment* can impact the ‘number of recharge wells required' in the *hydraulic assessment*), and whether there were any connections made in the SPT for which the reasons were unclear. The SPT performed well in unifying knowledge from different aspects of the tool thereby providing the users with a better understanding of the interconnections. The users felt that the connections did not always come across however this may be because modelling was not carried out during the assessment and majority of connections relate to modelling. Other connections were more subtle.

Connectivity was assessed during observation by logging questions on the relevance of "reminders" provided, whether the users were navigating back to previous sections to make sense of the reminders, questions on why sections were connected, any disagreement about the influence of different sections on each other, or any other comments related to connectivity. Users were clear on the purpose of the reminders, able to follow the logic appropriately and did not need to keep navigating between pages to understand/answer the requirements of various sections. They also understood and agreed with the connections formed between different sections.

Ease of use was evaluated by debriefing users on the clarity of the logic and whether there were any aspects of the SPT that were difficult to understand/use. Overall the tool was found to be relatively easy to follow however it was suggested that the home page could have been clearer on which sections were completed and which remained to be completed. This along with a progress bar would have made progress clearer to the users. A part of the SPT identified as unclear was that on 'the suitability of the aquifer for recharge and recovery' section of the *hydraulic assessment*, where a question is asked whether 'the storage capacity is sufficient', and the users did not have information on the amount of storage required. This was investigated further and it was determined that the amount of storage required is addressed in the 'source water considerations' section of the *strategic assessment* however the connection was missing with the *hydraulic assessment*, and so the reminder with information on the storage required was not shown in the *hydraulic assessment*. This was an oversight in the tool's development which can be corrected.

During observation, ease of use was evaluated by logging if the users navigated away from the page before an answer was given, pages that were left blank due to confusion, if the users understood how to populate the answer, how long it took to complete a run through the tool and any other observations relating to the ease of use. The main entries related to understanding how to populate the answer. In the ‘need for scheme’ section of the *strategic assessment*, the users felt that the table of water resources comparison was too long, however this is likely as this part of the viability investigation was not in the scope of their work therefore seemed of little relevance. The ‘objectives of the scheme’ in the same section was wrongly populated which was also likely due to the rush to get through this section as it was not in the user’s scope. There was some uncertainty as to whether the ‘regulatory requirements’ in the *strategic assessment* were to be answered from Anglian Water’s point of view or the Environment Agency’s, although the explanations (see Appendix B) seem clear in that the whole tool is to be answered from Anglian Water’s perspective. The confusion is likely due to the rush to get through this section as once again it was not in the scope of their work. The users were unsure what was meant by some of the terminology such the “width of the aquifer” in the ‘suitability of the aquifer for recharge and recovery’ section of the *hydraulic assessment*, and the difference between “robust” and “reliable” in the ‘pre-treatment and post-treatment’ section of *hydrogeochemical assessment*. However, these were quickly resolved when the questions and explanations were re-read more carefully. Overall the SPT seemed to be relatively easy to use and was completed in thirty minutes, however it should be noted that it was not fully completed due the restricted scope of the work contracted to the users.

The format of the report produced following completion of the SPT was assessed during the debrief by considering if it could be used as a skeleton for viability study and whether the report adequately represented the information input into the tool. The users determined that the report produced could be used as a skeleton for a viability study, although not in this particular case as the scope of the tool is wider than the scope of the investigation tasked. Overall, the report adequately represented information input in the tool however the format of the report could be improved. Furthermore, it would be useful to have the traffic light buttons (rather than words indicating the level of confidence) next to the answers. Some problems in the reporting ability were identified, such as in the *initial cost assessment*, whereby the report only shows the content of the comment boxes without the heading of the cost being referred to. It is therefore difficult to differentiate between costs in the report. This is an oversight in the coding of the web-app and is relatively simple to rectify. In the ‘suitability of the aquifer for recharge section and recovery’ of the *hydraulic assessment*, the question “Is the aquifer appropriately confined?” comes up twice however there is only an answer visible for one occurrence. This is because the report is pulling information from both the physical and chemical storage methods, even though only one of the storage methods is chosen and investigated further. This can also be corrected relatively easily.

The final attribute of the SPT that was assessed was its clarity, by observing and recording whether clarification on the requirements of any part of the tool was required, if help was required to understand the logic, if the users needed to re-read the question and if differences arose between the user’s interpretation of the questions and the intended interpretation. Any other observations made relating to the clarity of the tool were also recorded. Two points of clarification were made, firstly there was some uncertainty about what “purge water” was in the ‘regulatory requirements’ section of the *strategic assessment* and when it would be a concern. The term “purge water” is not clearly defined in the tool as the knowledge is assumed, however it is noted that it should be defined more clearly. This can be incorporated relatively easily, by enhancing the explanation of the term and requirements. Secondly, in the ‘initial flow modelling’ section of the *hydraulic assessment* there was some confusion about re-questioning if chemical/physical storage is used, as it is already asked in the ‘suitability of the aquifer for recharge and recovery’ section. This can be resolved by adjusting the logic path to ensure that the user is only asked to define the type of storage once, in the ‘suitability of the aquifer for recharge and recovery’ section.

Some help was occasionally required to understand the logic such as in the ‘clogging potential’ section of the *hydrogeochemical assessment*, where the users wondered why actual limits/guidelines for appropriate dissolved organic carbon were not provided. As discussed in Chapter 3, there is no defined guideline for this, since appropriate levels vary greatly depending on specific site conditions, therefore this is unfeasible. This was explained to the users however it would be useful to include this explanation in the tool. Where several considerations were grouped onto one page, the users were unsure whether the confidence indicators refer to individual questions or to the whole page. It was clarified that the indicators should be for each question, however only one appears per page even in cases where multiple questions are asked on the page. It is recognised that this needs to be altered so that there is one confidence indicator per question.

Finally, in the ‘pre-treatment and post treatment requirements’ section of the *hydrogeochemical assessment*, there was confusion as to why the users were again asked to adjust the potential pre-treatment required, after a new injectant water quality is input into the PHREEQC model, when this was already input once (see logic diagram in Appendix A). There is a loop whereby PHREEQC modelling is used to determine if the injectants quality will likely cause adverse reactions during storage. If it is, then an option is offered to adjust the pre-treatment to minimise adverse reactions, following which the user is asked to model the new injectant to determine if adverse reactions are likely. The confusion by the users is likely due to the fact that they did not perform PHREEQC modelling therefore did not “adjust the pre-treatment further” in the model and re-check for adverse water quality changes. They attempted to simply deduce potential changes and therefore did not see the need for the rest of the loop.

The only section where the users needed to re-read the question was in the ‘regulatory requirements’ in the *strategic assessment*. This was mainly because a regulatory evaluation was not in the user’s scope of work, therefore they were not confident in what was being asked.

There was one occasion where the user’s interpretation of the question differed from the intended interpretation. When considering the “acceptability of the water” in the ‘source water considerations’ section of the *strategic assessment*, acceptability of the water was considered from purely an operational point of view. The intention of this element is to determine the suitability of the water from a public and regulatory point of view, as operational considerations are tackled in the *hydrogeochemical assessment*. Although an example of public acceptance of recycled water is provided, the explanation of the requirements could have been clearer.

Other points which indicated a lack of clarity included occasional confusion on the use of some comment boxes and whether they were required. In some cases the reason for the comment box is not obvious however they are present in case the user has any notes to make for their reference. In the *initial costs assessment*, reminders from chemical storage were shown even though physical storage was selected as the method of storage required. This is an oversight in the writing of the web-app which can be corrected. A final comment was made when the run through the SPT was complete, that the end was abrupt and it was unclear that they had completed running through the tool and what the next steps were. A more obvious end can be incorporated to ensure the users are aware that they have finished and what the next steps should be.

Changes to the SPT as a result of testing during deployment

Appendix J provides a summary of the suggestions made on potential changes from the debriefing and observation during use of the tool, which can be actioned to improve the tool as a function and an attribute. It should be noted that only the changes to the logic of the tool and explanations can currently be made, and these have been highlighted in Appendix J and shown in Appendix K. Changes made to the logic diagrams have been shown in a different colour, and changes made in the explanations have been highlighted. Changes to the actual web-app could not however be implemented due to a lack of funds and time. The changes required have however been logged and can be implemented at any time.

2.7 Conclusions

A lack of precedence for ASR in the UK and uncertainties with respect to regulatory requirements, and abstracted water quality and quantity means ASR is perceived as a high risk option. To effectively evaluate the feasibility of a potential scheme, the acceptable level of investment needs to be established by assessing the risk to business. Risk assessment frameworks focus on the risks to human health, the environment and/or operations, therefore do not account for the risks to the business. Furthermore, risk assessment frameworks are hazard oriented, which limit their use where the proponent is unfamiliar with the potential hazards they may encounter. The decision support tool developed in this research evaluates potential threats to the business, environment, human health and operations in the context of UK regulations. The process oriented methodology breaks down the complexities associated with hazard oriented risk assessments by calling attention to the variety of processes that may result in hazards, and the conditions that would promote these hazards. This allows businesses unfamiliar with ASR to understand the potential threats to a scheme, thereby improving confidence in the scheme.

3 Critical review of current knowledge on clogging in ASR schemes

3.1 Introduction

Clogging is a significant barrier to the successful operation of ASR schemes since it has the potential to reduce injectivity which increases the pressure head required (and energy consumption) to maintain the injection rate (Bloetscher et al., 2004). Although clogging is an operational issue, it can also become a regulatory compliance issue, since higher injection pressures increase the risk of over-pressurization of the aquifer and/or overlying confining beds (Martin, 2013b) , and can intensify mounding and drawdown which in turn increases the impact of operations on the environment and other users. As discussed in Chapter 2 clogging is one of the most important causes of operational failures in ASR schemes and therefore deserves consideration at the earliest point in the planning process. It is strongly related to the quality of recharge water, however the interaction between the source water, the native groundwater and the aquifer minerals, borehole construction and the design of recharge facilities also have a significant influence. The potential sites for clogging are the recharge wells, the gravel pack or surrounding aquifer matrix and the recovery wells.

Injection wells are vulnerable to clogging which increases resistance to flow. Clogging in recharge wells generally occurs in the wall of the borehole, in the gravel pack and in the formation immediately surrounding the bore (Bloetscher et al., 2004). If injection rates are to be maintained then regular well redevelopment is required, which increases costs. Potential clogging of the aquifer matrix itself is more difficult to predict as it can occur due to factors unrelated to water quality such as mechanical compaction, air entrapment and clay dispersion. The higher injection pressures required as a result of clogging can also result in mechanical compaction of the aquifer matrix, which exacerbates the problem by further increasing the recharge pressures (Pyne, 2005b). The clogging mechanisms that may impact an ASR scheme include physical clogging, biological clogging, particle rearrangement, geochemical reactions, air entrainment and gaseous binding, clay swelling and dispersal (Pavelic et al., 2008). This chapter aims to provide information on potential clogging mechanisms that may impact an ASR scheme, evidenced by a thorough literature search and will address the following research questions:

1. What are the factors which influence/increase the potential for clogging?
2. Can available literature be used to help operators assess potential clogging mechanisms that may impact their ASR scheme?

3.2 Research Approach

Knowledge on clogging in ASR schemes has been generated through laboratory studies, field studies and reviews of pilot and operational sites as reported in Sections 3.4 and 3.5, all of which have been used to investigate the occurrence and mechanisms of clogging in a variety of hydrogeological settings. Academic and grey literature available in this field was reviewed to understand the variety of clogging mechanisms that may impact an ASR scheme and the parameters that influenced these mechanisms. Initially, a targeted review of field investigations was carried out, to identify the clogging mechanisms reported at various operational and pilot ASR sites using a variety of recharge water qualities and aquifer types. This was further dissected to identify the clogging mechanisms reported at ASR sites using Sandstone aquifers, in order to determine if there were any clear differences in the type of clogging experienced at sandstone sites as compared to other aquifers. There was a particular interest in sandstone aquifers as this is the target formation for the potential ASR site in Newton on Trent, Lincolnshire which would be operated by Anglian Water Services, who are the project sponsors. Further research included a review of laboratory studies, as well as field studies and reviews of pilot and operational to provide an overall evaluation of the influence of different parameters on clogging. An overview of the research approach is illustrated in Figure 3.1.

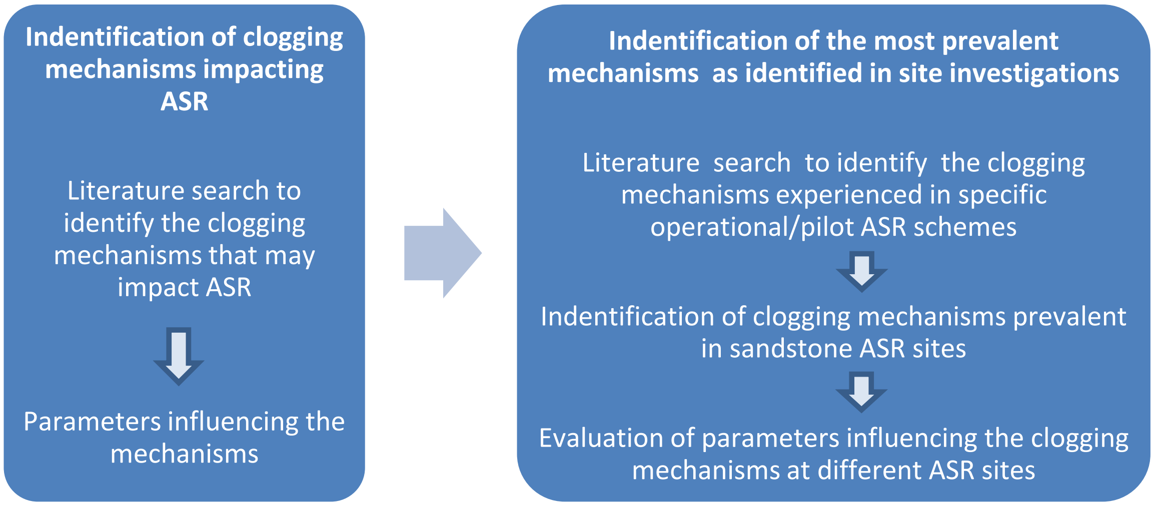


Figure 3.1: Approach to provide recommendations on managing clogging

The information provided in this chapter will be used to discuss the potential clogging mechanisms which may influence the proposed ASR scheme, potential pre-treatment to minimize clogging potential and techniques currently available to manage clogging, since prevention is not always possible. This will be done in the context of water quality changes and the overall impact of the scheme's viability in Chapter 5.

3.3 Overview of clogging mechanisms impacting ASR schemes

3.3.1 Physical clogging - Filtration

Particulates in injected water fill the aquifer/filter pack pore space, resulting in the formation of a filter-cake around the borehole wall. Even a small increase in suspended solids can have an appreciable effect on head build-up (Vecchioli and Ku, 1972). The extent of clogging by this mechanism depends on the relationship between pore size distribution within the aquifer and the nature, size, velocity and loading of the particulates in the injectant. Aquifers/filter packs that are composed of fine grains and small pores are more susceptible to clogging than those with larger pore spaces (Bichara, 1986; Wood et al., 2004). Furthermore, aquifers with a secondary porosity are less susceptible to clogging than those with mostly primary inter-particle porosity (Pitt and Magenheimer, 1997). Physical clogging could potentially be a problem for the selected site as the Sherwood Sandstone mostly has a primary inter-particle porosity (Gale et al., 2002).

The Membrane Filtration Index (MFI) was introduced to measure the physical clogging potential of a source of water by Bouwer, (2000), and is defined as “the suspended-solids content of the water in terms of the slope of the straight portion of a plot of time/volume versus volume in a membrane filter test, using, for example, a 0.45-µm Millipore filter”. Clogging by filtration has been described as a three step process by Huisman and Olsthoorn (1982) and Pyne, (2005) as illustrated in Figure 3.2 which shows the results of a typical MFI test.

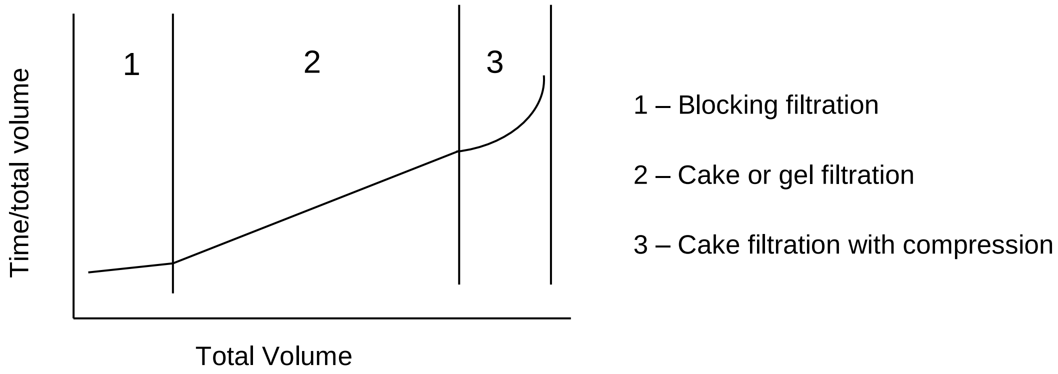


Figure 3.2: Stages of clogging on a membrane filter (adapted from Hutchinson, 1997; Pyne, 2005)

Blocking filtration is the initial stage whereby particulates physically block the pore spaces. As injection continues the filter cake thickens and undergoes compression which is indicated by a linear increase in injection pressures with time. The final stage (cake filtration with compression) results in a severe increase in injection pressure. Increasing recharge pressures to maintain recharge rates can therefore have a negative impact on recovery as this process compresses the clogged layer which exacerbates the resistance. It is therefore important not to ignore increasing recharge pressures and to address it at an early stage, as the longer it is left, the more difficult remediation can get.

3.3.2 Biological clogging

Microbes will grow in both anaerobic and aerobic conditions so long as sufficient nutrients are present, usually at the well screen openings and the filter pack (Huisman and Olsthoorn, 1982). Wood et al. (2004) have clearly shown that the grain size of the receiving aquifer has a significant impact on the amount of biological clogging, with a smaller grain size increasing the risk. This implies that extra precautions should be taken to prevent biological clogging when injecting into a fine grained aquifer such as the consolidated Sherwood Sandstone aquifer.

The microbes produce extracellular polymers (polysaccharides) which create a biofilm that reduces aquifer permeability (Shaw et al., 1985; Taylor and Jaffé, 1990). Microbial clogging can develop over varying timeframes and can act as a catalyst for other forms of clogging. For example, the biofilm can trap particles present in the water, which further decreases permeability and accelerates clogging (Shaw et al., 1985). This was shown clearly by Rinck-Pfeiffer et al. (2013), where a combination of the micro-organisms and suspended solids produced a rate of clogging which exceeded the sum of clogging rates of water containing only suspended solids and only microorganisms.

3.3.3 Particle rearrangement

When flow is reversed during recovery, aquifer fines can be mobilized and rearranged into a lower porosity (hence permeability) configuration. This clogging mechanism has a minor impact as it only occurs in the initial injection and recovery cycles, but the process is irreversible (Maliva and Missimer, 2010). Particle rearrangement is not generally experienced in consolidated aquifers, but can still be prevalent in the gravel pack rather than the aquifer itself (Pitt and Magenheimer, 1997). The effect on the ASR system in this situation would be identical to that if the aquifer was clogged.

3.3.4 Geochemical reactions

Introducing water that is incompatible with the native groundwater or the aquifer minerals can result in chemical reactions that alter the aquifer's hydraulic properties (Pavelic et al., 2008). Dissolution, precipitation, ion-exchange, ion-adsorption and oxidation-reduction are among the reactions that may occur. Dissolution is more likely to occur in carbonate aquifers where calcite dissolution can increase permeability and therefore has the opposite effect to clogging, thereby mitigating some of its effects (Rinck-Pfeiffer et al., 2000, 2013). Dissolution can also mobilise dissolved materials and produce turbid water, increase the potential for well instability and create preferential flow paths, all of which are undesirable. Calcium carbonate precipitation is also relatively common where it is present in the native water and its precipitation is dependent on the partial pressure of CO_2 gas in the water and the pH. Potential for precipitation can be assessed by calculating the pH and temperature of the mixed recharge and native water, determining the pH that would result in precipitation and the concentration of calcium carbonate in the native water (Pitt and Magenheimer, 1997). Carbonate dissolution and precipitation are unlikely to be an issue in the proposed scheme since the target aquifer is composed of sandstone.

Introduction of water containing oxygen into a reducing environment may result in precipitation of iron and manganese hydroxides (Maliva and Missimer, 2010), which cause clogging in the aquifer matrix and wells. This precipitation can in turn stimulate bacteria (e.g. iron and manganese bacteria) which further develops the clogging process as explained in Section 3.3.2. Ion-exchange and ion-adsorption are discussed in the clay dispersion and adsorption sections respectively.

3.3.5 Air entrainment and gaseous binding

Air entrainment occurs when water cascades into the well, forming bubbles of air which can block pore spaces in the well screen, filter pack or aquifer formation and restrict flow in a similar fashion to suspended solids. Air bubbles can flow out from the ASR well and will move through the aquifer until they encounter a pore through which they cannot pass. It should be noted that entrained air will only reach the storage zone if the down-hole flow velocity is greater than the bubble-rise velocity (Huisman and

Olsthoorn, 1982; Pyne, 2005b) as gas bubbles have a higher buoyancy than water and will therefore move upward if the downward flow is less than the bubble-rise velocity. Huisman and Olsthoorn (1982) noted that resistance to flow due to air entrapment is rapid initially and then levels off as the rate of bubble migration into the filterpack/formation equilibrates with the rate of bubble dissolution. A system should be designed to minimize the potential for water cascading.

Dissolved gases may also be released from solution during storage (gaseous binding) due to an increase in temperature (e.g. when cold water is injected into a warmer aquifer) or a drop in the water pressure to below atmospheric (Huisman and Olsthoorn, 1982; Pitt and Magenheimer, 1997). This mechanism needs to be particularly considered where recharge is occurring in the winter as in the case of the proposed ASR scheme, since the recharge water is likely to be colder than the native water. Gas bubbles may also be released due to biological reactions such as the release of nitrogen gas due to denitrification of nitrates in the injected water (Maliva and Missimer, 2010).

There is an associated change in the redox potential in the area where air entrainment/gaseous binding occurs, which can influence the geochemical reactions and microbial activity in the area, further exacerbating clogging (Pyne, 2005b). CO_2 coming out of solution can result in precipitation of calcium carbonate, O_2 coming out of solution can create iron precipitates/promote microbial activity and bubbles of H_2S can provide nutrients for sulphate reducing bacteria (Pitt and Magenheimer, 1997). A site in the City of Tea Tree Gully, Australia experienced air entrainment at the onset of injection due to an oversight in the engineering design, which in turn encouraged growth of iron bacteria (Martin, 2013a). A simple air entrainment problem developed into a complicated clogging process driven by multiple mechanisms.

3.3.6 Clay swelling and dispersal

Displacing saline water with freshwater plumes can reduce hydraulic conductivity due to clay swelling and dispersion (Konikow et al., 2001). Where water is recharged into a brackish/saline aquifer, there is a large reduction in the electrolytic concentration when compared to the native groundwater. This encourages ion exchange between cations in solution and those associated with clays within the aquifer, encouraging either clay swelling or dispersion (Pavelic et al., 2008). Potential for dispersion is highest in swelling clays, and permeability reductions can be significant with clay contents as low as 1% (Konikow et al., 2001).

Swelling clays such as montmorillonite adsorb water in the interlayer molecular spaces, causing them to expand and block the pores. The degree of expansion depends on the quantity of exchangeable cations available in the clay (Maliva and Missimer, 2010). Dispersion is similar to swelling in that water is adsorbed during this process, however pore throats are blocked due to the deflocculation and mobilization of the clay particles (Maliva and Missimer, 2010). Dispersion is more serious than swelling as it causes a largely irreversible reduction in permeability, unlike the reduction in porosity due to swelling which is largely a reversible process if original salinity conditions are restored (Brown and Silvey, 1973).

Clay dispersal depends on the difference in salinity between the injectant and native water, and the quantity of swelling clays present in the aquifer. Increasing the native water salinity and swelling clay (e.g. montmorillonite) content can result in a larger reduction in permeability when fresh water is introduced (Konikow et al., 2001). However, an aquifer with a high montmorillonite content may not experience significant clay dispersal even where freshwater is injected into a brackish aquifer, if the injectant has a significantly lower Sodium Adsorption Ratio (SAR) compared to the SAR of the native groundwater (Barry et al., 2013). Chang et al. (2005) and Vanderzalm et al. (2013) found that source waters with the lowest salinity which also had a low SAR did not pose a risk to clay mobilisation. It should be noted that the target aquifer for the potential ASR scheme is a fresh water aquifer therefore clay swelling/dispersal is unlikely to be a problem at the site.

3.4 Review of clogging mechanisms reported at various ASR sites

The literature was queried to identify operational or pilot ASR schemes and the types of clogging experienced, the results of which are summarized in Figure 3.3 and Table 3.1 below. It can be seen that clogging is a problem at many ASR projects worldwide, with physical clogging being the most prevalent followed by biological clogging. Geochemical clogging is the third most common form of clogging, followed by air entrainment, particle rearrangement, clay swelling & dispersal and finally the least common mechanism was gaseous binding. It is worth noting that geochemical clogging is not widely reported, as reactions that result in clogging take long periods of time to develop (Pavelic et al., 2008) and often coincide with other forms of clogging such as biological clogging due to the presence of iron, which promotes growth of iron bacteria (Martin, 2013a). These results are supported by Rinck-Pfeiffer et al. (2000), who also found that physical clogging was the most common clogging mechanism reported followed by biological clogging.

The results were further broken down to identify the clogging mechanisms that are prevalent in consolidated sandstone formations as illustrated by Figure 3.3, as this is the target formation for the Newton on Trent ASR scheme. Physical clogging was still the most common mechanism however unlike the general results, this was followed by air entrapment, clay dispersal and particle rearrangement, and geochemical reactions and biological clogging were least common. These results should be viewed in context since the source of water has a significant impact on the clogging mechanisms. For example, biological clogging seems to be less prevalent in Figure 3.3 however this could be explained by the quality of source water used in these schemes, which was often treated to drinking water standards and disinfected. This is not to say that biological clogging is less common in Sandstone formations, rather that it is dependent on the quality of the recharge water. Sandstone is not a common target formation for ASR schemes as evidenced by the results of the sites surveyed where only 12 of the 87 were formed predominately of sandstone. Extreme care should be taken when making conclusions from this data.

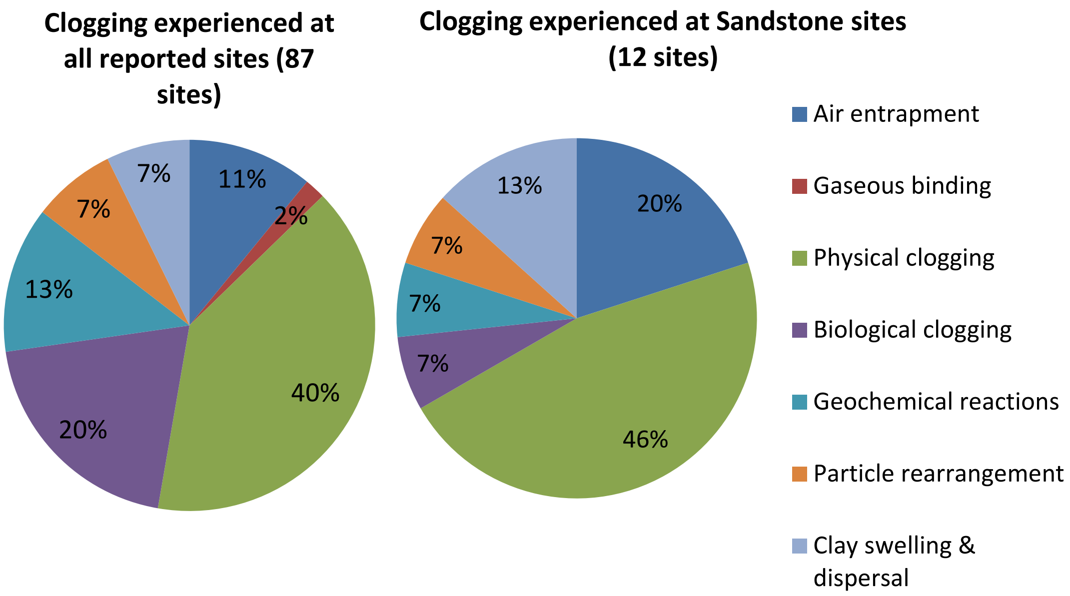


Figure 3.3: Type of clogging experienced at ASR sites – a compilation from the literature

Table 3.1: Summary of clogging experienced at all reported ASR sites

Clogging mechanism	Sites impacted	References
Air entrapment	Calleguas, California, USA	Brown, et al., 2006
	Las Vegas, Nevada, USA	Katzer and Brothers, 1989
	Centennial Water, Colarado, USA	Pyne, 2005b
	Grand Prairie area of Southern Arkansas, USA	Maliva and Missimer, 2010
	Kuwait ASR pilot	Pyne, 2005b
	City of Tea Tree Gully	Martin, 2013
Gaseous binding (due to microbial activity)	Myrtle Beach, South Carolina, USA	Maliva and Missimer, 2010
Physical clogging (including Algae in recharge water)	Jandakot, Western Australia	Johnston et al., 2013
	Cloudbreak Mine, Western Australia	Willis-Jones and Brandes de Roos, 2013
	Rosedale Golf Course, Aspendale, Australia	Page et al., 2011
	Urrbrae Wetland, Adelaide, Australia	Pavelic et al., 2008
	Highline, Seattle, USA (Algae in recharge water)	Brown, et al., 2006
	SE Salt Lake City, Utah, USA (Algae in recharge water)	Brown, et al., 2006
	Calleguas, California	Brown, et al., 2006
	Antelope Valley, California, USA	Brown, et al., 2006
	Highlands Ranch, Denver, USA	Pyne, 2005b
	Greenbay, Wisconsin, USA	Brown, et al., 2006

	Oak Creek, Wisconsin	Miller, 2001
	Hilton Head Island, South Carolina, USA	Brown, et al., 2006
	Myrtle Beach, South Carolina, USA	Brown, et al., 2006
	Wildwood, USA	Brown, et al., 2006
	Seattle Water, Washington, USA (Diatoms)	Pyne, 2005b
	Chesapeake, Virginia, USA	Pyne, 2005b
	Swimming River, New Jersey, USA (alum floc from backwash in the treatment plants)	Pyne, 2005b
	Kuwait ASR pilot	Pyne, 2005b
	Kingswood, Australia	Barry, et al., 2013
	Bolivar, Adelaide, Australia	Pavelic et al., 2007
	Bay Park, Long Island, NY	Vecchioli and Ku, 1972
	Lee County, FL	Fitzpatrick, 1986
Biological growth	Waalsdorp, Netherlands	de la Loma Gonzalez, 2013
	Amsterdam, Netherlands (iron reducing bacteria)	de la Loma Gonzalez, 2013
	Rosedale Golf Course, Aspendale, Australia	Page et al., 2011
	Urrbrae Wetland, Adelaide, Australia	Pavelic et al., 2008
	Antelope Valley, California, USA	Brown, et al., 2006
	Myrtle Beach, South Carolina, USA	Brown, et al., 2006
	Kingswood, Australia	Barry, et al., 2013
	City of Tea Tree Gully (iron bacteria)	Martin, 2013
	Bolivar, Adelaide, Australia	Pavelic et al., 2007
	Bay Park, Long Island, NY	Vecchioli and Ku, 1972
	Lee County, FL	Fitzpatrick, 1986
Geochemical reactions	Waalsdorp, Netherlands (iron precipitates)	de la Loma Gonzalez, 2013
	Watervlak, Netherlands (iron precipitates)	de la Loma Gonzalez, 2013
	Langerak, Netherlands (iron precipitates)	Pérez-Paricio and Carrera, 1999
	Rosedale Golf Course, Aspendale, Australia (iron precipitates)	Page et al., 2011
	Swimming River, New Jersey, USA (iron precipitates)	Pyne, 2005b
	Hermitage Dam ASR trial, Queensland, Australia	Vanderzalm et al., 2013
	Bolivar, Adelaide, Australia (de-clogging - dissolution)	Pavelic et al., 2007
	South London Aquifer Recharge Scheme, London	Anderson et al., 2004
Particle rearrangement (including mobilization of drilling muds or aquifer fines)	Mirrabooka, Western Australia	Johnston et al., 2013
	Urrbrae Wetland, Adelaide, Australia	Pavelic et al., 2008
	San Antonio, Twin Oaks, Texas, USA	Pirnie and Jackson, 2011
	South London Aquifer Recharge Scheme, London	Anderson et al., 2004
Swelling and dispersal of clay	Rosedale Golf Course, Aspendale, Australia	Page et al., 2011
	Norfolk, Virginia (clay dispersal)	Maliva and Missimer, 2010, Konikow et al., 2001
	Hermitage Dam ASR trial, Queensland, Australia	Vanderzalm et al., 2013
	Kingswood, Australia	Barry, et al., 2013

3.5 Managing Clogging

Studies on clogging in ASR schemes are abundant and laboratory studies, field studies and reviews of different sites have all been used to investigate the occurrence and mechanisms of clogging in ASR schemes in a variety of hydrogeological settings. Literature available in this field was reviewed to understand this risk and is summarized in Table 3.2 below. It should be noted that while Table 3.1 is simply a compilation of clogging mechanisms reported in field investigations, Table 3.2 additionally includes column investigations.

Table 3.2: Summary of literature on clogging

Study	Parameters investigated	Methodology
Rinck-Pfeiffer et al., 2000	Physical, biological and mechanical clogging, and carbonate dissolution Limestone Aquifer	Continuous flow column experiment using treated wastewater
Rinck-Pfeiffer et al., 2013	Physical and biological clogging, and carbonate dissolution. Limestone aquifer	Continuous flow column experiment using treated wastewater three columns – one with both suspended solids and microorganisms, one with only suspended solids and one with only microorganisms.
Vanderzalm et al., 2013	Iron precipitation, clay dispersion and swelling Fresh Sandstone aquifer	Pilot trial: pumping tests, SAR examined (clay dispersal), analysis of cores, PHREEQC analysis. Batch test for clay dispersion Column studies - 4 different source waters used
Konikow et al., 2001	Relationship between permeability changes and clay mineralogy, clay content and initial water salinity – clay dispersal	Column experiments using fine sand with 0-5% clay minerals were used to measure changes in permeability as a function of changes in salinity.
Hartwig et al., 2013	Physical clogging due to particle mobilisation.	One dimensional horizontal flow column
Holländer et al., 2004	Clogging due to physical deposition, air entrapment and biological effects. Effects of backwashing were also investigated.	Sand columns fed by water with suspended solids only, water with added air and a third water with micro-organisms.
Wood et al., 2004	Impact of grain size of the porous media on the rate and degree of biological clogging.	Column experiments with three grain sizes – fine, medium and coarse.
Pavelic et al.,	Local hydrogeology, ASR system	Review of an ASR trial that was shut

2008 (Urrbrae Wetland, Adelaide, Australia)	design, clogging and unclogging, water quality and efforts to remediate clogging. Unconsolidated fine-grained siliceous aquifer	down due to excessive well clogging.
Page et al., 2011 (Rosedale golf course, Australia)	Water quality targets to minimise clogging. Physical, biological and chemical mechanisms considered. Low permeability fractured sandstone aquifer	Full scale field study using potable and treated stormwater
Page and Dillon, 2013 (Rosedale golf course)	Water quality targets for injection and comparison between clogging experienced when treated stormwater injected Vs. potable water. Considered clay dispersal and physical clogging processes in detail. Chemical and biological clogging considered briefly. Low permeability fractured sandstone aquifer	Investigation at full scale scheme. MFI index to characterise potential for physical clogging and Emerson method for clay dispersal, DOC & BDOC for biological clogging
Willis-Jones and Brandes de Roos, 2013 (Cloudbreak mine, Australia)	Air entrainment, suspended solids, biofouling, clay swelling & dispersion. Application of pragmatic measures to control clogging evaluated. Former limestone formation that has undergone significant silicification	Field study at operational site. Potential for mineral precipitation was assessed with PHREEQC model
de la Loma Gonzalez, 2013 (Waalsdorp, Watervlak and Amsterdam dunes, Netherlands)	Physical clogging potential (MFI), biological clogging potential (AOC) of recharged water and effect of different types of rehabilitation and construction options. Unconsolidated aeolian deposits	Data from 3 deep well artificial recharge systems reviewed over a 23 year period to describe their clogging behaviour
Johnston et al., 2013 (Jandakot, Mirrabooka and Beenyup, Australia)	Degree and type of clogging using different water types and the management of clogging. Sandstone aquifer	Evaluation of three different sites (two trials and one operational)
Barry et al., 2013 (Kingswood, Australia)	Causes for clogging and potential solutions. Considered, well construction, clay dispersal, physical & biological clogging. Quaternary alluvial aquifer	Domestic scale pilot site set up - Quality of injectant and recovered water was also measured.
Martin, 2013	Clogging mechanisms in ASR, approach	Review of an operating ASR system.

(City of Tea Tree Gully)	to identifying clogging using the aquifers hydraulic response, and mitigation measures. Quaternary gravels, fractured shale, dolomite and quartzites.	Analysis of data in water quality and head build-up over time to determine the type of clogging. Further tests (including pumping tests) conducted to confirm hypotheses
Anderson et al., 2004 (South London Artificial Recharge Scheme (SLARS))	Processes causing borehole turbidity, aquifer clogging and well deterioration were assessed. Chalk aquifer	Cycle testing at a pilot site. Water quality sampling and field measurements analysed to evaluate change in hydraulic conductivity and the turbidity. PHREEQC modelling was used to identify the processes causing the turbidity events
Pavelic et al., 2007 (Bolivar, Australia)	Rates of clogging and unclogging, causes of clogging, water quality needed for sustainable injection and the effectiveness of various remediation measures. Sandy limestone Aquifer	Field scale study. Analysis of injectant, groundwater and backwash quality, particulate loadings of backwash water, MFI testing of injectant, microbial growth kinetics and periodic step testing.
Vecchioli and Ku, 1972 (Bay Park, Long Island, NY)	Parameters that could have contributed to clogging and effect of redevelopment Fine grained sand aquifer	Pumping tests, analysis of hydraulics, and quality of recharged and recovered water. Several cycles of storage and recovery
Fitzpatrick, 1986 (Lee county, FL)	Potential water quality changes and clogging that may occur during ASR, and recoverability of the stored water Limestone aquifer	Several cycles of ASR using treated and untreated river water as the source for recharge. Water quality, recovery efficiency and clogging compared between cycles.
Bouwer, 2002	Introduces the concept of using MFI (Suspended solids), AOC (Micobial growth) and PFI (Clogging of aquifer) to compare relative clogging potential of various waters.	Experience from designing and operating various ASR schemes
Brown at al., 2006	Degree of well clogging experienced at various sites.	A review of 50 operating ASR sites to provide data and lessons learned.
Hutchinson, 1997	Clogging potential of suspended solids	Clogging potential assessed using MFI which considers concentration, size and composition of the suspended solids. Sites in the US used to compare the MFI and clogging rates
Pitt and Magenheimer, 1997	Clogging of aquifer storage zone due to physical, chemical, biological and mechanical factors. Causes, methods for prevention, early detection and remediation discussed.	Experience, review of sites and literature.
Morris, 2007	Impact of well construction, development and operation on clogging.	Performance analysis of existing sites.

MFI – Membrane filtration index, AOC – assimilable organic carbon, PFI – parallel filter index

All the clogging mechanisms except for physical clogging are influenced by multiple factors. Biological clogging is encouraged in the presence of organic matter, nutrients or elements such as iron and manganese (Pyne, 2005b), while clay dispersal depends on the native water quality and the aquifer mineralogy as do geochemical reactions (Pavelic et al., 2008). Gaseous binding depends on the concentration of nitrate/sulphate (among others) and aquifer conditions (Pitt and Magenheimer, 1997). The mere presence of organic matter, nutrients or elements such as iron and manganese will not result in biological clogging/gaseous binding as conditions in the well and aquifer need to be suitable for microbiological growth. Additionally, gaseous binding may also occur due to an increase in temperature of the recharge water or a drop in water pressure in the aquifer (Huisman and Olsthoorn, 1982). Introduction of oxygenated water will not always result in geochemical clogging as the aquifer material or native water will need to contain iron/manganese in order to form the precipitates (Moorman et al., 2002), and similarly, dissolution will not occur unless the recharge water is incompatible with the native water (Maliva and Missimer, 2010). Finally, recharge water with a low salinity will not result in clay dispersal unless its SAR is higher than the native groundwater and swelling clays are present in the aquifer (Barry et al., 2013). Physical clogging only depends on the suspended solids content of the water, that is, just the presence of suspended solids will cause physical clogging, although the degree of clogging is dependent on the type of aquifer and method of well construction used. Several attempts have therefore been made to define an acceptable concentration of suspended solids, in terms of treatment costs, that would minimize potential for physical clogging.

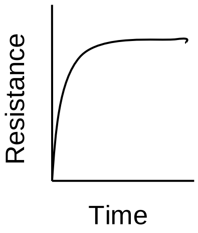
In a review of three ASR sites, de la Loma Gonzalez (2013) found that MFI values below $3s/L^2$ did not produce clogging due to suspended solids in an unconsolidated Aeolian deposit, while Johnston et al. (2013) found that MFI values of up to $14s/L^2$ were acceptable in a coarse Sandstone aquifer. MFI is a useful indicator however it cannot be relied upon to predict clogging in actual recharge wells, which also depend on well construction and aquifer characteristics (Bouwer, 2002). Turbidity is also commonly used to measure the potential for physical clogging. Page et al. (2011) found that a turbidity of $\leq$0.6 NTU minimised clogging due to suspended solids, while Pavelic et al. (2007) identified a turbidity of <3NTU as being suitable to prevent physical clogging. This illustrates the variation in standards at different sites since the clogging potential of a source water is highly dependent on the characteristics of the aquifer, native water, quality of the injectant, well construction methods and recharge facilities design (Pyne, 2005b). Clogging is very complex and although indicators such as MFI, TSS and turbidity can provide some guidance, it is essential to perform pilot field tests to identify the dominant clogging mechanisms (Pérez-Paricio and Carrera, 1999).

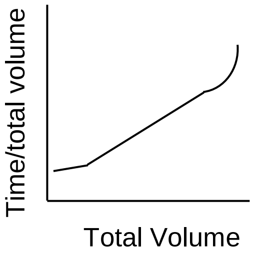
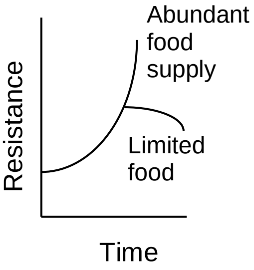
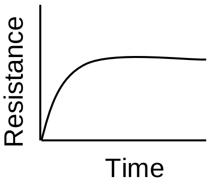
Clogging can be problematic and expensive to manage in some cases, however in most ASR operations it can be controlled by implementing appropriate management techniques such as ensuring satisfactory pre-treatment of the injectant and a regular borehole rehabilitation program. The quality of the injectant is important in determining the type and degree of clogging and it is possible to treat water to a standard that will minimise clogging however as discussed above, this standard varies with the type of source water used and the nature of the aquifer that is recharged. It should be noted that air entrainment and particle rearrangement occur due to the design of the recharge well rather than the quality of the recharge water.

Minimizing clogging is a very important consideration when designing an ASR scheme. Timely identification of potential clogging mechanisms presents an opportunity to redevelop the well and restore its initial capacity (Murray, 2009). In order to define measures to prevent and/or control clogging, methods to assess the water quality parameters responsible for clogging are required.

Table 3.3 (below) provides some guidance on identifying clogging mechanisms, the key parameters involved in the type of clogging and mitigation measures for these mechanisms. It illustrates that clogging can be managed by adequate pre-treatment of the recharge water, monitoring of injection pressure and tailored backwashing/rehabilitation programs. It should be stressed that it is only a guideline which should be used with care since as already explained, clogging is a site specific phenomenon and site specific investigations should be implemented before making any conclusions.

Table 3.3: Clogging mechanisms that may impact an ASR scheme, parameters controlling the mechanism, indicator of occurrence, and potential mitigation measures (Adapted from Brown and Silvey, 1973; Huisman and Olsthoorn, 1982; Okubo and Matsumoto, 1983; Pitt and Magenheimer, 1997; ASCE 2001; Wood et al., 2004; D. Pyne, 2005a; Martin, 2013a).

Clogging mechanism	Key parameters	Indicators	Suggested prevention/mitigation measures
Air entrapment	Entrained air in recharge water	Rapid increase in resistance to flow during injection, which levels of in hours (Huisman and Olsthoorn, 1982) 	1. Appropriate well head design and management to ensure air doesn't enter recharge piping 2. Installation of an air release and vacuum release valve at the well head 3. Prevent water cascading in the well casing where well head isn't airtight 4. Maintain positive pressure in the injection pipe prior to injection 5. If water contains entrained air, ensure downward velocity is not greater than 0.3m/s as this is the rate at which 0.1-10mm bubbles rise in still water (Pyne, 2005a)
Gaseous binding	Dissolved oxygen (DO) Temperature Microbial activity	N/a	1. Maintain concentration of DO < 10mg/l (Huisman and Olsthoorn, 1982) 2. Try and match temperature of the injectant to the temperature in the aquifer as gasses come out of solution with an increase in temperature (cold water injected into a warmer aquifer). 3. Minimize microbial activity (release gas as a metabolic by-product)
Suspended solids	Total suspended solids	Initial slow increase followed by a linear increase in injection pressure with time when injection rate is constant, followed by a sharp increase in	1. Try and eliminate pressure transients as these can result in a large influx of solids 2. Keep TSS in injectant as low as economically possible, especially if injecting into a single

		resistance to flow at the last stage (Pyne, 2005a)  	porosity/permeability aquifer 3. The gravel/filter pack should be sized appropriately –fine packs encourage physical clogging, while coarse packs allow material to move into the formation, which cannot be removed during redevelopment (American Americal Soceity of Civil Engineers/Environmental & Water, 2001).
Biological growth –	BDOC Temperature	Exponential increase in resistance (which stabilizes where food supply is limited) (Pyne, 2005a)  	1. Minimize biodegradable dissolved organic carbon in the injectant 2. Maintain chlorine residual in source water 3. Maintain a trickle flow of chlorinated water between periods of recharge and recovery to maintain chlorine residual in the well (Pyne, 2005a) 4. The gravel/filter pack should be sized appropriately –fine material encourages biological clogging (Wood et al., 2004)
Geochemical reactions	Aquifer mineralogy, Eh, pH, DO, TDS	N/a	1. Conduct investigations e.g. column studies/modelling to determine geochemical reactions that may occur. Native water quality, injectant quality and aquifer mineralogy need to be considered. 2. Try and match quality of injectant to the native water quality
Particle rearrangement	Fine materials in the aquifer Drilling fluids and muds.	Initial increase in resistance during startup of injection. Further clogging due to this process is not likely in subsequent cycles (Pyne, 2005a)  	1. Process is irreversible – impact of this is generally small therefore is not usually considered to be a problem

Swelling and dispersal of clay	Clay content (type and quantity of cations in exchangeable position) in the aquifer Ionic strength of recharge water SAR of recharge water Salinity of native water	N/a	1. Try and ensure the sodium adsorption ratio of the injectant is lower than ambient groundwater. This will minimize the potential for ion exchange between recharge water and clays in the aquifer hence minimise the likelihood for clay dispersal which may occur due to a reduction in groundwater salinity. This is more important when recharging in a brackish/saline aquifer 2. Injection of a calcium-chloride solution (or preflush) prior to the injection of freshwater would suppress clay dispersion and reduce aquifer clogging (Brown and Silvey, 1973)
Mechanical compaction	Compressibility of the aquifer Injection pressures	N/a	1. Try and minimize the injection pressures required 2. Ensure recharge pressures are not increased as a response to clogging
Adsorption	Adsorption capacity of aquifer Presence of ions in the injectant	N/a	1. Minimize the quantity of ions in the recharge water. This is more important if the scheme is required over a long period since the adsorption capacity would reduce over time. In the long term, there is a potential for breakthrough to occur and all adsorbed ions would be released

An increase in the injection pressure required is the main indicator for the occurrence of clogging therefore monitoring injection pressure is essential. The hydraulic response i.e. the rate and persistence of the increase in injection pressure required, can also provide an indication of the clogging mechanism responsible as shown in Table 3.3. For example a rapid increase in injection pressure which levels out in a matter of hours is an indicator of air entrapment, a linear increase followed by a sharp increase is indicative of physical clogging and an exponential increase implies biological clogging.

In general, higher quality recharge water will reduce the clogging potential, however this may not always be the case. For example, more stringent water quality standards and a focus on removing organic micropollutants prompt the use of advanced oxidation treatments such as UV/H_2O_2, which results in higher assimilable organic carbon, increasing the potential for biological clogging (de la Loma Gonzalez, 2013). Stacking treatment should be avoided and instead the pre-treatment requirements should be balanced to ensure that reducing the clogging potential is not undertaken at the expense of other water quality changes that would influence recovered water quality. This is discussed further in Chapter 5.

3.6 Conclusions

Clogging is a significant barrier to the successful operation of ASR schemes because it limits the recovery of stored water. Improper design/construction of the recharge well can result in clogging however the quality of the injectant is most important in determining the type and degree of clogging. Higher concentrations of suspended solids, nutrients, organic matter and chemical incompatibility with the native groundwater all increase the potential for clogging. In general, higher quality recharge water will reduce the clogging potential however this may not always be the case. There are no agreed standards for the recharge water to prevent/minimise clogging since the clogging potential of a source water is highly dependent on the characteristics of the aquifer, native groundwater and injectant quality, well construction methods and recharge facilities design. Existing literature can provide an indicative starting point to prevent/limit clogging however pilot tests and site specific investigations are unavoidable if the potential for clogging is to be estimated accurately.

4 Water Quality Changes during Storage in a Sherwood Sandstone Aquifer

4.1 Introduction

The survey reported in Chapter 2 suggested that potential changes in water quality are the biggest threat to ASR schemes. Interactions between water used for aquifer recharge, the aquifer material, and native groundwater can affect the quality of the water ultimately abstracted for reuse and can therefore constitute an operational risk to ASR schemes. This risk is site specific and its magnitude is difficult to quantify without detailed environmental, hydrogeological and geochemical characterisation studies combined with pilot-scale investigations. The water used for recharge typically interacts with both the native groundwater and the aquifer rock through a combination of physical, chemical and biological processes that are also linked to subsurface conditions.

When considering the water quality aspect of an ASR scheme three classes of influence need to be taken into account. The first of these is the required quality of the recharge and recovered water. The recharge water is subjected to alterations in redox states, pH, nutrient supplies and temperature and thus the quality of the recovered water will inevitably differ from the quality of recharge water (Dillon et al., 2006). The required recharge and recovered water quality can be defined by operational considerations (e.g. clogging of the boreholes), regulatory considerations (e.g. permit requirements) or strategic requirements (e.g. end-use of recovered water). The second class of influences pertains to the quality of the native groundwater and its influence on the interactions between the recharged and native water which in turn influences the quality of the abstracted water (Mirecki et al., 1998). This is more important if mixing between the waters is expected. Mixing can cause significant changes in water quality, especially where substantial elemental concentration differences exist between the recharge and native water (Eastwood and Stanfield, 2001; Pavelic et al., 2006). Finally, water-rock interactions also require consideration as once water is recharged into the aquifer, it may react with the geology, changing the quality of the abstracted water. A geochemical assessment of the rock and the possible interactions are important in determining whether the abstracted water would be of an acceptable quality. For example, large differences in the pH or Redox condition between the two waters can mobilise trace elements. Dual purpose injection wells can have rapidly changing redox conditions which can promote mobilisation and precipitation of compounds such as iron, manganese and arsenic, which not only contaminate the water but also exacerbate clogging of the wells (Fox, 2008). The possible influences of all the interactions need to be considered holistically.

An investigative study commissioned by Anglian Water (Diamanti and Hardisty, 2015) to select a site for an ASR scheme identified Newton on Trent, Lincolnshire, UK as the most preferable site (see Section 4.2.1) where treated water from the River Trent would be injected into the underlying Sherwood Sandstone aquifer. The main purpose of this ASR scheme would be to increase the resilience of drinking water supplies in the area. Understanding the envelope of potential changes in water quality during storage in the aquifer is therefore crucial if the scheme is to be designed appropriately and risks managed effectively. Four methods that may be used to improve this understanding include a literature search for reported water quality changes where similar water was injected into the Sherwood Sandstone aquifer, modelling potential changes that may occur, a laboratory scale investigation using the aquifer material and potential source of recharge water, and finally a pilot scale investigation at the potential site.

A literature review is useful in understanding the current state of knowledge and determining whether further investigations are required, therefore was the first step in the research (see Section 4.1.1and 4.1.2). The knowledge required was however very specific to the site, and to obtain this, either modelling, lab scale or pilot scale investigations are required.

Geochemical modelling can provide an estimate of potential water quality changes that may occur during ASR, however a model is only as good as the data and assumptions informing it. ASR schemes require site specific information, and modelling in the absence of good quality data and conceptual models would be of limited value and may be misleading. Reactions in British aquifers such as the Sherwood Sandstone aquifer are not well understood (Gale et al., 2002) thus there is limited data available to inform the model. Modelling would be best used in the initial feasibility investigations to provide a better basis for a conceptual design and planning the pilot investigations, and after constructing a pilot site, as at this point site specific data to calibrate and verify the model would be available (Pyne, 2005a). It is for this reason modelling was incorporated into the SPT, and laboratory scale investigations were chosen to provide more detailed site specific information on potential water quality changes that may influence an ASR scheme in the Sherwood Sandstone aquifer. Pilot scale investigations would have been the preferred option as a pilot would provide the most accurate information, however budgetary constraints did not allow for this.

To date, significant research has been undertaken to understand the risks associated with water quality changes in aquifer recharge schemes using infiltration techniques at a lab scale such as SAT (Drewes et al., 2001; Fox and Shah, 2006; Maeng et al., 2012; Rauch et al., 2006; Rauch-Williams, et al., 2010) and River Bank Infiltration (Horner, et al. 2006). It should be noted that storage following injection differs from storage after infiltration, since the soil's natural attenuation and filtration capacity provides a level of treatment during infiltration. Literature from infiltration investigations therefore cannot be used to inform ASR investigations which use injection via wells as the method of recharge.

Studies of ASR processes at lab scale are scarce, likely because infiltration techniques are more common than ASR and therefore more research is dedicated to this field. A desktop investigation of the Newton on Trent site (Macdonald, 2010) identified the release of metals and major ions during storage, following injection of oxidised water into a reducing environment, as a risk requiring further investigation. Furthermore, discussions with the Water Resources team in Anglian Water identified the fate of disinfection by products (DBPs) such as Trihalomethanes (THMs) and Haloacetic acids (HAA) during storage as requiring further investigation, because the water treatment works near the proposed site does not currently have the capacity to treat DBPs. There was therefore a need to determine if the abstracted water would contain DBPs.

A literature search was implemented to determine whether there was knowledge available on changes in water quality during storage, following injection of treated surface water into an aquifer, with respect to metals, major ions, THMs and HAAs.

4.1.1 Fate/Behaviour of Metals and Major ions during ASR

The purpose of this ASR scheme would be to increase the resilience of drinking water supplies therefore the abstracted water would need to adhere to drinking water standards. Since metals and major ions are regulated compounds in drinking water in the UK (DWI, 2010c), they were selected for the experimental analysis. Organic carbon, nitrate, sulphate, ammonia and general parameters such as pH can all influence the release of metals and major ions during storage in an aquifer (Johnson et al., 1999; Overacre et al., 2006; Patterson et al., 2010; Riches et al., 2007; Vanderzalm et al., 2010), therefore these were also investigated.

Research on the fate/behaviour of metals and major ions in ASR was reviewed to understand the current state of knowledge and determine whether further investigations are required (see Section 4.1.3). The papers reviewed are summarised in Table 4.1. It should be noted that although some of the studies investigated other parameters such as micro-contaminants, pathogens, radionuclides etc., only the outcomes with respect to the behaviour/fate of metals, nutrients, organic carbon and general parameters such as pH are discussed further, as these are the compounds of interest in this study.

Table 4.1: Summary of field and laboratory investigations on the fate of metals and major ions during ASR

Study site	Aquifer material	Compounds sampled	References
Field investigations			
Chandler, Arizona;	Alluviam	General parameters (Cl, Na, alkalinity, DO, pH, Eh), nutrients (N, P) , total organic carbon, metals, radionuclides, DBPs (THM, HAA), microorganisms, micro-contaminants	Overacre et al., 2006
Englewood, Florida;	Carbonate	General parameters (Cl, Na, alkalinity, DO, pH, Eh), nutrients (N, P) , total organic carbon, metals, radionuclides, DBPs (THM, HAA), microorganisms, micro-contaminants	Overacre et al., 2006
Manatee, Florida;	Carbonate	General parameters (Cl, Na, alkalinity, DO, pH, Eh), nutrients (N, P) , total organic carbon, metals, radionuclides,	Overacre et al., 2006

		DBPs (THM, HAA), microorganisms, micro-contaminants	
Bolivar, South Australia.	Sandy Limestone	General parameters (Cl, Na, alkalinity, DO, pH, Eh), nutrients (N, P) , total organic carbon, metals, radionuclides, DBPs (THM, HAA), microorganisms, micro-contaminants	Overacre et al., 2006
		As, pH, temperature, DO, EC and Eh, NO_3 and SO_4	Vanderzalm et al., 2007, Vanderzalm et al., 2005
Salisbury, South Australia	Limestone	General parameters, nutrients (N, P, NO_3, NO_2, NH_3), total organic carbon, biodegradable organic carbon., metals and major ions (Fe, Mn, As, Ni, Pb, Zn)	Vanderzalm et al., 2010
Andrews Farm, South Australia	Limestone	Major cations (Na, K, Ca, Mg, SO_4), general parameters (pH, EC, DO, temperature, alkalinity, Cl), total organic carbon	Herczeg et al., 2004
Field and Laboratory investigations			
Bolivar, South Australia;	Sandy limestone,	Pathogen attenuation, endocrine disrupting compounds, THMs and metals	Vanderzalm et al., 2009
Bradenton, Florida;	Limestone and sandstone	Pathogen attenuation, endocrine disrupting compounds, THMs and metals	Vanderzalm et al., 2009
Thames Water, North London, UK	Chalk	Pathogen attenuation, endocrine disrupting compounds, THMs and metals	Vanderzalm et al., 2009
Laboratory investigations			
Scottsdale, AZ	Unconsolidated sand and gravel aquifer	pH, major ions, trace metals, dissolved inorganic carbon, alkalinity	Johnson et al., 1999
Perth, Western Australia	Pyritic sandstone	trace organic compounds, metals, NO_3, DOC, pH	Patterson et al., 2010
South Florida, USA	Limestone	Metals (As, Mo, Sb, U), general parameters (pH, temperature, DO, Eh, EC)	Arthur et al., 2007
Horton Kirby, England, UK	Lower Greensand	Major ions, general parameters (pH, EC, temperature, alkalinity), total organic carbon, NO_3, NH_4, SO_4, P	Riches et al., 2007

As illustrated in Table 4.1, several field investigations have been conducted to investigate changes in metals and major ion concentration during storage, however only Overacre et al. (2006) and Vanderzalm et al. (2010) include general parameters (such as pH, DO, EC), nutrients and organic carbon in their evaluation of the metals and major ion concentrations. Laboratory investigations of the fate of metals and major ions during storage are less abundant, however it should be noted that all the lab investigations include an analysis of general parameters. Patterson et al. (2010) additionally consider organic carbon and Riches et al. (2007) consider organic carbon and nutrients in their evaluation of the metals and major ion concentrations.

Both the field and laboratory investigations show that the aquifer provides passive treatment through nutrient removal which is accompanied by changes in the organic matter concentration (Vanderzalm et al., 2010). These changes are highest close to the well, supporting the concept of higher biological activity near the injection site (Overacre et al., 2006). Organic matter is an important parameter to consider in ASR as mineralisation of organic matter in anaerobic conditions can lead to iron oxide (ferric iron) reduction which can release ferrous iron and other previously adsorbed species (Lovley and Phillips, 1986; Vanderzalm et al., 2009). Iron oxides have a large sorptive capacity, and can reduce the concentration of trace species such as arsenic (Vanderzalm et al., 2009). Arthur et al. (2007), Vanderzalm et al. (2007) and Vanderzalm et al. (2005) demonstrated the importance of iron oxides for control of arsenic concentrations by showing that the increase of arsenic was coincident with reductive dissolution of iron oxides, which released previously sorbed species. It should be noted that other metals and metalloids such as nickel and zinc can also be sorbed onto iron oxides and the aquifer material (Vanderzalm et al., 2005) although the extent of this will vary in different aquifers.

In sandy aquifers, pyrite (FeS_2) oxidation is one of the most important reactions influencing water quality during ASR (Riches et al., 2007; Vanderzalm et al., 2009; Vanderzalm et al., 2005) and the release of As, Co, Ni, and Zn are often coincidental with pyrite oxidation (Dillon et al., 2010; Vanderzalm et al., 2009). Oxidation of pyrite can also release iron in both dissolved and precipitate phases (Riches et al., 2007), which in turn influences the concentration of trace species which can sorb onto these precipitate phases.

In addition to the aquifer material, the quality of water injected has an influence on the water quality changes that may occur during storage. Treating water to a very high purity by using reverse osmosis for example, can result in more aggressive water which will dissolve more minerals in the aquifer (Dillon et al., 2010; Johnson et al., 1999). Dissolution is important not only because it can add contaminants into the water, but in the long term, these reactions could result in collapse of the well. Dissolution is mainly a concern in carbonate aquifers as carbonate mineral dissolution has been found to have a dominant influence on recovered water quality (Herczeg et al., 2004; Page et al., 2009; Dillon et al., 2010; Vanderzalm et al., 2010).

4.1.2 Fate/Behaviour of DBPs during ASR

As explained in Section 4.1, the DBP's of concern were identified as Trihalomethanes (THMs) and Haloacetic acids (HAAs) therefore the literature was reviewed to understand the current state of knowledge with respect to the fate of THMs and HAAs in ASR schemes (see Section 4.1.3). These two types of DBPs have been studied in a number of field investigations as well as in some laboratory studies (Table 4.2).

Table 4.2: Summary of field and laboratory investigations on the fate of disinfection by products during ASR

Study site	Aquifer	Compounds	References
Field Investigations			
Chandler, Arizona;	Alluviam	THM's and HAA	Overacre et al., 2006
Antelope Valley, California	Sand and gravel deposits (aerobic aquifer)	THMs	Fram et al., 2003
Charleston, South Carolina	Alluvial gravel and sand plus fines	THM's	Pavelic et al., 2006
Memphis, Tennessee	Fluvial sand and gravel	THM's	Pavelic et al., 2006
Talbert Gap, California	Alluvial gravel and sand plus fines	THM's	Pavelic et al., 2006

Centennial, Colombia	Unconsolidated sandstone siltstone and shale	THM’s and HAA	Singer et al., 1999
East Bay, California	Sandstone	THM’s	Pavelic et al., 2006
Oak Creek, Wisconsin	Sandstone	THM’s	Pavelic et al., 2006
Las Vegas, Nevada	Cemented sand and gravel (aerobic aquifer)	THM’s	Pavelic et al., 2006
		THM’s and HAA	Singer et al., 1999
		chloroform (THM compound) and chloroacetic acid (HAA compound)	Landmeyer et al., 2000
		THMs and HAAs	Thomas et al., 2000
		THMs and HAA	Pavelic et al., 2005
Bolivar, South Australia	Sandy limestone	THM’s and HAA	Pavelic et al., 2006
		THM’s and HAA	Pavelic et al., 2005
		THM’s and HAA	Overacre et al., 2006
Jandakot, Western Australia	Limestone and fractured sandstone	THM’s and HAA	Pavelic et al., 2006
Peace-Manasota, Arcadia;	Brackish sandy limestone	THM’s and HAA	Singer et al., 1999
Thames Water, London	Chalk aquifer	THM’s and HAA	Singer et al., 1999
Englewood, Florida;	Carbonate	THM’s and HAA	Overacre et al., 2006
Manatee, Florida;	Carbonate	THM’s and HAA	Overacre et al., 2006
Upper Guadalupe, Kerrville, Texas	Aggregates of sedimentary rock	THM’s and HAA	Singer et al., 1999
Monterey, California	Weakly cemented Sandstone	THMs	Vanderzalm et al., 2009
Laboratory investigations			
Laboratory study using Bolivar aquifer material	Sandy limestone	THMs	Vanderzalm et al., 2009
Antelope Valley, California	Sand and gravel deposits (aerobic aquifer)	THMs	Fram et al., 2003
Laboratory using glass beads to grow biofilm on	N/A	THMs	Bouwer and Wright, 1988
Laboratory study	Sand media	THMs and THM pre-cursors	McQuarrie and Carlson, 2003

As shown in Table 4.2, the fate of DBPs have been studied in a variety of field investigations, some of which have shown attenuation (Bouwer and Wright, 1988; Fram et al., 2003; Landmeyer et al., 2000; McQuarrie and Carlson, 2003; Overacre et al., 2006; Pavelic et al., 2005; Pavelic et al., 2006; Singer et al., 1993; Thomas et al., 2000) while others have shown formation of DBPs (Fram et al., 2003; Pavelic et al., 2006; Singer et al., 1993; Vanderzalm et al., 2009) during storage in the aquifer.

DBP degradation is highly dependent on the type of DBP compound and on the geochemical conditions in the aquifer (Pavelic et al., 2005; Singer et al., 1993). Even within the same aquifer, geochemical conditions and hence degradation can vary (Pavelic et al., 2006; Vanderzalm et al., 2009). For example, in Monterey California in 2004 there was a degradation of THM's with a half life of 41-50 days, however in 2005 aerobic conditions persisted and half life increased to 1700 days. The reported rate of degradation is highly variable with half-lives varying from < 1day to 76 days for HAA's and <1 day to 480 days for THM's, according to the sites. Therefore it is not possible to estimate the potential for degradation (or formation) using existing literature, and site specific investigations would be required.

It should be noted that across the studies listed in Table 4.2 only THMs were formed during storage while none of them reported formation of HAA. This is because HAAs are degraded much faster than THMs and can degrade under aerobic conditions while THM degradation requires anaerobic conditions and longer storage periods for degradation (Singer et al., 1993; Thomas et al., 2000; Pavelic et al., 2005; Overacre et al., 2006; Pavelic, Dillon and Nicholson, 2006). The literature therefore suggests that the DBP that would pose the bigger threat to abstracted water quality would be THM's.

The potential for THM formation needs to be understood because THM levels are regulated, and formation during storage could result in abstracted water having a higher than permitted concentration of THM. If the abstracted water is to be used without any post treatment then the point of compliance would be the recovery well. If post treatment is required then the point of compliance would be at the water treatment works outlet. It follows that if THMs are formed during storage, post-treatment to reduce levels will be required. This is potentially a fatal problem for the proposed ASR scheme as the water treatment works near the site does not currently have the capacity to treat THMs. This would likely increase the cost of ASR to the point that it is no longer affordable.

The factors promoting formation of THM's in the aquifer include the presence of natural organic matter and residual chlorine in the injected water (Fram et al., 2003; Pavelic et al., 2005; Vanderzalm et al., 2009). A small chlorine residual of 1 to 2mg/l can produce up to 48µg/l THM although pH buffering by calcareous aquifer material and a low organic carbon content can reduce THM formation (Vanderzalm et al., 2009). As explained in Section 4.1.1, it is likely that the injectant will be drinking water quality and since water companies in the UK typically maintain a chlorine residual of 0.5mg/l (DWI, 2010a), there is potential for THM formaton during storage. It is therefore vital that other factors which promote THM formation such as presence of natural organic matter are reduced.

DBP formation is rapid and can start immediately after injection (Dillon et al., 2005a) and continue for up to four weeks after injection depending on aquifer conditons (Fram et al., 2003). Where conditions do not support degradation, they are likely to persist in the recovered water. An important finding is that where THM formation was reported, storage had taken place in aerobic aquifers such as in Monterey, California (Vanderzalm et al., 2009), Memphis, Tennessee (Singer et al., 1993), Antelope Valley, California (Fram et al., 2003) and Las Vegas, Nevada (Pavelic, Dillon and Nicholson, 2006), where THMs cannot be degraded. As the target aquifer for ASR in this study is a confined anaerobic aquifer, the potential for formation is less likely.

As shown in Table 4.2 above, whilst the behaviour of DBPs during storage in an aquifer has been extensively studied during field investigations, laboratory scale investigations are limited. Although results from field investigations are useful, it is difficult to distinguish between reduction due to dilution with the native water and actual degradation of the DBP's (Pyne, 2005a). Laboratory studies under controlled conditions are therefore useful in determining the fate of DBP's during storage, even though all the aquifer conditions cannot be reliably simulated.

Laboratory investigations have also concluded that no significant degradation of THMs occur in aerobic conditions (Bouwer and Wright, 1988; Fram et al., 2003). It is however possible for bacteria capable of degradation to be present, therefore in anaerobic microzones that are developed during storage, acclimation of the bacterial community could promote degradation (Fram et al., 2003). This hypothesis is supported by Singer et al. (1993) who found the concentration of THMs reduced during storage in an aerobic aquifer in Las Vegas, Nevada. This reduction was attributed to the heterogeneity of the aquifer which could result in pockets where degradation occurs. Chlorinating water prior to injection in anaerobic aquifers is unlikely to have an adverse impact on the abstracted water quality with respect to THMs since they can be reduced substantially during aquifer storage (McQuarrie and Carlson, 2003). As well as the redox state of the aquifer, the aquifer material is also an important factor influencing the rates of THM formation, as shown by Vanderzalm et al. (2009), who found that an increase in residual chlorine produced less THMs during storage where a calcareous aquifer material with a low organic content was used. This was attributed to pH buffering by the aquifer material which raised the pH of the water, thereby reducing the rate of THM formation. Although these studies provide valuable information, none address the fate of THMs in an anaerobic sandstone aquifer. Furthermore, none of these investigations included HAAs.

4.1.3 Gap in Knowledge

Water quality changes during storage in a sandstone aquifer with respect to nutrients, metals, major ions, TOC, THMs and HAAs have been studied at both the laboratory and field scale (See Table 4.1 and Table 4.2), however no literature was found with respect to these changes when treated surface water is recharged into a consolidated, confined Sherwood Sandstone aquifer, and the influence of recharge water quality on the recovered water quality. Some literature on the fate of these parameters during storage in sandstone aquifers is available, however it is important to note that each sandstone aquifer varies in its mineralogical composition and will influence recovered water quality in a different manner. Differing qualities of recharge water and native groundwater will also influence the recovered water quality. Site specific data is therefore required to assess potential water quality issues that may impact an ASR scheme at the Newton on Trent site. In order to address this, the following research questions were set:

1. What is the fate of metals, major ions and DBPs when treated surface water is stored in a confined Sherwood Sandstone aquifer, and how does this impact the recovered water quality?
2. How does the recharge water quality and retention period influence the fate of these parameters and the recovered water quality?

A simulated ASR study using Sherwood Sandstone aquifer material was implemented using columns, to investigate the fate of trace metals, major ions, DBPs and influencing parameters such as organic carbon, nitrate, sulphate, ammonia and pH, during simulated storage, and the influence of recharge water quality and retention period on these.

The Sherwood Sandstone group forms the second most important aquifer in the UK (Allen et al., 1997) therefore the knowledge generated by this research has the potential to improve understanding of water quality changes during ASR across a variety of potential sites in the UK. The laboratory investigations also extend the general understanding of the mechanisms that may influence the fate of metals, major ions and DBPs during storage. This provides the basis for a discussion on the appropriateness of the current water quality requirements set out by the regulators when permitting ASR schemes in the UK, and the need to promote a risk based approach to scheme approval (Chapter 5).

4.2 Methods and Materials

Newton on Trent, Lincolnshire, UK has been identified as a potential ASR site through a staged water resource and hydrogeological study (Diamanti and Hardisty, 2015). Water from the River Trent will be treated at Hall water treatment works (WTW) following which it will be recharged into the confined Sherwood Sandstone aquifer with the purpose of recovering it to provide potable water when required. The treatment train includes a granular activated carbon (GAC) roughing filter, submerged ultrafiltration (UF) membrane, advanced oxidation (H_2O_2 and UV), GAC polishing filter, UV and finally chlorination (see Section 4.2.3).

4.2.1 Aquifer characterisation

The ASR scheme will be located within the deep, confined Sherwood Sandstone aquifer. This aquifer is the second most important aquifer in the UK and it provides an essential source of water for industry, agriculture and homes in northern and central England (Price et al., 2007). It comprises predominantly sandstone with few inter-layered fine-grained horizons (Macdonald, 2010). The sandstone is overlain and confined by the Triassic Mercia Mudstone formation, which is up to 250 m thick. At the Newton-on-Trent source, 210m of Mercia Mudstone overlies 240m of Sherwood Sandstone (Macdonald, 2010). Both the Sherwood Sandstone and Mercia Mudstone dip gently to the east. As such, the Sherwood Sandstone is unconfined in the west and becomes more deeply confined towards the east.

The aquifer has a moderate intergranular hydraulic conductivity enhanced by fractures close to abstraction boreholes, however these fractures tend to close with depth, resulting in a reduction in transmissivity (Macdonald, 2010). Pumping tests at Newton on Trent provided information on the transmissivity and storativity (which is dimensionless) values which were 60-100m^2/d and 4x10^{-4} respectively (Macdonald, 2010).

The native groundwater quality at Newton is almost fully compliant with drinking water standards, with only iron and turbidity exceeding the prescribed concentrations or values. The high iron content of the water means that changing redox conditions are likely to result in the precipitation of iron out of solution (Diamanti and Hardisty, 2015). It is therefore essential to investigate this further, along with any other water quality issues that may arise from injecting oxygenated water into a reduced aquifer.

To provide information on the mineralogy of the aquifer material used in this study, six samples of crushed Sherwood Sandstone were analysed using an FEI XL30 Scanning Electron Microscope (SEM) coupled with Energy Dispersive Spectroscopy (EDS), with two sites analysed for each sample (total of 12 sites analysed). The sample was also analysed using a Siemens D5005 Diffractometer for x-ray diffraction (XRD) analysis to determine the mineralogical composition of the aquifer material.

4.2.2 Column set-up

Potential changes in water quality during storage in this aquifer that could impact the quality of abstracted water were investigated using ASR simulating columns. For this purpose, a core sample of the Sherwood Sandstone was utilised. The sample was collected in 2014 from a site located approximately 11 miles west of the potential pilot ASR site. This sample was cored many years ago during the investigation programme for a borehole. The sample was weathered on the exposed areas, but relatively fresh inside. The sample was taken to the British Geological Survey (BGS) where the weathered surface was removed, following which the sample was crushed to achieve a maximum particle size of 2mm.

Although using the whole core would have maintained the structure of the rock i.e. the porosity and permeability, which could improve extrapolation of the results to a field scale, the core was crushed to ensure homogeneity of the column media, as opposed to using different cores each varying in structure and composition. In order to assess the impact of varying recharge water quality on recovered water quality, replication with different waters was necessary. Using crushed material focuses attention on changes in recovered water quality as a result of the different recharge water qualities only, and avoids confounding due to differences in the structure and composition of the core. This is a common approach as evidenced by its use in Arthur et al. (2007), Riches et al. (2007), Patterson et al. (2010), Rinck-Pfeiffer et al. (2013) and Vanderzalm et al. (2009, 2013).

In order to explore the influence of different recharge water qualities on recovered water, four different water qualities were to be recharged into the columns (See section 4.2.3). The crushed material was therefore packed into four PVC columns with a diameter of 9 cm and length of 40 cm, and set up as shown in Figure 4.1. The columns were sized to ensure they could yield 500 ml of water - the quantity required to complete all the required analysis. The column size was determined by first using a small column packed with material to determine the yield per volume of aquifer material, which was then used to extrapolate the volume of material, hence size of the column required to attain the desired yield. A 0.1mm stainless steel mesh was placed in the endcaps to support the aquifer material and to help spread the inflow laterally through the columns, following which the columns were sealed.

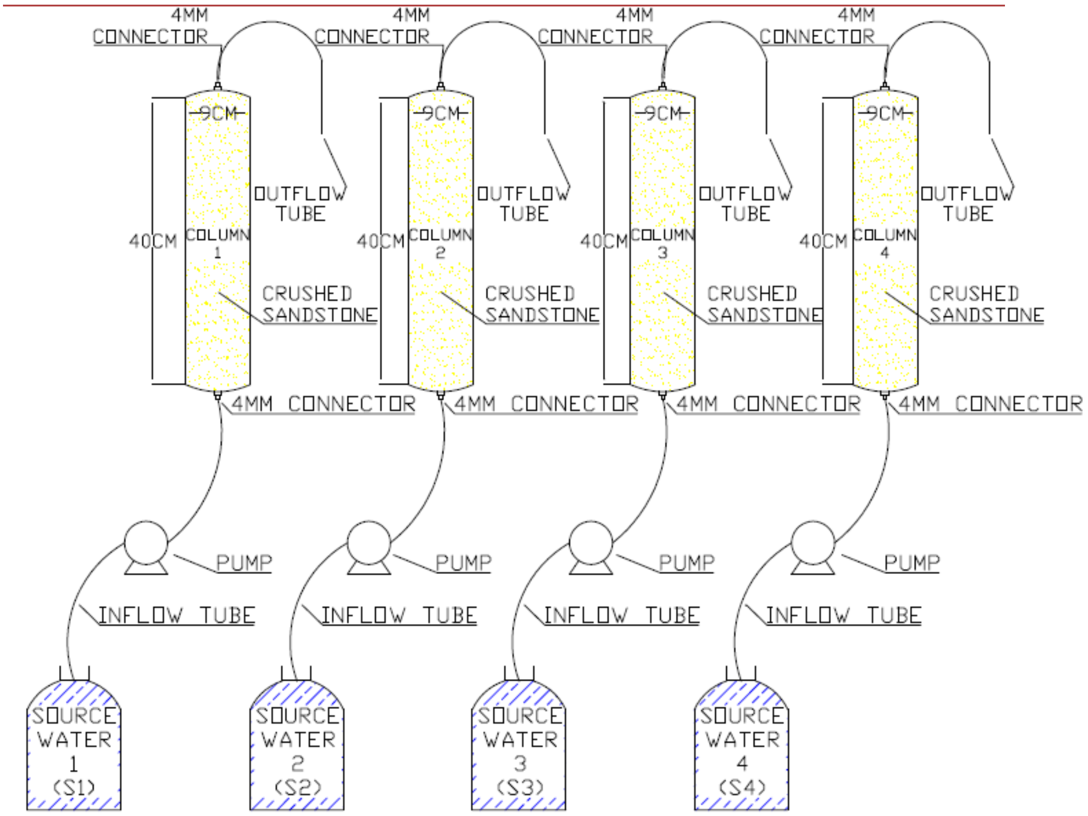


Figure 4.1: Schematic of the experimental setup – not to scale

The columns were initially flushed with fresh native groundwater in an upward flow to remove all free oxygen, allow stabilisation and inoculation of the columns (Arthur et al., 2007; Patterson et al., 2012; Rinck-Pfeiffer et al., 2013; Vanderzalm et al., 2013). The flushing period was determined by measuring TOC removal rate in the columns (Appendix L) to determine when an approximate steady state with respect to DOC removal was achieved (Sharma et al., 2007). The TOC removal appeared to level off after seven days, therefore a flushing period of ten days was used to err on the side of caution.

Once the flushing was complete, the columns were drained of excess water. The groundwater that was held in the pores of the material remained in the column, the volume of which was estimated as 700ml. This was determined by subtracting the volume of water recovered under gravity (300ml) from the volume of water introduced into the initial dry material (1L).

The columns were then purged with nitrogen gas to create anaerobic conditions representative of natural aquifer conditions. The source water was introduced, following which the inlet and outlet of the columns were sealed. It should be noted that the batches were not run simultaneously due to limitations in space availability, thus only two batches could be run at a time. This meant that the recharge water was sampled at different times and so the initial water quality varied between the batches. However this is not seen as a problem as the experiment is concerned with the difference in concentrations before and after storage rather than absolute values of concentration in the recovered water.

4.2.3 Water sources

In order to assess the impact of differing recharge water sources on abstracted water quality, water was sampled from different points of the Hall works treatment process as illustrated in Figure 4.2. These sampling points were chosen to determine the influence of membrane treatment and chlorination on the reactions that may occur during storage. Sampling points were therefore chosen pre and post membrane treatment, and pre and post chlorination.

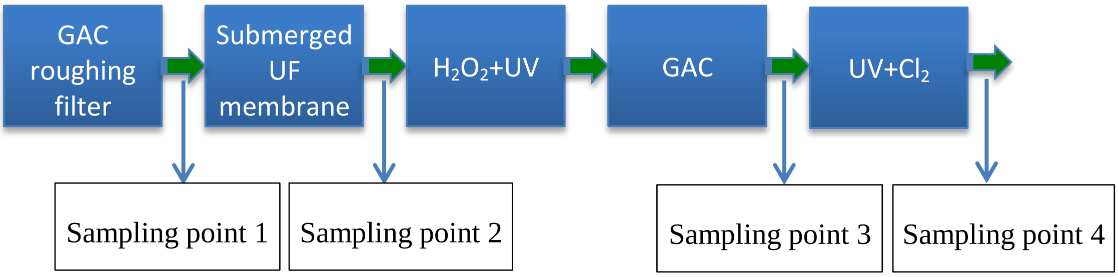


Figure 4.2: Hall WTW treatment train and sampling points used as source water for the columns

Water from the four sampling points (S1, S2, S3 and S3) were introduced into columns 1, 2, 3 and 4 respectively and left for pre-determined retention times of 15, 20, 30 and 60 days, to allow any microbiological and geochemical reactions to occur before the water was extracted, and to provide information on the temporal variability of the parameters chosen for analysis. The quality of the abstracted water was then compared to the source water to determine changes that had occurred during storage over the different retention periods.

4.2.4 Water sampling and quality analysis

Source water was collected in 1litre glass Duran bottles to ensure there was sufficient water for feeding the column as well as the required analysis of the water before introducing it into the columns. At the end of each test, the water was recovered from the bottom of the column into a 500ml glass Duran bottle.

Both source water and column output were immediately analysed (in duplicates) for nitrates, sulphates, ammonium and pH. Samples for metals and major ions were acidified and analysed within three months of acidification. TOC samples were preserved by adding concentrated hydrochloric acid (S.G. 1.18) to achieve 0.1% v/v, and analysis was completed within 5 days of sampling. Samples for HAA analysis were dechlorinated using 10% ammonium chloride and THM samples were dechlorinated using 10% sodium sulphate, following which a buffer of 1% Sodium Phosphate dibasic and 99% Potassium Phosphate monobasic was added to the THM vials. No buffer is required for HAA analysis. The parameters chosen for the evaluation of water quality changes during storage are shown in Table 4.3.

Table 4.3: Parameters measured to determine changes in water quality during storage

Parameter	Reason for selection	Analytical methods
Total Organic Carbon (TOC) – (Non purgeable)	• Indicates the quantity of organic matter: o Potential impact on redox conditions (biogeochemical reactions) and metal mobilization. o Impact on pH o Influences biological growth • TOC method chosen over BDOC as it is quicker to complete and equipment was more readily available	Shimadzu TOC-5050A Analyser was used as this was the equipment available for the analysis
Nitrate & sulphate	• Oxidants – Dissolved organic carbon can be mineralised (and concentrations reduced) by reacting with injected oxygen, nitrate and sulphate • To ensure regulatory compliance	Spectroquant cell test kit (Merck Millipore) 1.0 – 50.0 mg/l NO_3-N 5 – 250 mg/l SO_4 Cell tests chosen as method of analysis as they are quick, reliable and readily available.
Ammonium	• Indicator of growth of anaerobic bacteria (nutrient) • To ensure regulatory compliance	Spectroquant cell test kit (Merck Millipore) 0.20 – 8.00 mg/l NH_4-N cell test Cell tests chosen as method of analysis as they are quick, reliable and readily available.
pH	• Influences microbial activity, • Influences biogeochemical reactions • Influences dissolution	pH probe (JENWAY 3540 pH and Conductivity Meter). This was the equipment available
Metals, Major ions & Phosphorus	• Release of inorganic compounds during storage. • Phosphorus is a nutrient for microbes • To ensure regulatory compliance	Digestion – 1.5ml nitric acid added to 30ml unfiltered sample and digested in a Mars Xpress microwave using EPA method 3015. Analysis – Inductively coupled plasma mass spectrometry (ICP-

		MS) for all but Fe and Na which were measured using Atomic absorption spectroscopy (AAS, Perkin Elmer Analyst 800). This method of analysis was chosen as it is reliable and the equipment and training was readily available.
THMs and HAAs	• To understand the fate of THM’s and HAA’s during storage • To ensure regulatory compliance	THMs- GCMS and a single quadrupole mass spectrometer operating in SIM mode. Detailed method of analysis is not available as samples were sent to a UKAS (United Kingdom Accreditation Service) accredited lab to be analysed. HAAs were sent to a UKAS accredited laboratory to be analysed. Method of analysis is not available

4.2.5 Crushed Sandstone sampling and analysis

A virgin sample of the crushed sandstone, and the material recovered from the column once water has been extracted were sent off for analysis at a UKAS accredited laboratory for metals and major ions using the following methods:

1. Magnesium and potassium - samples were prepared in advance by drying and grinding. 5ml of the material was placed into a disposable pot, following which 25ml of 1M ammonium nitrate is added. This mixture was shaken for 30 minutes at a speed of 250 rpm after which it was filtered immediately through a Whatman no.2 filter paper into a Sterilin tube. The extracts were then analysed for magnesium and potassium by Inductively Coupled Plasma - Optical Emission Spectrometry (Optima 3) (ICP-OES).
2. Phosphorus - 5ml of the sample was extracted in a standard manner as defined by ADAS. The extract was analysed by air segmented continuous flow

methodology, involving the generation of phosphomolybdenum blue complex in accordance with Beer and Lambert’s laws. The colour generated was measured by a twin-beam dichroic filter colorimeter, and the data generated was processed by a computer system in order to derive the concentration of phosphorus by comparison with the data from standard solutions.

3. Metals - Samples were prepared by drying, grinding and microwave digestion following which they were diluted 1 in 10 using a Hamilton 503a dilutor with 1.1ppm gold prior to analysis. Once diluted, each sample was mixed “tube to tube” with a clean polypropylene test tube and analysed by Inductively Coupled Plasma-Mass Spectrometry (PerkinElmer Elan DRC II).

4.2.6 Data analysis and Error representation

Once all the data was collected, the full data set was processed by formatting and organising the data into a spreadsheet to allow further analysis. This was followed by data cleaning which involved identifying and correcting errors (<1% of the results were corrected) introduced as a result of the method of data entry and the process of formatting the data, and replacing values below detection with a “0”. The data set was then analysed using various data visualisation techniques to reveal the relationships, patterns and trends, all of which are discussed in the following sections.

Standard deviation is the most common approach to represent the spread of the data around the mean result however it requires a minimum of triplicate results. Due to the variety of the parameters measured in this study and the cost of all the analysis, a decision was made to use duplicates rather than triplicates. This meant that standard deviation could not be used to represent the error, therefore Min-Max error bars were used to represent the spread of the results around the mean.

4.3 Results

4.3.1 Aquifer material and native groundwater composition

EDS analysis of the aquifer material used in this study showed that it was composed of mostly oxygen (68.1%) and silica (22.1%) with noteworthy contributions of zinc (16.6%), aluminium (4.3%) and barium (4.1%). Trace amounts of potassium, iron, magnesium, sodium, calcium and chloride were also detected with atomic % ranging from 1.7% to 0.2%. Results of the XRD are shown in Figure 4.3 below. In terms of the position and intensity of the peaks shown, the XRD pattern generated form the aquifer sample matched with the database models of three crystalline phases namely Quartz (SiO_2), Microcline ($KAlSi_3O_8$) and Orthoclase ($K(Al,Fe)Si_2O_8$). It should be noted that numerous crystalline phases including a combination of elements detected with the EDS were searched. Although iron was detected by the EDS, its mineral form could not be identified. This analysis was completed at the start of the experiment.

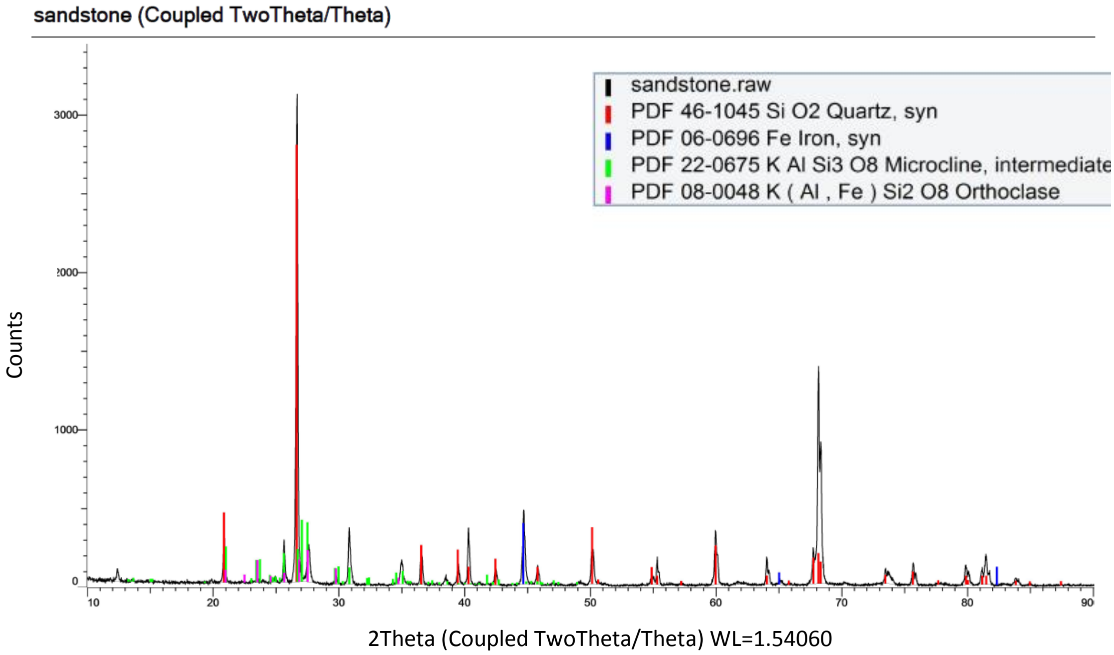


Figure 4.3: Spectrum of the aquifer material XRD analysis

The results from the experiment showed large differences in the concentrations of metals and major ions in the water before and after storage (see Section 4.3.2), therefore their concentrations in the crushed aquifer material was analysed at the end of the experiment, with a view to explaining these differences with a mass balance analysis (see Section 4.3.2). The results are shown in Table 4.4. It should be mentioned that not all the parameters were measured; Ba and U were not measured as the lab to which the samples were sent for analysis could not measure these parameters. Due to constraints in the budget, Mo was also removed from the analysis as there was no discernible difference in the water before and after storage.

Table 4.4: Concentration of metals and major ions in the Sherwood Sandstone

Parameter	Unit	Concentration
Mn	mg/kg	62.5
Fe	mg/kg	4350
Ni	mg/kg	4.84
As	mg/kg	2.28
P	% P2O5	<0.20
Mg	mg/kg	2500
Na	% Na2O	-
Co	mg/kg	1.19
Zn	mg/kg	19.1
K	%K2O	<0.05

The concentrations of all the measured parameters in the groundwater are shown in Table 4.5. Only the concentration of iron exceeds the prescribed concentration or value (PCV) for drinking water in the UK.

Table 4.5: Concentration of the measured parameters in the groundwater used to flush the columns

Parameter	Units	Concentration	PCV (Prescribed concentration or value) in drinking water in UK
As	µg/L	0.96	10
Ba	µg/L	43.59	N/a
Co	µg/L	0.11	N/a
Mn	µg/L	4.26	50
Mo	µg/L	2.60	N/a
Ni	µg/L	4.32	20
P	µg/L	53.81	N/a
U	µg/L	0.76	N/a
Zn	µg/L	32.83	N/a
K	mg/L	4.41	N/a
Mg	mg/L	25.95	N/a
Fe	mg/L	0.24	0.2
Na	mg/L	6.90	200
NH_4	mg/L	<0.20	0.5
NO_3	mg/L	4.27	50
SO_4	mg/L	70.67	250
TOC	mg/L	0.43	N/a
pH	-	7.73	N/a

4.3.2 Metals and Major ions

The full results of this experiment can be found in Appendices M-Q and this section will focus on the parameters that exceed the PCV for drinking water in the UK as this is the intended end-use, and other water quality parameters that showed significant changes during storage. Table 4.6 shows the parameters with defined PCVs and the maximum concentration observed in the recovered water along with the sample, storage time and initial concentration which produced this maximum concentration. It also provides an overall count of the samples of recovered water which exceeded the PCV, to show the parameters most likely to require further pre/post-treatment. Parameters where values higher than PCV were observed are highlighted.

Table 4.6: Details of samples where the maximum concentration was observed after storage and the overall number of recovered water samples exceeding the PCV for drinking water in UK

Parameter	PCV	Maximum value after storage	Corresponding value before storage	Sample point	Storage time	Number of samples exceeding the PCV
Arsenic	10 µg/L	16.7 µg/L	1.5 µg/L	S3	60 days	5
Manganese	50 µg/L	6205 µg/L	0.6 µg/L	S4	60 days	15
Nickel	20 µg/L	52.8 µg/L	12.7 µg/L	S1	30 days	5
Iron	0.2 mg/L	16.0 mg/L	0.1 µg/L	S3	60 days	14
Ammonium	0.5 mg/L	4.7mg/L	<0.2mg/L	S4	60 days	3
Nitrate	50 mg/L	7.8 mg/L	8 mg/L	S4	15 days	-
Sodium	200 mg/L	44.2 mg/L	52.8 mg/L	S4	15 days	-
Sulphate	250 mg/L	132 mg/L	140 mg/L	S4	15 days	-

The concentration of the measured parameters in the different source waters prior to storage is summarised in Table 4.7 and Table 4.8 and the following sections will provide the impact of different storage periods on the recovered (final) water quality.

Table 4.7: Average concentration of measured parameters in the water before 15 and 20 days storage in the columns

		15 days				20 days			
Parameter	Unit	s1	s2	s3	s4	s1	s2	s3	s4
As	µg/L	2.00	1.83	1.87	1.51	1.93	1.56	1.62	1.49
Ba	µg/L	82.85	81.11	80.69	75.02	83.06	79.80	84.79	79.43
Co	µg/L	0.28	0.27	0.22	0.19	0.23	0.20	0.20	0.19
Fe	mg/L	0.05	0.05	0.05	0.04	0.12	0.05	0.05	0.05
K	mg/L	9.64	9.37	9.42	7.94	7.57	7.91	8.12	7.90
Mg	mg/L	22.89	22.58	22.31	19.90	20.16	20.16	22.42	20.74
Mn	µg/L	6.35	3.98	2.13	0.90	3.44	0.81	0.81	1.03
Mo	µg/L	2.30	2.14	1.56	1.89	2.40	1.95	2.25	2.08
Na	mg/L	48.68	48.82	49.11	49.46	49.56	48.19	48.86	49.88
NH4	mg/L	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Ni	µg/L	6.45	15.02	59.38	31.45	4.45	14.02	3.80	3.86
NO3	mg/L	10.60	9.95	14.05	7.80	7.85	8.10	8.10	8.20
P	µg/L	238.88	262.50	334.43	761.25	412.65	307.65	391.65	365.93
pH	-	7.55	7.75	7.78	8.14	8.33	8.22	7.92	7.70
SO4	mg/L	139.00	142.50	143.00	121.50	113.50	123.50	111.00	117.00
TOC	mg/L	1.78	1.48	1.09	1.62	2.23	3.58	1.58	1.61
U	µg/L	0.53	0.51	0.34	1.04	1.03	0.99	1.12	1.04
Zn	µg/L	71.19	72.19	77.96	26.67	22.58	51.82	42.63	25.36

Table 4.8: Average concentration of measured parameters in the water before 30 and 60 days storage in the columns

		30 days				60 days			
Parameter	Unit	s1	s2	s3	s4	s1	s2	s3	s4
As	µg/L	1.83	1.56	1.50	1.78	1.44	1.46	1.49	1.44
Ba	µg/L	67.57	79.80	74.03	67.67	77.86	83.79	88.41	85.16
Co	µg/L	0.30	0.20	0.20	0.62	0.20	0.21	0.19	0.16
Fe	mg/L	0.05	0.05	0.05	0.30	0.05	0.09	0.05	0.08
K	mg/L	8.74	7.91	7.80	9.03	7.25	7.08	6.98	6.83
Mg	mg/L	18.01	20.16	19.53	18.53	19.01	18.48	18.38	17.69
Mn	µg/L	0.98	0.81	0.92	6.10	2.13	0.47	0.68	0.55
Mo	µg/L	2.46	1.95	1.86	10.25	2.19	2.25	2.22	2.15
Na	mg/L	39.85	48.19	48.41	41.75	44.98	44.45	44.50	44.48
NH4	mg/L	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Ni	µg/L	9.76	14.02	136.50	44.10	10.16	20.79	48.62	2.71
NO3	mg/L	9.20	8.10	8.15	8.10	9.15	9.55	8.90	9.90
P	µg/L	330.75	307.65	302.40	593.78	108.15	101.38	97.55	303.45
pH	-	7.82	8.22	8.12	7.67	7.94	7.79	7.75	7.69
SO4	mg/L	126.00	123.50	119.00	129.00	122.00	133.50	125.00	126.00
TOC	mg/L	4.27	3.58	1.94	2.69	2.33	1.74	2.26	1.40
U	µg/L	1.00	0.99	1.04	0.90	0.89	0.90	0.86	0.81
Zn	µg/L	34.28	51.82	54.23	34.70	202.65	54.23	81.59	33.86

Iron

Overall the concentration of iron in the water increased during storage in the columns over all four retention periods tested (15, 20, 30 and 60 days) (Table 4.9). However none of the source waters seemed to promote release of iron from the aquifer material to a greater extent than others. During 15 days storage, S1 (GAC treated water) resulted in the largest difference in concentration before and after storage with a difference of 2.13mg/l which is a 4160% increase. During the 20 and 30 days storage period S2 (column receiving GAC and UF treated water) resulted in the largest difference of 3.02mg/l and 6.82mg/l which is a 5940% increase and 13540% respectively. S3 (GAC+UF+H2O2/UV+GAC treated water) showed the largest increase during 60 days storage, with a difference of 15.99mg/l which is a 31880% increase, the largest increase seen in the experiment.

Table 4.9: Average concentration of Fe (mg/l) in the water before (initial) and after (final) storage in the columns. PCV for Fe = 0.2mg/l

	Storage time							
Source water	15 days		20 days		30 days		60 days	
	initial	final	initial	final	initial	final	initial	final
S1	0*	2.13	0*	1.02	0*	0*	0*	14.27
S2	0*	1.49	0*	3.02	0*	6.82	0.10	12.88
S3	0*	1.17	0*	1.58	0*	4.12	0*	15.99
S4	0*	0.65	0*	0.84	0.30	0.80	0*	14.11

** values below the limit of detection (0.1mg/l).*

All recovered waters had a concentration higher than the PCV following storage in the column, with the exception of S1 after 30 days storage. Generally the concentration of iron in the recovered page water increased with longer retention times, and this was investigated further by plotting the differences in concentration of iron before and after storage over the different retention periods (Figure 4.4 below). There is an excellent linear correlation between the increase in concentration during storage and the storage time for S3 and S2 with R^2 values of 0.98. S1 and S4 have lower R^2 values of 0.82 and 0.90 respectively which is likely due to the lower concentration of iron observed in the recovered water after 30 days of storage. A linear trend-line was chosen as it offered the best fit to the results.

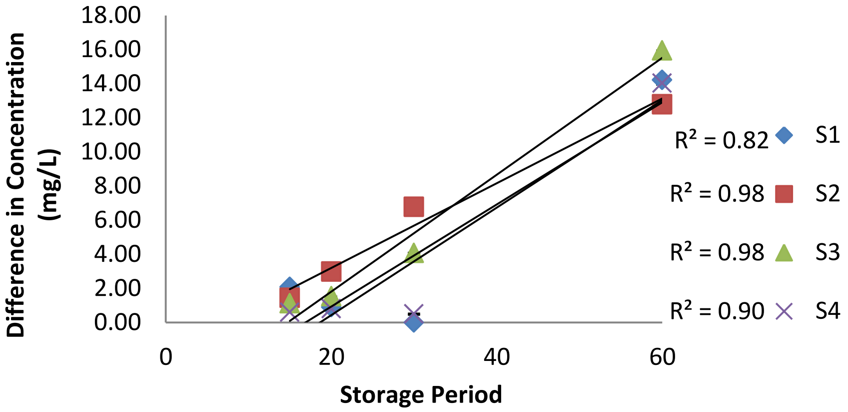


Figure 4.4: Relationship between storage period and concentration of iron in the recovered water

As the literature search showed that metals such as iron in recovered water could be present in both soluble and insoluble form, the water from three columns were analysed using both filtered (through a 0.45μm filter) and unfiltered samples as shown in Table 4.10. It should be noted that in order to perform this analysis, a separate batch had to be employed as the water recovered from the columns was not sufficient to perform this analysis. It is for this reason that this analysis was not performed on all the columns. The results show that filtered samples had iron concentrations an order of magnitude lower than the unfiltered samples. Insoluble iron precipitation was also evidenced by the darkening of the aquifer material after storage, which was noticed when the columns were dismantled.

Table 4.10: Results from filtered and unfiltered recovered water from three columns; S2 20 days storage, S2 30 days storage and S3 30 days storage. Filtered values are highlighted

Element	Unit	Sample Name	Storage period	Value
Fe	mg/L	s2	20	0.1932
Fe	mg/L	s2	20	0.29715
Fe	mg/L	s2	20	2.95785
Fe	mg/L	s2	20	3.08385
Fe	mg/L	s2	30	0.28665
Fe	mg/L	s2	30	0.29085
Fe	mg/L	s2	30	6.7851
Fe	mg/L	s2	30	6.8502
Fe	mg/L	s3	30	0.11025
Fe	mg/L	s3	30	0.12075
Fe	mg/L	s3	30	4.1055
Fe	mg/L	s3	30	4.14225

Arsenic

The concentration of arsenic increased in all the columns, albeit to different extents (Table 4.11). The data shows that storage of S3 (GAC+UF+H2O2/UV+GAC treated water) resulted in the highest concentration after all storage periods except for 20 days, which is the only period where S2 (GAC and UF treated water) produced the highest concentration of As in the recovered water with 6.10 µg/l. Storage of S4 (GAC+UF+H2O2/UV+GAC+ Chlorinated water) for 15 and 30 days produced the lowest concentration of As in the recovered water, 3.10µg/l and 3.11µg/l respectively.

Table 4.11: Average concentration of As (µg/l) in the water before (initial) and after (final) storage in the columns. PCV for As = 10µg/l

	Storage time							
	15 days		20 days		30 days		60 days	
Source water	initial	final	initial	final	initial	final	initial	final
S1	2.00	4.60	1.93	3.48	1.83	7.21	1.44	13.65
S2	1.83	3.77	1.56	6.10	1.56	6.17	1.46	12.76
S3	1.87	4.97	1.62	5.03	1.50	8.70	1.49	16.70
S4	1.51	3.10	1.49	3.58	1.78	3.11	1.44	15.86

As in the case of iron, the concentration of arsenic generally increased with longer retention times, and this was investigated further by plotting the differences in concentration of arsenic before and after storage over the different retention periods as shown in Figure 4.5.

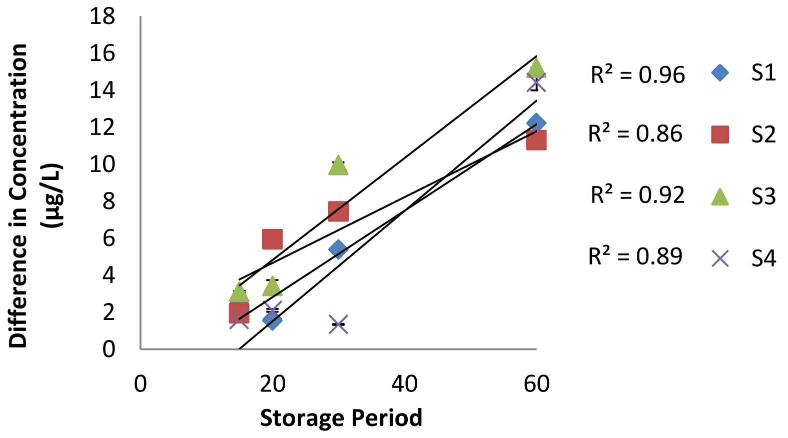


Figure 4.5: Correlation between the storage period and the concentration of As in the recovered water for S1, S2, S3 and S4

Once again, a linear trend-line was chosen as it offered the best fit to the results. The strongest correlation between the storage time and concentration in recovered water was in S1 (R^2 = 0.96) followed by S3 (R^2=0.92), S4 (R^2=0.89) and S2 (R^2=0.86). Since the literature review suggested a relationship between iron and arsenic exists, and the results of this experiment showed both increased with time, the concentration of both in the recovered water were plotted as shown in Figure 4.6 to explore this relationship. There is a partial relationship between these parameters since an increase in one coincides with an increase in the other in all but two measurements (discussed further in Section 4.4.1).

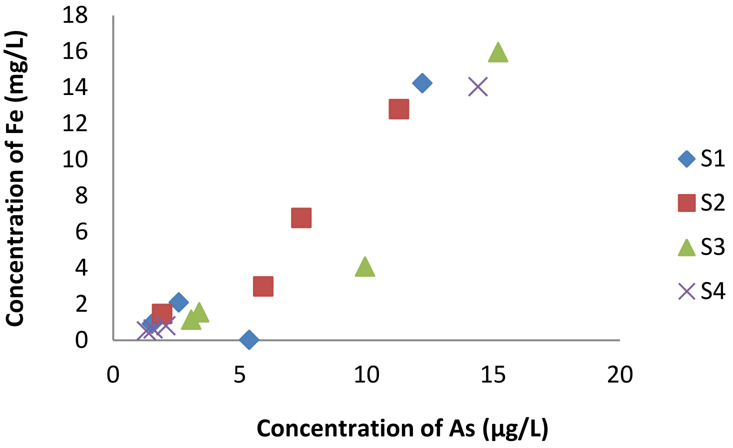


Figure 4.6: Relationship between the concentration of arsenic and iron in the recovered water

Since there seems to be a relationship between the concentration of iron and arsenic in the recovered water, water from three columns that were analysed for iron using both filtered and unfiltered samples was also analysed for arsenic. The results of this analysis (Table 4.12) show that the filtered samples contained much lower concentrations of arsenic than the unfiltered samples.

Table 4.12: Results from filtered and unfiltered recovered water from three columns; S2 20 days storage, S2 30 days storage and S3 30 days storage. Filtered values are highlighted

Element	Unit	Sample Name	Storage period	Value
As	µg/l	s2	20	4.4205
As	µg/l	s2	20	4.9665
As	µg/l	s2	20	7.2135
As	µg/l	s2	20	7.791
As	µg/l	s2	30	3.2865
As	µg/l	s2	30	3.381
As	µg/l	s2	30	8.925
As	µg/l	s2	30	9.072
As	µg/l	s3	30	5.8905
As	µg/l	s3	30	6.027
As	µg/l	s3	30	11.34
As	µg/l	s3	30	11.55

This along with the apparent correlation between the concentration of iron and arsenic in the recovered water shown in Figure 4.6 suggests there is a relationship between the concentration of iron and arsenic in recovered waters, which is discussed in Section 4.4.1.

Manganese

The concentration of manganese increased significantly during storage in all the columns with concentrations in the recovered water being significantly higher than the PCV, except for S4 (GAC+UF+H2O2/UV+GAC+Chlorinated treated water) after 30 days storage, which had the lowest increase in concentration during storage (Table 4.13) and remained below the PCV. The largest increase in manganese of 6131.32 µg/L was found in S3 after 60 days storage in the column, however interestingly almost double the amount of manganese was released during 15 days storage of S1 (4209.10µg/L) and

S2 (4983.52µg/L) than during storage for 60 days of the same water (2276.37µg/L and 1810.78µg/L respectively). There is no apparent relationship between the concentration of manganese in the recovered water and the period of retention.

Table 4.13: Average concentration of Mn (µg/l) in the water before (initial) and after (final) storage in the columns. PCV for Mn = 50µg/l

	Storage time							
	15 days		20 days		30 days		60 days	
Source water	initial	final	initial	final	initial	final	initial	final
S1	6.35	4,215.75	3.44	482.48	0.98	326.03	2.13	2,278.50
S2	3.98	4,987.50	0.81	1,808.63	0.81	1,708.88	0.47	1,811.25
S3	2.13	2,971.50	0.81	1,869.00	0.92	1,420.13	0.68	6,132
S4	0.90	1,417.50	1.03	950.25	6.10	13.97	0.55	6,084.75

The initial concentration of manganese in S4 in the 30 days batch is much higher than the other batches except for S1 in the 15 days batch, and the concentration is higher than S1, S2 and S3 in this batch while the final concentration in S4 is lower than the other waters in all other batches. Another inconsistent result was the concentration of manganese in the recovered water after storage of S1 and S4 for 20 (482.48µg/L and 950.25µg/L respectively) and 30 days (326µg/L and 13.97µg/L respectively), which have a significantly lower concentration of manganese in comparison to the rest of the results.

Since manganese released during storage could also be in either soluble or insoluble form as in the case of iron, water from three columns was analysed using both filtered and unfiltered samples as shown in Table 4.14. There was little difference in the concentration of manganese in the filtered and unfiltered samples. These results are discussed in Section 4.4.1.

Table 4.14: Results from filtered and unfiltered recovered water from three columns; S2 20 days storage, S2 30 days storage and S3 30 days storage. Filtered values are highlighted

Element	Unit	Sample Name	Storage period	Value
Mn	µg/L	s2	20	1764
Mn	µg/L	s2	20	1806
Mn	µg/L	s2	20	1764
Mn	µg/L	s2	20	1900
Mn	µg/L	s2	30	1680
Mn	µg/L	s2	30	1722
Mn	µg/L	s2	30	1659
Mn	µg/L	s2	30	1775
Mn	µg/L	s3	30	1407
Mn	µg/L	s3	30	1418
Mn	µg/L	s3	30	1418
Mn	µg/L	s3	30	1439

Nickel

The concentration of Ni was higher than the PCV in all waters after storage with the exception of S1, S2 and S3 after 15 days storage, S2, S3 and S4 after 30 days storage and S1, S2, S3 and S4 after 60 days storage (Table 4.15).

Table 4.15: Average concentration of Ni (µg/l) in the water before (initial) and after (final) storage in the columns. PCV for Ni = 20µg/l

	Storage time							
	15 days		20 days		30 days		60 days	
Source water	initial	final	initial	final	initial	final	initial	final
S1	6.45	4.46	4.45	24.47	9.76	49.14	10.16	0*
S2	15.02	10.90	14.02	21.79	14.02	5.07	20.79	0*
S3	59.38	11.76	3.80	33.65	136.50	9.60	48.62	15.01
S4	31.45	25.73	3.86	42.32	44.10	12.97	2.71	0*

**Values below the limit of detection (0.1 µg/l).*

The fate of Ni during storage was highly variable with concentrations reducing in all the waters during 15 and 60 days, increasing in all waters during 20 days storage and increasing in S1 during 30 days storage while reducing in S2, S3 and S4. Where the concentration reduced during storage, the largest reduction was seen in S3 with a reduction of 47.62µg/l, 129.85µg/l and 33.61µg/l after 15, 30 and 60 days storage respectively. The initial concentration of Ni in all these waters was also among the highest concentrations.

Other Water quality changes

The concentration of nitrate reduced during storage in all the columns, except the column fed with water from S4 after 15 days storage as shown in Figure 4.7. The retention period with the largest reduction was 60 days with almost all nitrate being removed, however the largest reduction in concentration of 9.4mg/l was observed after 15 days storage of S3. A temporal variation in nitrate concentration can be noticed in S1 and S4 whereby the removal during storage increases with a longer retention period, however this is less obvious in S2 and S3 which show a lower removal rate during 30 and 20 days storage.

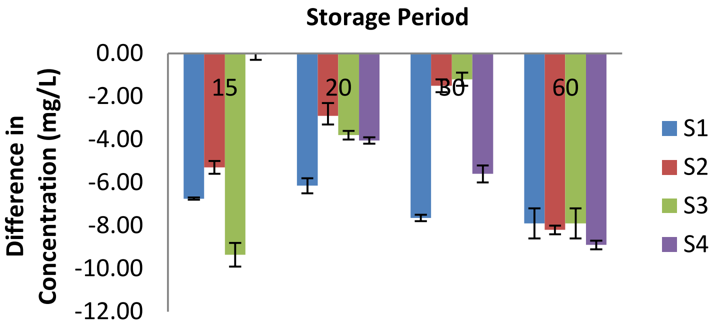


Figure 4.7: Variation in concentration of Nitrate in the water before and after storage in the columns

The TOC concentration increased during storage in all columns except for S4 after 30 days storage, where the concentration reduced by 1.7mg/l (Figure 4.8). The smallest increase in TOC concentration was in S4 after 15 days storage, with an increase of 0.1mg/l. Overall, the largest increase in TOC was seen after 60 days storage with S4 showing the largest increase from 1.4mg/l to 136mg/l, and this storage period also corresponds to the largest overall reduction in nitrates. The lack of nitrate removal in S4 after 15 days corresponds to the lowest increase in TOC concentration, however a slight reduction in TOC in S4 after 30 days was found, even though the nitrate concentration reduced by 4.05mg/l.

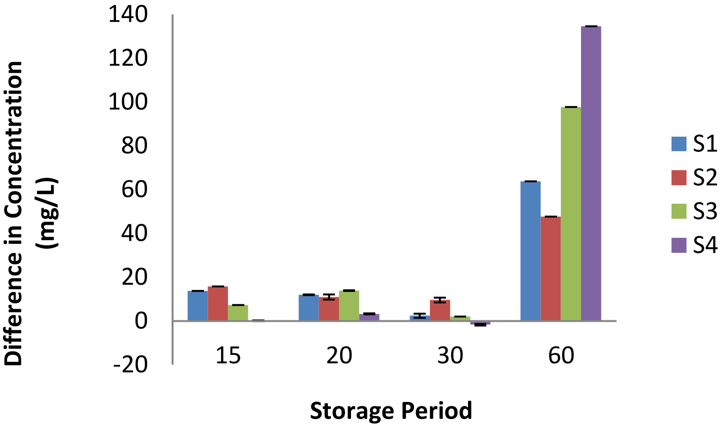


Figure 4.8: Difference in concentration of TOC in the water before and after storage in the columns

Table 4.16 shows the concentration of ammonium in the waters before and after storage in the columns. There was no detectable change in the concentration of ammonium during storage except for S1 after 20 days, S3 after 30 days and all waters after 60 days. Of these, only S1 after 20 days, and S4 60 days resulted in a concentration higher than the 0.5mg/l PCV, with concentrations of 1.83mg/l and 4.64mg/l respectively.

Table 4.16: Concentration of NH_4 (mg/l) in the water before (initial) and after (final) storage in the columns. PCV for NH_4 = 0.5mg/l

	Storage time							
	15 days		20 days		30 days		60 days	
Source water	initial	final	initial	final	initial	final	initial	final
S1	0*	0*	0*	1.83	0*	0*	0*	0.35
S2	0*	0*	0*	0*	0*	0*	0*	0.28
S3	0*	0*	0*	0*	0*	0.42	0*	0.35
S4	0*	0*	0*	0*	0*	0*	0*	4.64

** values below the limit of detection (0.2mg/l).*

The concentration of sulphate also reduced during storage in all the columns as shown in Table 4.17, however the most significant reduction was seen after 60 days storage, with the largest reduction of 71mg/l observed for S2. Overall the decrease in concentration after 15 days storage was greater than 20 and 30 days (where measured), with larger reductions in S1 and S2.

Table 4.17: Concentration of SO_4 (mg/l) in the water before (initial) and after (final) storage in the columns. PCV for SO_4 = 250mg/l.

	Storage time							
	15 days		20 days		30 days		60 days	
Source water	initial	final	initial	final	initial	final	initial	final
S1	139	101	114	87	126	-*	122	54
S2	143	108	124	87	124	92	134	62.5
S3	143	107	111	101	119	93	125	66
S4	122	103	117	101	129	-*	126	61

**Not measured*

The concentration of sodium also reduced during storage (Table 4.18), however the storage period had little impact on the magnitude of this decrease. No trends in the reduction can be ascertained with respect to the source of water or storage that resulted in the largest decrease in concentration.

Table 4.18: Concentration of Na (mg/l) in the water before (initial) and after (final) storage in the columns. PCV for Na = 200mg/l

	Storage time							
	15 days		20 days		30 days		60 days	
Source water	initial	final	initial	final	initial	final	initial	final
S1	48.68	34.62	49.56	22.28	39.85	22.91	44.98	37.50
S2	48.82	39.85	48.19	29.09	48.19	36.05	44.45	37.31
S3	49.11	32.47	48.86	37.77	48.41	40.18	44.50	30.36
S4	49.46	34.69	49.88	32.70	41.75	16.56	44.48	34.40

Mass Balance Analysis

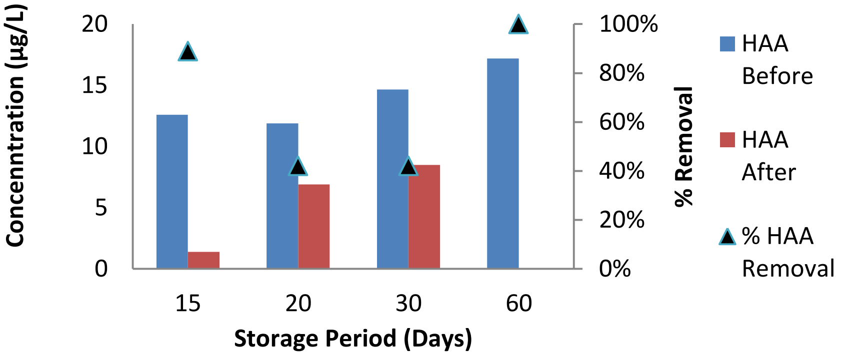
In order to determine the sources and sinks of the trace metals, a mass balance analysis was attempted, the results of which are shown in Appendix R. The mass of the trace metals in the different sources of water before and after storage are shown over the different storage periods, as well as the mass in the groundwater. The difference in mass of the element in the raw aquifer material before any water was introduced and the mass of the element in the aquifer material after storage is shown in the table within the graph.

The expectation of a mass balance analysis is that an increase in the mass in one phase (e.g. the water) should correspond with a decrease in the mass in another phase (e.g. the aquifer material). This was not found to be the case in this analysis as often an increase in the water corresponded to an increase in the aquifer material. One explanation for the lack of a discernible relationship in these results can be the analytical method used to determine the mass of the elements in the aquifer material. Only 5ml of the sandstone sample is required to complete the analysis, out of the two litres that was in the column. This makes it extremely difficult to obtain a sample representative of the whole column especially since it is highly improbable that all reactions took place equally throughout the column. Ideally several samples would have been taken from each column, however as the samples were sent to external labs for analysis, funding limitations meant this was not possible. The results from this analysis will therefore not be discussed in Section 4.4.

4.3.3 DBP's

The concentration of THMs and HAAs in S4 (chlorinated water) before and after storage in the columns are shown in Figure 4.9. The largest decrease in the recovered water concentration was seen during 60 days of storage of S4, with a 100% removal for both HAAs and THMs. The second largest reduction in concentration was seen after 15 days storage which saw the HAAs reduced by 89% and THMs reduced by 97%, followed by a 42% reduction in HAA and 52% reduction in THM after 20 days storage, and 43% and 82% respectively after 30 days storage.

(a)



(b)

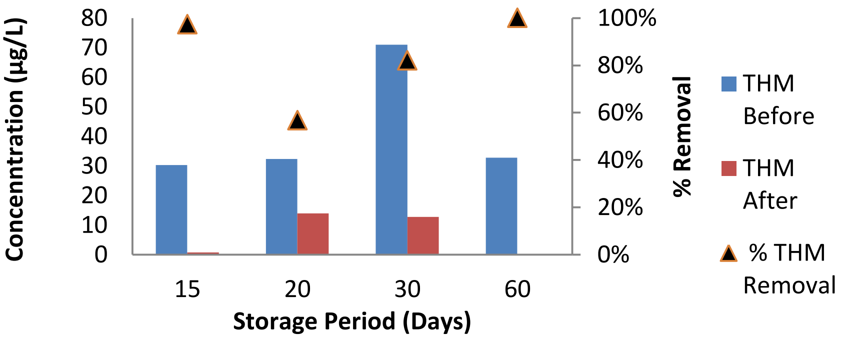


Figure 4.9: Concentration of (a) HAA and (b) THM in S4 before and after storage over time

4.4 Discussion

4.4.1 Metals and major ions

Water in aquifers is usually in geochemical equilibrium with the aquifer matrix. The introduction of aerated water with a different composition to the native groundwater into anaerobic aquifers can induce geochemical reactions such as mineral precipitation and dissolution, cation exchange, and redox reactions (Pavelic et al., 2006). Mixing with the native groundwater can either increase or reduce concentrations of metals and major ions in the recovered water depending on the concentrations present in the groundwater, and sorption onto the aquifer matrix can reduce concentrations. This section discusses the results presented in Section 4.3 to determine the parameters that pose the main threat to potential ASR scheme in the Sherwood Sandstone aquifer. Although the influence of different recharge water qualities on recovered water quality was explored, it should be noted that the results showed that it is difficult to ascertain which source of water would be the most suitable in terms of minimising unfavourable changes in water quality during storage using this data, due to the variability of the results over different storage periods. Even though the suitability of the water for recharge will not be discussed, the variability between the concentrations of the measured parameters in the recovered water and the recharge water will be. Furthermore, the impacts of these results on the viability of a potential ASR scheme will be discussed in Chapter 5.

Iron

It is difficult to establish whether a particular source of water had a distinguishable impact on the concentration of iron in the recovered water, as almost all the recovered waters had a concentration higher than the PCV following storage in the column, with the exception of S1 after 30 days storage. This is an important finding as it implies that release of iron during storage is a likely outcome in the potential ASR scheme, thereby post-treatment to deal with this will be required. The results from S1 after 30 days storage is likely erroneous as the concentrations of other parameters (i.e. arsenic, barium, potassium, molybdenum, uranium and zinc) measured in the water recovered from the columns fed with S1 in the 30 days batch also differ from the overall trends observed (see Appendix Q). One possible explanation for this is an incomplete digestion of the water prior to analysis, as a result of equipment malfunction.

Overall, there is a relatively strong correlation between the retention period in the columns and the concentration of iron in the recovered water as indicated by the R^2 values in Figure 4.4 (0.82, 0.98, 0.98 and 0.90, for S1, S2, S3 and S4 respectively) which implies a directly proportional relationship between the two. The possible sources for the increase in iron concentration are the native groundwater that remained in the column, or the aquifer material. Since the concentration of iron increased with an increasing storage time, the increase of iron in the water is most likely to be due to the dissolution of iron from the aquifer material. Dissolution of iron bearing mineral oxides is known to be the key contributor to the increasing concentration of iron in the recovered water (Vanderzalm et al., 2009). It is therefore likely that eventually a state of equilibrium will be reached with regards to the iron concentration in the water and the mineral phase. At this point, the linear relationship between storage time and concentration of iron in the recovered water would taper off and an increase in storage time would not result in an increase in Fe concentration.

Analysis of the crushed raw aquifer material indicated that iron was present at relatively high concentrations (4350mg/kg). Although the XRD could not identify the mineral form of the iron detected, the dominant mineral source of reduced iron in most sandstone formations is pyrite (FeS_2) (Stuyfzand, 1998; Vanderzalm and Le Gal La Salle, 2005). The release of iron in the water during storage may suggest presence of pyrite in the aquifer material. The predominant reactions that can initiate pyrite oxidation include oxygen, nitrate or ferric iron as the electron acceptors (Vanderzalm and Le Gal La Salle, 2005).

$4FeS_2 + 15O_2 + 16HCO_3^- \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16CO_2 + 2H_2O$ *Reaction 1*

$5FeS_2 + 14NO_3- + 4H^+ \rightarrow 5Fe^{2+} + 10SO_4^{2-} + 7N_2 + 2H_20$ *Reaction 2*

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$ *Reaction 3*

Pyrite oxidation produces sulphate (Stuyfzand, 1998; Ruiter, 2005), however this study did not see an increase in sulphate concentrations during storage in any columns as shown in Section 4.3.2. In fact the sulphate concentrations consistently decreased during storage. Considering that sulphate does not have any other sources or sinks during storage in an aquifer (Stuyfzand, 1998), pyrite is unlikely to be present in this aquifer material.

Edmunds et al. (1982) conducted a detailed hydrogeochemical study of the Sherwood Sandstone aquifer in the same area from which the core was obtained, and found the main mineral sources of iron included iron oxides such as haematite (Fe_2O_3), lepidocrocite (γ-FeO(OH)) and geoethite (α-FeO(OH)).

The native groundwater has a relatively high concentration of iron (0.24mg/L), which is soluble (Fe^{2+}). Introduction of oxic water into the reducing environment will result in the oxidation of ferrous (Fe^{2+}) iron to ferric (Fe^{3+}) iron via the following reaction (Maliva and Missimer, 2010):

$O_2 + 4Fe^{2+} + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$ *Reaction 4*

This reaction will impact the mineral stability of the aquifer material as the decrease in concentration of the Fe^{2+} ion will promote dissolution of minerals containing reduced iron, and the increase in concentration of the Fe^{3+} ion will promote precipitation of minerals containing oxidised iron (e.g. goethite and lepidocrosite). This will in turn increase the concentration of iron (ferric and ferrous) in the recovered water. Once all the oxygen has been consumed, mineralisation of organic matter in anaerobic conditions can lead to iron hydroxide reduction which can release ferrous iron and other previously adsorbed species (Lovley and Phillips, 1986; Vanderzalm et al., 2009) via the following reaction (Schreiber et al., 2003).

$4Fe(OH)_3 + 8H^+ + CH_2O \rightarrow 4Fe^{2+} + 11H_20 + CO_2$ *Reaction 5*

Reductive iron (III) dissolution due to the introduction of organic matter was also reported in the South London Aquifer Recharge Scheme, where pyrite oxidation was not reported (MWH, 2004). In order to explore the evidence for this mechanism, the presence of both ferrous and ferric iron was tested by analysing the recovered water from S2 after 20 days storage and S2 and S3 after 30 days storage using both filtered (0.45µm) and unfiltered samples. Ferric iron (Fe^{3+}) forms precipitates which are insoluble in water and therefore easily filtered, while ferrous iron (Fe^{2+}) is soluble and therefore remains in the water even after filtration. From the results in Table 4.10, it is evident that the filtered samples had significantly less iron than the unfiltered samples, which suggests that the recovered water contained mostly ferric iron, which supports Reaction 4.

This is an important finding because iron oxide precipitates have a large sorptive capacity and therefore play a key role in the adsorption and immobilisation of other trace metals such as arsenic (Vanderzalm et al., 2009). Reductive dissolution of iron oxides can lead to increases in the concentration of trace metals such as arsenic as previously sorbed species are released (Arthur et al., 2007; Vanderzalm et al., 2007; Vanderzalm et al., 2005).

Arsenic

As in the case with the behaviour of iron, it is difficult to establish whether a particular source of water had a distinguishable impact on the recovered water quality in this experiment. It is however very clear that the storage period has a significant influence on the concentration of As in the recovered water, with a longer storage time corresponding to a higher concentration of As in the water as illustrated in Figure 4.5.

It should be noted that the correlation suggesting a linear relationship between storage period and concentration of As in recovered water is valid for a storage period of <60 days. However, an increase in storage time beyond 60 days would not necessarily result in a continuous increase in As concentration, which is likely to taper off eventually. This is because the main source of arsenic in the recovered water is dissolution of iron oxides, and as explained, this dissolution would eventually taper off.

Analysis of the crushed raw aquifer material indicated that arsenic was present at concentrations of 2.28mg/kg. The main sources of arsenic during ASR are either sulphides or iron oxides (Vanderzalm et al., 2009; Maliva and Missimer, 2010). As explained in the case of iron, sulphides are unlikely to be present in the Sherwood Sandstone material and the most likely source of arsenic in this study is therefore from the reductive dissolution of iron oxides, which release previously sorbed trace metals such as arsenic (Arthur et al.. 2007, Vanderzalm et al., 2007 and Vanderzalm et al., 2005). The results of the experiment support this hypothesis, as the increase in concentration of arsenic in the recovered water coincides with the increase in iron concentrations as shown in Figure 4.6. As the concentration of iron increases in the recovered water, so does the concentration of arsenic.

Further evidence of the relationship between the iron oxides and arsenic was provided by finding that the filtered (0.45µm) samples contained a concentration of almost half of the unfiltered samples (Table 4.12). This implies that as the iron oxides are filtered out, the sorbed arsenic is also removed, lowering the concentration of arsenic.

Arsenic has been reported as a major issue in several ASR schemes where recharge occurs in a sandstone aquifer such as in Florida (Arthur et al., 2007), Wisconsin (Brown et al., 2006), Netherlands (Stuyfzand, 2001) and Australia (Vanderzalm et al., 2007). It is therefore not a new issue however it can be a major problem in ASR systems because the very low PCV of 10 µg/l means a small amount of leaching could lead to the drinking water quality standards being violated, leading to more extensive post recovery treatment requirements. Although the concentration of arsenic increased during storage in all the columns, the PCV was only exceeded after 60 days storage. This implies that if longer storage periods are required, then concentration of arsenic in the recovered water is more likely to be a problem.

Manganese

The concentration of manganese in the recovered water was significantly higher than the recharge water with a thousand fold increase in all waters except S1 and S4 after 20 days storage (482.48µg/L and 950.25µg/L respectively) and 30 days storage (326µg/L and 13.97µg/L respectively). As discussed for iron, the low concentration in S1 after 30 days storage may be attributed to an incomplete digestion of these waters, however the lower concentration in the other recovered waters suggests another mechanism may be responsible. The water recovered from these columns also had the highest pH values of 8.32, 7.97, 7.86 and 7.95 respectively, and since manganese is less soluble at pH values above 8 (Pyne, 2005a; Patterson et al., 2010), it makes sense to have lower concentrations of manganese in these waters.

A discrepancy was noted in the initial concentration of manganese in S4 in the 30 days batch, which is much higher than the other batches. This result did not fit with the rest therefore it was checked against the treatment works sampling data. As S4 is the final water produced from the treatment works, it was sampled by Anglian Water on the same date a sample for this experiment was taken. The sample was found to contain a concentration of manganese of <1 µg/l which is consistent with the concentrations is S4 in the other batches. It is therefore likely that the S4 30 days sample was contaminated at some point in the analytical process.

The magnitude of the increase in manganese concentration during storage found in this experiment is not uncommon, for example Antoniou (2015) found the concentration in recovered water to have increased by 1098µg/L after storage in an anoxic sand aquifer in Herten, Netherlands, Pyne (2005a) found the concentration of manganese in the recovered water increased by 1030µg/L after storage in a sandy aquifer in Chesapeake, Virginia, and Stuyfzand et al.(2005) who found a concentration of 1208.64 µg/L in the recovered water after storage for 106 days in a sandy aquifer in Netherlands.

The largest increases in manganese of 6131.3µg/L and 6084.2µg/L were found in S3 and S4 respectively after 60 days storage, which makes sense since a longer storage period provides more opportunity for biogeochemical reactions to take place, however the increase in concentration in S1 and S2 was not as high 2276.4µg/L and 1810.8µg/L. This coupled with the fact that the second highest increase in concentration was seen in S1 (4209.10µg/L) and S2 (4983.52µg/L) after 15 days storage implies that there is another influencing factor besides pH and storage time. Solubility of manganese in alluvial aquifers has been found to vary seasonally, with higher concentrations observed in the summer months (Bourg and Bertin, 1994). The 15 days batch was implemented in summer while the 60 days batch was implemented in spring. It was not possible to regulate the temperature around or inside the columns and therefore the 15 days columns were exposed to a slightly higher temperature than the 60 days columns, which may explain the high concentrations in the recovered water in the 15 days batch.

The concentration of manganese in the recovered water is therefore most likely influenced by a combination of pH, storage time and temperature. Other factors such as the redox state, levels of mixing with native groundwater and the species of manganese would also influence the concentration in recovered water (Maliva and Missimer, 2010). As in the case of iron and arsenic, it is difficult to determine if a particular source of water had a higher impact on concentrations of manganese in the recovered water, as the concentrations were highly variable between the storage periods and source water types.

The source of manganese was determined to be the aquifer material, since the concentration of manganese in the native groundwater was only 4.26µg/L and therefore could not have resulted in the increases observed in the recovered water. The SEM and XRD analysis did not detect the presence of manganese in the aquifer material but analysis of the crushed raw aquifer material indicated that manganese was present at a concentration of 62.5mg/kg. Mn-siderite is an important source of manganese during storage in sand aquifers (Antoniou et al., 2012), as is manganese oxide (Petrunic et al., 2005), therefore both or one of these are likely the source of manganese in the aquifer material.

Although the concentration of manganese in the aquifer material was much lower than that of iron (4350mg/kg), the increase in concentration of manganese was much higher with approximately a thousand fold increase during storage. This is most likely because unlike iron, most of the manganese measured in the recovered water was in its soluble form as evidenced in Table 4.14, which shows that filtered samples had similar concentration to non-filtered. This implies manganese precipitates did not form and most of the manganese was present in its soluble form Mn^{2+}. This along with the fact that Mn^{2+} is a very stable form of manganese (Hem, 1985), could explain the much higher concentration of Mn in comparison to iron. The column would filter out some of the iron precipitates during recovery, reducing its concentration, however this would not occur for manganese since it is all in soluble form (Stuyfzand et al., 2005).

The concentration of manganese in recovered waters was higher than the PCV (50µg/L) in all but one column, therefore it is very likely that post treatment to deal with this would be required. This will be discussed further in Chapter 5.

Nickel

The fate of nickel was highly variable with concentrations generally increasing in all waters during 20 days storage and reducing in all waters during 15, 30 and 60 days storage, with the exception of S1 during 30 days storage where concentration increased relative to the initial concentrations. Storage period does not seem to influence the quality of the recovered water with respect to nickel, however it seems that initial concentrations were more important.

Where the initial concentrations were low, Ni was released during storage, while higher initial concentrations resulted in a lower concentration after storage in all cases except for during 15 and 60 days storage where even low initial concentration resulted in removal during storage. It is possible that injecting water with a low concentration of Ni results in leaching from the aquifer material. Analysis of the crushed raw aquifer material indicated that Nickel was present at a concentration of 4.84mg/kg of Ni, therefore the aquifer material is likely responsible for the increase of Ni during storage.

Ni can be adsorbed onto iron or manganese precipitates (Vanderzalm et al., 2005) however this does not appear to have occurred in this experiment as there is no apparent relationship between the concentration of nickel and iron/manganese. The decrease in concentration of Ni during storage is most likely as a result of either adsorption onto the aquifer material or mixing with the native groundwater which had a low concentration of nickel (4.32 µg/l). It is however difficult to make any conclusive comments on the fate of nickel during storage in a Sherwood Sandstone for any of the waters using this data and information with regards to the fate of nickel during storage in an aquifer is also scarce. Since the recovered water frequently exceeded the PCV, it would be useful to conduct further investigations on the fate of nickel during storage.

Other Water quality changes

In situ bio-denitrification is the most important attenuation mechanism for nitrates in groundwater and occurs when nitrate is biologically reduced to nitrogen gas during anaerobic respiration (Aravena and Robertson, 1998; Vidal-Gavilan et al., 2014).

Organic carbon is the main electron donor in denitrification, catalysed by the heterotroph *Pseudomonas denitrificans* as shown in Reaction 6 (Dillon et al., 2005a).

$$4NO_3^- + 5CH_2O + 4H^+ \longrightarrow 2N_2 + 5CO_2 + 7H_2O \qquad \text{Reaction 6}$$

This means that a longer storage period would reuslt in a larger reduction of nitrates, as the microbial community has more time to consume the nitrates. The concentration of nitrates generally reduced during storage in the columns except in the column where S4 was stored for 15 days, where no change in concentration was seen. This could be because the S4 was chlorinated, thereby reducing the microbial activity in the column and limiting degradation. In the longer storage periods, a reduction in concentration was seen, and this could be because the microbial community had a longer period to grow and aclimatise. This is supported by the finding that the largest reduction in nitrate concentration was seen after 60 days of storage, as well as a temporal variation in the nitrate concentration over time particulary for S1 and S4 which suggest that a longer storage period reduces concentration of nitrates. This was however not the case for S2 and S3 during 30 and 20 days storage which show a lower removal rate, and S3 during 15 days storage, which resulted in the largest reduction in concentration. Other factors which may impact the microbial community such as changes in pH, phosphorus content and organic carbon content did not provide any supporting evidence from which conclusions may be drawn, as no patterns between any of the parameters were evident. The reason for this variation could therefore not be determined using the data from this experiment, however since a reduction in concentration was seen in all the columns except S4 after 15 days storage, the likely reason for which was explained, it would be safe to assume that nitrate concentrations would reduce during storage, even though the extent of the reduction cannot be determined in this experiment.

Although bio-denitrification results in an improvement in water quality, it may trigger reducing conditions as a result of anaerobic degradation of organic matter during the process of denitrification (Stuyfzand, et al., 2005; Vanderzalm et al., 2002), which may influence the release of trace metals (as discussed in case of iron). Dahab (1993) reported reductions in nitrate of 50 to 100% due to bio-denitrification, however this meant that the recovered water quality would likely have high residual organic material.

Over extended storage periods, the microbial communities that have developed die off due to lack of nutrients and oxygen during storage (Antoniou, 2015), which can increase concentrations of the TOC levels in the recovered water.

This is supported by the results of this experiment which found that while the nitrate concentration in the recovered water reduced over time (Figure 4.7), the TOC concentration increased (Figure 4.8). These results do not show an obvious correlation between the TOC concentration and nitrate concentration, however they do show that overall the concentration of nitrate reduced during storage with a corresponding increase in TOC concentration. It is difficult to establish which source of water promotes the largest reduction in nitrate concentration during storage due to the variability of the results, however the results show that the concentration of nitrate is likely to reduce during storage, with a corresponding increase in TOC concentration.

Although TOC is not a regulated parameter for drinking water in the UK, its concentration needs to be controlled due to its influence on DBP formation which is regulated. The increase in concentration of TOC during storage increases the DBP formation potential of the water once it has been recovered. This will be discussed further in Chapter 5.

Mineralisation of organic matter may also release ammonium into the water during storage (Dillon et al., 2005a). Anaerobic degradation of organic matter is a slow process (Takizawa, 2008), thus it makes sense that the longest storage period of 60 days resulted in a higher concentration of ammonium in the recovered water. An increase was also seen in S1 after 20 days, S3 after 30 days, however the reason for this could not be determined, and further investigations may be useful to understand the fate of ammonium in the aquifer. Of these increases, only S1 after 20 days, and S4 60 days resulted in a concentration higher than the 0.5mg/l PCV, with concentrations of 1.83mg/l and 4.64mg/l respectively, therefore there is a possibility that post-treatment would be required for ammonium.

Sulphate reduction is a microbial process where the anaerobe *Desulfovibrio desulfuricans* uses sulphate as an electron acceptor under anaerobic conditions with an accessible organic carbon substrate (Dillon et al., 2005a) (Reaction 7). It therefore makes sense that the longest retention period of 60 days showed the largest sulphate reduction. The sulphate is reduced to hydrogen sulphide which can be identified by its odour of rotten eggs. When the columns were opened to recover the water, there was a distinct smell of hydrogen sulphide, which was noticeably stronger after 60 days storage.

$SO_4^{2-} + 2CH_2O \longrightarrow H_2S + 2HCO_3^-$ Reaction 7

The larger reduction in sulphate concentration in the 15 days batch than in the 20 and 30 days batch may be due to the columns being exposed to a slightly warmer temperature. As mentioned in the manganese section of Section 4.4.1, it was not possible to regulate the temperature. Since sulphate reduction is a microbiologically mediated process it is appropriate that overall, larger decreases were noticed in S1 and S2, since these had the highest concentration in TOC before storage (Appendix Q). Furthermore, S1 and S2 were not disinfected while S3 had undergone UV disinfection and S4 was additionally chlorinated, thereby impeding microbiological activity.

The concentration of sodium also reduced during storage, however no real difference in magnitude was seen over the different storage periods which implies that microbiology is not involved in the removal of sodium. The reduction is therefore most likely as a result of mixing with the groundwater present in the column, which has a sodium concentration of only 6.9mg/l. Cation exchange would release sodium in exchange for divalent cations, however the scale of this is generally very small (Maliva and Missimer, 2010).

4.4.2 DBP's

The final stage of most drinking water process in the UK is chlorination, which eliminates harmful microorganisms from the water. The presence of natural organic matter in the water during chlorination can result in the formation of disinfection by products such as THMs and HAAs, which are considered to be carcinogenic, hence harmful to human health. The PCV for THMs is 100µg/l and although HAAs are not currently regulated in the UK, it is likely that they will be in the near future. The USEPA standard of 60µg/l can be used as a guideline since their standard for THMs of 80µg/l is similar to the UK's PCV. As can be seen in Figure 4.9, none of the recharge or recovered waters exceeded the PCV or USEPA standard for THMs or HAAs. Furthermore, the concentration of both HAAs and THMs reduced during storage in all the columns. It should be noted that only the columns recharged with S4 were analysed for DBPs, since it was the only recharge water that was chlorinated.

The primary processes that can influence the DBP concentrations during storage include sorption of the DBP to aquifer material, mixing between injected and groundwater, chemical hydrolysis and biodegradation by aquifer bacteria (Fram et al., 2003; Pavelic et al., 2006).

In order to determine the role of sorption, breakthrough data for HAAs and THMs relative to a conservative ion such as chloride would be required. Although this was not carried out in this experiment, Buszka et al. (1994); Dillon et al. (2005b); Fram et al. (2003) and Pavelic et al. (2006) all found that sorption onto the aquifer material was not considered to be a significant removal mechanism due to the low sorption coefficient of DBPs, coupled with low organic carbon content of aquifer material.

Although mixing with the native groundwater in the column would have provided some dilution in concentrations, the difference in removal rates over the storage periods as can be seen in Figure 4.9 suggests there is another mechanism in play, since the quantity of groundwater remaining in the columns was constant across all storage periods. This implies that the most significant removal process is likely to be either hydrolysis or biodegradation, as this would explain the increased removal over time.

Hydrolysis involves a reaction between the halogenated compound and water resulting in an exchange of one of the halogens with a hydroxyl group from water (Buszka et al., 1994). Table 4.19 below reports the THM and HAA hydrolysis rates reported in the literature. It should be noted that the HAA hydrolysis rates reported in Lifongo et al. (2010) were for natural waters and not aquifers, and although specific data for aquifers is not currently available, this data provides an indication of time scales for hydrolysis to occur.

Table 4.19: THM and HAA hydrolysis half-lives at different sites

Site	HAA hydrolysis half life	THM hydrolysis half life	References
Hueco Bolson, El Paso, Texas		chloroform 3,500 years bromoform 687 years	Buszka et al. (1994)
Laboratory study		Chloroform 3500 years Bromodichloromethane 137 years Dibromochloromethane 274 years Bromoform 686 years	Stated in Vogel et al. (1987)
Laboratory study for natural waters – not aquifers	Tribromoacetic acids -103 days Trichloroacetic acids -46 years Trifluoroacetic acids -40,000 years monobromoacetic acids – 2 years dibromoacetic acids – 12 years monochloroacetic acids – 15 years dichloroacetic acids - 68 years bromochloroacetic acids – 6 years chlorodifluoroacetic acids - 83 years		Lifongo et al. (2010)

Whilst THMs and HAAs can potentially be degraded by chemical hydrolysis, half-lives are extremely long. The lack of these compounds in the recovered water following after 60 days of storage, implies the process responsible for their decrease occurs at a much faster rate, thus hydrolysis is not considered to be the removal mechanism responsible for the decrease in concentration in this experiment. This leaves biodegradation as the most likely removal mechanism, a conclusion supported by Bouwer and Wright (1988) and Thomas et al. (2000). Table 4.20 summarises the biodegradation rates of THMs and HAAs reported in the literature, and shows that the half-life for biodgradation is much shorter than that for hydrolysis, and is therefore more likely to be responsible for the removal of DBPs during storage in the columns.

Table 4.20: THM and HAA biodegradation rates at different sites

Study	HAA biodegradation rate	THM biodegradation rate	References
East Bay, California		Chloroform was dominant. Half-life = 480 days	Pavelic et al., 2006
Jandakot, Western Australia	Half-life = 13 days	All THMs were removed during the storage phase prior to pumping. Half-life = 11 days	Pavelic et al., 2006
Bolivar, South Australia	Half-life = <1 days	All THMs were removed during the storage phase prior to pumping at. Half-life = 14 days	Pavelic et al., 2006
	Half-life = <1 days	Half-life = <1 to 65 days	Pavelic et al., 2005
Charleston, South Carolina		Half-life = <1 days	Pavelic et al., 2006
Oak Creek, Wisconsin		Half-life = 10-16 days	Pavelic et al., 2006
Las Vegas, Nevada		60% more TTHMs were recovered than injected No Net removal at a different well. Half-life >120 days	Pavelic et al., 2006 Miller et al
	Concentrations less than detection within one month of storage in one well. Concentrations less than detection after 43 to 76 days of storage in three other wells. Another cycle showed Concentrations less than detection after 51 to 85 days of storage from eight wells.	Continued formation of THMs in the aquifer – no degradation observed	Thomas et al., 2000
	HAA concentrations were decreased to non-detectable levels by day 29	TTHM concentration decreased consistently throughout the short storage	Singer et al., 1999

		period (only 48 days)	
Memphis, Tennessee		Almost 8 times more TTHMs recovered than injected. Half-life = 79 days	Singer et al., 1999
Peace River, Minnesota, Arcadia;	THAA concentration fell to non-detectable levels between days 1 and 21	TTHM concentrations began to decline after day 43	Singer et al., 1999
Upper Guadalupe, Kerrville, Texas	HAAs were eliminated by the time the first storage sample was taken on day 41	TTHM concentration decreased most significantly after day 71	Singer et al., 1999
Centennial, Colombia	HAAs were completely eliminated by day 9.	The TTHM concentration decayed appreciably between days 9 and 16, and were not detectable by day 56	Singer et al., 1999
Thames Water, London	HAAs were eliminated by day 3	TTHM concentration decreased significantly Between days 3 and 22 and were not detectable after day 78	Singer et al., 1999
Monterey, California		2004 half-life = 41-50 days 2005 half- life = 1700 days. Aerobic conditions persisted in 2005	Vanderzalm et al., 2009
Laboratory study using sand media		44% reduction after 34 days retention in column	McQuarrie and Carlson, 2003

The largest decrease in the recovered water concentration was seen after 60 days of storage, with a 100% removal for both HAAs and THMs. This is as expected since the longer storage provides more time for biodegradation to occur. The second largest reduction in both THMs and HAA was seen after 15 days storage followed by 30 days and 20 days storage. In the context of this experiment the large decrease in concentration after 15 days storage does not follow the trend of biodegradation since a lower removal rate was found after 20 and 30 days storage in comparison to 15 days. Biodegradation would imply a graduated decrease in concentration rather than a large decrease initially followed by lower rate of removal over time. The most likely explanation for the anomalous 15 day result is that the water samples for DBP analysis were sent to external labs at a particularly busy time therefore it is possible that samples were not analysed within the required timeframes.

The reported rate of degradation is highly variable with half-lives varying from < 1day to 76 days for HAA's and <1 day to 480 days for THM's, according to the sites studied. The occurrence and rate of attenuation depends on the aquifer conditions such as the redox status, temperature and nutrient content of the water (Pavelic et al., 2006). These conditions are highly variable and can vary with time and distance from the injection point and at different points in the aquifer. This is demonstrated in Table 4.20 by the variability in degradation rates reported at the same ASR site, for example at the Las Vegas site, Singer et al. (1993) found THMs were degraded, while Pavelic et al. (2006) and Thomas et al. (2000) found them to form and accumulate. The heterogeneity of aquifer could result in pockets where degradation occurs, which is another reason why column experiments with homogenous aquifer material and controlled conditions is useful in determining the fate of DBPs during storage.

The results of this experiment confirm that DBPs would be degraded during storage rather than increase in concentration due to formation following injection, as was the case in Las Vegas, Nevada (Pavelic et al., 2006; Thomas et al., 2000) and Memphis Tennessee (Singer et al., 1993). THMs are formed in the aquifer mainly due to residual chlorine in the injected water however the presence of organic matter also has an impact (Singer et al., 1993; Fram et al., 2003; Vanderzalm et al., 2009). It is worth noting that only THM formation during storage has been reported in the literature and where this occurred, aerobic aquifers were used for storage. This is because HAA's can be degraded under both aerobic and anaerobic conditions, while reducing conditions are usually required for effective biodegradation of THMs (Pavelic et al., 2006; Singer et al., 1993). A lack of biodegradation can result in persistence and accumulation of THMs in the aquifer, over several injection cycles.

Overall, the concentrations of both HAAs and THMs reduced during storage in the columns for all storage periods, albeit to different extents, with the overall THM concentrations reducing faster than the HAA concentrations. These results differ from those reported in the literature (Singer et al., 1993; Thomas et al., 2000; Pavelic et al., 2005; Overacre et al., 2006), which suggested that HAA removal precedes THM removal, as they are biodegraded under both anaerobic and aerobic conditions. As biodegradation is presumed to be the removal mechanism at play, it is possible that the microbial community present in the columns were more inclined to the THMs than the HAAs. This would explain the inconsistency of the findings of this experiment to that in the literature, however detailed microbiological studies would need to be conducted to confirm this.

4.5 Conclusions

Utilising the Sherwood Sandstone aquifer to provide storage is likely produce water with high concentrations of iron, arsenic, manganese and potentially nickel, with the most substantial increase seen in the manganese concentration. Longer storage periods promote higher concentrations of arsenic and iron in the recovered water however the impact of storage time on manganese concentration in the recovered water is less clear, as pH and temperature also had an influence. The fate of nickel was dependant on its concentration in the recharge water, with low concentrations in the recharge water promoting release from the aquifer material and vice versa. Water quality also improved during storage with respect to nitrates, sulphates and DBPs, with longer storage periods producing the most significant improvements, and this was attributed to microbial activity. These improvements were accompanied by an increase in TOC, which increases the DBP formation potential of the recovered water. This is a significant threat since the recovered water is likely to be disinfected before being distributed as drinking water. The concentration of sodium also reduced during storage, however since no real difference in magnitude was seen over the different storage periods, the reduction is attributed to mixing with the groundwater. Overall, the column experiments suggest that an increase in iron, arsenic and manganese above the PCV could be a substantial threat to an ASR scheme in the Sherwood Sandstone aquifer, especially if longer storage periods are required, since post treatment requirements for these would impact the viability of the scheme. Concentration of nickel also increased above the PCV on some occasions, however there is less certainty as to the level of threat posed by these exceedances.

5 Overall Discussion

The results of the experiment show that ASR in the Sherwood Sandstone aquifer can result in water quality improvements such as biodegradation of DBPs, denitrification and reduction of sulphate. However, water quality also deteriorated with respect to trace metals such as iron, arsenic, manganese and nickel (on occasion), as well as total organic carbon concentrations in the recovered water. The mechanisms responsible for these are discussed in Chapter 4, and this chapter aims to discuss the overall implication of these changes in water quality to the viability of a potential ASR Scheme.

5.1 Water quality improvements and the regulatory agenda

A decrease in concentration of contaminants such as DBPs (THMs and HAAs) nutrients, nitrates and sulphate have been demonstrated at various ASR sites and in laboratory investigations as shown in Chapter 4. The intentional use of the natural attenuation processes to improve water quality has been referred to as natural aquifer treatment (NAT) by Maliva and Missimer (2010). Although it is important to ensure ASR does not compromise the quality of the groundwater, NAT has important implications in terms of regulation and operation of ASR schemes. If a water quality parameter is shown to decrease in concentration during storage, then the requirement for water quality standards to be met at the point of injection can be argued to be unnecessarily restrictive. A more appropriate approach would be to set the compliance point at a monitoring well as this would take the NAT into consideration (Pyne, 2005b). This is a particular issue for ASR schemes in the UK since the point of compliance for the recharge water is at the injection well. There is no legislation dedicated to ASR in the UK, however schemes are required to adhere to all existing regulations and standards.

In the context of injection water standards, the most important regulation is the Groundwater Daughter Directive (GWDD), which falls under the Water Framework Directive (WFD). The main objective of the GWDD is to prevent deterioration in the quality and quantity of the groundwater and achieve “good status” with respect to these. The directive requires that all necessary measures are taken to prevent inputs of hazardous substances into groundwater, and to limit the input of non-hazardous substances to prevent pollution, deterioration in status or a significant and sustained upward trend. The difference between these should be noted. Hazardous substances are not permitted to enter the groundwater regardless of whether they would pollute the groundwater or not, while non-hazardous substances may be allowed entry provided they do not pollute the groundwater.

The survey of ASR sites conducted in Chapter 2 found that there is little experience in authorising ASR projects under existing legislation in the UK. The main area of contention with regards to injectant standards is the “no deterioration in water quality” requirement of the GWDD (Dixon, 2012). Interpretation of the GWDD is unclear with regards to ASR, since it is possible for the injectant to be drinking water quality, however if the concentrations of non-hazardous substances such as trace metals and nutrients are higher than that in the groundwater, then it could be interpreted as a deterioration in the water quality. This kind of interpretation would seriously threaten the viability of this ASR scheme, since the concentration of all measured parameters were higher in most of the recharge waters with the exception of manganese, molybdenum, magnesium and iron which were higher in the groundwater. It should be noted that trace metals and nutrients are classed as “non-hazardous”.

UKTAG (2011) interprets “the control of non-hazardous substances to ensure there is no significant and sustained upward trend, and no deterioration in status” requirement to mean that inputs should not cause pollution. A slight deterioration in the groundwater quality due to the higher concentrations of non-hazardous substances in the injectant is not in itself regarded as “pollution”, which requires a risk “receptor”. Receptors include any connected ecosystems or any other users. Since the water adheres to drinking water standards, it can be argued that there is no risk to other users or connected ecosystems (unless the connected ecosystems require the standards higher than those imposed for drinking water).

It is recognised that ASR could prove to be very beneficial, especially in terms achieving a good quantitative status therefore there are some exemptions stated in Article 6(3) of the Directive that may be applicable to ASR schemes as highlighted by UKTAG (2011). Under GWDD Article 6 (3)(a) and 6 (3)(d) respectively, “direct discharges of pollutants to groundwater authorised under Article 11(3)(j) of the WFD and artificial recharges authorised under Article 11(3)(f) are exempted from the requirement to take all measures to prevent or limit, but must otherwise meet the environmental objectives of the groundwater body". The environmental objective as set out in Article 4(1)(b)(ii) of the WFD is to "protect, enhance and restore all bodies of groundwater, ensure a balance between abstraction and recharge of groundwater, with the aim of achieving good groundwater status". Furthermore, under Article 6.3(e)(i) of the GWDD, the competent authority, which in this case is the Environment Agency, may exempt the requirement to take all measures to prevent/limit inputs that are technically feasible if they result in increased risk to human health or the quality of the environment as a whole.

These exemptions provide a possibility of balancing the risks to the groundwater with the risk to the wider environment, which is an important factor when considering ASR. The use of ASR for local consumption significantly reduces the energy requirements for pumping water over long distances and infrastructure requirements, and the reliance on NAT can reduce the engineering requirements for treatment (Dillon et al., 2008; Dillon et al., 2010), thereby increasing the overall benefit to the environment. Regulation of groundwater quality to meet good chemical status should not be at the expense of meeting good quantitative status.

Over a quarter of groundwater bodies in England are at risk of failing the environmental objectives set in the WFD due to over-abstraction (Environment Agency, 2006). An opportunity is provided by artificial recharge projects to maintain sustainable abstractions and meet good quantitative status in these over-abstracted bodies. Wider implementation of ASR should be encouraged by the regulations rather than imposing unnecessarily restrictive standards. Of course the quality of the groundwater must not be neglected, and the Environment agency has stated that a minimum standard of drinking water quality will be imposed on all ASR sites as they consider all aquifers to be potential drinking water sources regardless of the native water quality. It is therefore argued, that as long as the concentrations of all non-hazardous substances are below the drinking water standards, there should be no requirements for further treatment before injection, regardless of the concentration of these substances in the native groundwater.

When considering DBPs, the NAT capacity could provide an essential argument for allowing their introduction into the aquifer. Chloroform, which is a component of THMs, is classed as a hazardous substance, therefore it is not permitted to enter the groundwater regardless of whether it would pollute the groundwater or not. It would not be economically feasible to remove DBPs before injection, and an alternative would be to dechlorinate the water after chlorination. Although this is more feasible, it would encourage biological clogging, which in turn could increase the well maintenance cost, thereby increasing the overall cost of the scheme. This will be discussed further in Section 5.4.

Under the GWDD, the Environment Agency has the discretion to apply a “de minimis” exemption if they are satisfied that the inputs of pollutants will not result in deterioration of groundwater quality. Considering that the experimental work in Chapter 4 showed that the introduction of DBPs would not result in a deterioration of groundwater quality since they were biodegraded during storage, it seems there is no substantial reason to prevent DBPs entering the aquifer. The exemptions noted above should therefore be applicable to the DBPs since the environmental objectives of the groundwater body are not compromised.

The viability of the scheme would be further enhanced if NAT with respect to nitrates and sulphate could be used as a treatment process, rather than just a beneficial by-product of the system. However, due diligence is required when attempting to use the aquifer as a treatment step, as a benefit in one parameter could be at the expense of another. For example, NAT of nitrates is achieved via bio-degradation, which may trigger reducing conditions as a result of anaerobic degradation of organic matter during the process of denitrification (Stuyfzand, et al., 2005; Vanderzalm et al., 2002), and potentially decrease the pH, both of which may encourage the release of trace metals. Furthermore, bio-denitrification during storage is often accompanied by a high concentration of organic matter in the recovered water (Dahab, 1993), which increases the DBP formation potential of the recovered water. It is therefore a possibility that using NAT for nitrates may result in the recovered water containing a higher concentration of metals and organic matter, both of which may require post-treatment.

In trying to reduce the cost of pre-treating one parameter, it is possible that post-treatment requirements would increase, thereby increasing the overall cost of the scheme more than what would have been if the recharge water was pre-treated for this parameter. This kind of inter-relationship between the parameters is site-specific therefore pilot investigations would be required to assess the potential for NAT. However, preliminary results from the column investigations suggest that although bio-denitrification does not impact the release of trace metals in this aquifer, it does increase the concentration of organic carbon in the recovered water. A unified, holistic risk based approach to authorising ASR schemes could allow NAT to be considered if the pilot investigations can show that there would be no associated negative impacts.

5.2 Influence of the regulatory agenda on ASR and the role of the Strategic Planning Tool

The impact of inconsistent and unclear regulations is not unique to the UK. A survey of 46 ASR sites in USA commissioned by American Waterworks Association (AWWA, 2002) found that regulatory inconsistencies within and across states in relation to planning and developing ASR schemes is a significant barrier to more widespread implementation of the technology due to higher perceived risks. An interesting finding is that despite the regulatory constraints, in March 2005 there were 72 ASR systems operating in the USA, with an estimated further 100 in various stages of development (Pyne, 2005a). This is because high population and industrial growth in the most water stressed areas has pushed water suppliers to look for alternative water resources.

Transfer of water between states is common practice in America however as the climate changes and droughts become more frequent, there is a need to reduce the reliance on other states. Increasing concerns about the sustainability and security of importing water drove investigations into alternative supplies of water (Durham et al., 2003). Desalination is a viable alternative, however it has a high environmental and economic cost compared to ASR (P. Dillon et al., 2010), and water-reuse is limited by public opposition due to the “yuck factor” and the potential for contaminant accumulation. ASR has been growing in the US as it improves the resilience and security of water, and so despite the regulatory barriers, ASR continues to grow. In the US, ASR proponents regularly lobby regulators to develop a more integrated framework since the regulatory requirements provide constraints within which projects need to work, and can impact the viability of a scheme (Brown, 2005). This should be a lesson for the UK in that ASR proponents need to unite and lobby the regulators to ensure that investment in ASR is not stifled by unclear or overly restrictive regulations.

This was the case in Australia where the regulators worked with the water utilities, public health experts, academics and other stakeholders/experts, to form the Australian guidelines for MAR (NRMMC-EPHC–NHMRC, 2009) which provide a scientific basis for implementing MAR schemes. The main driver for these guidelines was the implementation of the National Water Initiative (NWI) in 2004 which was an intergovernmental agreement (between the Australians, state and territory governments) on how to manage the nation's water resources (Australian National Water Commission, 2006). The main aim of the NWI was to minimise the adverse effects on water bodies, which were being experienced due to prevailing drought and over-abstraction (Australian Bureau of Statistics, 2007). Sustainable levels of abstraction were required of both the surface and groundwater bodies and in the case of aquifers, ASR would allow a higher quantity of water to be abstracted sustainably. The NWI is similar to the WFD in principle as it aims to improve the quality and quantity of both surface and groundwater. Standards for water reuse were established and codes of practice guidelines for ASR were set. The UK is currently in a position similar to Australia in 2004 in terms of the implementation of the WFD, therefore there is a prospect that guidelines and standards for ASR will soon be established. The lesson from the US of lobbying the regulators should also be abided - it is important for water utilities to be more proactive and work with regulators to form the regulatory agenda. In order to improve confidence in ASR, an improvement in planning and governance of these schemes is required.

What is clear from the foregoing discussion is that regulators need a sound basis for policies relating to ASR, as it has the potential to create conflict between water conservation and water-quality protection (NRMMC-EPHC–NHMRC, 2009), both of which are requirements of the WFD. It is important to have separate policies where water is intentionally recharged into an aquifer as in the case of ASR, since the rechargers intent is to increase water supply security and therefore they have a vested interest in protecting water quality in the aquifer (Dillon et al., 2013). This was recognised in Australia, where ASR was very slow to establish in areas where recharge was governed under groundwater pollution regulations, while it developed quickly where groundwater replenishment was recognised as an environmentally advantageous solution, and as such was managed from both a quantity and quality perspective (Parsons et al., 2012). Potential ASR operators in the UK would benefit from a more consistent and holistic regulatory approach as in Australia, where ASR increased following formation of the Australian Guidelines for MAR. It should be realised that setting arbitrary standards for the recharge water is not appropriate for ASR. For example, simply treating the recharge water to drinking water standards does not ensure protection of the aquifer or of the recovered water quality (NRMMC-EPHC–NHMRC, 2009). This is because water with a high purity results in stronger dissolution of aquifer minerals, while a low concentration of nutrients can impede the biodegradation of trace organics (Dillon et al., 2010). It is therefore more appropriate to adopt a risk based approach to determining standards in an ASR scheme.

The SPT offers a framework which can be used to do this, as it would promote a risk based approach to approval. It has the potential to be an important part of the development of ASR in the UK as it provides a holistic and unified framework in the context of UK regulatory requirements, which not only helps proponents determine the viability of a scheme, but may also enable the regulators to take a risk based approach and understand the overall implications of their requirements when evaluating proposed ASR projects. The SPT recognises that aquifers behave as biochemical reactors and adopts an open ended approach that accounts for the interaction of the recharged water with the aquifer. It does not set limits for acceptable qualities of the recharge water as these have not been published by the regulators, however it does provide a holistic view of the impacts of recharge water quality on operations and abstracted water quality. It considers the end-use of the water as a primary basis for determining the acceptability of the recovered water quality. The SPT can therefore be used by the both regulators and operators to negotiate requirements.

5.3 Water quality deterioration and the impact on viability of the scheme

The column investigations (Chapter 4) suggest that the concentration of iron, arsenic and manganese are likely to increase above PCV during storage. This would mean that the abstracted water would require further treatment with regards to these parameters, before the water could be distributed as drinking water, which is the intended end-use. The increase in iron coincided with an increase in arsenic, which was attributed to the reductive dissolution of iron oxides which have a large sorptive capacity for trace species such as arsenic (Vanderzalm et al., 2009). Filtered samples of recovered water had significantly lower concentrations of iron and arsenic as ferric oxides are removed, with iron concentrations reducing by an order of magnitude and arsenic concentrations halved. Although concentration of arsenic increased in all columns, the PCV was exceeded only after 60 days of storage, while all but one of the recovered waters had concentrations higher than the PCV for iron. The increase in manganese was markedly high, with all but one of the recovered waters exceeding the PCV, and this was attributed to the dissolution of Mn-siderite and/or Mn-oxides. Further treatment for these parameters is therefore a likely requirement. Concentration of nickel also increased above the PCV on some occasions, however there is less certainty as to the level of threat posed by these exceedances due to the inconsistent increases.

Post treatment for iron and manganese would most commonly entail aeration to transform soluble iron and manganese into their insoluble forms, followed by rapid sand filtration to remove the precipitates (Buamah, 2009). Nickel would be adsorbed onto iron or manganese precipitates (Vanderzalm et al., 2005), therefore it would also be removed during this process. Since the experimental work showed that ferric oxides are present in the recovered water, it would be more beneficial if the pre-treatment is adjusted to minimise iron (and arsenic) precipitation, rather than to treat the water following recovery. This is because ferric oxides also promote clogging of the wells, the implications of which are discussed in Section 5.4.

The most common pre-treatment to manage iron, arsenic and manganese release from the aquifer material is pH adjustment upward of 8.5 (Pyne, 2005b; Maliva and Missimer, 2010; Antoniou, 2015). Addition of sodium hydroxide to increase the pH of the recharge water has been successful in reducing the concentrations of these trace metals at several sandstone sites including Chesapeake Virginia (Pyne, 2005b), Herten Netherlands (Antoniou, 2015) and Swimming River New Jersey (Pyne, 2005b; Maliva and Missimer, 2010). Information with regards to the fate of nickel during storage in an aquifer is scarce, however the solubility of nickel is also lower at high pH (Bernard et al., 2007) therefore pH adjustment will likely reduce its concentration in the recovered water.

It should be noted that pH adjustment will reduce concentrations of soluble iron, arsenic, manganese and nickel however their precipitates (ferric and manganese oxides) will not be impacted. Deoxygenation of the recharge water is effective in reducing precipitation of these oxides, thereby also reducing the concentration of arsenic since dissolution of iron oxide is the main source of arsenic in this aquifer. It should be noted however, that the presence of free chlorine will provide some oxidative capacity (Vanderzalm et al., 2013). The potential for biological clogging should be weighed up against the risk of iron oxide precipitation due to the presence of free chlorine, in order to determine if dechlorination would be beneficial in this respect (Section 5.4).

Alternatively, the aquifer itself can be treated/conditioned, to reduce its reactivity by accelerating the oxidation reactions, allowing them to occur in the initial conditioning phase. Initial conditioning of a sandstone aquifer using permanganate which is a strong electron acceptor, increases the oxidation capacity of the injected water substantially, thereby reducing the number of treatment cycles required (Antoniou, 2015). Additionally, generation of manganese oxide precipites during this oxidation will increase the sorptive capacity of the aquifer, and the oxidation reaction will consume protons and increase the pH, further reducing the solubility of metals such as manganese, iron and nickel.

So long as a buffer zone is maintained, that is the zone at the edge of the stored water that mixes with the native groundwater, the beneficial effects of this treatment will continue as manganese oxides continue to scavenge soluble manganese, iron, arsenic and other trace metals (Buamah, 2009). A buffer zone is maintained by leaving a small percentage of the recharged water in the aquifer during each recovery cycle, thereby ensuring that the native water is not reached. If the buffer zone is not maintained then native water will enter the conditioned reaction zone, circumventing the conditioning and so a repetition of the permanganate treatment may be required (Antoniou, 2015). It should be noted however, that sorption is not considered to be sustainable since a breakthrough is likely following several cycles of ASR (NRMMC-EPHC–NHMRC, 2009). Pre-treating the water to limit release of these metals during storage should therefore be the preferred option.

5.4 Potential for Clogging at the Newton on Trent ASR site

Clogging is purely an operational issue and it has a significant impact on the viability of ASR operations as it increases the cost of injection, recovery and maintenance of the scheme (see Chapter 3). Following the experimental work and a review of the likely pre-treatment requirements, the clogging mechanisms that have a potential to impact the ASR scheme in Newton on Trent have been deduced as geochemical clogging, biological clogging, gaseous binding, and potentially physical clogging.

The experimental work showed that the recovered water is likely to contain iron oxide precipitates which can cause clogging in the wells and potentially the aquifer matrix close to the injection point. After the water was recovered from the columns and they were dissembled, iron precipitation was visible through darkening of the aquifer material close to the injection point. Biofilm (slime) was also visible on the darkened aquifer material, which is an indication of bacterial growth. Precipitation of iron most likely promoted the growth of iron bacteria which are common in groundwater (Martin, 2013a). Not only does the biofilm reduce the permeability, it can act as a catalyst for physical clogging by trapping particles present in the recharge water, further reducing permeability (Shaw et al., 1985; Rinck-Pfeiffer et al., 2013). Considering that release of iron increases the potential for clogging and also poses a risk to the abstracted water quality, pre-treating the water as suggested in Section 5.3 is recommended.

Biological clogging could also be a problem if the water is dechlorinated before injection, to prevent DBPs entering the aquifer or to reduce the oxidative capacity of the recharge water. Field studies at Monterey ASR site showed that dechlorination prior to injection in 2005 was successful in inhibiting THM formation, but instead resulted in well clogging problems (Vanderzalm et al., 2009). At an ASR site in Fountain Hills Sanitary district, Arizona, a rapid decline in well performance due to biological clogging was observed after the disinfection method was changed from chlorination to UV disinfection (Small et al., 2007). This shows the importance of maintaining a chlorine residual, a finding which is further substantiated in experimental investigations by Fox et al. (1998). On the other hand, dechlorination would eliminate the amount of free chlorine hence reduce the oxidative capacity, which would in turn reduce the potential for iron oxides forming. This was not noticed in the experimental work, as the chlorinated water (S4) did not show any significant difference in iron concentration when compared to the non-chlorinated waters. It is therefore difficult to provide a treatment recommendation at this stage, however it is recommended that potential for geochemical and biological clogging and the effects of free chlorine on these mechanisms is closely monitored during proposed pilot investigations.

The experimental work also showed that denitrification and sulphate reduction was prevalent therefore there is also a potential for gaseous binding due to the release of N_2, CO_2 and H_2S (see Section 4.4.1). This could influence the geochemical reactions and microbial activity in the area, further exacerbating clogging. For example, release of H_2S can provide nutrients for sulphate reducing bacteria (Pitt and Magenheimer, 1997), thereby promoting biological growth and clogging. Gaseous binding is not a common clogging mechanism and only one site in Myrtle Beach, South Carolina, USA (Maliva and Missimer, 2010) was found in the literature where its occurrence was reported. It is therefore unlikely to cause any significant problems at the proposed site.

Finally, physical clogging is also likely at the proposed site, since it is the most widely reported cause of clogging in ASR sites (see Section 3.4), and the target site has a primary inter-particle porosity which is more susceptible to clogging (Pitt and Magenheimer, 1997). Potential for this clogging mechanism can be reduced by keeping the suspended solids content of the injectant as low as economically possible and minimising pressure transients, which can result in a large influx of solids into the system.

Although prevention is the best option, it may be more economical to allow some clogging to occur and then rehabilitate the well. Often there is a trade-off between the cost of pre-treatment and the type and frequency of redevelopment required (Pavelic et al., 2008). The main aim of well redevelopment is to restore the hydraulic properties of the injection well, the frequency of which depends on the rate of clogging, and can vary from daily to annually. The frequency of redevelopment is also dependent upon the aquifer material with sand aquifers requiring more frequent redevelopment than karstic limestone aquifers (Brown at al., 2006). This is because aquifers with secondary porosity/ permeability such as limestone aquifers are less likely to clog than those with just primary porosity/permeability such as sandstone aquifers (Pitt and Magenheimer, 1997).

Rehabilitation is a necessary part of ASR if the long term injectivity is to be maintained, however if the frequency and cost are not in proportion to the economic value of the scheme, it may be seen as a disadvantage. It should be noted that the approach to managing well clogging will differ in each scheme as it depends on the quality of water injected, aquifer characteristics and design of the well, therefore there is no optimal strategy. What works at one site may not work at another site. The most critical element in effective well rehabilitation is to accurately diagnose the cause of clogging, as this ensures the correct technique is employed. Table 3.3 can assist in this diagnosis.

5.4.1 Well redevelopment

There are a variety of mechanical and chemical techniques that may be implemented to redevelop an injection well. Mechanical methods such as jetting, surging and pumping rely on physical agitation to remove incrustations that may form in the screen, filter-pack and aquifer formation during injection. Chemical methods involve the addition of acids, flocculants and disinfectants to dissolve or loosen and clogging materials, making them easier to remove.

Mechanical Techniques

Well clogging issues have been managed successfully through the use of a regular back flushing program in several ASR schemes (Brown at al., 2006). It is effective against physical clogging, removing mineral deposits as a result of geochemical reactions, and may also reverse the effects of air entrapment, however is not effective against biological clogging (Holländer et al., 2004). Backwashing should be performed at a higher rate than the injection rate to ensure deposits are dislodged and removed. This would require the pump installed in the well to be able to accommodate this higher pumping rate, which is usually twice the recharge rate (Morris, 2007). Furthermore, backwashing uses water stored in the aquifer, therefore there is a loss in quantity of stored water which needs to be considered when planning the storage requirements and determining the viability of the scheme.

Well surging and jetting are also effective in removing in incrustations, and do not use the stored water, therefore there is no loss in storage capacity. Well surging involves using a plunger in the casing to force water to flow into and out of a screen, thereby loosening the material and drawing it into the well. This repeated change in direction can provide more beneficial results than simply backwashing (Cash, 2010). Jetting involves high pressure fluid (air or water) removing material deposited in the formation and well screen. It is important to note that surging and jetting may cause damage to screens, the well and even the formation if not done properly. Furthermore, neither of these techniques remove the material that has been loosened, therefore the well would need to be pumped following surging and jetting in order to remove the loosened material.

An alternative method that may be used is carbon dioxide injection, whereby gaseous and liquid carbon dioxide are injected under pressure. First gaseous carbon dioxide is injected which produces an abrasive carbonic acid, then liquefied carbon dioxide is injected, which upon contact with the water expands and causes the water to freeze, thereby cracking and loosening the incrustation. It is possible for the aquifer itself to crack which may further increase the yield. This technique would also get rid of bacteria, particularly iron bacteria (Pitt and Magenheimer, 1997), and therefore is capable of mitigating physical, geochemical and biological clogging mechanisms. After the zone has been rehabilitated, the well needs to be surged and redeveloped.

Chemical techniques

Chemical techniques need to be used in conjunction with mechanical techniques, especially for remediating against biological clogging. Acidification using hydrochloric, sulphuric or nitric acid may be used to remove biofilm and incrustation, however deterioration of the well materials is likely and therefore needs to be weighed up against the removal of the biofilm (Bloetscher et al., 2004). Chlorine (such as sodium hypochlorite) is often used to dissolve the biofilm which then needs to be removed via backwashing/surging (Maliva and Missimer, 2010). Initial acidization, combined with regular backwashing was used to successfully remediate biological clogging at the Bolivar ASR site in Australia, where injection rates were sustained via regular maintenance in this way (Pavelic et al., 2007).

5.5 Implications of using experimental results at a field scale

Predictions regarding potential concentrations of the measured parameters at field scale based on the experimental data, should be made with caution for the following reasons; Firstly, the size of the soil columns used pale in comparison to the extent and heterogeneity of an actual aquifer. Although attempts were made to ensure the columns were representative of aquifer conditions, the aquifer material was obtained from one point in the aquifer and therefore may not truly represent the formation. Secondly, the material used in the columns was crushed, which increases the reactivity of the sediment because surfaces that were not previously in contact with water are exposed. This suggests that not all the changes seen in recovered water during the experiment would correspond to the changes seen in the field, and the magnitude of these changes may be lower in the field. The results of this study however are still very useful in predicting potential changes that may occur since the increased reactivity of the columns provide a "worst case" scenario of changes that may occur.

6 Overall Conclusions

An increase in iron, arsenic and manganese above the PCV during storage in the Sherwood Sandstone aquifer poses a substantial threat to the Newton on Trent ASR scheme. Along with soluble iron in the recovered water, iron oxide precipitates were also formed, which promote growth of iron bacteria. This increases the potential for geochemical and biological clogging, if the water is not pre-treated to address the release of iron. Furthermore, the biofilm produced by iron bacteria can trap suspended solids in the recharge water, which promotes physical clogging. Considering that the release of iron during storage not only poses a risk to the abstracted water quality, but also increases the potential for clogging, pre-treatment is recommended rather than post-treatment. The recharge water should be deoxygenated to reduce precipitation of iron oxide and the pH should be adjusted above 8.5 to reduce concentrations of soluble iron, arsenic, manganese and nickel.

ASR in the Sherwood Sandstone aquifer is technically feasible however the current interpretation of regulations threatens the cost effectiveness of such schemes. ASR improves the quantitative status of groundwater however current interpretation of the "no deterioration in water quality" requirement of the WFD is limiting wider implementation of ASR, due to overly onerous recharge water quality requirements. A more appropriate approach to regulating ASR schemes is required. Adopting a risk based approach to determining recharge water quality standards rather than setting arbitrary standards provides an opportunity to regulate ASR operations from both a quantity and quality perspective. The SPT offers a framework which can be used to implement this, as it provides a holistic and unified framework in the context of UK regulatory requirements, which not only helps proponents determine the viability of a scheme, but may also enable the regulators to take a risk based approach and understand the overall implications of their requirements. The SPT therefore has the potential to be an important part of ASR development in the UK

This thesis has fulfilled its objectives by developing the SPT to better characterise threats to ASR schemes, using existing knowledge on clogging mechanisms to evaluate their influence on the viability of the proposed ASR scheme and determining the potential changes in water quality during storage when treated surface water is stored in the Sherwood Sandstone aquifer. This knowledge was then used to evaluate the relationship between water quality changes, clogging and pre/post treatment, which in turn informed a commentary on the influence of current regulations on wider implementation of ASR and the importance of a risk based approach to scheme approval. By attaining these objectives, the following gaps in knowledge/practice were addressed:

1. What are the potential changes in water quality when treated surface water is stored in a Sherwood Sandstone aquifer, and what is the influence of recharge water quality and storage time, on the recovered water quality?
2. How does the regulatory agenda influence wider implementation of ASR in regions where it is not yet established?
3. Is there a viability assessment that could encourage wider implementation of ASR schemes in the UK?

This research has therefore reduced the uncertainties surrounding the design and operation of ASR schemes and provided a commentary which can be used to inform the regulatory agenda in the UK. The outputs of this research may also be used in a broader context. Although the experimental work focused on the Sherwood Sandstone aquifer, the knowledge generated on the mechanisms responsible for water quality changes during storage in an aquifer, can be used to inform ASR schemes in a variety of aquifers. The discussion on the role of regulations in wider implementation of ASR schemes can be used in other regions where ASR is not yet established, as a step towards informing the regulatory agenda. Finally the SPT can be used by ASR operators around the UK, using a variety of aquifers and recharge waters, to improve the viability assessment process. It could also be used internationally however the 'regulatory requirements' section would need to be adapted to reflect the local regulations.

Limitations of the research

Due to the time and budget constraints the scope of the work had to be carefully managed. Some limitations of the research as a result of this include:

1. The Strategic Planning Tool could not be tested in the different stages of an ASR schemes development. It was only tested at the initial desktop investigation stage since at the time of this research, the only scheme being investigated by the sponsor (Anglian Water Services) was in the pre-feasibility investigation stage.

2. The changes suggested during deployment of the tool could not be incorporated due to time and budgetary constraints. These changes have however been documented in detail.

3. The column investigations were undertaken over the course of different seasons and the temperature of the columns could not be controlled. Biogeochemical reactions that are influenced by temperature (e.g. manganese solubility, sulphate reduction, biodegradation of DBP) were therefore observed more prominently in the warmer season, which makes comparison between the results more challenging.

4. Although the water quality analysis was replicated, the columns were not due to time and space constraints. The lack of column replication prevented a more definitive explanation of the results, especially with regards to the impact of different recharge water qualities on the recovered water quality.

5. The experimental work was a high level investigation of potential water quality changes that may occur during storage, therefore detailed evaluation on the mechanisms responsible for these changes was not always possible.

Recommendations for future work

During the course of this research, several areas where additional research could improve knowledge in the field were identified. Further work as relevant to the context within which this research was conducted include:

1. The tool advises the use of various modelling however no modelling was actually implemented during testing. It would be useful to undertake some

modelling at a pilot site and evaluate if the tool can be adjusted to improve the evaluation of the modelling results.

2. Implement the Strategic Planning Tool at the detailed investigation stage of the potential ASR scheme at Newton on Trent, should the scheme progress. This would allow an evaluation as to the value and usability of the tool at this stage in a similar manner to the evaluation in Section 2.6.4.

3. Test the tool at a variety of ASR investigation sites by different proponents, to determine the applicability of the tool across different schemes.

4. Implement the changes suggested during deployment of the tool (Appendix K)

5. Investigate the DBP formation potential during storage in the Sherwood Sandstone aquifer, to improve understanding on the impact of storage on post treatment requirements, and the recovered waters potential risk to human health.

6. Dissolution and precipitation experiments for the parameters of concern such as iron, manganese, arsenic and nickel to determine the factors influencing these reactions in the Sherwood Sandstone aquifer.

7. Leaching/sorption experiments to determine the source/sinks for metals during storage in the Sherwood Sandstone aquifer would provide valuable information for future schemes in this aquifer.

8. Determining the proportions of soluble and insoluble factions of the metals (particularly iron and manganese) released during storage in this aquifer, to distinguish between potential impacts on abstracted water quality and clogging mechanisms.

9. Validation of experimental work with results from pilot site to fully assess the potential water quality changes and clogging mechanisms that may impact the ASR scheme.

Broader recommendations that would improve knowledge/practice in this field of research include:

1. Breakthrough tests for THM and HAA at this site to determine the role of sorption as a removal mechanism. This will provide stronger evidence that biodegradation is the mechanism responsible for the decrease in concentration and if sorption plays a role, this test could quantify the extent of its impact.

2. Identify the bacteria responsible for THM and HAA degradation in an aquifer so that future investigations can use the presence of these bacteria as an indication of whether DBP degradation is likely to occur.

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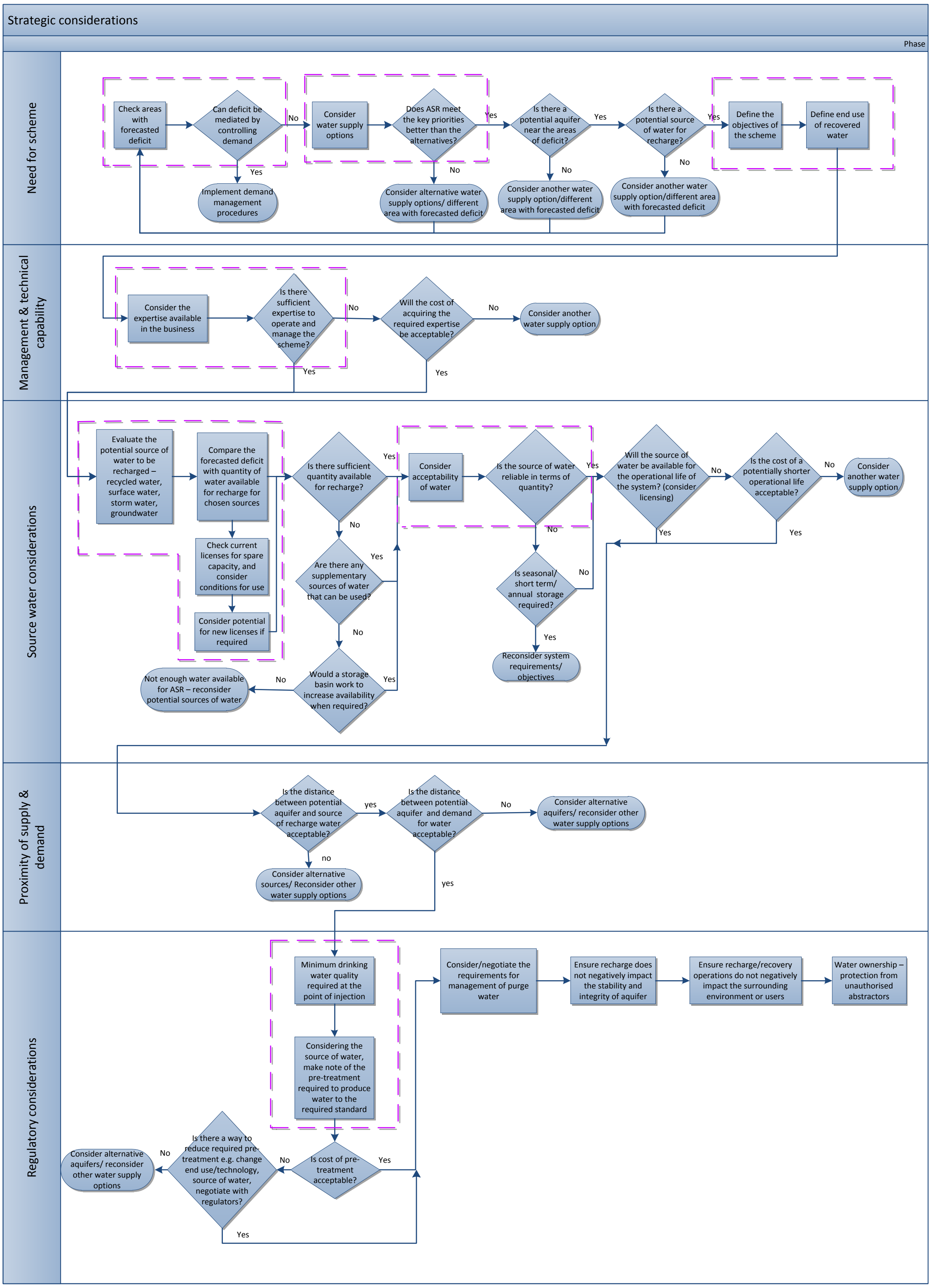
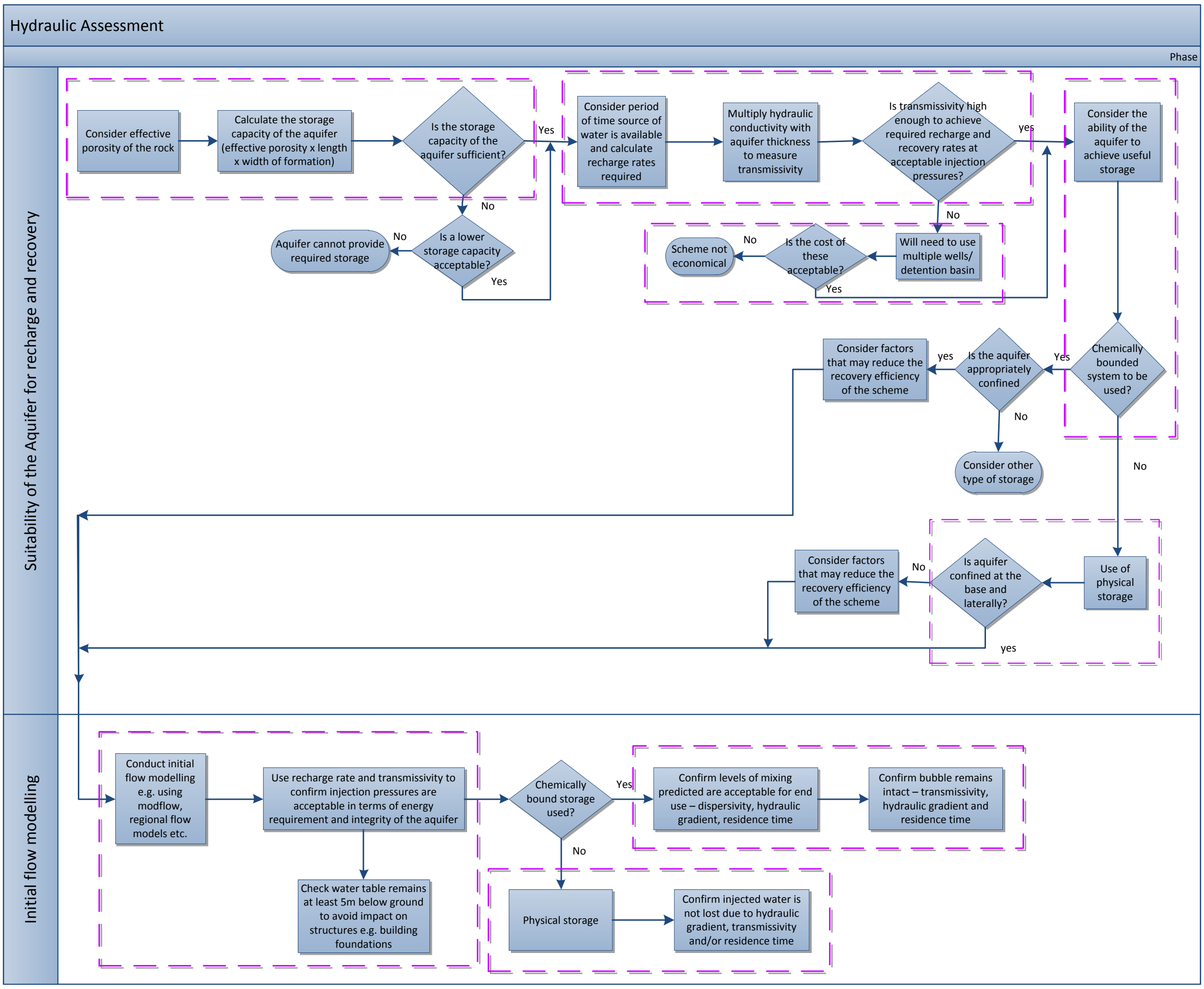
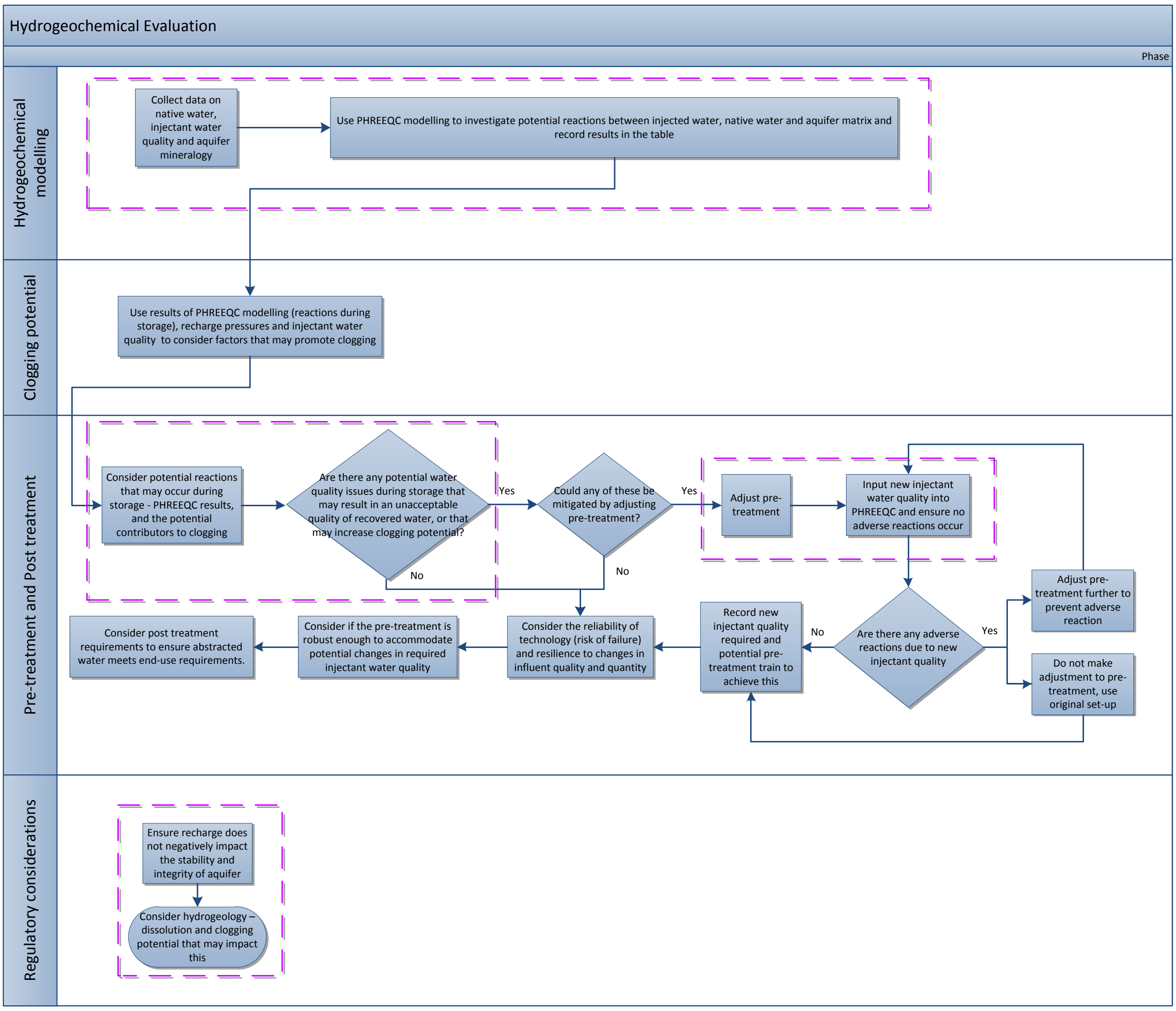
APPENDICES

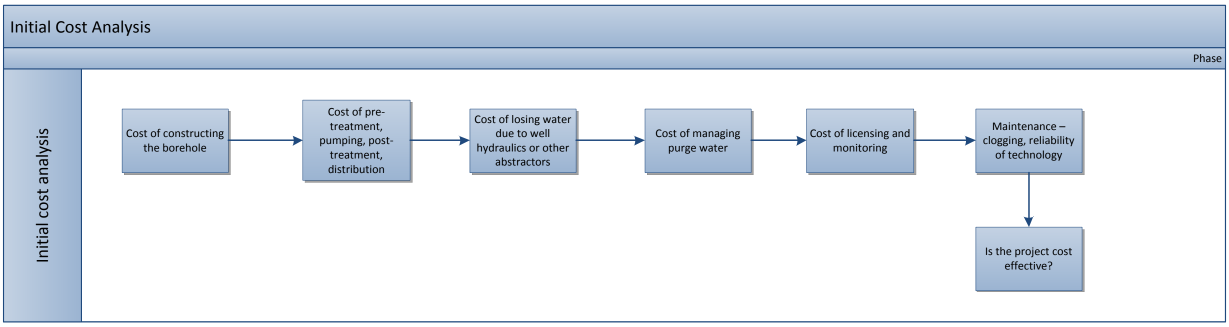
Appendix A Process diagrams illustrating the logic of the Strategic Planning Tool

The diagrams below represent the structure of the logic used to form the Strategic Planning Tool web-app shown in Chapter 1.




Hydraulic Assessment
Phase
Suitability of the Aquifer for recharge and recovery
Consider effective porosity of the rock
Calculate the storage capacity of the aquifer (effective porosity x length x width of formation)
Is the storage capacity of the aquifer sufficient?
Yes
No
Is a lower storage capacity acceptable?
No
Yes
Aquifer cannot provide required storage
Consider period of time source of water is available and calculate recharge rates required
Multiply hydraulic conductivity with aquifer thickness to measure transmissivity
Is transmissivity high enough to achieve required recharge and recovery rates at acceptable injection pressures?
yes
No
Will need to use multiple wells/ detention basin
Is the cost of these acceptable?
No
Yes
Scheme not economical
Consider the ability of the aquifer to achieve useful storage
Chemically bounded system to be used?
Yes
No
Is the aquifer appropriately confined
yes
No
Consider factors that may reduce the recovery efficiency of the scheme
Consider other type of storage
Use of physical storage
Is aquifer confined at the base and laterally?
No
yes
Consider factors that may reduce the recovery efficiency of the scheme
Initial flow modelling
Conduct initial flow modelling e.g. using modflow, regional flow models etc.
Use recharge rate and transmissivity to confirm injection pressures are acceptable in terms of energy requirement and integrity of the aquifer
Check water table remains at least 5m below ground to avoid impact on structures e.g. building foundations
Chemically bound storage used?
Yes
No
Confirm levels of mixing predicted are acceptable for end use – dispersivity, hydraulic gradient, residence time
Confirm bubble remains intact – transmissivity, hydraulic gradient and residence time
Physical storage
Confirm injected water is not lost due to hydraulic gradient, transmissivity and/or residence time


Hydrogeochemical Evaluation
Phase
Hydrogeochemical modelling
Collect data on native water, injectant water quality and aquifer mineralogy
Use PHREEQC modelling to investigate potential reactions between injected water, native water and aquifer matrix and record results in the table
Clogging potential
Use results of PHREEQC modelling (reactions during storage), recharge pressures and injectant water quality to consider factors that may promote clogging
Pre-treatment and Post treatment
Consider potential reactions that may occur during storage - PHREEQC results, and the potential contributors to clogging
Are there any potential water quality issues during storage that may result in an unacceptable quality of recovered water, or that may increase clogging potential?
Yes
No
Could any of these be mitigated by adjusting pre-treatment?
Yes
No
Adjust pre-treatment
Input new injectant water quality into PHREEQC and ensure no adverse reactions occur
Are there any adverse reactions due to new injectant quality
Yes
No
Adjust pre-treatment further to prevent adverse reaction
Do not make adjustment to pre-treatment, use original set-up
Record new injectant quality required and potential pre-treatment train to achieve this
Consider the reliability of technology (risk of failure) and resilience to changes in influent quality and quantity
Consider if the pre-treatment is robust enough to accommodate potential changes in required injectant water quality
Consider post treatment requirements to ensure abstracted water meets end-use requirements.
Regulatory considerations
Ensure recharge does not negatively impact the stability and integrity of aquifer
Consider hydrogeology – dissolution and clogging potential that may impact this


Initial Cost Analysis
Phase
Initial cost analysis
Cost of constructing the borehole
Cost of pre-treatment, pumping, post-treatment, distribution
Cost of losing water due to well hydraulics or other abstractors
Cost of managing purge water
Cost of licensing and monitoring
Maintenance – clogging, reliability of technology
Is the project cost effective?

Appendix B Explanations to clarify the requirements of each aspect of the Strategic Planning Tool

The text below represents the explanations accompanying the logic shown in Appendix A, to help the user understand the requirements of the questions/assessments presented to them. The section associated with the explanation under each assessment is shown by the text in red italics and the red text under each section represents to the actual questions/assessments presented to the user. Text in black are the explanations.

Strategic Assessment

Need for Scheme – justify the need for the scheme to gain business backing

3 &4 **Consider water supply options** – consider desalination, water reuse, additional groundwater sources, inter-catchment transfers. Does ASR meet AW key priorities better than the alternatives – The table compares the main water supply options to the Anglian Water key priorities. Rate each water supply option in relation to the key priorities to provide a comparison between them.

1 – Low/negative effect on the priority
2 - Medium impact
3 – High/positive impact

It should be noted that some cells under the ASR heading are split – this is because the impacts of these depend on the source of water used for recharge. For example where treated wastewater is used as the source the reliability, resilience and security would be higher than where treated surface water is used.

	Transfers	Desalination	Reuse	Reservoirs	ASR	
Reliability & Resilience						
Security						
Improve environment						
Adapt & mitigate against climate change						
Efficiency & flexibility						
Keep bills affordable						
Overall score						

4. **Is there a potential aquifer near area of deficit** – ensure there are potential aquifers that may be used for ASR close to the deficit area to minimise infrastructure costs.
5. **Is there a potential source of water for recharge** – ASR requires a source of water that can be used to recharge the aquifer
6. **Define the objectives of the scheme** – Long-term storage (> 1 year), Seasonal storage (< 1 year), increase acceptability of recycled water, prevent saline intrusion, water quality improvement, groundwater management, improve environmental flows etc. Requirements of each system differ thus need to be defined before risk assessment implemented.
7. **Define end use of recovered water** – requirements of the system differ according to the end use e.g. lower water quality required for non-potable uses compared to potable uses.

Management & Technical capability – ensure business has, or can economically acquire the capability to implement and operate the scheme.

Source water considerations – ASR requires a source of water that can be used to recharge aquifers, therefore availability, reliability, acceptability, quality and quantity of source needs to be evaluated. The table below provides some guidance on the availability, reliability, quality, quantity and acceptability of the different potential sources of water in the UK

Source of water	Availability	Reliability	Quality	Quantity	Acceptability
Surface water	Variable	Variable	Variable	High	High
Recycled water	Consistent	High	High	High	Low
Storm water	Variable	Variable	Variable	Low - Moderate	Moderate

1 & 2 Evaluate the potential source of water to be recharged – recycled water, surface water, storm water, groundwater. Compare forecasted deficit with quantity of water available for recharge for chosen sources – Ensure quantity of water available for recharge is sufficient to meet demands

a. Check current licenses for spare capacity and consider conditions for use – licenses with spare capacity should be listed to compare with the deficit areas and suitable aquifer sites at a later stage
b. Consider potential for new licenses if required – communicate with the regulator to judge future strategies and their potential effect on licensing. Attempt to get confirmation of licensing for source water for the duration of the ASR scheme, and the cost of the licenses.

3. Is there sufficient quantity available for recharge
    a. Are there any supplementary sources that can be used
    b. Would a storage basin increase availability when required – if injection is seasonal then storage basin can be used to store quantities required before recharge.

4. Consider the acceptability of water - The acceptability of water should be considered as it may impact permitting of the scheme. This is most important for recycled water as this is an area where public opposition could result in problems.

5. Is the source of water reliable in terms of quantity – For example, surface water and storm water rely on rainfall which is increasingly less reliable as the climate changes, recycled water is very reliable since as long as water is consumed, wastewater is produced. Consider the quantity of assured yield and the risk of undersupply.
    a. Is seasonal storage required - < 1 year cycle of recharge & recovery. If seasonal storage is required then source of water needs to be more reliable as if the water is recovered annually, then an equal amount needs to be recharged annually. If long-term storage needed then reliability of water is less important low recharge in one year is less important over a longer period of time – water is banked.

6. Will the source of water be available for the operational life of the system – consider potential licensing issues in the future, e.g. if surface water used, how likely is a reduction in abstraction licenses? Could other demands reduce the amount of water available for recharge?

7. Is the cost of a potentially shorter operational life acceptable – operational life cycle has a direct impact on the cost effectiveness of a scheme, and impacts the acceptable Capex and Opex. The impact of a potential shorter operational life on these should therefore be considered.

Proximity of supply and demand – potential ASR site should be close to demand for water as well to the source of recharge water to minimise transport and infrastructure costs.

Regulatory considerations – need to ensure regulatory requirements are considered as these will impact the requirements of the system. The Environment Agency will take a risk based approach to permitting therefore it is important to take into account what they will consider.

1. Minimum drinking water quality required at the point of injection – The Environment Agency has stated that the recharge water will need to meet at least drinking water standards at the point of injection regardless the quality of native groundwater. However it is worth noting that if a potable aquifer is recharged then it is possible that a “better than

drinking water" standard is enforced. Potable/near potable aquifers would likely have more onerous treatment and monitoring requirements than brackish aquifers.

   a. Considering the source of water, make note of the pre-treatment required to produce water to the required standard – The quality of the source water needs to be considered and an assessment of the source water catchment land-use should be conducted to account for the impact of land use on the source water quality. The required standard is determined by regulatory requirements, as well as the end-use of the water and objectives of the system. Therefore these need to be defined to determine the pre-treatment requirements.

2. Consider/negotiate the requirements for management of purge water – The potential disposal methods and the regulatory requirements to do so need to be considered. The method of disposal will depend on both the quality of the purge water and the regulatory requirements for disposal. Some examples of discharge methods include to a storm water system, to sewers, to nearby river and to nearby industry/ irrigation. Purge water can contain suspended solids, pathogens, metals, nutrients and organics, therefore the requirements for potential methods of disposal need to be considered.

3. Ensure recharge does not negatively impact the stability and integrity of the aquifer – any potential improvements or degradation in recharge water quality during storage will not be considered by the Environment Agency, except in circumstances where it negatively impacts the stability/integrity of the aquifer e.g. dissolution and clogging both of which increase recharge/recovery pressures which can destabilise wells and the aquifer.

4. Ensure recharge/recovery operations do not negatively impact the surrounding environment/users – a general requirement of minimal impact on the surrounding environment/users, e.g. dehydration/flooding of nearby wells or the environment during recovery/recharge. The hydraulic connection to the environment and other users should be considered.

5. Water ownership, protection from unauthorised abstractors - once an ASR scheme is set up, it would be protected from large abstractions. However the Water Act 2003 allows abstractions up to 20 m^3/d without a licence or a requirement to inform nearby scheme operators. The proximity of other potential uses should be noted and an inventory of existing wells/ potential users should be conducted to understand this risk.

Hydraulic Assessment

Suitability of the Aquifer for recharge and recovery   The three main considerations when choosing an aquifer for an MAR scheme are achievement of useful storage, the storage capacity and the hydraulic properties of the aquifer.

1. Consider effective porosity of rock - Effective Porosity is the pore space in a unit volume of rock in which the water can move freely, and differs from void porosity which also considers the water that is bound e.g. by absorption, therefore is not able to move freely. The table below illustrates the difference between the two porosities in different rocks. It is therefore imperative that effective porosity is used.

Type of rock	Void porosity (%)	Effective porosity (%)
Clay	40-35	1-10
Sand	35-40	10-30
Gravel	30-40	25-30
Sand and gravel	20-25	15-25
Sandstone	10-20	5-15
Limestone	1-10	0.5-2

2. Calculate the storage capacity of the aquifer the space available for recharged water should also consider the historical water levels and abstraction data

3. Is the storage capacity of the aquifer sufficient? – compare storage capacity available and the amount of storage required.

4. Consider period of time source of water is available and calculate recharge rates required - If water is available for short periods then higher recharge rates required and vice versa.

5. Multiply hydraulic conductivity with aquifer thickness to measure transmissivity – transmissivity is the ability of an aquifer to transmit water, i.e. it is the rate of flow of water through a defined thickness.

6. Is transmissivity high enough to achieve required recharge and recovery rates at acceptable injection pressures? - The minimum transmissivity required of an aquifer would mostly depend on the target recharge rate which is dependant on the period of time the source of water used for recharge is available. A high recharge rate would require a high transmissivity and vice versa. Low transmissivity increases the injection pressures and drawdown during recovery (which increases the area impacted by abstraction).
    a. Will need to use multiple wells/detention basin – multiple wells allow injection of volume at lower pressures, while detention increases period available for injection thus accommodates a lower rate of recharge. The difference between the recharge rate required and the achievable required recharge can be used to provide a rough

calculation of the number of wells/detention capacity required. It should be noted that both measures will increase the cost of a scheme.

7. Consider the ability of the aquifer to achieve useful storage – two main methods to achieve useful storage are chemically bounded storage and physical storage

8. Chemically bounded storage used? - In this case fresh water is stored in an aquifer of lesser water quality. The injected water displaces the native water and forms a "bubble" of water. The injected water is chemically bounded such that the walls of the "tank" are the boundary between the injected and native water, i.e. the mixing zone.
   a. Is the aquifer appropriately confined? – this type of storage works best in confined aquifers to maintain "bubble" of water. The aerial extent, thickness and depth of the confining layer should be considered - If the confining layer is thin and the aquifer is relatively shallow then there is a risk of ground movement during injection and recovery. The depth of the aquifer and the thickness of the confining layer will also influence the cost of drilling a borehole.

   b. Consider factors that may reduce the recovery efficiency of the scheme – Use table below to understand all the factors that may reduce the recovery efficiency of the scheme. The more factors that apply to the scheme, the higher the impact on the recovery efficiency.

Factors that may reduce recovery efficiency	**How factors impact recovery efficiency**	Place "x" in all that apply
Native water TDS > 5000mg/l	5000mg/l is used as a guideline value above which density stratification would contribute significantly to mixing between the native water and stored "bubble".	
High dispersivity (evaluated by considering the aquifer heterogeneity & hydraulic conductivity (includes fractures))	Dispersivity determines how the "bubble" of water moves in the aquifer and will impact the mixing between the native and injected water.	
High transmissivity (hydraulic conductivity x aquifer thickness)	High transmissivity promotes migration of the bubble. The highest acceptable transmissivity can be defined by the degree of migration of the recharged water, and the mixing between native and recharge water that would be acceptable.	
High hydraulic gradient (groundwater flow models)	If aquifer is at a high hydraulic gradient relative to its surroundings then water will move from the high hydraulic gradient (the aquifer) to a low gradient and the water will be lost. More	

	important if the water is stored over longer periods of time.	
Long Residence time (objectives of the scheme)	Impacts levels of mixing due to hydraulic gradient, transmissivity and dispersivity. Duration of storage is more important in more saline aquifers because of potential mixing due to density stratification.	

9. Use of physical storage – Introduction of water into an aquifer causes an increase in the water level (pressure head). Recharge water in the aquifer does not need to form a bubble however it does need to remain within the aquifer and not leak out.
    a. Is the aquifer confined at the base and laterally? - Small area unconfined aquifers that are confined at their base and laterally (bounded on all sides) to limit leakage are the ideal candidates.
    b. Consider factors that may reduce the recovery efficiency of the scheme – Use table below to understand all the factors that may reduce the recovery efficiency of the scheme. The more factors that apply to the scheme, the higher the impact on the recovery efficiency.

Factors that may reduce recovery efficiency	**How factors impact recovery efficiency**	Place "x" in all that apply
High transmissivity (hydraulic conductivity x aquifer thickness)	High transmissivity promotes migration of the stored water, and this is exacerbated if the aquifer is at a high hydraulic head or with long residence times (however it can still have a significant impact on its own)	
High hydraulic gradient (groundwater flow models)	If aquifer is at a high hydraulic gradient relative to its surroundings then water will move from the high hydraulic gradient (the aquifer) to a low gradient and the water will be lost. It is more relevant where it is coupled with a high transmissivity or a long residence time.	
Long Residence time (objectives of the scheme)	Long residence times, coupled with either a high transmissivity or a high hydraulic gradient can promote migration of the stored water. It is less relevant where transmissivity and hydraulic gradients are low.	

Initial flow modelling – use a flow model to get a better understanding of the feasibility of the scheme/confirm Hydraulic Assessment. It should be noted that this modelling would be based on assumptions/predicted data and not actual data.

1. Use recharge rate and transmissivity to confirm injection pressures are acceptable in terms of energy requirement and integrity of the aquifer – consider the recharge/recovery pressures that could destabilise wells and the aquifer, and ensure modelled pressures are below this level. Interference with other users should also be considered and minimised.

Hydrogeochemical Assessment

Hydrogeochemical modelling

1. Collect data on native water, injectant water quality and aquifer mineralogy – use nearby boreholes to measure quality of native water. Since a minimum of drinking water quality is required, this can be assumed to be the injectant water quality (unless the injectant quality is otherwise known). The mineralogy can be estimated by considering the type of rock. The table below provides some parameters that should be measured as a starting point for the Hydrogeochemical Assessment.

Parameter	**Concentration in native water**	**Concentration in injectant water**	**Concentration in recovered water**
Salinity Related Parameters			
Sodium			
Chloride			
Sulphate			
Total Dissolved Solids			
Carbonate Mineral Equilibrium Parameter			
Calcium			
Magnesium			
Bicarbonate (Bicarbonate Alkalinity)			
pH			
Measure Redox Mineral Reaction			
Iron			
Manganese			
Eh			
Dissolved Oxygen			
Dissolved Sulphide			
Redox Couple			
Measure Leachable Metals And Metalloids			

Arsenic			
Uranium			
Molybdenum			
Nickel			
Zinc			
Cobalt			
Measure Silicate Mineral And Miscellaneous Parameters			
Dissolved Silica			
Potassium			
Fluoride			
Barium			

2. Use PHREEQC modelling to investigate potential reactions between injected water, native water and aquifer matrix, and record results in the table –PHREEQC can model potential geochemical reactions including dissolution/ precipitation, ion exchange, ion adsorption, redox and many more. Details of PHREEQC including the user manual can be found at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/. The programme can also be downloaded from this website.

Clogging potential

1. Use results of PHREEQC modelling (reactions during storage), recharge pressures and injectant water quality to consider factors that may promote clogging – Clogging is a major operational risk associated with aquifer recharge. It reduces the recovery efficiency and increases the injection/recovery pressures required, which in turn increases the energy requirements, reduces the recharge rates and increases the drawdown during recovery. Use table below to understand all the factors that may promote clogging - the more factors that apply to the scheme, the higher the potential for clogging.

Types of clogging	**Causes of clogging**	**Place "x" in all that apply**
Clogging of injection wells (that injection wells are vulnerable to clogging)	Where the injectant water has a level above 3NTU (and >3mg/l TSS), clogging of injection wells is more likely. Does injectant contain suspended solids?	
	If the injectant contains biodegradable dissolved organic carbon then microbial clogging (biofouling) is likely. Does injectant contain biodegradable dissolved organic carbon?	
Clogging of aquifer matrix	Air entrained in the recharge water enters the aquifer formation and lodges into the pore spaces, increasing resistance to flow. There is also an associated change in the redox potential in the	

	area which can influence the geochemical reactions and microbial activity in the area, further exacerbating clogging. Does the injectant contain air?	
	Gaseous binding from gasses coming out of solution can also block the pores of the aquifer e.g. the release of nitrogen gas due to denitrification of nitrates in the injected water. Will reactions during storage release gases?	
	High injection pressures can result in mechanical compaction of the aquifer matrix. High injection pressures required?	
Clogging of aquifer matrix and/or recovery wells (recovery wells are less vulnerable to clogging)	Dispersal of clay particles/swelling of clay colloid – may occur due to ion exchange between the recharged water and aquifer material. Is dispersal of clay particles/ swelling of clay colloids likely?	
	Geochemical reactions (e.g. precipitation of minerals such as iron and manganese) can clog the recovery well and the aquifer matrix. Geochemical reactions likely?	

Pre-treatment and post-treatment

1. Are there any potential water quality issues during storage that may result in an unacceptable quality of recovered water, or that may increase clogging potential? – Water quality issues include release of inorganic minerals (such as arsenic, iron, manganese, trace species or hydrogen sulphide), organic compounds (such as disinfection byproducts), radionuclides (such as radium, radon and uranium), and increase in turbidity due to dissolution and precipitation reactions.
    a. The acceptable quality for the recovered water depends on strategic considerations (such as the end-use of the water and the acceptable cost for post-treatment) and operational considerations (such as clogging).

2. Adjust pre-treatment – if the modelling shows abstracted water would NOT be of an acceptable quality, consider changing pre-treatment methods to improve abstracted water quality. In the model, quality of injected water can be adjusted to produce the required abstracted water quality.

3. Record new injectant quality required and potential pre-treatment train to achieve this

Parameter	**Concentration in injectant water**
Salinity Related Parameters	
Sodium	

Chloride	
Sulphate	
Total Dissolved Solids	
Carbonate Mineral Equilibrium Parameter	
Calcium	
Magnesium	
Bicarbonate (Bicarbonate Alkalinity)	
pH	
Measure Redox Mineral Reaction	
Iron	
Manganese	
Eh	
Dissolved Oxygen	
Dissolved Sulphide	
Redox Couple	
Measure Leachable Metals And Metalloids	
Arsenic	
Uranium	
Molybdenum	
Nickel	
Zinc	
Cobalt	
Measure Silicate Mineral And Miscellaneous Parameters	
Dissolved Silica	
Potassium	
Fluoride	
Barium	

4. Consider the reliability of technology (risk of failure) and resilience to changes in influent quality and quantity – pre-treatment is a vital barrier therefore it is important to ensure the chosen technology is resilient to changes in influent quality and quantity (as these may vary temporally, depending on the source of water used), and is capable of producing the quality and quantity of water required reliably. it is usually possible to produce the required quality of water, however the reliability of the technology (maintenance costs) and its resilience will impact the viability of the pre-treatment process and the overall integrity of a scheme.

5. Consider if the pre-treatment robust enough to accommodate potential changes in required injectant water quality – The required quality for the injectant may change due to a change in the regulatory standards, end-use of water, unforeseen water quality changes during

storage etc. This should be kept in mind when designing the pre-treatment to ensure the process is flexible enough to accommodate changing requirements.

6. Consider post treatment requirements to ensure abstracted water meets end-use requirements - The technology chosen should have the ability to adapt to varying quality of water, to accommodate potential changes in water quality during storage. It would also be advantageous to have a robust process, which could accommodate changes in future requirements of the final water e.g. in case of a change to the enduse.

Initial Cost Assessment

Please consider the costs for both a pilot scheme and a full scale scheme.

1. Cost of constructing the borehole – consider the number of boreholes (and size of the detention basin if required) to estimate cost of constructing the borehole (and detention basin if required).

2. Cost of pre-treatment, pumping, post-treatment, distribution - The cost of treatment can be estimated using the pre-treatment and post treatment requirements determined. Distribution cost can be estimated by considering the distances from source of water to aquifer and aquifer to demand area. Cost of pumping during injection and recovery can be estimated by considering the required injection pressures and recharge rated as found in the initial flow modelling.

3. Cost of losing water due to well hydraulics or other abstractors - Water can be lost during storage either due to other abstractors or due to the hydraulics during storage. Consider the number of wells in the storage area and the quantity of water abstracted to estimate the water lost to other abstractors.

4. Cost of managing purge water – Purge water is produced when ASR wells are flushed during testing and as a part of clogging management. Purge water needs to be disposed of therefore the infrastructure required to do this needs to be accounted for.

5. Cost of licensing and monitoring - Estimated cost for abstraction licenses for source of water and recovering water after storage, license for injecting the water in the aquifer, and license for disposing purge water during flushing. On-going monitoring will be required therefore the cost of this should be estimated. This should include the cost of drilling and maintaining monitoring boreholes, water quality testing, frequency of testing and reporting etc.

6. Maintenance – clogging, reliability of technology - Considering the potential clogging mechanisms that may impact the scheme, estimate the cost of mitigation. The potential cost of maintaining the technology in the treatment train and boreholes should also be factored in.

7. Is the project cost effective – considering the costs estimated reconsider all the water supply options and re-evaluate if ASR is still the best water supply option. The minimum recharge to make the project worthwhile should also be considered.

Appendix C Data and Skills requirement sheet

Data requirements	Skills requirement
Strategic considerations	
Need for scheme	
1. Water resources management plan a. Supply-demand deficit forecast map b. Summary of feasible options for maintaining supply demand balance 2. Hydrogeological map of Anglian region (can be found at http://bgs.ac.uk/research/groundwater/datainfo/hydromaps/home.html)	1. Hydrogeologist (preferably with some knowledge of ASR) 2. Water resources manager (strategic considerations) 3. Supply demand planning specialist – water
Management and technical capability	
	1. Water resources manager (strategic considerations)
Source water considerations	
1. Water resources management plan a. Supply-demand deficit forecast map b. Information on potential sources of water in each planning zone 2. Availability (including seasonality) of water sources 3. License costs	1. Hydrogeologist (preferably with some knowledge of ASR) 2. Water resources manager (strategic considerations) 3. Supply demand planning specialist – water 4. Water resources licensing
Proximity of supply and demand	
1. Hydrogeological map of Anglian region (can be found at http://bgs.ac.uk/research/groundwater/datainfo/hydromaps/home.html)	1. Water resources manager (strategic considerations)
Regulatory considerations	
1. Nature and vulnerability of environment surrounding the potential ASR site 2. Well inventory (can be found at http://www.bgs.ac.uk/research/groundwater/datainfo/NWRA.html) – abstraction volumes, distance from potential ASR site 3. Hydrogeology of the aquifer and vulnerability to	1. Hydrogeologist (preferably with some knowledge of ASR) 2. Water resources manager (strategic considerations) 3. Water resources licensing 4. Water treatment engineer

dissolution, injection pressures etc.	
Hydraulic Assessment	
Suitability of aquifer for recharge – hydraulic evaluation	
1. Effective porosity, hydraulic conductivity, dispersivity, confinement, and dimensions of the potential aquifer 2. Volume of storage required (deficit in supply demand balance can be used to estimate this) 3. Period of time source of water is available 4. Quality of water currently in the potential aquifer 5. Hydraulic gradient (potentiometric map and well inventory)	1. Hydrogeologist (preferably with some knowledge of ASR)
Initial flow modelling	
1. Hydraulic properties of the aquifer e.g. dispersivity, transmissivity 2. Recharge rates, hydraulic gradient, residence time 3. Sources and Sinks for the aquifer	1. Hydrogeologist (preferably with some knowledge of ASR) 2. Modeler (preferably familiar with flow models)
Hydrogeochemical Evaluation	
Hydrogeochemical modelling	
1. Data on quality of native water – Sodium, chloride, sulphate, total dissolved solids, calcium, magnesium, bicarbonate (bicarbonate alkalinity), pH, iron, manganese, Eh, dissolved oxygen, dissolved sulphide, redox couple, arsenic, uranium, molybdenum, nickel, zinc, cobalt, dissolved silica, potassium, fluoride, barium. 2. Data on injectant quality - drinking water standards 3. Data on mineralogy – consider the type of rock and estimate mineral composition of the rock.	1. Hydrogeologist (preferably with some knowledge of ASR) 2. Hydrogeochemist 3. Modeler (preferably familiar with PHREEQC)
Clogging potential	
1. Quality of injectant – TSS, BDOC, nitrates, air content 2. Injection pressures required (hydraulic evaluation) 3. Presence and type of clay (aquifer mineralogy – hydrogeochemical modelling) 4. Geochemical reactions results (output of	1. Hydrogeologist (preferably with some knowledge of ASR) 2. Hydrogeochemist

PHREEQC – hydrogeochemical modelling)	
Pre and post treatment	
1. Output of PHREEQC – hydrogeochemical modelling and Clogging potential 2. Quality of injectant 3. Pre-treatment requirements and technology 4. Water end-use requirements	1. Hydrogeologist (preferably with some knowledge of ASR) 2. Water treatment engineer
Initial Cost Analysis	
1. Supply/demand distances and Distribution costs 2. Pumping/energy costs 3. License costs 4. Cost of different water treatment technologies 5. Cost of borehole construction	1. Hydrogeologist (preferably with some knowledge of ASR) 2. Water resources manager (strategic considerations) 3. Supply demand planning specialist – water 4. Water resources licensing

Appendix D Survey sent to ASR operators

Introduction

Managed Aquifer Recharge (MAR) provides a more sustainable method to store water when compared to reservoirs. However, potential changes in water quality that may occur during storage in the aquifer, regulatory uncertainty and high initial investigation costs are all deterrents to wider application of the technology. There is a need to address these issues if MAR is to be promoted.

The aim of this survey is to characterise the risks associated with MAR schemes and the management responses to characterising and coping with such risks. Your responses to the questions below will provide a good idea of the risk frameworks that are being used in MAR schemes and the experiences of using them, recalcitrant threats associated with schemes and any possible indicators that may be used to identify high risk schemes. This can then be used to improve the risk assessment process and reduce the uncertainty associated with MAR.

This survey only comprises of 12 questions and should take 15-20 minutes to complete. Your time and effort is greatly appreciated.

Your rights

- All data collected through this survey will be stored securely with pin either online or on a hard drive for three years, after which it will be deleted or destroyed. Data obtained will be used for research purposes only.
- You have the right to withdraw from participation in this survey at any time before submitting your responses. However, once you have submitted your data, it cannot be withdrawn as it will be submitted anonymously.
- As this is anonymous research; your name will not be required. Neither the researchers nor anyone else will be able to identify you from the data.
- If you have any questions regarding this research, you may contact Mital Pindoria at mpindoria@anglianwater.co.uk

Context

1. Please provide us with some details of the scheme you will focusing your answers on below

Name of Scheme (optional): ☐

Location (optional): ☐

Contact details (optional): ☐

Any Reference documents (e.g. reference to a document/webpage containing relevant information on the scheme): ☐

Methods for Assessing Risk in ASR

This section of the survey asks for your insights into the risk assessment frameworks/methodologies used in ASR schemes Examples of risk assessment frameworks and methodologies include HAZOP, FMECA, QMRA or perhaps bespoke national or commercial frameworks.

2. Which risk assessment frameworks/methodologies were used to assess potential risk associated with the ASR scheme you told us about in answer to Question 1

Risk assessment framework/methodology 1:
Risk assessment framework/methodology 2:
Risk assessment framework/methodology 3:
Risk assessment framework/methodology 4:

3. Please indicate which project development stage the risk assessment/assessments were implemented in.

Pre-feasibility/desktop study - mainly strategic risks e.g. need for water, availability, reliability, quantity and acceptability of source water, proximity of supply & demand, regulatory requirements etc.
Investigation stage - more detailed analysis e.g. site selection, hydrological studies etc.
Feasibility/pilot stage - pilot testing
Implementation - full scale operation

	Pre-feasibility/desktop study	Investigation stage	Feasibility/pilot stage	Implementation stage
Risk assessment framework/ methodology 1	☐	☐	☐	☐
Risk assessment framework/ methodology 2	☐	☐	☐	☐
Risk assessment framework/ methodology 3	☐	☐	☐	☐
Risk assessment framework/ methodology 4	☐	☐	☐	☐

4. Did the risk assessment in the "pre-feasibility and investigation" stages identify all major risks to the scheme?

○ Yes

○ No

○ If "no", which major risks were not identified

Risks associated with ASR schemes

When responding to the questions in this section, please use the numbers as an identification key for the response and use the same order throughout the section - i.e. if a particular threat is listed as number "1." in response to Question 5, all following questions labelled "1." will refer to this same threat.

5. Post commissioning, what were the four main threats to the long term success of the scheme? Please rate these in terms of their impact on the scheme – 1 = highest impact, 4 = lowest relative impact.
NB. These could be threats to any dimension of performance (e.g. regulatory, strategic, financial, operational, environmental, etc.)

1:
2:
3:
4:

6. In hindsight, what were the specific causes of these threats? Please maintain the same order as Question 5. (Cause 1. for Threat 1. etc.)

1:
2:
3:
4:

7. Were there any indicators that provided warning for the occurrence of these threats? Please maintain the same order as Question 5. (Indicator 1. for the occurrence of Threat 1. etc.)

1:
2:
3:
4:

8. In hindsight, do you feel a more comprehensive risk assessment could have offered any benefits?

☐ Yes

☐ No

☐ If yes, please elaborate

9. What mitigation measures were used to minimise the impact of these threats? Please maintain the same order as Question 5 (Mitigation measure 1. for Threat 1. etc)

1:
2:
3:
4:

10. How effective were these mitigation measures?

	Ineffective	Satisfactory	Good
Mitigation measures 1	☐	☐	☐
Mitigation measures 2	☐	☐	☐
Mitigation measures 3	☐	☐	☐
Mitigation measures 4	☐	☐	☐

11. Could the threats which emerged post implementation of the scheme have been identified during the planning phases of the scheme? Please maintain the same order as Question 5

	Yes	No
Threat 1.	☐	☐
Threat 2.	☐	☐
Threat 3.	☐	☐
Threat 4.	☐	☐

12. If you could re-design the scheme, what would you do differently?

1: ☐
2: ☐
3: ☐
4: ☐

Appendix E Summary of survey responses – Frameworks used

Scheme	Framework used	Stage implemented	Identify all risks in pre-feasibility/investigation stages?
batería de pozos de infiltración del Alto Guadiana (Spain) ASTR scheme	own methodology Australian risk assessment (AWA) South African (CSIR)	All stages investigation stage feasibility/pilot stage	yes
Torreele/St-Andre water reuse/ dune aquifer recharge scheme	HACCP	Feasibility/pilot and implementation stage	yes
Mesa northwest water reclamation plant	None		No
Sand hollow reservoir spreading basin MAR	None		While only minimal water-quality risk assessment was conducted, the main concern is flushing of vadose-zone salts and arsenic
Great Horksley	Decision tree - decision plus package (generic and customised for use. Criteria and weighting assigned) Internal investigation programme - logical staged approach requiring justification of risk	pre-feasibility/ desktop stage and feasibility/pilot stage pre-feasibility/ desktop stage, investigation stage and feasibility/pilot stage - ALL	No
Bucklesham	Internal investigation programme - logical staged approach requiring justification of risk	pre-feasibility/ desktop stage, investigation stage and feasibility/pilot stage - ALL	yes
NLARS	Expert judgement	Throughout	N/a

Horton Kirby ASR	Modelling done after core removed - geochemical and mixing	investigation stage (hydrogeochemical modelling done when core drilled) and Feasibility stage (hydraulic modelling done as part of operations)	No - only hydrogeochemical modelling done at this point
Lytchett Minster	None - time criticality meant results were needed quickly to show business value of such schemes. Expert judgement (D. Pyne) used		No risk assessment implemented Missed out the impact of dual porosity (BGS said it would be an issue that would cause mixing). Supply demand issues identified - demand died off)
	hydraulic modelling - Modflow	End of feasibility/pilot THUS IMPLEMENTATION	
	geochemical modelling - phreeqc	End of feasibility/pilot THUS IMPLEMENTATION	
	dual porosity diffusion model - SWIFT/486	End of feasibility/pilot THUS IMPLEMENTATION	
Australia (NSW)	Australian Guidelines	ALL	No - How the ecological status of the local stream could be adversely affected by changes to seasonal flow wasn't identified
Las Vegas Valley Water District ASR program	Internal process - hydraulics, retrofitting existing wells, attenuation studies etc. (desktop), well design & construction methods (implementation)	Pre-feasibility/desktop and implementation stages. Just started doing it at full scale, learnt from experience and expanded	No - however, no one could have anticipated eventual signing of a tri-state agreement between California, Arizona and Nevada relating to water rights that undercut the ability to store water due to low availability.
San Antonio Water System Twin Oaks ASR Well field	Pyne approach.	ALL	No - Potential for lateral movement of the stored water was not initially identified as a risk, however became potential risk when objective of scheme changed
Bradenton ASR program	Pyne approach	All Pre-feasibility/desktop Pre-feasibility/desktop	Yes - However changing team in the middle who didn't understand reasoning behind previous plan and changed it, resulted in Arsenic mobilisation. This meant deoxygenation was needed in pre-treatment - expensive

Greenville Utilities Commission ASR Well	Pyne approach	All Pre-feasibility/desktop Pre-feasibility/desktop	No - Kaolinite bed made the recovered drinking water cloudy white. However cores geophysical logs and drill cuttings were analysed, which didn't detect the Kaolinite. Everything that could be justified economically was done therefore unlikely anything else could have been done
Hilton Head public service district ASR	Pyne approach	All Pre-feasibility/desktop Pre-feasibility/desktop	Yes
Nottinghamshire ARR schemes	PHREEQC modelling	feasibility/pilot	No - NB. there was already a working scheme nearby
Irton ASR, Scarborough, Yorkshire	Internal process - value management and risk study	pre-feasibility/desktop and feasibility/pilot	No - cost of the scheme and added cost of re-treatment required after abstraction was not identified. The intent was only disinfection after re-abstraction but changes during storage not identified. scheme was benched as too expensive due to extra treatment and replaced by a pipeline which solved more than one problem (~10mld)
	Numerical modelling - to assess technical feasibility	Feasibility/pilot stage	
Stockburry ASR pilot	Rough technical assessment	pre-feasibility/desktop and investigation	No - geochemical reactions were not adequately identified. When chalk water was stored in greensand, Fe, Mn etc. were released. Post and pre-treatment too expensive
	groundwater flow and some geochemical modelling	Pre-feasibility/desktop	
Perth Groundwater Replenishment Scheme	Strategic Advice on Managed Aquifer Recharge Using Treated Wastewater on the Swan Coastal Plain	pre-feasibility/desktop and investigation	Yes, The preliminary risk assessment identified the three key objectives/risks of GWR; technical feasibility, development of policy and

Australian Drinking Water Guidelines. National Water Quality Management Strategy 6	pre-feasibility/desktop and investigation	regulation and stakeholder and community engagement and acceptance. This allowed the Water Corporation to identify required research to characterise source water (wastewater), define the treatment processes, quality of the recycled water and characterisation the aquifer. This allowed the development of appropriate guidelines to protect the environmental values of the receiving environment, appropriate monitoring plans to gather the required information to define and address the risks at future risk assessments
National Water Quality Management Strategy 21 Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 1)	Investigation, feasibility/pilot and Implementation	
National Water Quality Management Strategy Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2) – Augmentation of Drinking Water Supplies	Investigation, feasibility/pilot and Implementation	
National Water Quality Management Strategy 24 Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2) Managed Aquifer Recharge	Feasibility/pilot and Implementation	

Appendix F Summary of survey responses – threats, causes, indicators and mitigation measures used

Scheme	**Threats**	**Causes**	**Indicators**	**More comprehensive risk assessment benefit?**	**Mitigation**	**effectiveness of mitigation**	**Could threats which emerged post implementation be identified earlier?**	**Re-design scheme - what would you do differently**
batería de pozos de infiltración del Alto Guadiana (Spain)	water availability	weather	long term forecast	Yes - all rights of farmers not taken into account and compensation has been required	-	ineffective	yes	bigger storage cells to slow down recharge rate
	clogging	pre-treatment cannot be too demanding as it is an opportunity scheme	detection in wells via video camera		replace sand and gravel filters when possible	good	yes	install pre-treatment and filters easier and cheaper to replace
	air clogging	quick injection due to short availability	Genesis of decalcification clay from mudstone, Fe2O3 concentration in Groundwater, clogging crusts in slotted cases		recharge at lower speed	ineffective	yes	advertising directed to related people to promote scheme
	economical guarantee for future maintenance	economic crisis, psycho-social perception of scheme	Media appearance, complaints submitted		compensation to affected people, technical articles, scientific explanation to complainers	satisfactory	yes	more dissemination sessions in the affected municipalities
Torreele/St-Andre water reuse/ dune aquifer recharge scheme	recontamination of the infiltrated water in the open pond	Water obtained after RO, thus free of bacteria and viruses, comes back in open air	sampling of the infiltration pond shows low levels of bacteria	no	none		yes	cannot avoid this unless scheme is put underground
	clogging of the pond	By organic material present at site and by the faeces of the birds	infiltration rates reduce - cleaning required every 4-5 years		minimise trees around the pond	satisfactory	yes	cut all trees that can drop leaves into pond

	high temperature of abstracted water	Water in open air warms in summer and can lead to increased temperatures when extracted causing biological instability	Temperature measurement showed fluctuations along the season but as the distance from the wells to the pond varied, the increase was not 'problematic'		distance from wells to pond is varied	good	yes	Did as should have
Mesa northwest water reclamation plant	Jurisdiction - the site is on the edge of a federal waterway and an Indian Reservation	The methods to recover the water were not implemented so the recharged water plume keeps expanding		No	The location of the recharge basins was moved and recharge was implemented further upstream from the neighbouring cities	ineffective	no	The methods to recover the water would have been implemented correctly
	Groundwater transport to the neighbouring City of Tempe						no	
Sand hollow reservoir spreading basin MAR (USA)	clogging and reduced infiltration rates	inflowing stream water with suspended sediments	Virgin River occasionally has high turbidity	Yes - More hydrochemical modelling for mixing and mobilization of arsenic would have been helpful	: Stream water is not diverted to the reservoir when turbidity is high (visual inspection only)	Satisfactory	yes	More effort to characterize effects of hydrochemical mixing of native groundwater with MAR water
	Water-quality decline (increased salinity and arsenic)	borehole chemistry vadose zone under reservoir showed high natural solute accumulation during Holocene	(same answer as above)		None so far	ineffective	yes	
	Water logging in areas down gradient of surface-water reservoir	Steep hydraulic gradient of regional water table once reservoir established hydraulic connection	Rising groundwater levels during decade since reservoir was completed		: A series of shallow wells and french drains were installed and pumped to lower	good	yes	

		with underlying aquifer			groundwater levels below land surface			
Great Horksley	water quality - fissured system	diffusion exchange - high K in abstracted water	no				yes	choose a site with a higher yield
	low yielding borehole	chalk permeability low - tight chalk	previous work indicated system was in a low-medium permeability area	yes	N/a - scheme was benched	N/a - scheme was benched	yes	
	clogging of borehole	turbidity in injected water - physical clogging	Yes – low permeability				yes	
Bucklesham	legislation - sustainability reductions removed source of water	WFD	no - were in discussion with EA in whole process - possible communication breakdown between 2 teams dealing with project	no	N/a - scheme benched. There is however a possibility to use another source of water, transfer pipelines already exist	N/a - scheme was benched	yes	Have another source of water
NLARS	maintenance of assets - drought management scheme	Not used often thus is low priority for maintenance. However failure during drought is critical.	dialogue with the EA and agreements made	Yes - maintenance risks would be identified and more regular use negotiated. Area without London clay would also have been identified.			yes	other sources for recharge
	resilience of the scheme	Growing demand for water thus less recharge water available. Low pressure in the network during recharge	modelling done (after) to identify network low pressures		recharge in lowest demand periods		yes	more flexible use - not only drought management

	water quality (1 borehole abandoned)	release of iron into water due to redox reactions causing leaching	Chemistry of the sands - geochemical studies done & indicated as threat. NB only a threat at one site due to lack of confinement i.e. area lacked London clay		blending and keeping water levels below the sands	good	yes	
Horton Kirby ASR	Impact on the environment	This layer of Lower green sand (LGS) - although K is high, T is low results in larger drawdown which reaches the River Darrent. This river already has low flow this impact is very high	N/a (except hydraulic modelling which was done later)	yes	N/a	N/a	N/a	Do the hydraulic modelling earlier - with the hydrogeochemical modelling when core drilled and tested rather than as part of operations.
	source of water not readily available	n/a	N/a					
	water quality	LGS is reactive and can cause a lot of clogging	severe clogging at other sites - however no clogging at other similar sites					
	hydraulic gradient	natural hydraulic gradient	BGS maps					
Lytchett Minster	Water quality - F	Mixing due to dual porosity	Modelling studies (done after pilot testing though). Nature of dual porosity	Yes - Supply demand balance to identify lack of demand. Identify high levels of mixing	N/a - scheme abandoned as F treatment too expensive	N/a	yes	Risk assessment first with modelling. Choose different aquifer - deeper and in demand area. Not waste as much time and resources with mitigation for borehole integrity (Environmental
	Fe and Mn release - potential clogging	Iron in Chalk released due to introduction of O2	mineralogy				yes	

								Concerns WRT blow out during injection)
Australia (NSW)	Pollution to the local stream from associated Reverse Osmosis (RO) treatment plant	Maintenance and monitoring of RO treatment plant	Historical failures on similar RO plant infrastructure - that we were not aware of at the time	Yes - However, the diversity of MAR schemes is such that no single set of guidelines could cover all aspects. The most important factor in covering all the potential risks is to ensure experienced and qualified professionals are involved in every specialist stage of the project.	Maintenance schedule of the RO plant infrastructure was improved	Good	yes	Reliability and monitoring of the RO treatment plant
	River Bank erosion	Construction of the shallow recharge system	Observations from the pilot scheme should have provided warning		Monitoring of the river channel and flows rates was improved	satisfactory	yes	Pre-MAR (i.e. natural condition) monitoring of the stream and river bank conditions
	Unacceptable change to seasonal flow regime in river	Continued recharge to river bed altering seasonal flow characteristics and therefore ecology of the river	Regulatory recommendations at the pre-feasibility stage provided a warning of this		Better understanding of the natural seasonal flow and how this can be reflected in the system (moving some shallow recharge away from the river)	satisfactory	yes	Pre-MAR (i.e. natural condition) monitoring of the seasonal river flow conditions
	Failure of the RO treatment plant	No redundancy in the RO treatment plant and limited surface storage dams should temporary storage be required	Records of the reliability of the RO plant at other locations		As response 1 - more monitoring and maintenance of the RO plant and associated infrastructure.	good	yes	Reliability and monitoring of the RO treatment plant
Las Vegas Valley Water District ASR program	Lack of water to store…this is the current situation, pursuant to an interstate agreement	Original yield estimates were overstated decades ago. Now the states are dealing with the resulting water shortages	Water availability consistently below expectations	Yes - ASR program was managed at a low level within the LVVWD organisation, perhaps better liaison with	Change well field operation from mostly ASR to mostly production, accepting the resultant loss of storage, declining water levels, and	satisfactory in short term only	No	Improve integration of ASR into the tri-state negotiated settlement agreement. This may eventually happen. California has recently made

				regulators could have provided some warning to LVVWD/ provided regulators with an idea of the importance of ASR is Las Vegas	subsidence. UNSUSTAINABLE			significant regulatory policy changes that favour storing water underground instead of in surface reservoirs
San Antonio water system Twin Oaks ASR wellfield	Concern regarding adequate control over stored water - Texas water law & politics	Change in operating plan after design and construction due to political opposition by land owners.	Local landowner opposition from the beginning. SAWS proceeded regardless, without addressing their concerns	No - the original conceptual design and site selection process may have been flawed, at least in hindsight. This caused increased cost and risk. However the resulting project has been highly successful anyway, meeting demands during a recent/current severe drought. SAWS probably understood the risk that they were taking 15 or so years ago and moved forward	Well field mitigation program to address landowner concerns - wells were deepened and pumps replaced, etc.	Good	yes	Locate the ASR well field in san Antonio, not 30 miles south of town in a different county. This option was not considered to be viable politically at the time.
	Politics of funding - SAWS will be competing their share of funds with major water projects e.g. desalination - not everyone interested in the lowest cost viable option	Big, expensive, above ground projects have more political appeal than wells	Capital investment decisions for major water projects are not necessarily based upon considerations of feasibility and cost. The more money available, the less likely that the selected plan will be cost-effective		Campaigning and building relations with relevant authorities to ensure some funding goes to ASR	unknown	No - state funding then available	NOTHING
	Lack of understanding of need for buffer zone by top water managers - operators aware	Currently not an operational concern, may become one if they try and recover buffer zone and then have to treat the poor quality recovered water.	Nothing specific - but the buffer zone technical approach is relatively new and a lot of technical people don't understand it yet, let along water managers.		Efforts to educate top managers about these seemingly minor and unimportant technical issues are, in fact, important.	unknown	no - buffer zone concept in early development back then	clearly establish the buffer zone up front, as part of the operations plan for the well field

	Doubt about the schemes cost effectiveness, risk and uncertainties	The accounting system includes many elements not needed to support the ASR scheme - doesn't reflect costs accurately	Texas legal framework - maintaining control over water stored necessitates acquisition of huge tracts of land for well field development	anyway. In hindsight that was a good move.	Education opportunities are being sought, such as conference presentations, etc.	unknown	no - not an issue until threat 1 became real	suggest to SAWS that they set up their ASR accounting system differently, relating ASR costs and benefits
Bradenton ASR program	Technical: arsenic mobilization	changing teams mid-stream, who changed the cycle plan and got rid of the required buffer zone	Yes - the original investigations showed Arsenic mobilisation was a risk		Deoxygenation. Ultimately successful but was more complicated, time-consuming and expensive than expected.	Good	Yes - They were identified	Don't change horses in mid-stream and hand over project control to folks who do not understand ASR science and technology.
	Financial: cost of ASR compared to other water supply options, after the city opted for deoxygenation Vs forming and maintaining a buffer zone	Arsenic mobilisation meant that expensive deoxygenation was required	Everyone involved at the time knew that deoxygenation would be expensive, however it was the only way forward that the regulators could approve at the time	NO	None (Option to reform and maintain buffer zone?? Has this been done now?)			
Greenville Utilities Commission ASR Well	Regulatory changes - low flow restrictions recently changed, reducing the need for ASR	Regulators change their policies very slowly - low flow restrictions have been in place for around ~20 years	Low flow diversion restrictions on GUC have been a widely-known political/regulatory issue for at least 20 years. However planning and implementation of projects had to be based on the current restrictions.	No - GUC would not have agreed to include in the original budget a doubling or tripling of the geochemical tasks, and we (as the consultants) would not have recommended	None. It would have been unreasonable and unacceptable to plan and implement an ASR program based on the long-range assumption that regulatory policy would be changed in favour of GUC	N/a	No	Nothing

	Strategic considerations - changes in GUC priorities	reduction in water sales and associated revenues - capital investments deferred and priorities adjusted as necessary	Few people foresaw the economic collapse that began in 2008, affecting strategic decisions across the globe, including for GUC	that anyway, based on the available information at the time.	Overall strategy was to achieve a successful ASR program, so GUC could meet its seasonal water storage needs	ineffective - so far at least	No	
	Turbidity due to occurrence of kaolinite in recovered water	Insufficiently detailed geochemical investigations and plain bad luck	no way to foresee the occurrence of kaolinite in the recovered water until cycle testing began		-	-	No	
Hilton Head public service district ASR	Potential interference between ASR wells and the brackish water production wells, causing loss of performance for all wells - desalinated water from a deeper brackish aquifer is one source of recharge water. The same brackish aquifer is being utilized for ASR and for brackish water supply to the reverse osmosis plants.	Utility operations personnel lack of awareness of the potential for such well interference. This is an educational process that is now being addressed	Yes, fairly extensive monitoring of water levels and water quality at many wells on Hilton head island, plus associated steady improvement of the local groundwater model. This is a potential threat that is being addressed	NO	Monitoring, groundwater modelling, updating of long-range water plans so that new wells are located and operated in such a way as to avoid significant well interference. All of this is underway.	Good	Yes - They were identified in phase one planning	Nothing

Nottinghamshire ARR	getting yield from limestone - could get water in but couldn't get it back out	tightly packed & need fracturing locally to get yield	Other boreholes were drilled in the area and got no yield. Desk study was conducted to try and identify fractured areas	NO	changed the siting strategy and used acid to open the fractures (condition the aquifer)	good	Yes	Nothing
	Regulatory barrier - abstraction from sandstone not acceptable to EA. Embargo in place for further schemes	Hydraulic connection between limestone and the fully allocated sandstone means water is being abstracted from the sandstone	Post scheme so no real indicators		negotiation with the EA - however no plans for expansion so no real requirement to push for the embargo to be lifted at the moment	N/a	No	
	expensive - uses 3 pumps							
Irton ASR, Scarborough, Yorkshire	Cost of scheme	Increased risks due to the lack of data in the UK which increased uncertainties and made costing the scheme difficult. Available information limited to theoretical geological interpretation backed up with a very small diameter investigation borehole	data restrictions were known - the small borehole provided the only available info concerning the osgodby aquifer in the vicinity of Irton	Yes - A better economic assessment could have indicated the cost effectiveness of the scheme, and the acceptable levels of risk	pilot borehole testing, hydraulic modelling, geochemical analysis & a comparison with other schemes	Good	No	
	Large drawdown meant that target yield couldn't be achieved with 1 borehole. Would need 2 which	high transmissivity	Hydraulics + transmissivity was roughly known, however there was not enough data		two wells used to achieve the target yield	Good	No	

	increases costs							
	Microbial contamination of recovered water	inflow from the corallian groundwater - big threat especially as system is designed to be operated when the corallian groundwater is contaminated (when R.Derwent polluted)	N/a		Re-engineer the borehole - over drilling and grouting of borehole, or grouting via existing main	N/a - didn’t get to this stage	No	
	High ammonium which degrades the disinfection capability	Ammonium is present in the native groundwater and behaves conservatively - mixing	N/a - had to drill the pilot to do testing		design disinfection to be able to deal with the presence of ammonium	N/a - didn’t get to this stage	No	
Stockburry ASR pilot	water quality - release of Fe & Mn resulted in a loss of storage capacity due to clogging of the aquifer	geochemistry of the greensand	Issues with the greensand were known, however the geochemistry of deeply confined greensand not as well known - needed to experiment and see as the deep confinement could have resulted in different reactions	Yes - better geochemical investigations such as taking core samples could have provided a better understanding of the potential geochemical changes and better understanding of treatment hence cost	N/a	N/a	yes	More investigation on the hydrogeochemisty
	pre-treatment was considered expensive	need for the scheme was not enough to justify the costs, and it was a small scale - 0.5MLD	there was an idea of the possible reactions that could take place				yes	

Perth Groundwater Replenishment Scheme	Stakeholder and public support	Misinformation causing lack of trust in Water Corporation to manage the recycling process and regulators to oversee	Yes, failure of other recycled water schemes in Australia	No	Extensive community and stakeholder engagement	Good	Yes and they were identified	Nothing, Trial was a very conservative approach to progressing a GWR Scheme
	Policy and Regulation	Lack of policy and regulation and process not determined to progress a GWR Scheme	No MAR policy in place, had to ensure good engagement with regulators to ensure appropriate governance and guidelines in place		Interagency working group established several years before our trial to keep regulators informed on activities, research to allow policy development	Good	Yes and they were identified	
	Technical Feasibility	Lack of understanding/capability to characterise recycled water and aquifer. Lack of capability to operate AWRP to produce recycled water to meet drinking water guidelines	Lack of data – however we were able to design our research programs to address the unknowns		Appropriate research program	Good	Yes and they were identified	

Appendix G Comparison of existing guidelines and proposed Strategic Planning Tool

Below is the spread sheet used to evaluate the existing guidelines and DST's against each other and the Strategic Planning Tool. It shows the parameters considered in each category when comparing the guidelines/DSTs. An "x" was placed in the cells where the parameter was considered in the corresponding guideline/DST. Parameters with a strikethrough were the adjustments made when the Strategic Planning Tool was evaluated against the others, bearing in mind the UK context and the aim of the tool. The reason for excluding it is given in the last column under "proposed DST".

	South African guidelines	Dutch guidelines	Pyne guidelines	Australian guidelines	Brown DST	Kazner DST	Proposed DST
Hydrological limitations							
will aquifer receive water	x	x	x	x	x		x
will water be retrievable	x	x	x	x	x		x
Storage capacity of the aquifer - also consider space for water using historical water levels and abstraction data	x	x		x	x	x	🟥 x
will aquifer achieve required recharge rates (injection/pumping tests)	x	x	x	x	x		x
groundwater flow regime and potential gradients	x	x	x	x		x	x
confining layer properties (aerial extent, thickness & depth)		x	x	x		x	x
aquifers aerial extent, thickness and depth		x	x	x		x	🟥 x
method of recharge	x	x	x	x		x	x
~~Additional data collection - geophysical exploration and borehole logging, hydraulic analysis of cores~~		~~x~~	~~x~~	~~x~~	~~x~~		This is investigated after the desktop stage
impact of storage time on quantity			x	x			x
Water quality issues							
source water quality and suitability for recharge	x	x	x	x	x	x	x
native water quality	x	x	x	x	x	x	x
effects of mixing and rock water interaction	x	x	x	x	x	x	x
Pre-treatment and post-treatment requirements	x	x	x	x	x	x	x
Hydrogeological simulation modelling			x	x	x		x
Target storage volume/buffer zone			x	x			🟥
~~Source water catchment land use assessment~~			~~x~~	~~x~~	~~x~~	~~x~~	Integrated in pre-treatment considerations
~~Additional data collection - geochemical analysis of cores, hydrochemical survey of native water~~		~~x~~	~~x~~	~~x~~	~~x~~		This is investigated after the desktop stage
impact of storage time on quality			x	x	x		x
Clogging							
comment on clogging concerns, types, prevention and management	x			x			x
describe how design will minimise clogging	x	x	x	x			x
Source water availability							
quantity and availability of water	x	x	x	x	x	x	x
quantity of assured yield (monthly) and risk of undersupply	x		x				🟥
reliability of source of water					x		x
Acceptability of source of water				x			x

Regulatory approval/water rights								
potential environmental benefits, risks, constraints including impact on aquifer	x	x	x	x	x	x	x	
any legal constraints e.g. securing water rights	x	x	x	x	x		x	
existing groundwater license and conditions for use	x	x	x				x	
authorisation needed for feasibility tests	x	x	x	x			x	
Impact on other users			x	x	x		x	
Economics/funding (including maintenance)								
define objectives	x		x	x	x	x	x	
evaluate AR relative to other options to meet objective	x		x	x	x	x	x	
cost of feasibility study	x	x	x	x			🟥 x	
~~existing and planned monitoring systems~~	~~x~~			~~x~~		~~x~~		This would be determined after the investigation and pilot stages
skills needed to manage, operate and maintain scheme - current & needed	x			x			x	
minimum recharge to make project worthwhile	x		x	x	x	x	🟥 x	
infrastructure needed to treat, inject and extract water	x	x	x	x	x	x	x	
Storage requirements - source water availability+demand (quantity and period) and objectives impact no. of wells	x		x	x	x	x	x	
describe/cost all economic benefits	x	x	x	x	x	x	🟩	
economic assessment and comparison with alternative options	x	x	x		x		🟨	
recovery efficiency			x	x	x		x	
Management of purge water (testing and clogging management)			x	x			🟥	
Other impacts on the business								
Meeting with parties involved		x	x	x		x	🟥	
Site selection		x	x	x	x	x	x	
Similarity to successful projects - confidence to stakeholders				x			🟥	
~~Hazard identification and preventative measures - source, effect, management~~				~~x~~	~~x~~			Tool intended to provide a process oriented viability assessment, not hazard oriented risk assessment thus not needed
preliminary infrastructure design for treatment, conveyance and recharge (conceptual design)	x	x	x	x	x	x	🟩	
detailed implementation plan	x		x	x	x		🟩	
establish requirements for full scale operation	x		x	x			🟩	
Meets business priorities?							x	

The cells shaded red under “Proposed DST” are parameters that were missing and needed to be included in the Strategic Planning Tool. The cells shaded green indicate that these will be outputs of the Strategic Planning Tool and the cells shaded yellow will be available in studies done prior to implementing this tool, for example in the Water Resource Management Plan.

It is important to mention that most of the guidelines considered in the evaluation had a sufficient about of detail to form the comparison except the Dutch guidelines which were essentially a checklist. In this case, there was significant inference as to the meaning of points on the checklist and the parameters that would be included.

Appendix H Templates used to test the Strategic Planning Tool during deployment

Template used to debrief the user following deployment of the Strategic Planning Tool. Responses are shown in red.

Performance Attribute	Data source – Questions asked during debriefing	Data collection method	Data evaluation method
Tool as an artefact – clarity and reliability			
Connectivity between relevant sections of the tool – the user should understand why different sections are connected to each other and how one will influence the other	1. Do you feel you have a better understanding of the interconnections between different aspects (e.g. how availability of water can impact number of recharge wells required) of an ASR viability study? If not, please elaborate Yes 2. Where there any connections made in the tool for which the reasoning was unclear? Please elaborate Connections didn't really come across	Notes taken during debriefing	Analysis of notes and recording for indications where user doesn't seem to understand why some sections are connected Comparing the number of connections not understood to overall number of connections
Ease of use – the overall logic should be clear and easy to follow	1. On a scale of 1 to 5, with 1 being poor and 5 being excellent, how clear was logic of the tool? 3 – It was relatively easy to follow however the home page could have been clearer on which sections were completed and which were not. A progress bar would also have been useful.	Notes taken during debriefing	Analysis of notes and recording to determine if the user found the tool difficult to understand/use

	2. Were there any parts of the tool in particular that were difficult to understand/use? Please elaborate In Hydraulic Assessment a question is asked whether the storage capacity is sufficient however information on the amount of storage required is not provided.		
The format of the report – The report should provide a skeleton for a viability study.	1. Could the report be used as a skeleton for a viability study? If not, please elaborate Potentially 2. Does the report adequately represent the information input into the tool? If not, please elaborate Yes however the format of the report could be better. Also it would be useful to have the traffic light buttons (rather than words indicating the level of confidence) next to the answers In the ‘suitability of the aquifer for recharge and recovery’ section, the question “Is the aquifer appropriately confined?” comes up twice however there is only an answer visible for one occurrence Finally in the Initial Cost	Notes taken during debriefing	Analysis of notes and recording to determine the impact of the reporting function.

	Assessment, the report only shows the content of the comment boxes without the heading of the cost being referred to. It is therefore difficult to differentiate between costs in the report		
Tool as a function – ability to achieve the intended outcomes			
Provide a unified, holistic methodology to assess viability of ASR in the UK	1. Does the tool integrate all the elements (pre-treatment, injection, storage, recovery and post-treatment) of ASR? If not, please elaborate They are not experts all the aspects of ASR therefore cannot be confident in their response however as far as they know, Yes. 2. Does the tool consolidate all the elements of ASR? If not, please elaborate A holistic investigation was not in the scope of their work	Notes taken during debriefing	Analysis of notes and recording to determine if the tool helped the user to think systemically (e.g. appreciate other perspectives and get a bigger picture understanding)
Provide a methodology that would allow businesses unfamiliar with ASR to assess viability of such schemes	1. Does the tool enable businesses unfamiliar with such schemes to understand the potential threats involved, and the factors that need to be considered when planning and designing an ASR scheme? If not, please elaborate Yes however some questions may be difficult to answer as there is little guidance on what to do if the user does not know how to approach the question. It was recognised however that this is not feasible to do and	Notes taken during debriefing	Analysis of notes and recording to determine if the tool can be used by inexperienced businesses to assess viability of ASR

	contractors should be hired to investigate the unknowns.		
Provide a process oriented methodology that promotes the tools use across different sites	1. Is the tool versatile enough to use across different sites? If not, please elaborate Yes	Notes taken during debriefing	Analysis of notes and recording to determine if a versatile, process oriented methodology has been developed
Provide a cost effective methodology to assess viability of such schemes	1. Effectiveness - how do the outputs compare to the desired outcome? No – expected a tick box method. 2. Efficiency - how do the outputs stack up to the resources spent to produce them? As the work was contracted out it is up to Anglian Water to decide this. 3. Economy – Is the time invested appropriate considering the outputs provided? Please elaborate Yes	Recording time taken to complete Notes taken during debriefing	Analysis of notes and recording to determine if the tool provides a cost effective method of assessing viability of ASR
Provide guidance specific to the UK context by considering the regulations in the UK.	1. Are there any regulatory requirements with regards to ASR in the UK that the tool has neglected? If yes, please elaborate This was not in the scope of their work however it seemed to include all requirements.	Notes taken during debriefing	Analysis of notes and recording to determine if sufficient guidance with regards to regulatory requirements of ASR in UK is provided.
Provide some indication of the complexity and cost of the scheme as well as provide a scope for investigation during a	1. Does the tool provide an indication of the complexity of the scheme? If not, please elaborate Yes – however the	Notes taken during debriefing	Analysis of notes and recording to determine if the tool provides an initial indication of the complexity and cost of a scheme, and a scope

pilot	consultant was mostly concerned with specific aspects therefore are not able to confidently answer 2. Does the tool provide the ability to roughly cost the scheme? If not, please elaborate Yes however the section seems more like "write what you feel". It would be better to have a separate box to put the cost and have a £ sign with explicit instructions that only numbers should be entered. The ability to sum up all the costs entered would also be useful. 3. Are there any factors that have not been considered which would prevent the tool from informing a pilot scheme? If yes, please elaborate Identifying faults and fractures in the geology, potential sources of contamination around the borehole, size of distribution pipes, existing infrastructure e.g. roads.		for investigation during pilot testing.

Observation template

Performance Attribute	Data source	Data collection method	Data evaluation method
Tool as an artefact – clarity and reliability			
Ease of use – the *overall logic* should be clear and easy to follow	Log of queries and help provided /comments from user during use	Notes taken during use	Analyse for comments which indicate difficulty understanding/following the overall logic of the tool
Clarity – the requirements of *each page* should be clearly understood	Log of queries/comments from user during use	Notes taken during use	Analyse for comments/ queries which indicate confusion or indecision about the requirements of a page
Connectivity between relevant sections of the tool – the user should understand why different sections are connected to each other and how one will influence the other	Log of queries/comments from user during use	Notes taken during use	Analyse for comments/ queries which indicate the user does not: 1. Understand why certain sections are connected 2. Agree with the influence of the sections on each other

Performance criteria associated with each attribute – to be used during observation

Performance Attribute	Performance Criteria	Comments including a note of the section of tool being evaluated
Ease of use – the logic should be clear and easy to follow	Navigation away from the page before answer given	
	Pages left blank	
	Understanding how to populate the answer	• Table of water resources – users felt it was too long • Objectives of the scheme – wrongly populated • Regulation – from Anglian Water point of view not the Environment Agency • Width of the aquifer – a bit of confusion • How is robust and reliable different?
	Completion time	30 mins – (not completed fully as was not in their scope)
	Other	
Clarity – the requirements of each page should be clearly understood	Clarification on requirements	• Purge water – unsure about what it is/when it is a concern • Initial flow modelling – confusion about re-asking if chemical/physical storage is used
	Queries/ help required to understand logic	• Clogging – actual quantity of DOC not provided • Confidence indicators – do they refer to confidence in the whole page or individual questions? • Potential pre-treatment required after new injectant quality input – unclear of why its asked again and again
	Re-reading the question	• Regulatory section
	Difference between users interpretation and intended interpretation	• Acceptability of water – answered from only an operational point of view?

	Other	• What is the box after “is transmissivity high enough” for? • Can’t tell from home page what had been completed • “Is it finished? What now?” Unclear when finished and what next steps are • Initial costs – physical chosen but reminder shown as “level of mixing/integrity of the bubble” • Storage capacity – what is “enough” – need to ask before this what storage capacity is needed
Connectivity between relevant sections of the tool – the user should understand why different sections are connected to each other and how one will influence the other	Questions on relevance of “reminders”	No
	Are they navigating back to the previous section to make sense of the “reminders”?	No
	Questions on why the sections are connected	None
	Disagreement on influence of different sections on each other	
	Other	

Appendix I Summary of responses from debriefing and observation during deployment of the Strategic Planning Tool

Summary of responses from user's debriefing on the tool as an artefact and the tool as a function, and the observations made during deployment of the tool are shown below. A brief commentary on the validity of the comments is also provided. It should be noted that some of the enquiries (e.g. "is storage capacity of the aquifer sufficient?", "changes to home page") identified in the debriefing were included in the observational template as well (see Appendix H), however to avoid repetition, these were only recorded once in the tables below.

Debriefing – Tool as an artefact		
Performance attribute	**Summary of response**	**Notes**
Connectivity between relevant sections of the tool	User had a better understanding of the interconnections between different aspects	Tool performed well in unifying different aspects.
	Connections did not always come across	This may be because modelling was not carried out during the assessment and majority of connections relate to modelling. Other connections were more subtle.
Ease of use	The tool was relatively easy to follow however the home page could have been clearer on which sections were completed and which remained to be completed. A progress bar would also have been useful.	This can be implemented
	A part of the tool identified as unclear was in Hydraulic Assessment, where a question is asked whether the storage capacity is sufficient, however information on the amount of storage required is not provided.	The amount of storage required is addressed in the Strategic Assessment however the connection was missing – This was an oversight in the tools development which can be easily corrected.

Format of the report	The report produced could be used as a skeleton for a viability study	Not in this particular case as the scope of the tool is wider than the scope of the investigation tasked.
	The report adequately represented information input into the tool however the format of the report could be improved upon. Furthermore it would be useful to have the traffic light buttons (rather than words indicating the level of confidence) next to the answers	This can be implemented
	In the Initial Cost Assessment, the report only shows the content of the comment boxes without the heading of the cost being referred to. It is therefore difficult to differentiate between costs in the report	This is an oversight in the coding of the web-app and is relatively simple to rectify.
	In the ‘Suitability of the aquifer for recharge and recovery’ section, the question “Is the aquifer appropriately confined?” comes up twice however there is only an answer visible for one occurrence.	This is because the report is pulling information from both the physical and chemical storage methods. This can be corrected
Debriefing – Tool as a function		
Provide a unified, holistic methodology to assess viability of ASR in the UK	The tool seems to integrate and consolidate all the elements (pre-treatment, injection, storage, recovery and post-treatment) of ASR. However the users were not experts in all aspects of ASR therefore cannot be confident in their response. Furthermore a holistic investigation was not in the scope of their work	
Provide a methodology that would allow businesses unfamiliar with	The tool enables businesses unfamiliar with such schemes to understand the potential threats involved, and the factors that need to be considered when planning and designing an ASR scheme.	

ASR to assess viability of such schemes	However some questions may be difficult to answer as there is little guidance on what to do if the user does not know how to approach the question. It was recognised however that this is not feasible to do and contractors should be hired to investigate the unknowns.	
Provide a process oriented methodology that promotes the tools use across different sites	The tool is versatile enough to use across different sites	
Provide a cost effective methodology to assess viability of such schemes	The outputs of the tool did not meet the desired outcome (effectiveness) as the user expected a tick box exercise	It should be noted that this expectation was likely due the briefing given to the users by Anglian Water
	No comment was offered on whether the outputs stack up to the resources spent to produce them (efficiency).	This is because it was not their resources spent. Anglian Water's opinion was required to answer this.
	The time invested was seen as appropriate considering the outputs provided (Economy)	It only took 30 minutes to complete.
Provide guidance specific to the UK context by considering the regulations in the UK.	Although regulatory requirements were not in the scope of the contracted work, the user felt most regulatory requirements with regards to ASR in the UK were covered.	
Provide some indication of the complexity and cost of the scheme as well as provide a scope for	The tool does provide an indication of the complexity of the scheme however the user was mostly concerned with specific aspects therefore were not able to answer with confidence.	
	The tool provides the ability to roughly cost the scheme however it was	The main reason for this is that it is not always easy to get costs

investigation during a pilot	suggested that presentation of the section could have been improved. For example having a box to input the cost with a £ sign along with explicit instructions that only numbers should be entered would be beneficial. The ability to sum up all the costs entered would also be useful.	at such an early stage, therefore the user could make notes on factors that would influence costs, and this could be taken further at the next stage on investigations.
	Factors that were identified as missing which may impact the viability of the scheme include the identification of faults and fractures in the geology, potential sources of contamination around the borehole, size of distribution pipes and existing infrastructure e.g. roads.	These could be included in the logic

Observation – Tool as an artefact		
Performance attribute	**Summary of response**	**Notes**
Connectivity between relevant sections of the tool		
Questions on relevance of “reminders”	No	Users seemed to be clear on the purpose of the reminders
Are they navigating back to the previous section to make sense of “reminders”?	No	Users seemed to be able to follow the logic appropriately and did not need to keep navigating between pages to understand/answer the requirements of various pages.
Questions on why the sections are connected	None	Users seemed to understand the connections
Disagreement on influence of different	No	There was no disagreement or confusion on the connections formed between different sections

sections on each other		
Ease of use		
Understanding how to populate the answer	The users seemed to feel the table of water resources comparison in the 'need for Scheme' section of the Strategic Assessment was too long.	This is likely as this part of the viability investigation was not in the scope of the users work therefore seemed of little relevance.
	The users wrongly populated the "Objectives of the scheme" in the 'need for scheme' section.	This is likely due to the rush to get through this section as it was not in their scope.
	There was some uncertainty as to whether the 'regulatory considerations' were to be answered from Anglian Water's point of view or the Environment Agency's	The explanations seem clear in that the whole tool is to be answered from Anglian Water's perspective. Confusion is likely due to the rush to get through this section as it was not in their scope.
	There was some confusion as to what the "width of the aquifer" meant in the Hydraulic Assessment	This was quickly resolved when the question was re-read
	There was some confusion with regards to the difference between "robust" and "reliable" in the 'pre-treatment and post-treatment requirements' section of "Hydrogeochemical Assessment"	This was clarified when the explanations were read more carefully
Completion time	The completion time was 30 minutes.	It was not fully completed due the scope of the work contracted to the user.
Clarity		
Clarification on requirements	There was some uncertainty about what "purge water" is in the 'regulatory requirements' section of the Strategic Assessment, and when it would be a concern.	The term "purge water" is not defined as the knowledge is assumed. It should be defined more clearly in the tool. Instances when it would be a concern are however explained.

	In the 'initial flow modelling' section of the Hydraulic Assessment there was some confusion about re-asking if chemical/physical storage is used.	The logic path could be adjusted to ensure that the user is only asked which type of storage is only asked once in the 'suitability of the Aquifer for recharge and recovery' section.
Queries/ help required to understand logic	Clogging table - actual DOC levels not provided?	As discussed in Chapter 3, there is no defined guideline for this therefore this is unfeasible.
	Confidence indicators – do they refer to confidence in the whole page or individual questions?	The indicators should be for each question, however only one appears per page even in cases where multiple questions are asked on the page. This can be altered.
	Potential pre-treatment required after new injectant quality input – unclear of why its asked again and again	This confusion is likely due to the fact that the user did not perform PHREEQC modelling therefore did not "adjust the pre-treatment further" in the model and re-check for adverse water quality changes.
Re-reading the question	'Regulatory requirements' section	This was mainly because a regulatory evaluation was not in the user's scope of work.
Difference between users interpretation and intended interpretation	When considering the acceptability of the water in 'source water considerations' in the Strategic Assessment, acceptability of the water is considered from purely an operational point of view.	The intention of this consideration is to determine the suitability of the water from a public and regulatory point of view - operational considerations are tackled in the Hydrogeochemical Assessment. Although an example of public acceptance of recycled water is provided, the explanation of the requirements could be clearer.
Other	Occasionally comments were made on the use of some comment boxes and whether they were required	In some cases the reason for the comment box is not obvious however they are present in case the user has any notes to make for their reference

	It was unclear when they had completed running through the tool and what the next steps were	A more clear end can be incorporated
	In the Initial cost Assessment, reminders from chemical storage were shown even though physical storage was shown as the method of storage required.	This is an oversight in the writing of the web-app which can be changed

Appendix J Changes suggested by users during deployment of the Strategic Planning Tool

The table below provides a summary of actionable comments from both the debriefing and observation, as identified from Appendix I. Items in black relate to the tool as an artefact and items in red to the tool as a function. Items highlighted in yellow have been actioned as shown in Appendix K.

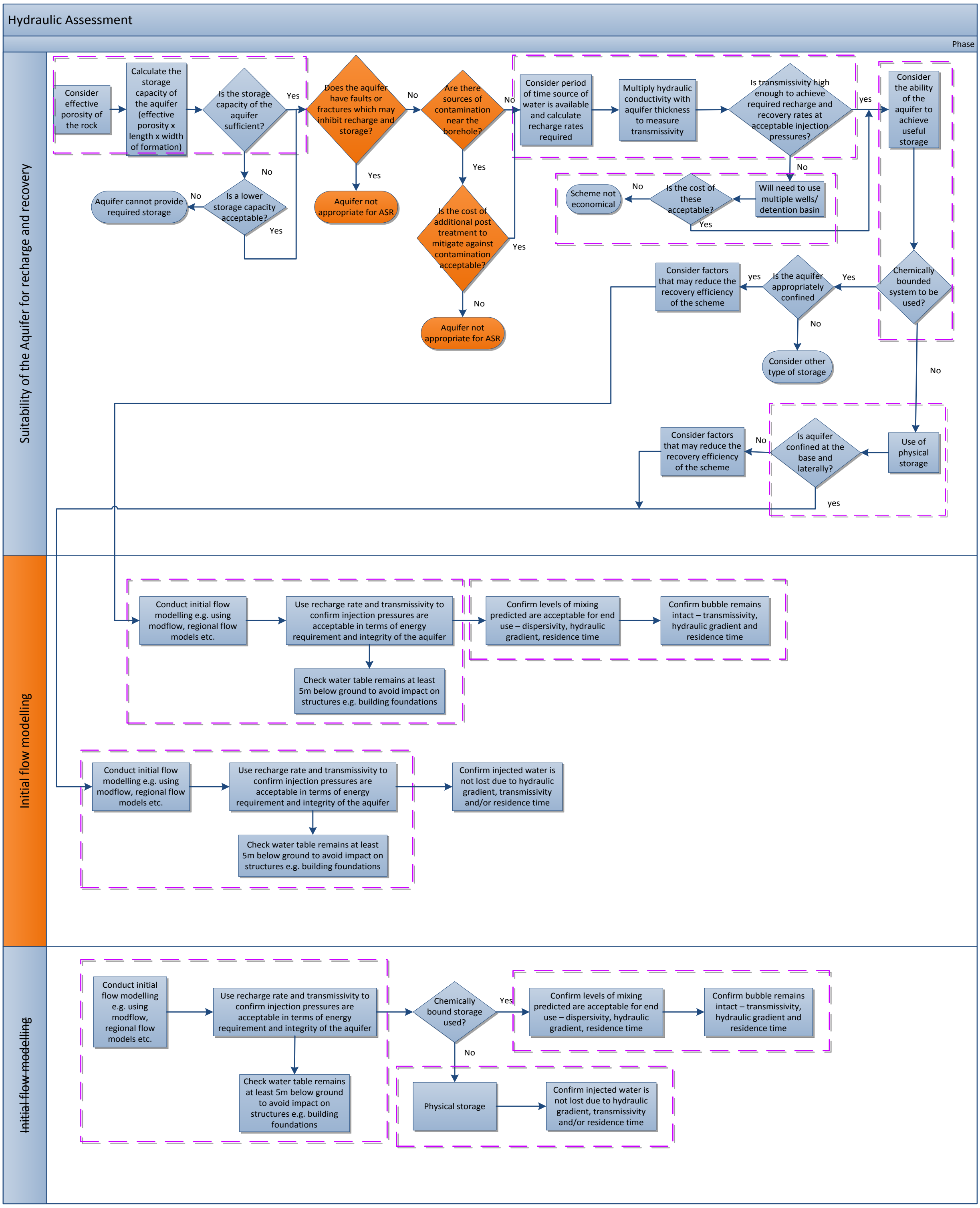
Performance attribute	**Comment**	**Action**
Debriefing		
Ease of use	Home page to indicate which sections were complete and which remained	This could be implemented, however due to the lack of funds and time, the change could not be incorporated
Ease of use	A progress bar would be useful	This could be implemented, however due to the lack of funds and time, the change could not be incorporated
Format of the report	Format of the report could be improved upon.	This could be implemented, however due to the lack of funds and time, the change could not be incorporated
Format of the report	Have the traffic light buttons (rather than words indicating the level of confidence) next to the answers	This could be implemented, however due to the lack of funds and time, the change could not be incorporated
Format of the report	Lack of headings in report for the Initial Costs Assessment- the report only shows the content of the comment boxes without the heading of the cost being referred to. It is therefore difficult to differentiate between costs in the report	Oversight in coding - This could be implemented, however due to the lack of funds and time, the change could not be incorporated
Format of the report	In the ‘suitability of the aquifer for recharge and recovery’ section, the question “Is the aquifer appropriately confined?” comes up twice however there is only an answer visible for one occurrence.	This is because the report is pulling information from both the physical and chemical storage methods. This is an error in the data source. However due to the lack of

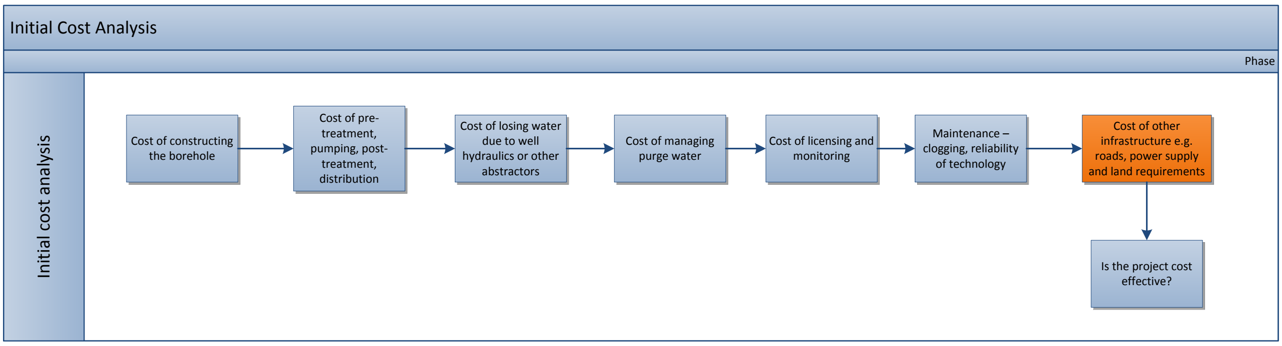
		funds and time, the change could not be incorporated
Factors that would impact viability and identified as missing	Factors that were identified as missing which may impact the viability of the scheme include: - the identification of faults and fractures in the geology, - potential sources of contamination around the borehole, - size of distribution pipes and - existing infrastructure e.g. roads	These could all be included in the logic of the tool, however due to the lack of funds and time, the change could not be incorporated
	Observational	
Clarity - Clarification on requirements	Uncertainty about what purge water is and when it is a concern in 'regulatory considerations' section	Better define what "Purge water" in the explanation
Clarity - Clarification on requirements	Confusion about re-asking if chemical/physical storage is used in the 'initial flow modelling' section	Adjust logic path in initial flow modelling so there is no need to re-ask if physical or chemical storage is required.
Clarity - Queries/ help required to understand logic	Confidence indicators – do they refer to confidence in the whole page or individual questions?	The indicators should be for each question, however only one appears per page even in cases where multiple questions are asked on the page. However due to the lack of funds and time, the change could not be incorporated
Clarity - Difference between users interpretation and intended interpretation	When considering the acceptability of the water in 'source water considerations', acceptability of the water was considered from purely an operational point of view. There was some uncertainty about whose perspective should be used.	The intention of this consideration is to determine the suitability of the water from a public and regulatory point of view – operational considerations are tackled in the Hydrogeochemical Assessment. Although an example of public acceptance of recycled water is provided, the explanation of the requirements could be clearer.

Clarity - Other	In the Initial Costs Assessment, reminders from chemical storage were shown even though physical storage was shown as the method of storage used.	This is an oversight in the writing of the web-app. However due to the lack of funds and time, the change could not be incorporated

Appendix K Changes made to the logic of the tool and explanations in the tool

Some additions were made to the logic to incorporate some of the suggestions made in Appendix J. These have been highlighted in the diagrams below.





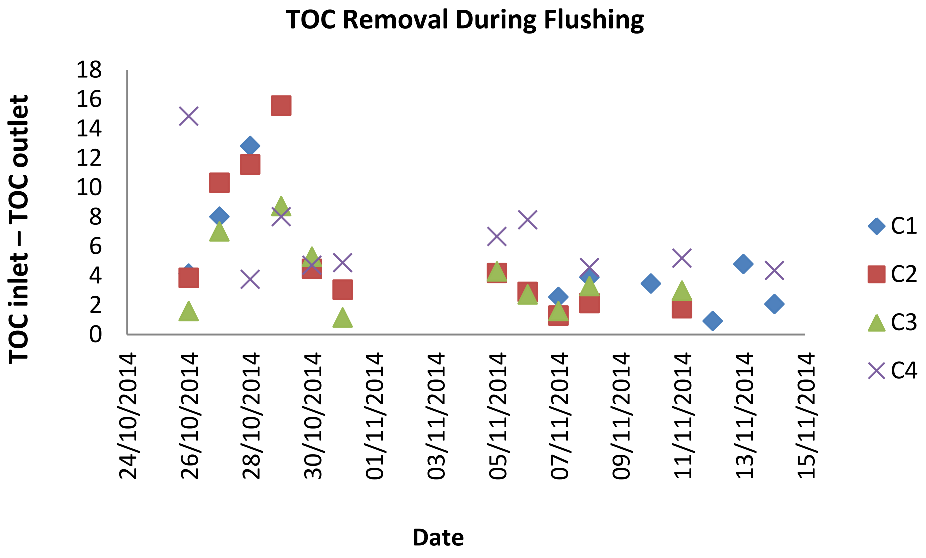
The table below shows the changes made to the explanations as suggested in Appendix J. As in Appendix B, the texts in red are the actual questions/assessments presented to the user. Changes that have been made are highlighted in yellow.

Original explanation	New explanation
Consider the acceptability of water - The acceptability of water should be considered as it may impact permitting of the scheme. This is most important for recycled water as this is an area where public opposition could result in problems.	Consider the acceptability of water - The acceptability of the water should be considered from a regulatory and public point of view as it may impact permitting of the scheme. This is most important for recycled water as this is an area where public opposition could result in problems.
Consider/negotiate the requirements for management of purge water – The potential disposal methods and the regulatory requirements to do so need to be considered. The method of disposal will depend on both the quality of the purge water and the regulatory requirements for disposal. Some examples of discharge methods include to a storm water system, to sewers, to nearby river and to nearby industry/ irrigation. Purge water can contain suspended solids, pathogens, metals, nutrients and organics, therefore the requirements for potential methods of disposal need to be considered	Consider/negotiate the requirements for management of purge water – Purge water is essentially waste water that is produced during drilling, test pumping and well rehabilitation. The potential disposal methods and the regulatory requirements to do so need to be considered. The method of disposal will depend on both the quality of the purge water and the regulatory requirements for disposal. Some examples of discharge methods include to a storm water system, to sewers, to nearby river and to nearby industry/ irrigation. Purge water can contain suspended solids, pathogens, metals, nutrients and organics, therefore the

	requirements for potential methods of disposal need to be considered.
None – new addition to the logic of the tool	Does the aquifer have faults or fractures which may inhibit recharge and storage? – Faults can act as barriers to flow, e.g. when faulting juxtaposes an older, lower transmissivity formation against the newer formation. This limits the transmissivity at depth.
None – new addition to the logic of the tool	Are there sources of contamination near the borehole? Where confined aquifers are being assessed, potential sources of contamination such as onshore oil fields should be considered. Where unconfined aquifers are being evaluated, other sources such as landfills, farmlands etc. which may contaminate the water table should also be considered. Contamination of the stored water would require further treatment when the water is recovered, increasing the cost of the scheme.

Cost of pre-treatment, pumping, post-treatment, distribution - The cost of treatment can be estimated using the pre-treatment and post treatment requirements determined. Distribution cost can be estimated by considering the distances from source of water to aquifer and aquifer to demand area. Cost of pumping during injection and recovery can be estimated by considering the required injection pressures and recharge rated as found in the initial flow modelling	Cost of pre-treatment, pumping, post-treatment, distribution - The cost of treatment can be estimated using the pre-treatment and post treatment requirements determined. Distribution cost can be estimated by considering the distances from source of water to aquifer and aquifer to demand area. Cost of pumping during injection and recovery can be estimated by considering the required injection pressures and recharge rated as found in the initial flow modelling. It should be noted that the costs could be lowered significantly where there is existing infrastructure such as pipelines, nearby treatment works etc. The suitability of existing infrastructure should therefore we evaluated.
None – new addition to the logic of the tool	Cost of other infrastructure e.g. roads, power supply, land requirements - existing infrastructure such as, access roads, power supply reduce the investment requirements and vice versa. The land requirements for the scheme should also be considered.

Appendix L TOC removal during initial flushing of columns with groundwater



Appendix M Full results from experimental work – 15 days batch

		Column 1		Column 2		Column 3		Column 4	
Parameter	**Unit**	Before	After	Before	After	Before	After	Before	After
As	µg/L	2.00	4.60	1.83	3.77	1.87	4.97	1.51	3.10
Ba	µg/L	82.85	166.95	81.11	176.40	80.69	152.25	75.02	126.53
Co	µg/L	0.28	5.75	0.27	8.66	0.22	5.74	0.20	7.08
Fe	mg/L	0	2.13	0	1.49	0	1.17	0	0.65
HAA	µg/L	-	-	-	-	-	-	12.60	1.40
K	µg/L	9,639.00	8,473.50	9,371.25	9,791.25	9,423.75	8,137.50	7,943.25	7,728.00
Mg	µg/L	22,890.00	37,485.00	22,575.00	40,110.00	22,312.50	34,230.00	19,897.50	33,967.50
Mn	µg/L	6.35	4,215.75	3.98	4,987.50	2.13	2,971.50	0.90	1,417.50
Mo	µg/L	2.30	2.81	2.14	2.34	1.56	1.91	1.89	2.82
Na	mg/L	48.68	34.62	48.82	39.85	49.11	32.47	49.46	34.69
NH4	mg/L	0	0	0	0	0	0	0	0
Ni	µg/L	6.45	4.46	15.02	10.90	59.38	11.76	31.45	25.73
NO3	mg/L	10.60	3.85	9.95	4.65	14.05	4.70	7.80	7.75
P	µg/L	238.88	113.93	262.50	117.60	334.43	71.40	761.25	45.10
pH	-	7.55	7.46	7.75	7.42	7.78	7.54	8.14	8.21
SO4	mg/L	139.00	101.00	142.50	108.00	143.00	107.00	121.50	102.50
THM	µg/L	-	-	-	-	-	-	30.30	0.80
TOC	mg/L	1.78	15.50	1.48	17.20	1.09	8.33	1.62	1.72
U	µg/L	0.53	0.40	0.51	0.57	0.34	0.39	1.04	0.70
Zn	µg/L	71.19	29.03	72.19	40.85	77.96	37.70	26.67	25.46

Appendix N Full results from experimental work – 20 days batch

		Column 1		Column 2		Column 3		Column 4	
Parameter	**Unit**	Before	After	Before	After	Before	After	Before	After
As	µg/L	1.93	3.48	1.56	7.50	1.62	5.03	1.49	3.58
Ba	µg/L	83.06	91.09	79.80	177.98	84.79	150.68	79.43	118.13
Co	µg/L	0.23	9.41	0.20	8.24	0.20	11.29	0.19	6.45
Fe	mg/L	0.12	1.02	0	3.02	0	1.58	0	0.84
HAA	µg/L	-	-	-	-	-	-	11.90	6.90
K	µg/L	7,570.50	7,381.50	7,911.75	7,103.25	8,116.50	6,804.00	7,901.25	6,315.75
Mg	µg/L	20,160.00	34,177.50	20,160.00	32,497.50	22,417.50	26,775.00	20,737.50	24,937.50
Mn	µg/L	3.44	482.48	0.81	1,808.63	0.81	1,869.00	1.03	950.25
Mo	µg/L	2.40	2.77	1.95	2.20	2.25	2.37	2.08	3.02
Na	mg/L	49.56	22.28	48.19	29.09	48.86	37.77	49.88	32.70
NH4	mg/L	0	1.83	0	0	0	0	0	0
Ni	µg/L	4.45	24.47	14.02	17.33	3.80	33.65	3.86	42.32
NO3	mg/L	7.85	1.70	8.10	5.20	8.10	4.30	8.20	4.15
P	µg/L	412.65	174.83	307.65	49.72	391.65	78.80	365.93	70.51
pH	-	8.33	8.32	8.22	7.25	7.92	7.68	7.70	7.97
SO4	mg/L	113.50	86.50	123.50	87.25	111.00	101.00	117.00	100.50
THM	µg/L	-	-	-	-	-	-	32.40	14.00
TOC	mg/L	2.23	14.20	3.58	14.48	1.58	15.45	1.61	4.80
U	µg/L	1.03	1.00	0.99	0.64	1.12	0.75	1.04	0.77
Zn	µg/L	22.58	41.79	51.82	40.16	42.63	22.00	25.36	15.80

Appendix O Full results from experimental work – 30 days batch

		Column 1		Column 2		Column 3		Column 4	
Parameter	**Unit**	Before	After	Before	After	Before	After	Before	After
As	µg/L	1.83	7.21	1.56	9.00	1.50	11.45	1.78	3.11
Ba	µg/L	67.57	302.93	79.80	357.00	74.03	256.73	67.67	69.93
Co	µg/L	0.30	2.93	0.20	4.15	0.20	3.07	0.62	0.53
Fe	mg/L	0	0	0	6.82	0	4.12	0.30	0.80
HAA	µg/L	-	-	-	-	-	-	14.65	8.50
K	µg/L	8,736.00	6,142.50	7,911.75	6,754.13	7,801.50	6,562.50	9,030.00	7,827.75
Mg	µg/L	18,007.50	30,555.00	20,160.00	37,721.25	19,530.00	35,306.25	18,532.50	29,190.00
Mn	µg/L	0.98	326.03	0.81	1,708.88	0.92	1,420.13	6.10	13.97
Mo	µg/L	2.46	2.88	1.95	2.20	1.86	2.29	10.25	2.88
Na	mg/L	39.85	22.91	48.19	36.05	48.41	40.18	41.75	16.56
NH4	mg/L	0	0	0	0	0	0.42	0	0
Ni	µg/L	9.76	49.14	14.02	0.72	136.50	6.65	44.10	12.97
NO3	mg/L	9.20	1.55	8.10	6.60	8.15	6.95	8.10	2.50
P	µg/L	330.75	29.93	307.65	47.25	302.40	49.77	593.78	124.43
pH	-	7.82	7.86	8.22	7.18	8.12	7.37	7.67	7.95
SO4	mg/L	126.00	-	123.50	91.50	119.00	92.50	129.00	-
THM	µg/L	-	-	-	-	-	-	71.00	12.80
TOC	mg/L	4.27	6.63	3.58	13.10	1.94	3.91	2.69	0.97
U	µg/L	1.00	1.04	0.99	0.36	1.04	0.44	0.90	1.09
Zn	µg/L	34.28	87.36	51.82	54.23	54.23	25.25	34.70	36.23

Appendix P Full results from experimental work – 60 days batch

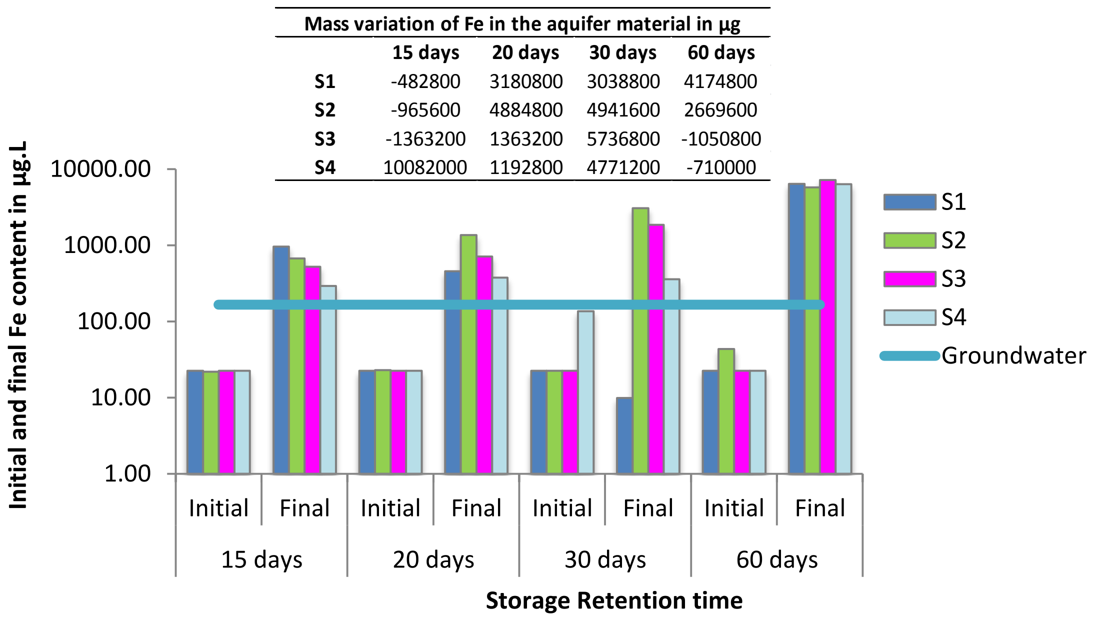
		Column 1		Column 2		Column 3		Column 4	
Parameter	**Unit**	Before	After	Before	After	Before	After	Before	After
As	µg/L	1.44	13.65	1.46	12.76	1.49	16.70	1.44	15.86
Ba	µg/L	77.86	685.13	83.79	626.85	88.41	388.50	85.16	344.40
Co	µg/L	0.20	6.21	0.21	2.97	0.19	13.91	0.16	9.40
Fe	mg/L	0	14.27	0.10	12.88	0	15.99	0	14.11
HAA	µg/L	-	-	-	-	-	-	17.20	-
K	µg/L	7,245.00	6,646.50	7,082.25	6,678.00	6,982.50	7,491.75	6,830.25	8,552.25
Mg	µg/L	19,005.00	44,152.50	18,480.00	47,040.00	18,375.00	40,950.00	17,692.50	40,845.00
Mn	µg/L	2.13	2,278.50	0.47	1,811.25	0.68	6,132.00	0.55	6,084.75
Mo	µg/L	2.19	1.90	2.25	2.10	2.22	3.50	2.15	2.91
Na	mg/L	44.98	37.50	44.45	37.31	44.50	30.36	44.48	34.40
NH4	mg/L	0	0.35	0	0.28	0	0.35	0	4.64
Ni	µg/L	10.16	-	20.79	-	48.62	15.01	2.71	-
NO3	mg/L	9.15	1.25	9.55	1.35	8.90	1.00	9.90	1.00
P	µg/L	108.15	74.24	101.38	56.28	97.55	371.70	303.45	433.65
pH	-	7.94	7.01	7.79	7.07	7.75	6.90	7.69	7.41
SO4	mg/L	122.00	53.50	133.50	62.50	125.00	66.00	126.00	61.00
THM	µg/L	-	-	-	-	-	-	32.80	-
TOC	mg/L	2.33	66.00	1.74	49.40	2.26	100.00	1.40	136.00
U	µg/L	0.89	0.15	0.90	0.26	0.86	0.20	0.81	0.16
Zn	µg/L	202.65	39.22	54.23	25.15	81.59	33.55	33.86	26.15

Appendix Q Difference in concentration of the elements over the different storage periods

		Days	15	15	15	15	20	20	20	20	30	30	30	30	60	60	60	60
Element	**Unit**	**Sample**	s1	s2	s3	s4	s1	s2	s3	s4	s1	s2	s3	s4	s1	s2	s3	s4
As	µg/L		2.6	1.9	3.1	1.6	1.5	5.9	3.4	2.1	5.4	7.4	9.9	1.3	12.2	11.3	15.2	14.4
Ba	µg/L		84.1	95.3	71.6	51.5	8.0	98.2	65.9	38.7	235.4	277.2	182.7	2.3	607.3	543.1	300.1	259.2
Co	µg/L		5.5	8.4	5.5	6.9	9.2	8.0	11.1	6.3	2.6	3.9	2.9	-0.1	6.0	2.8	13.7	9.2
Fe	mg/L		2.1	1.4	1.1	0.6	0.9	3.0	1.5	0.8	-	6.8	4.1	0.5	14.2	12.8	15.9	14.0
HAA	µg/L		-	-	-	-11.2	-	-	-	-5.0	-	-	-	-6.2	-	-	-	-17.2
K	µg/L		-1,165.5	420.0	-1,286.3	-215.3	-189.0	-808.5	-1,312.5	-1,585.5	-2,593.5	-1,157.6	-1,239.0	-1,202.3	-598.5	-404.3	509.3	1,722.0
Mg	µg/L		14,595.0	17,535.0	11,917.5	14,070.0	14,017.5	12,337.5	4,357.5	4,200.0	12,547.5	17,561.3	15,776.3	10,657.5	25,147.5	28,560.0	22,575.0	23,152.5
Mn	µg/L		4,209.4	4,983.5	2,969.4	1,416.6	479.0	1,807.8	1,868.2	949.2	325.0	1,708.1	1,419.2	7.9	2,276.4	1,810.8	6,131.3	6,084.2
Mo	µg/L		0.5	0.2	0.4	0.9	0.4	0.2	0.1	0.9	0.4	0.3	0.4	-7.4	-0.3	-0.2	1.3	0.8
Na	mg/L		-14.1	-9.0	-16.6	-14.8	-27.3	-19.1	-11.1	-17.2	-16.9	-12.1	-8.2	-25.2	-7.5	-7.1	-14.1	-10.1
NH4	mg/L		-	-	-	-	1.6	-	-	-	-	-	0.2	-	0.1	0.1	0.2	4.4
Ni	µg/L		-2.0	-4.1	-47.6	-5.7	20.0	3.3	29.9	38.5	39.4	-13.3	-129.8	-31.1	-10.2	-20.8	-33.6	-2.7
NO3	mg/L		-6.8	-5.3	-9.4	0.0	-6.2	-2.9	-3.8	-4.1	-7.7	-1.5	-1.2	-5.6	-7.9	-8.2	-7.9	-8.9
P	µg/L		-125.0	-144.9	-263.0	-716.2	-237.8	-257.9	-312.8	-295.4	-300.8	-260.4	-252.6	-469.4	-33.9	-45.1	274.2	130.2
pH	-		-0.1	-0.3	-0.2	0.1	0.0	-1.0	-0.2	0.3	0.0	-1.0	-0.8	0.3	-0.9	-0.7	-0.9	-0.3
SO4	mg/L		-38.0	-34.5	-36.0	-19.0	-27.0	-36.3	-10.0	-16.5	-	-32.0	-26.5	-	-68.5	-71.0	-59.0	-65.0
THM	µg/L		-	-	-	-29.5	-	-	-	-18.4	-	-	-	-58.2	-	-	-	-32.8
TOC	mg/L		13.7	15.7	7.2	0.1	12.0	10.9	13.9	3.2	2.4	9.5	2.0	-1.7	63.7	47.7	97.7	134.6
U	µg/L		-0.1	0.1	0.0	-0.3	0.0	-0.3	-0.4	-0.3	0.0	-0.6	-0.6	0.2	-0.7	-0.6	-0.7	-0.7
Zn	µg/L		-42.2	-31.3	-40.3	-1.2	19.2	-11.7	-20.6	-9.6	53.1	2.4	-29.0	1.5	-163.4	-29.1	-48.0	-7.7

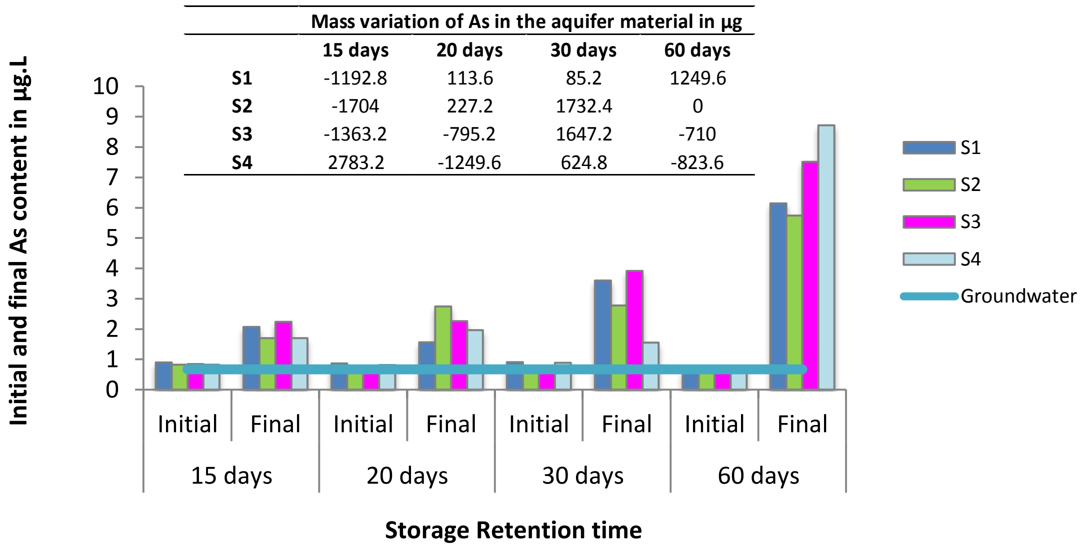
Appendix R Mass balance analysis

Evolution of the Iron (Fe) content in four water sources after storage in ASR simulating columns

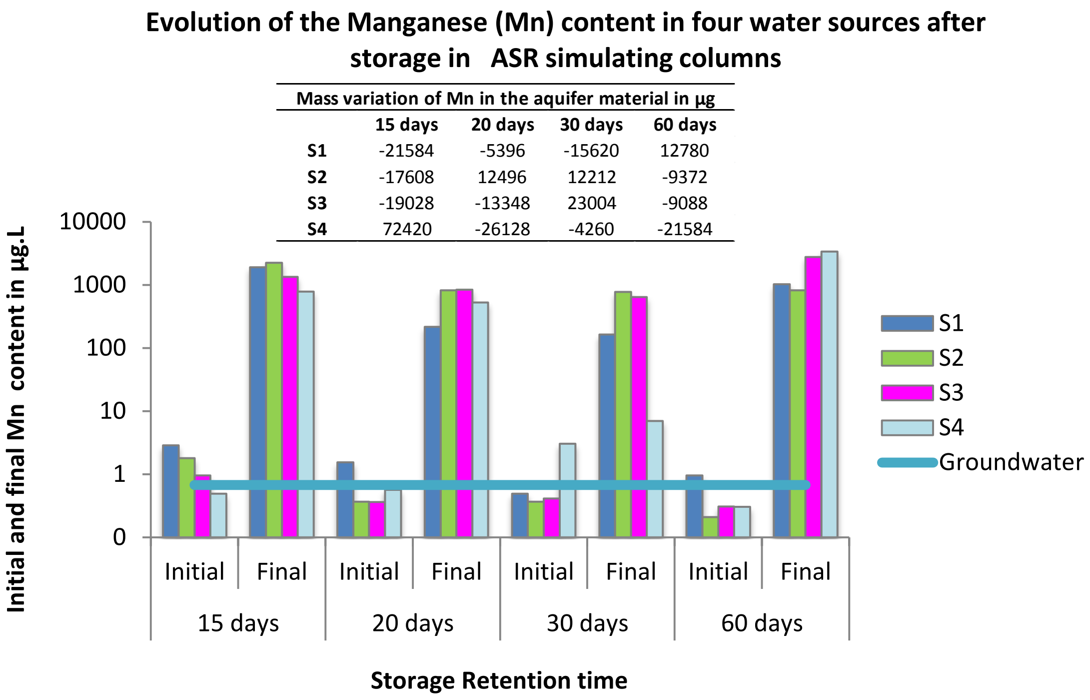


Mass variation of Fe in the aquifer material in µg				
	15 days	20 days	30 days	60 days
S1	-482800	3180800	3038800	4174800
S2	-965600	4884800	4941600	2669600
S3	-1363200	1363200	5736800	-1050800
S4	10082000	1192800	4771200	-710000

Evolution of the Arsenic (As) content in four water sources after storage in ASR simulating columns



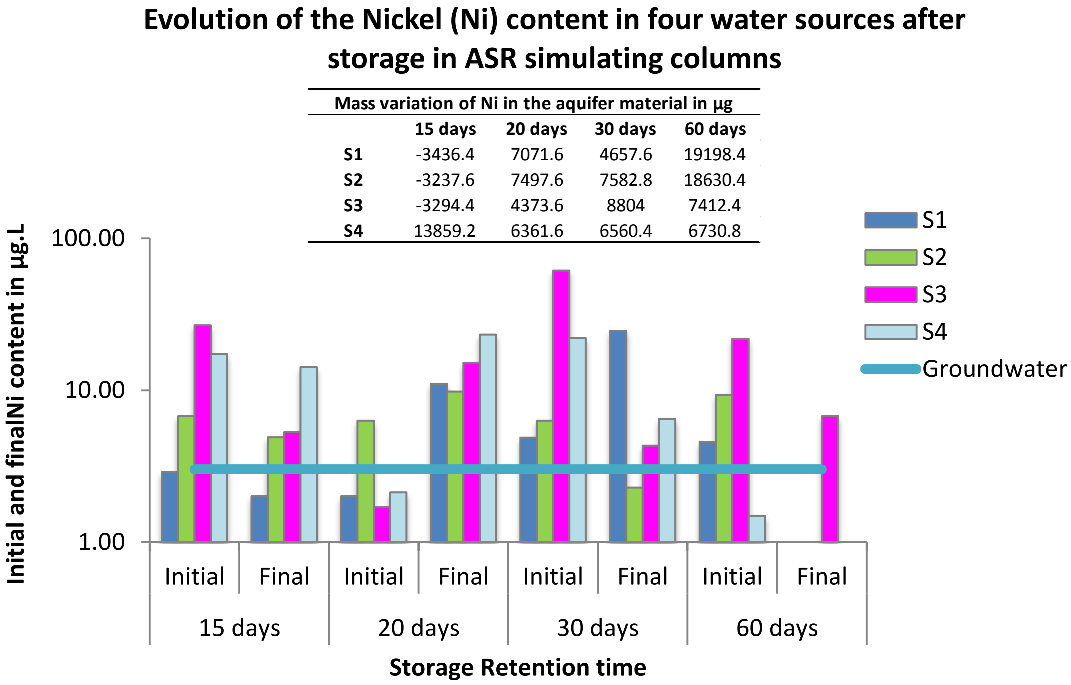
	Mass variation of As in the aquifer material in µg			
	15 days	20 days	30 days	60 days
S1	-1192.8	113.6	85.2	1249.6
S2	-1704	227.2	1732.4	0
S3	-1363.2	-795.2	1647.2	-710
S4	2783.2	-1249.6	624.8	-823.6



Evolution of the Manganese (Mn) content in four water sources after storage in ASR simulating columns

Mass variation of Mn in the aquifer material in µg

	15 days	20 days	30 days	60 days
S1	-21584	-5396	-15620	12780
S2	-17608	12496	12212	-9372
S3	-19028	-13348	23004	-9088
S4	72420	-26128	-4260	-21584



Evolution of the Nickel (Ni) content in four water sources after storage in ASR simulating columns

Mass variation of Ni in the aquifer material in µg

	15 days	20 days	30 days	60 days
S1	-3436.4	7071.6	4657.6	19198.4
S2	-3237.6	7497.6	7582.8	18630.4
S3	-3294.4	4373.6	8804	7412.4
S4	13859.2	6361.6	6560.4	6730.8