Isotopic Tracers of Surface Derived Components in Arsenic Rich Shallow Aquifers of South and South East Asia

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

2010

Michael Lawson

School of Earth, Atmospheric and Environmental Sciences
# Table of Contents

Table of Contents .......................................................................................................................... 1

List of Tables .................................................................................................................................. 5

List of Figures ................................................................................................................................. 7

Abstract ......................................................................................................................................... 8

Declaration ...................................................................................................................................... 9

Copyright Statement ..................................................................................................................... 10

Acknowledgements .......................................................................................................................... 11

The Author ..................................................................................................................................... 12

CHAPTER 1: INTRODUCTION ......................................................................................................... 13

1.1. The arsenic induced human health catastrophe ...................................................................... 14

1.2. Aims and objectives .................................................................................................................. 15

1.3. Approach and thesis structure .................................................................................................. 16

1.4. References ............................................................................................................................... 18

CHAPTER 2: A REVIEW OF THE SOURCE, OCCURRENCE AND BIOGEOCHEMICAL PROCESSES ASSOCIATED IN THE GENERATION OF ARSENIC RICH GROUNDWATER IN SOUTH AND SOUTH EAST ASIA: IMPLICATIONS FOR SECULAR CHANGES IN THE ARSENIC HAZARD ........................................................................................................... 21

2.1. Introduction ............................................................................................................................. 22

2.1.1 The extent of arsenic contamination in South and South East Asia ................................... 23

2.1.2 Geological setting of affected countries ............................................................................... 24

2.1.3 Arsenic speciation .................................................................................................................. 25

2.1.4 Arsenic solubility ................................................................................................................... 27

2.1.5 Source and occurrence of arsenic in Asian groundwaters ...................................................... 28

2.2. Arsenic Release mechanisms .................................................................................................. 30

2.2.1 Competitive exchange reactions .......................................................................................... 31

2.2.2 Oxidation of arsenic rich pyrite ........................................................................................... 32

2.2.3 Reductive dissolution of iron oxyhydroxides ....................................................................... 33

2.3. Role of micro-organisms in the As release process .................................................................. 36

2.4. Role of Organic Matter in arsenic release ............................................................................... 38

2.4.1 Subsurface sources of Organic Matter .................................................................................. 38

2.4.2 Surface sources of Organic Matter ....................................................................................... 41

2.5. Potential role of anthropogenic interference on arsenic release ............................................. 43

2.6. Variability in arsenic concentrations ....................................................................................... 47

2.6.1 Spatial variability in dissolved arsenic concentrations .......................................................... 47

2.6.2 Temporal variability in dissolved arsenic concentrations ..................................................... 49
2.7. Conclusions ......................................................................................................................... 50
2.8. References ............................................................................................................................. 52

3. CHAPTER 3: USE OF ISOTOPIC TRACERS IN ASSESSING ARSENIC MOBILIZATION ........... 65
3.1. Introduction ............................................................................................................................ 66
  3.1.1 Oxygen and Hydrogen isotopes in groundwater studies .................................................. 66
  3.1.2 Isotopic fractionation and partitioning of isotopes through the hydrological cycle ......................... 67
3.2. Carbon isotopes in groundwater studies ................................................................................ 73
  3.2.1 Carbon isotopes ................................................................................................................ 74
  3.2.2 Sources of carbon in groundwater ..................................................................................... 75
  3.2.3 Dating of older groundwaters using 14C ............................................................................ 79
3.3. Tritium in groundwater studies ............................................................................................ 80
3.4. References ............................................................................................................................. 84

CHAPTER 4: ANALYTICAL PROCEDURES AND EXPERIMENTAL TECHNIQUES ......................... 89
4.1. Field collection techniques .................................................................................................... 90
4.2. Analytical procedures .......................................................................................................... 91
  4.2.1 Aqueous chemistry analysis ............................................................................................. 91
  4.2.2 Stable isotope analysis ...................................................................................................... 91
  4.2.3 Carbon – 14 analysis ......................................................................................................... 92
  4.2.4 Tritium analysis ............................................................................................................... 93
4.3. Calculation of tritium concentrations .................................................................................... 97
4.4. Estimation of error associated with tritium measurements ................................................... 99
4.5. Data quality concerns .......................................................................................................... 101
4.6. References ............................................................................................................................. 105

5. CHAPTER 5: DATING OF OLDER GROUNDWATER USING 14C: A REVIEW OF EXISTING MODELS, LIMITATIONS AND A NEW APPROACH FOR MODELLING MEAN GROUNDWATER RESIDENCE TIMES .................................................................................................................. 108
5.1. Introduction ............................................................................................................................ 109
5.2. Correction of groundwater DIC 14C age for carbonate dissolution ........................................ 110
  5.2.1 Statistical Correction Models ........................................................................................... 111
  5.2.2 Geochemical models ....................................................................................................... 111
5.3. Application of models to field data ...................................................................................... 116
  5.3.1 Field sampling techniques and analytical procedures ....................................................... 116
  5.3.2 Groundwater chemistry ................................................................................................... 117
  5.3.3 Isotopic composition and model comparisons .................................................................... 119
5.4. Model sensitivities ............................................................................................................... 126
6. CHAPTER 6: PROVENANCING ORGANIC MATTER AND TRACING GROUND-SURFACE WATER INTERACTIONS IN SHALLOW CAMBODIAN GROUNDWATERS: IMPLICATIONS FOR ARSENIC RELEASE

6.1. Introduction .......................................................................................................................... 138
6.2. Field Area ............................................................................................................................ 140
6.3. Methods ............................................................................................................................... 142
  6.3.1 Tubewell installation ....................................................................................................... 142
  6.3.2 Groundwater and surface water sampling .................................................................... 143
  6.3.3 Analytical procedures .................................................................................................... 144
6.4. Results: ............................................................................................................................... 145
  6.4.1 Aqueous chemistry and aquifer mineral saturation status ............................................ 145
  6.4.2 Stable isotopes ............................................................................................................... 150
  6.4.3 Tritium ............................................................................................................................ 155
  6.4.4 Carbon – 13 isotope systematics .................................................................................... 159
  6.4.5 C-14 of dissolved inorganic carbon .............................................................................. 163
  6.4.6 C-14 ages of dissolved organic carbon ......................................................................... 166
6.5. Discussion ........................................................................................................................... 174
  6.5.1 Hydrological environment ............................................................................................ 175
  6.5.2 Sources of organic matter present in groundwater ....................................................... 177
  6.5.3 Vulnerability of groundwater to abstraction practices .................................................. 178
6.6. Conclusions ......................................................................................................................... 180
6.7. References .......................................................................................................................... 181
7. CHAPTER 7: PROVENANCING ORGANIC CARBON IN HIGH ARSENIC AND RELATED SHALLOW AND DEEP GROUNDWATERS OF WEST BENGAL .................................................................................. 187
7.1. Introduction ......................................................................................................................... 188
7.2. Field Area ............................................................................................................................ 190
7.3. Methods ............................................................................................................................... 192
  7.3.1 Groundwater and surface water sampling .................................................................... 192
  7.3.2 Analytical procedures .................................................................................................... 192
7.4. Results ................................................................................................................................. 194
7.4.1 Aqueous chemistry ......................................................... 194
7.4.2 Stable isotopes................................................................. 198
7.4.3 Tritium and groundwater dating................................. 200
7.4.4 C-14 ages of dissolved inorganic carbon.................. 206
7.4.5 C-14 ages of dissolved organic carbon...................... 209
7.5. Discussion........................................................................ 213
7.5.1 Ground-surface water interaction and contributions of DOC .... 213
7.5.2 Vulnerability of deep groundwater............................. 214
7.6. Conclusions ..................................................................... 215
7.7. References ...................................................................... 216
8. CHAPTER 8: THE GEOCHEMICAL AND ISOTOPIQUE COMPOSITION OF GROUNDWATERS IN WEST BENGAL: TRACING GROUND-SURFACE WATER INTERACTION AND ITS ROLE IN ARSENIC RELEASE...................................................................................... 222
9. CHAPTER 9: CONCLUSIONS .................................................. 223
9.1. The generation of high arsenic groundwaters in South and South East Asia .... 224
9.2. Characterisation of a Cambodian aquifer – An insight into pre-development conditions.................................................................................................................. 225
9.3. Characterisation of a Bengali aquifer: An insight into Cambodia’s future?........... 226
9.4. The effect of groundwater abstraction on the flow regimes and groundwater chemistry ............................................................................................................. 228
9.5. Implications for a sustainable source of As free groundwater in South and South East Asia .............................................................. 229
9.6. References ...................................................................... 230
10. APPENDIX 1 .................................................................. 234
11. APPENDIX 2 .................................................................. 239

Final Word Count: 87,088 words
List of Tables

Chapter 4
Table 4.1. C-14 correction factors 100
Table 4.2. Comparison of $\delta^{13}C$ data from ICSF and RCF-E laboratories 103
Table 4.3. Comparison of $\delta^{13}C$ of DIC and DOC in Bengali groundwater 105

Chapter 5
Table 5.1. Hydrochemistry of Cambodian groundwater 119
Table 5.2. Summary of modelled dilution factors for use in matrix exchange model 122
Table 5.3. Comparison of uncorrected and modelled groundwater residence times 126
Table 5.4. Summary of sensitivity analysis of matrix exchange model 133

Chapter 6
Table 6.1. Summary of major analytes in Cambodian groundwater 149
Table 6.2. Saturation indices of key mineral phases 151
Table 6.3. $^3H$ content of ground and surface water at Cambodian study site 158
Table 6.4. Comparison of uncorrected and modelled groundwater residence times in Cambodian groundwater 167
Table 6.5. C-14 age of DOC in Cambodian groundwater 168
Table 6.6. Modelled contributions of sediment and surface derived OM to DOC in Cambodian groundwater 172

Chapter 7
Table 7.1. Summary of major analytes in Bengali groundwater 195
Table 7.2. $^3H$ content of groundwater and river water at Bengal study site 206
Table 7.3. Comparison of uncorrected and modelled groundwater residence times in Bengali groundwater 208
Table 7.4. C-14 age of DOC in Bengali groundwater 211
Table 7.5. Modelled contributions of sediment and surface derived OM to DOC in Bengali groundwater 214
## List of Figures

### Chapter 2

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Map of As effected countries in South and South East Asia</td>
<td>24</td>
</tr>
<tr>
<td>2.2</td>
<td>Eh-pH plot of As speciation</td>
<td>26</td>
</tr>
<tr>
<td>2.3</td>
<td>Chemical composition of As-bearing groundwaters</td>
<td>29</td>
</tr>
<tr>
<td>2.4</td>
<td>Arsenic distribution with depth in Bangladesh groundwaters</td>
<td>30</td>
</tr>
<tr>
<td>2.5</td>
<td>Cartoon of As release process</td>
<td>35</td>
</tr>
<tr>
<td>2.6</td>
<td>Schematic of stratified groundwater column model</td>
<td>42</td>
</tr>
</tbody>
</table>

### Chapter 3

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Isotopic evolution of meteoric waters</td>
<td>70</td>
</tr>
<tr>
<td>3.2</td>
<td>Deuterium excess of precipitation</td>
<td>71</td>
</tr>
<tr>
<td>3.3</td>
<td>Variation in $\delta^{13}$C of carbon reservoirs</td>
<td>77</td>
</tr>
<tr>
<td>3.4</td>
<td>Time resolution of $^3$H/$^4$He method</td>
<td>84</td>
</tr>
</tbody>
</table>

### Chapter 4

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Schematic of Manchester degassing line</td>
<td>94</td>
</tr>
<tr>
<td>4.2</td>
<td>Schematic of noble gas processing line</td>
<td>95</td>
</tr>
<tr>
<td>4.3</td>
<td>Stability of $^3$He and $^4$He measurements</td>
<td>97</td>
</tr>
<tr>
<td>4.4</td>
<td>Enrichment of $\delta^{13}$C from residual DIC</td>
<td>104</td>
</tr>
</tbody>
</table>

### Chapter 5

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Variability of $\varepsilon^{13}$DIC with recharge conditions</td>
<td>127</td>
</tr>
<tr>
<td>5.2</td>
<td>Variability of $\delta^{13}$C with recharge conditions</td>
<td>127</td>
</tr>
<tr>
<td>5.3</td>
<td>Temporal record of $^{14}$C in atmospheric CO$_2$</td>
<td>130</td>
</tr>
<tr>
<td>5.4</td>
<td>Percent error of modelled groundwater residence times</td>
<td>132</td>
</tr>
</tbody>
</table>

### Chapter 6

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Aerial image of Cambodian study site</td>
<td>142</td>
</tr>
<tr>
<td>6.2</td>
<td>Spatial distribution of As concentrations at Cambodian study site</td>
<td>146</td>
</tr>
<tr>
<td>6.3</td>
<td>Distribution of major cations and anions in Cambodian groundwater</td>
<td>149</td>
</tr>
<tr>
<td>6.4</td>
<td>Stable water isotope composition of water bodies at study site</td>
<td>152</td>
</tr>
<tr>
<td>6.5</td>
<td>Temporal variability of $\delta^{18}$O in surface waters</td>
<td>153</td>
</tr>
<tr>
<td>6.6</td>
<td>Temporal variability of $\delta^{18}$O in groundwater</td>
<td>155</td>
</tr>
<tr>
<td>6.7</td>
<td>Tritium content of Bangkok precipitation</td>
<td>156</td>
</tr>
</tbody>
</table>
Figure 6.8. Depth distribution of As concentration in Cambodian groundwater

Figure 6.9. Variation in $\delta^{13}C$ of DOC and DIC in Cambodian groundwater

Figure 6.10. Evolution of $\delta^{13}C$ of total carbon

Figure 6.11. Variation in $^{14}C$ of DOC and groundwater in Cambodian groundwater

Figure 6.12. Modelled $^{14}C$ composition of DOC in Cambodian groundwater

Figure 6.13. Relationship between As and $^{14}C$ age of DOC in Cambodian groundwater

Figure 6.14. Relationship between $^{14}C$ age and concentration of DOC

Figure 6.15. Spatial distribution of tubewell locations with associated spatial and depth distributions of arsenic, sulphate, and tritium profiles

Chapter 7

Figure 7.1. Aerial image of Bengal study site

Figure 7.2. Distribution of As concentration with depth in Bengali groundwater

Figure 7.3. Spatial distribution of As concentration in Bengali groundwater

Figure 7.4. Distribution of major cations and anions in Bengali groundwater

Figure 7.5. Stable isotopic composition of Bengali meteoric and groundwater

Figure 7.6. Tritium content of Dhaka precipitation

Figure 7.7. Tritium groundwater depth distribution

Figure 7.8. Relationship between As and tritium in Bengali groundwater

Figure 7.9. $^{14}C$ age of $^3$H-dead Bengali groundwater

Figure 7.10. Variability in $^{14}C$ age of DOC with depth in Bengali groundwater

Figure 7.11. Relationship between groundwater residence time and DOC age

Chapter 8

Figure 8.1. Piper diagram showing the ionic composition of groundwaters

Figure 8.2. Stable isotopic composition of shallow and deep groundwater samples

Chapter 9

Figure 9.1. Comparison of depth distribution in $^{14}C$ age of DOC in Bengali and Cambodian groundwater
Abstract
The contamination of groundwater by naturally occurring arsenic (As) in South and South East Asia has resulted in the exposure of an estimated 100 million people to hazardously high concentrations of this known carcinogen. Whilst the biogeochemical processes and mechanisms responsible for releasing As to groundwater are now understood, the fundamental controls on these processes have yet to be resolved. In particular, the role of different sources of organic matter (OM) in controlling the rate and extent of As release and how the contributions of these different sources may be influenced by groundwater abstraction practices, remains poorly constrained. Indeed, it is the absence of such key information which currently limits our capability to accurately predict both where and when As will be released in to the groundwaters of this region. Elucidation of the controls of these processes is therefore of vital importance for aiding policy makers and those responsible for mitigating the effects of the current catastrophe in providing a sustainable source of As free drinking water to millions of people in the countries impacted.

We conducted investigations at two known As hotspots in West Bengal and Cambodia to assess the impact of groundwater abstraction practices on the composition of dissolved organic carbon (DOC) and As release. The radiocarbon age of DOC at both sites requires a contribution of young surface or near surface derived OM as well as contributions from older, sedimentary sourced OM. Mixing profiles at the Cambodian study site suggest this subsurface OM end member to have an age of between 1000 and 6000 years. A clear association is observed between high As concentrations in shallow groundwaters containing young DOC, with lower concentrations of As being associated with older DOC in deeper groundwater. This provides the first direct confirmation that younger, more labile sources of OM are able to support more extensive As release in these aquifers. Perhaps more importantly, it is shown that modern surface derived OM can be drawn into As contaminated groundwaters. Comparison of the residence times of groundwaters suggests that the extent of ground-surface water interaction is more extensive and extends to greater depths in aquifers that have been subjected to massive groundwater abstraction. Indeed, it is suggested that groundwater abstraction practices may be responsible for driving the downward transport of As contaminated shallow groundwater into deeper groundwater, and may potentially be driving changes in the composition of organic carbon within the groundwater. This could give rise to a more reactive, bioavailable organic carbon pool which has the potential to further influence As mobility in these groundwaters. The potential for secular changes in the groundwater As hazard in these regions must therefore consider the impact that changes in the DOC composition may have on the biogeochemical evolution of these aquifers.
Declaration

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification at this or any other university or other institute of learning.
Copyright Statement

The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”) and he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

The ownership of certain Copyright, patents, designs, trade marks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

Further information on the conditions under which disclosure, publication and commercialisation of this thesis, the Copyright and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP Policy (see http://www.campus.manchester.ac.uk/medialibrary/policies/intellectual-property.pdf), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see http://www.manchester.ac.uk/library/aboutus/regulations) and in The University’s policy on presentation of Theses.
Acknowledgements

I would first like to thank my academic supervisors (and friends) Professor Dave Polya and Professor Chris Ballentine for their guidance, support and financial backing (!) throughout the course of my PhD. I have learnt so much from our discussions, field trips and the numerous international conferences which they were happy to send me on, and for this I will forever be in their debt. A big thank you goes to the Natural Environment Research Council (NERC) that funded the project and the analysis of stable isotopes and carbon-14. Thanks to my collaborators Dr Adrian Boyce at SUERC and Dr Charlotte Bryant at the NERC RCL for their advice and analytical support throughout the course of this research. My thanks also go to Cath Davies for her huge support in helping prepare the equipment for each of my sampling programmes and for the welcome distractions from filtering in the chemistry lab. I am also grateful to Dave Blagburn, Bev Clementson, and Dr Zheng Zhou for their help during tritium and noble gas analysis.

I am hugely indebted to the numerous people who have helped during my sampling trips to India and Cambodia. In Cambodia, I would like to thank the late Mickey Sampson for convincing me, if it was needed, that this work really can contribute to making a difference to the lives of people who really need it. Seeing his commitment and passion for this cause gave me the fresh injection of energy and understanding that helped complete this work. Massive thanks to Andrew Schantz and all the people at RDI who made my sampling trip to Cambodia both enjoyable and successful. Thanks also to Laura, Heather and the cast of Greys Anatomy for providing the entertainment during my 3 months out there. In India, I would like to express my huge gratitude to Debapriya Mondal and her family for their logistical support and kind hospitality which made my work there possible.

I would like to thank all of my office colleagues and honorary members of 1.76: Nick, Jon, Claire, Steve, Aimee, Ashley and Vikki for the banter, support and distractions which helped maintain my sanity throughout my PhD. Thanks also to Greg for entertainment during the many hours spent in the lab. My biggest Manchester thanks goes to my cousin Joanne, who provided huge amounts of emotional support throughout the course of this PhD, and was always happy to offer welcome relief (and relaxants) from the stresses of work.

Finally, but most importantly, I would like to express my most sincere of thanks to my parents Mick and Christine, sister Emma and brother Lee, for their love and support (including financial!) throughout my 8 years of higher education – I promise this will be the last of it!
The Author

The author graduated from The University of Manchester in 2005 with a First Class honours BSc. Degree in Environmental Science. Since September 2006, the author has been engaged in the research reported in this thesis.
CHAPTER 1

Introduction
1.1. The arsenic induced human health catastrophe

Prior to the 1960s, the rural populations of South and South East Asia utilised surface waters as a source of water for drinking, cooking and irrigation. However, these water bodies were often contaminated by pathogenic bacteria which resulted in a high prevalence of water borne diseases such as cholera, typhoid and dysentery. In an attempt to provide these local populations with safe, bacteria-free drinking water, the World Health Organisation (WHO) established a programme of installing tubewells to tap the abundant groundwater reserves in the alluvial aquifer systems of the region. Indeed, in West Bengal and Bangladesh alone, 6 to 10 million tubewells were installed. However, following the identification of health conditions linked to chronic arsenic (As) exposure (CHAKRABORTY and SAHA, 1987; MAZUMDER et al., 1988), it was subsequently found that many of these wells tap groundwater where concentrations of naturally occurring arsenic (As) exceed the WHO maximum concentration limit (MCL) and Bangladesh MCL of 10 and 50 µg/l respectively (BGS and DPHE, 2001; SMEDLEY and KINNIBURGH, 2002). More extensive surveys of the region have found the problem not to be unique to the Bengal delta, with the groundwaters of Vietnam (BERG et al., 2001), Cambodia (POLYA et al., 2005; POLYA et al., 2003), and several other countries within the region also affected. In fact, it is now feared that as many as 100 million people within the region may be exposed to hazardously high concentrations of As (RAVENSCROFT et al., 2009), which is likely to result in numerous deleterious health effects and excess deaths from cancers of the skin, lungs, liver and other internal organs in many of those affected (BALGA and KAISER, 1996; MAZUMDER et al., 1998; SMITH et al., 2000; YU et al., 2003).

The As in these groundwaters is thought to be of natural origin and the general consensus is that it is released to solution following the reductive dissolution of As-bearing Fe(III) minerals (MCARTHUR et al., 2001; NICKSON et al., 1998; NICKSON et al., 2000). This process is driven by metal reducing bacteria, with organic matter (OM) critically implicated as an electron donor in the process (ISLAM et al., 2004). The OM is thought to be either derived from (i) peat or other diffuse sources within the sedimentary aquifers (SOM) (MCARTHUR et al., 2004; MEHARG et al., 2006; NICKSON et al., 1998) or (ii) to be modern surface-derived OM largely from ponds, potentially drawn in as a result of massive groundwater abstraction (HARVEY et al., 2002; LAWSON et al., 2008; NEUMANN et al., 2010). The nature and source of this OM, however, is a matter of considerable debate (e.g. VAN GEEN et al., 2003) and has recently been highlighted as one of the last remaining issues which limits our ability to accurately predict the distribution of As in these aquifer systems (FENDORF et al., 2010; POLYA and CHARLET, 2009). Indeed, it has been suggested that the rate of As release in these groundwaters is likely to be governed by the
source of OM present (GAULT et al., 2005; MLADENOV et al., 2010; ROWLAND et al., 2007). Labile sources of OM, which are stable much more highly reactive forms of organic carbon, are suggested to be able to support much more rapid rates of As release. In contrast, more recalcitrant sources of OM, which is a much more stable form of organic carbon that is less likely to be present in the soluble form, will support a much slower rate, but potentially longer period, of As release (FENDORF et al., 2010). Determining the relative contributions of different OM sources under different groundwater abstraction practices is therefore central to predicting future secular changes in the groundwater As hazard – a matter of great concern for policy-makers in the countries impacted.

1.2. Aims and objectives

The aim of this research is to provide an incremental improvement in our understanding of the origin of OM present in the groundwaters of As bearing aquifers in South and South East Asia and to determine how groundwater management practices may influence this distribution. To achieve this aim, investigations were conducted at study sites in West Bengal and Cambodia which previous studies have shown to be areas where extensive As contamination of the groundwater is prevalent (BERG et al., 2007; BUSCHMANN et al., 2007; CHARLET et al., 2003; CHARLET et al., 2007; CHATTERJEE et al., 2003; GAULT et al., 2005; KOCAR et al., 2008; METRAL et al., 2008; NATH et al., 2005; POLIZZOTTO et al., 2008; POLYA et al., 2005; ROWLAND et al., 2008). In West Bengal, massive groundwater abstraction has resulted in a complex subsurface hydrological environment and transient flow paths which have been influenced by anthropogenic activity (HARVEY et al., 2002). However, the absence of such extensive abstraction in the As-rich aquifers of Cambodia provides a largely pristine study environment within which it is possible to determine pre-development conditions that can be used as a baseline for comparison with sites that have been subjected to extensive anthropogenic disturbance (POLIZZOTTO et al., 2008).

The specific objectives are:

1. To elucidate and constrain the source(s) of recharge to the groundwater at each of these sites.
2. To determine the timescales over which hydrological processes operate and estimate mean groundwater residence times.
3. To provenance the source(s) of OM present in the groundwater of each of these aquifer systems and assess the distribution of the OM composition.
4. To understand how this information can be used to examine how high As groundwaters are generated, and how changes in the composition of groundwater chemistry can result in a further evolution of the As hazard

Combined, this information will be used to model and assess the role of the hydrological environment on the occurrence of arsenic in the groundwater of this region. This information will also provide a novel data set from which comparisons can be made to examine the influence of groundwater abstraction practices on current and potentially future As release rates.

1.3. Approach and thesis structure

This thesis has been written in a scientific paper format. Whilst this may lead to some repetition between chapters, this format will allow for a more efficient transfer of PhD thesis chapters for submission for publications. With the exception of chapters three and four, each chapter is either intended to be or is in the process of being submitted for publication, or has already been published (chapter eight).

Chapter two is a literature review written to be submitted to the Journal of Water Quality, Exposure and Health. This review discusses the contributions to the understanding of the source, biogeochemical processes and mechanisms that give rise to high As groundwaters in the reducing aquifers of the region investigated in this research. It discusses the current limitations in our understanding and knowledge and suggests where future directions of study should be targeted to provide an improvement in our ability to better predict the spatial distribution of the current As hazard and the temporal evolution of this hazard.

Chapter three discusses the background and application of each of the isotope systems employed in the research presented in this thesis in studying the role of the hydrological environment on As-bearing aquifer systems in South and South East Asia.

Chapter four presents and discusses the analytical techniques employed during the course of this research. It also describes how tritium concentrations and the errors associated with these concentrations have been derived. It also discusses any issues associated with data quality assurance that is presented in this thesis.
Chapter five discusses existing models that are used to determine mean groundwater residence times following the correction for contributions of $^{14}$C-dead dissolved inorganic carbon from carbonate dissolution. This chapter then presents a new model that applies geochemical and isotopic mass balance equations in conjunction with a calculation of the pH dependent $\delta^{13}$C$_{soil}$ at recharge in studies where direct measurements of this cannot be made. This chapter also discusses the sensitivity of each model discussed and provides a summary of how model errors can be estimated. This chapter is intended to be submitted to Water Resources Research.

Chapter six presents the results of the extensive isotopic studies conducted at the study site in Cambodia. This chapter discusses the role of contributions of modern surface water and associated organic carbon and how this may influence As release. The implications associated with these observations are discussed in the context of anthropogenic disturbance of natural groundwater systems and how this may or may not exacerbate As release in these groundwaters. This chapter is intended to be prepared for submission in Geochimica et Cosmochimica Acta.

Chapter seven presents the results of the isotopic studies conducted at the study site in West Bengal, where extensive groundwater pumping has continued for decades. The data presented here is used to assess the effect of groundwater pumping practices on the hydrological environment and to assess the vulnerability of the deep groundwater to As contamination at this site. This chapter is intended to be submitted to Applied Geochemistry.

Chapter eight presents a paper that has been published in Mineralogical Magazine (LAWSON et al., 2008). This paper utilises stable isotope and geochemical data collected from the study site in West Bengal to suggest a contribution of surface waters to shallow groundwater and a possible link between its presence and the generation of high As groundwaters at this site.

Finally, chapter nine compares and contrasts the observations and interpretations made for the two As bearing groundwater systems investigated in this research. It discusses the potential implications of such observations and the contributions of this comparison to the current knowledge of the kinetics associated with the As release process and the generation of high As groundwaters.
1.4. References


CHAPTER 2

A review of the source, occurrence and biogeochemical processes associated in the generation of arsenic rich groundwater in South and South East Asia: Implications for secular changes in the arsenic hazard
2.1. Introduction

The consumption of groundwater containing elevated levels of naturally occurring arsenic (As) in South and South East Asia has resulted in a humanitarian disaster, with an estimated 100 million people exposed to concentrations of As above the World Health Organisation (WHO) standard of 10 μg/l (RAVENSCRYPT et al., 2009). This is adversely affecting the health of millions of people in this region and is likely to cause numerous cancers of the skin, liver, lungs and other internal organs over the next several decades (BALGA and KAISER, 1996; CHOWDHURY et al., 2000; DAS et al., 1996; MANDAL et al., 1996; MAZUMDER et al., 1998; NRC, 1999; NRC, 2001; POLYA et al., 2010; SAMPSON et al., 2008; SMITH et al., 2000; VAN GEEN et al., 2003a; YU et al., 2003). This has led to the situation being described as “the largest poisoning of a population in history” (SMITH et al., 2000). Mitigation efforts aimed at reducing human exposure to As requires a knowledge of both the locations in which the high groundwater As hazard is currently present and how the As concentrations are likely to change in the future, and importantly at what rate. Understanding the processes which give rise to these high As groundwaters is therefore of paramount importance. In this article, the current knowledge on the generation of As-bearing groundwater in this region is reviewed, describing the occurrences of As, the controls on As mobility in these groundwaters, the biogeochemical processes which drive As mobilisation mechanisms, and the potential impact of anthropogenic interference on current and future As concentrations.

This review focuses strictly on the mechanisms and processes which have resulted in the high As groundwaters of South and South East Asia. A wealth of literature exists detailing the variety of other environments with groundwaters containing high concentrations of As, such as those associated with geothermal activity, sulfide oxidation or desorption at high pHs: these are beyond the scope of this review. An excellent review of all of the environments and processes associated with high As groundwaters has been provided in Ravenscroft et al. (2009), whilst previous reviews of the global distribution and causes of high As groundwater has also been extensively covered in Smedley and Kinniburgh (2002), with additional contributions from Valsami-Jones et al. (2005) and Mukherjee et al (2008), and more recently Fendorf et al (2010). This review, whilst discussing many of the key contributions covered in the aforementioned reviews, is focussed entirely on the As-contaminated groundwaters of South and South East Asia where the consumption of this groundwater is directly affecting the lives of tens of millions of people. In particular, this review focuses on discussing areas of research that are associated with the elucidation of key processes that may govern future changes in the groundwater As hazard because it is this science that may inform and direct
future mitigation efforts in this region. We also discuss the more recent groundbreaking studies published since the comprehensive review of Ravenscroft et al. (2009).

2.1.1 The extent of arsenic contamination in South and South East Asia

Following the initial discovery of elevated As in West Bengal, India in the mid 1980’s (CHAKRABORTY and SAHA, 1987) and in Bangladesh in the mid 1990’s (NICKSON et al., 1998), more extensive surveys have indicated that at least one third of the existing wells in Bangladesh contain water that does not meet the local drinking water standard of 50 μg/l for arsenic, with this figure rising to over one half of wells that do not meet the WHO guideline of 10 μg/l (BGS and DPHE, 2001). More recently, further investigation of analogous settings within other river basins in Asia have shown the problem not to be unique to West Bengal and Bangladesh, with several other states of India (CHAKRABORTI et al., 2003; CHAKRABORTI et al., 2004; CHAKRABORTI et al., 2008), the Mekong River and Red River plains of Vietnam (BERG et al., 2007; BERG et al., 2001), Cambodia (POLYA et al., 2005; POLYA et al., 2003), and Laos (JAKARIYA and DEEBLE, 2008), the Indus Plains of Pakistan (NICKSON et al., 2005), the Terai Plains of Nepal (SHRESTHA et al., 2003), the Lanyang Basin in Taiwan (HSU et al., 2003; LIU et al., 2006) and the Yellow River Basin, amongst others in China (LIN et al., 2002; SMEDLEY et al., 2003), all affected. Calibrated logistic regression models which utilise geological and surface soil parameters have further identified the eastern coast of Sumatra, the Irrawaddy Delta of Myanmar and the Chao Phraya Basin in Thailand as areas where groundwater is likely to contain As at concentrations greater than 10 μg/l (WINKEL et al., 2008a). Figure 2.1 below shows all areas where As contamination of groundwater has either been reported or where the groundwater has been predicted to be at risk from contamination.
2.1.2 Geological setting of affected countries

The As hazard in the Bengal delta is typically restricted to shallow Quaternary sediments of Pleistocene and Holocene age. Pleistocene sediments typically consist of gravels, sands and muds that are coated with iron oxide phases (ACHARYYA et al., 2000; GOODBRED and KUEHL, 2000). Holocene deposits overlay these and were deposited by the Ganges, Brahmaputra and Meghna rivers between 10,000 to 7,000 years BP under the combined influence of the Holocene sea level rise and the erosion of the Himalayas (ACHARYYA and SHAH, 2007). Organic rich peaty silts, grey muds and clays of the Joypur Alluvium form a surface aquitard which is found almost exclusively throughout the region that varies in thickness from 6 to 21 m. Peat is observed in many locations at a depth of about 15 m in this unit and has been reported to have a $^{14}$C age of 7.92 ka (MCARTHUR et al., 2008). This is marked in some locations by an impermeable stiff red clay paleosol at a depth of between 21 – 24 m which has been suggested to be a key factor in preventing As contamination of the underlying aquifer, in focussing
groundwater flow and hence controlling the observed spatial heterogeneity in As concentrations in the regions groundwaters (McArthur et al., 2004; McArthur et al., 2008). These units overlay 30 to 40 m of grey sands of the Barasat Formation which forms the shallow aquifer. These units are underlain by a 20 m thick clay aquiclude which separates the shallow and the deeper aquifer of yellow/brown Pleistocene sands which is almost always free of As contamination at depths in excess of 100 m (DPHE/MMI/BGS, 1999). The Holocene Pleistocene contact has been shown to range from depths of between 30 m to 150 m in these alluvial deposits (Van Geen et al., 2003c). Aquifer deposits in the Bengal delta extend to depths in excess of 300 m (BGS and DPHE, 2001). Solid phase As concentrations in these sediments range from 2 to 18 mg/kg, with the higher concentrations typically associated with near surface sediments (upper 15 m).

Broadly similar geological settings exist in neighbouring countries, although often the Quaternary deposits do not extend to the depths of those in the Bengal delta. In Vietnam for example, deposits extend to depths of the order of 50 – 90 m (Berg et al., 2001), whilst in Cambodia deposits typically extend tens of metres in Cambodia, with isolated occurrences of in excess of 100 m (JICA, 2002). In Cambodia, Quaternary deposits dominate the floodplains of the As affected region. Here young Holocene levee/overbank deposits of orange/grey clay containing laminations of peat and silt overlay fine grey aquifer sands (Kocar et al., 2008; Tamura et al., 2007). These clay deposits range in thickness between 3 and 20 m but typically are between 10 – 14 m thick. The peat here is generally about 5 m thick and typically extends from a depth of approximately 6 m to a depth of 11 m. The timing of this peat formation has been shown to be fairly consistent and comparable to that in the Bengal delta at 8.4 – 6.3 ka (Tamura et al., 2009). Solid phase As concentrations in these sediments, like Bengal, vary considerably, with concentrations of 12 mg/kg in the shallow clays decreasing to 2 mg/kg in the deeper aquifer sands (Kocar et al., 2008). Older Pleistocene deposits of orange sands and silts occasionally underlie the Holocene sediments, and have been reported at depths as shallow as 20 m (Tamura et al., 2007).

2.1.3 Arsenic speciation

Despite the fact that arsenic has a low abundance in the Earth’s crust it is still widely distributed in nature and is often associated with metal ores. Arsenic predominantly exists in one of four oxidation states: As(-III), As(0), As(III) and As(V) (Oremland and Stolf, 2003), and is sensitive to mobilisation under either oxidising or reducing conditions and in the pH range typical of natural waters, a property that makes it somewhat unique compared with other
heavy metals (SMEDLEY and KINNIBURGH, 2002). The oxidative weathering and dissolution of arsenic containing minerals forms inorganic As(III) (arsenite) and As(V) (arsenate) which can be transported in groundwaters and become adsorbed on soil and sediment particles (MANNING and GOLDBERG, 1997). The distribution between these two forms of arsenic is largely dependent on the prevailing redox conditions, although because of the slow redox transformations between arsenate and arsenite both are often found in either redox environment (MASSCHELEYN et al., 1991). From figure 2.2 below it can be seen that the predominant form of dissolved inorganic arsenic in aqueous aerobic environments at intermediate pHs is arsenate, which exists as deprotonated arsenic acid oxyanions (H₂AsO₄⁻ and HAsO₄²⁻). Under anaerobic, reducing conditions arsenite, an uncharged particle, dominates as As(OH)₃⁰.

Figure 2.2. Eh - pH diagram calculated in Geochemist’s Workbench® version 6.0 (BETHKE, 2006) for aqueous As species in the As – O₂ – H₂O system at 25°C and at 1 bar total pressure. This displays the dominant As species prevailing under different environmental conditions.
2.1.4 Arsenic solubility

The mobility of arsenic in natural waters is largely controlled by adsorption and desorption reactions to and from clay and metal oxide surfaces such as iron, aluminium and manganese (Belzile and Tessier, 1990; Foster et al., 2003; Fuller et al., 1993; Redman et al., 2002). These ad/de-sorption processes are dependent on both the prevailing pH and the microbially mediated redox conditions within the aquifer (Cummings et al., 1999; Islam et al., 2004; Oremland and Stolz, 2003). The reasons for this are twofold. Firstly, as discussed above, the dominant form that As is present as in solution is dependent on both the Eh and the pH. Secondly, the surface charge of metal oxides is also pH dependent. At low pHs the surface is positively charged and hence is ideal for sorption of negatively charged species such as HAsO$_4^{2-}$ from solution. The isoelectric point describes the pH above which the surface charge changes from negative to positive, and so surface adsorption of negative species such as HAsO$_4^{2-}$ is prevented by coulombic forces. Of the metal oxide surfaces known to exert a control on As concentrations in the aqueous environment, the oxides and oxyhydroxides of iron in particular have been shown to provide a significant collection of surfaces for the adsorption of trace metals, with hydrous ferric oxide (HFO) being the most effective because of its large specific surface area (Swedlund and Webster, 1999).

Iron(III) oxides have a strong affinity for arsenate which is strongly adsorbed to the surfaces of several mineral surfaces such as ferrihydrite and goethite where it forms inner sphere complexes (Manning and Goldberg, 1997; Redman et al., 2002). Arsenite has been shown to strongly sorb to iron oxide surfaces, with a sorption maximum greater than that of As(V) at pH 7 (Dixit and Herling, 2003; Herbel and Fendorf, 2006), contrary to previous reports which suggested it is less strongly adsorbed and to fewer minerals (Oremland and Stolz, 2003). However, desorption of As(III) is suggested to be more rapid and therefore is thought to be more mobile in aquifer systems (Herbel and Fendorf, 2006).

Of the iron oxide minerals found in aquifer sediments, many are present only as preliminary phases which are unstable but form as a result of the slow precipitation kinetics of other more stable minerals. The minerals formed, for example ferrihydrite, are poorly crystalline and have a high specific surface area, ideal to scavenge trace elements such as As from solution. However, over time these HFO’s undergo transformation to more crystalline forms such as goethite or hematite. These crystalline forms may then undergo future transformations, with goethite having been shown to be transformed to magnetite during reductive dissolution.
(FREDRICKSON et al., 1998). The mobilization of As during the transformation of these iron oxides will therefore depend on the relative affinity of the original and transformed minerals for the different As species.

In addition to oxides, sorption and or incorporation of As on or into metal sulfides may also exert a control on As mobility (MOK and WAI, 1994; MORSE and LUTHER, 1999). Mackinawite, a precursor phase of pyrite, is thought to be a major component of the acid volatile sulfide (AVS) fraction of sediments (MORSE and RICKARD, 2004), which have previously been reported in Bengali sediments (HARVEY et al., 2002). Disordered mackinawite has a large specific surface area and hence represents a potentially significant sink for As in the aquifers of this region (WOLTHERS et al., 2005).

2.1.5 Source and occurrence of arsenic in Asian groundwaters

The floodplains and basins of the different countries listed above may in some cases be located thousands of miles apart but the sediments which have accumulated all share important things in common. All available data demonstrates that the generation of the high As groundwaters in this region are not a function of elevated concentrations in the host sediments, which typically have a concentration close to that of the world average (BERG et al., 2001; BGS and DPHE, 2001; DPHE/MMI/BGS, 1999; KOCAR et al., 2008; SMEDLEY and KINNIBURGH, 2002). Instead, the high As groundwater in this region is a result of biogeochemical and hydrogeological processes that arise as a result of the combined influence of the source, rate and content of the sediment that is deposited and the topographic relief. The As in the groundwater of South and South East Asia ultimately derives from the rapid weathering of As-bearing rocks in the upper Himalayan catchments (POLYA et al., 2005). This As is then transported within or sorbed onto suspended particulates via the various great rivers of this region and deposited rapidly and buried in the young, low lying alluvial floodplains of the various river deltas. These include but are not restricted to the Ganges, Brahmaputra and Meghna river floodplains of India and Bangladesh, the Mekong river floodplains of Cambodia, Thailand and Laos, and the Red River floodplains of Cambodia and Vietnam. On deposition, initially under oxic conditions, this As either sorbs to the surface of metal oxides which coat the surface of sedimentary grains, or under reducing conditions can be incorporated into the mineral structure of Fe(II) minerals such as magnetite (COKER et al., 2006) or Fe and/or As sulfides (KIRK et al., 2004). During deposition, abundant supplies of OM are co-deposited with this As (MEHARG et al., 2006; VAN DONGEN et al., 2008). All of these groundwaters have topographically driven gradients which result in extremely slow aquifer flushing rates. This,
combined with the timing of deposition in relation to sea level change, means that the shallow sediments (< 60 m) associated with high As groundwaters within these aquifer systems have seen very few, of the order of 20 or fewer, pore volumes of water which has limited As removal from the sediment (DOWLING et al., 2002).

![Figure 2.3. Piper diagram showing chemical composition of Bengali (squares) and Cambodian (circles) groundwaters. Data taken from Lawson et al (2008) and Rowland et al (2008).](image)

The concentration of arsenic in groundwater has been found to vary by many orders of magnitude and is dependent on the source of arsenic, the amount that is available and the local geochemical environment (SMEDLEY and KINNIBURGH, 2002). Generally, low groundwater arsenic concentrations are found in relatively oxic Pleistocene aquifers, with the majority of affected aquifers being shallow and of Holocene age (BERG et al., 2001; DOWLING et al., 2002; MCARTHRU et al., 2001; POLYA et al., 2005; RAVENSROFT, 2001; RAVENSROFT et al., 2005). Arsenic rich groundwater in the regions affected occurs under highly reducing conditions, occasionally to the extent of methanogenesis, and generally is found in groundwaters with a distinct chemical composition (see figure 2.3 above) dominated by high concentrations of dissolved...
iron and phosphorus in these predominantly calcium, magnesium, and bicarbonate type groundwaters (BERG et al., 2001; HARVEY et al., 2002; LAWSON et al., 2008; RAVENSCROFT et al., 2005; ROWLAND et al., 2008). Sulfate concentrations are generally low in the Holocene aquifers, typically below 5mg/l. However, pockets of higher concentrations associated with elevated concentrations of sodium and chloride do occur, particularly in Cambodia, perhaps indicative of connate seawater trapped in the aquifer matrix. Nitrate concentrations are also generally low, although they have been recorded as being higher below areas of settlement, and range between 0 and 88 mg/l (RAVENSCROFT et al., 2005). High concentrations of As are almost universally restricted to the uppermost 150 m, with a few isolated occurrences at greater depths (see figure 2.4).

![Arsenic distribution with depth in Bangladeshi groundwaters](image)

Figure 2.4. Arsenic distribution with depth in Bangladeshi groundwaters. The dotted line marks the national maximum concentration limit for As of 50 μg/l. Data taken from BGS and DPHE dataset (2001).

2.2. **Arsenic Release mechanisms**

Several mechanisms have been postulated to describe the mobilization of As from aquifer sediments to the groundwaters in South and South East Asian aquifers. The three most commonly invoked mechanisms responsible for arsenic release are the reductive dissolution of Fe oxyhydroxides, competitive exchange reactions, and the oxidative dissolution of arsenic rich pyrite, each of which is described in more detail below.
2.2.1 Competitive exchange reactions

The concentration of As in groundwater can be many orders of magnitude lower than that of other inorganic aqueous species which directly compete for sorption sites on metal oxide surfaces. Of the species which compete for sorption sites with As, phosphate in particular has attracted a significant amount of attention. Acharyya et al. (1999) suggested that an increase in phosphate concentrations mobilized from fertilizers and the decay of natural organic materials may occur as a result of the extensive withdrawal of groundwater. This increase in phosphate concentrations may lead to the release of arsenic from the sediments as a result of competitive exchange of phosphate and arsenic for surface sorption sites. Similarities in the chemistries of phosphate and arsenate suggest that proposal may not be without merit. These two species have been shown to form identical surface species (WAYCHUNAS et al., 1993) and display comparable affinities for sorption sites (MANNING and GOLDBERG, 1997). The presence of phosphate has been shown to decrease the crossover points (the pH at which As(V) and As(III) are equally sorbed) for goethite and HFO and significantly reduced the fraction of As that could be bound to HFO (DIXIT and HERING, 2003). This effect may be substantial in aerobic systems where As(V) dominates, but is likely to be less significant in the reducing groundwaters of the region and hence is unlikely to be a major cause of As mobilisation in the areas affected.

Carbonate has also been proposed to have a similar competitive effect, with As(V) adsorption to ferrihydrite shown to be reduced because weak surface sites had become occupied by carbonate species (APPELO et al., 2002). Appelo et al (2002) suggest that this displacing effect may be an important cause of As release from the Holocene sediments of Bangladesh, which by virtue of the similarities of the geological and geochemical conditions prevailing within many of the affected areas can be extended to represent a potential mechanism of As release regionally. This is supported by results from Van Geen et al (1994) who suggest that many metal oxide surface sites that would normally determine the ratio of metal ions between the aqueous and solid phase are often bound to adsorbed carbonate species when it is present. Carbonate has also been shown to mobilise As as a result of carbonation of As bearing sulfide minerals (Kim et al., 2000). However, both laboratory experiments and field data suggest the interpretations from these studies may have been overly simplified for the circum-neutral, reducing groundwaters discussed here. Neuberger and Helz (2005) show that As solubility is increased by complexation with carbonate species in solution, but the effect of this is small and only significant in extremely carbonate rich waters more typical of interior drainage basins. On the field scale, very little evidence exists to support this theory. Indeed, the study
of McArthur et al (2004) reported that the highest concentration of bicarbonate (744 mg/l) was associated with an As concentration of below 5 μg/l at a known As hotspot in West Bengal.

These mechanisms discussed above suggest that competitive exchange reactions are unlikely to be the single dominant factor responsible for the generation of the high As concentrations in groundwaters of South and South East Asia. This does not mean to say, however, that such mechanisms may not contribute to the overall As budget in solution. Indeed, a reduction in the capacity of sediments to sorb both arsenate and arsenite as a result of competitive exchange reactions with natural organic matter (NOM) has been suggested to be sufficient enough to result in As release at concentrations that may exceed drinking water standards (BAUER and BLODAU, 2006; REDMAN et al., 2002). In the study of Redman et al (2002), NOM was shown to form aqueous complexes with both arsenate and arsenite and was also shown to have a direct effect on the redox speciation of As in solution, resulting in arsenate reduction as well as arsenite oxidation. Arsenite in particular was shown to have a decreased sorption capacity as a result of either competitive exchange reactions or through the complexation with NOM. Such interactions with NOM may partially explain the observed increased mobility of As(III) in these groundwaters.

2.2.2 Oxidation of arsenic rich pyrite

Chowdhury et al. (1999) suggested that the oxidation of arsenical pyrite, whilst perhaps not the sole cause of high As in the aquifers affected, could contribute As to the groundwater. They suggest that the reducing environment of the younger region of the Ganges delta may have resulted in the formation of As rich pyrite and that As may be mobilized by the oxidative dissolution of these minerals. Consistent with this theory, a study by Akai et al (2004) found the arsenic content of minerals to be highest in pyrite and decrease with precursor minerals of frambooidal pyrite, such as mackinawite, down to Fe oxides. The authors of this paper, despite accepting that the main source of As in the Holocene groundwaters are oxides of Fe and Mn, suggest the system is further complicated by the oscillation of oxidation and reduction fronts during sediment-water interactions. In such a situation pyrite could be partially oxidized and re-precipitated as Fe-hydroxide with concomitant sorption of As.

The validity of this theory, however, is often disputed for a number of reasons. Firstly, it has been suggested that the oxidation of pyrite would generate sulphate and so a positive correlation with arsenic in solution would be expected. However, Harvey et al (2002) found an
inverse relationship between the two at the sites they tested. Secondly, it has been suggested that for this to be happening, the process would require either dissolved O₂ or NO₃ as an electron acceptor and the process would result in the acidification of water: in general none of these conditions are met for most samples (DOWLING et al., 2002; MCARTHUR, 1999). It has also been suggested that the arsenic released from the oxidative dissolution of arsenic rich pyrite would adsorb onto or coprecipitate with FeOOH, the product of oxidation (MOK and WAI, 1994). Whilst pyrite has been noted in studies on aquifer sediments (HARVEY et al., 2002; NICKSON et al., 2000; POLIZZOTTO et al., 2005), it is thought to represent a sink for, not source of arsenic (ACHARYYA and SHAH, 2007; HARVEY et al., 2002; MCARTHUR et al., 2001). This is supported by the limited number of samples which were analysed for δ³⁴S in the study of Smedley et al (2001). Here, the data suggests that sulphate reduction, not sulfide oxidation, is occurring.

2.2.3 Reductive dissolution of iron oxyhydroxides

The most widely accepted theory is that the reductive dissolution of iron oxyhydroxides may lead to the release of arsenic into groundwater (BHATTACHARYA et al., 1997; MCARTHUR et al., 2001; MCARTHUR et al., 2004; NICKSON et al., 1998; POSTMA et al., 2007; STUBEN et al., 2003; ZHENG et al., 2004). Fe oxyhydroxides exist in aquifers as dispersed phases such as coatings on sedimentary grains, and these phases are known to scavenge As from solution (NICKSON et al., 2000). The reductive dissolution of these phases in reducing groundwaters solubilises Fe and its adsorbed load. This process of reductive dissolution is thought to be microbiologically mediated and driven by concentrations of sedimentary organic matter of up to 6% (ISLAM et al., 2004; NICKSON et al., 1998; VAN GEEEN et al., 2004). Consumption of this organic matter (OM) drives redox processes establishing a redox gradient over the upper few meters of sediment (POSTMA et al., 2007). Following the exhaustion of oxygen, a number of different electron acceptors are utilised until the onset of Fe-reducing conditions where Fe(III) is used as an electron acceptor in microbiologically mediated reactions. If sufficient OM is present to drive the process, sulphate reduction and even methanogenesis can result. The reductive dissolution of iron (oxy)hydroxides can be described by the following equation and is presented schematically in figure 2.5:

\[
4\text{FeOOH(s) + CH}_2\text{O(OM) + 7H}_2\text{CO}_3\text{(aq) } \rightarrow 4\text{Fe}^{2+}\text{(aq) + 8HCO}_3\text{(aq) + 6H}_2\text{O (aq)}}
\]  

(2.1)

Work by Islam et al (2004) supports the requirement for organic matter and showed, through the increased rate of reduction after the addition of acetate, that As release is limited by the
availability of an electron donor in the sediments. This study also showed that Fe reduction occurs before As release in sediments. The observed decoupled nature of arsenic and iron release from sediments has been used to suggest that Fe(III) phases may undergo transformation to Fe(II) minerals without necessarily resulting in the release of Fe to solution (HORNEMAN et al., 2004). In fact, numerous studies have found that the reductive dissolution of FeOOH leads to the precipitation of secondary Fe(II)/mixed valence phases such as magnetite (COKER et al., 2006; HANSEL et al., 2005; HERBEL and FENDORF, 2006; KOCAR et al., 2006), vivianite (ISLAM et al., 2005a; ISLAM et al., 2005b), and siderite (GUO et al., 2007), which are all capable of sequestering As from solution either by incorporation into the mineral structure or through sorption to its surface. Arsenite is less suitable for incorporation into the mineral structure of secondary Fe phases (COKER et al., 2006), and although it may subsequently be sorbed to the new mineral phase, sorption may be limited because of the decrease in surface area. In addition to the numerous secondary Fe phases which can form and sequester As under Fe reducing conditions, a number of studies have suggested As may be sequestered from solution under sulphate reducing conditions (cf. MCARTHUR et al., 2004). However, whilst As release has been shown to be rapid (HERBEL and FENDORF, 2006), sequestration of As from solution is rate limited by thermodynamic and kinetic restrictions on the formation of mineral phases and the rate at which As sorbs to the surface of these phases (KIRK et al., 2010; NATH et al., 2009), and As-sulfide formation may be inhibited by the presence of reactive Fe(III) or Fe(II) (KOCAR et al., 2010).

The studies suggest that reduction of Fe(III) alone is not sufficient to mobilize arsenic. Given the decreased retention of As(III), reduction of As(V) to As(III) prior to or concomitant with Fe reduction, coupled to a partial removal of adsorbants or a decrease in the number of available sorption sites, may be required for the significant release of As to groundwaters observed in South and South East Asia. The mobility of As in these groundwaters is therefore partly controlled by the supply and distribution of Fe, S and OM and the thermodynamic and kinetic limitations on mineral precipitation and dissolution processes.
The literature discussed above suggests that the reductive dissolution of FeOOH’s represents the single most significant mechanism of As release to groundwaters in South and South East Asia. However, in reality it is likely that multiple biogeochemical processes are occurring simultaneously that act to both release As to and sequester it from solution. It is therefore possible that two or even all of the mechanisms discussed above could be operating at the same time to generate As rich groundwaters. In the study of Swartz et al (2004), the authors suggest that high As groundwater is associated with sediments whose sorption capacity has been exceeded, and that the combined effect of the reductive dissolution of iron oxyhydroxides phases in the aquifer and competitive sorption contribute to maintain high As concentrations in the aquifer. Similarly, recent studies by Polizzotto et al (2005; 2006) support the suggestions of Akai et al (2004) and combine the oxidative dissolution of arsenic rich pyrite and the reductive dissolution of iron oxyhydroxides to propose a new mechanism for arsenic release from aquifer sediments. They suggest that arsenic-rich sulfides in surface sediments are oxidized during periods of oxic conditions, forming Fe(III) oxides which would sorb the As from solution. During subsequent reducing periods, for example during flooding which carries a high load of organic carbon, reductive dissolution of the minerals releases arsenic to
solution. However, because of the partial removal of sulphur via sulphate transport following oxidation, only a portion of the As release can adsorb to the re-precipitated sulfide minerals. The remaining As, present as arsenite because of the reducing conditions, is then easily transported to well depth because of the paucity of sorbents in the underlying sediment. Such oscillating redox conditions are expected to be common, particularly in areas such as West Bengal and Bangladesh where seasonal monsoon flooding and subsequent extensive groundwater irrigation raises and lowers the water table on a seasonal basis (POLIZZOTTO et al., 2006).

Whilst Polizzotto et al (2005; 2006) suggest seasonal variations in the groundwater level may result in the seasonal cycling of redox conditions, a study by Berg et al (2008) found that substantial groundwater abstraction for the water supply of Hanoi in Vietnam has lead to dramatic lowering of groundwater levels, resulting in a downshift of redox conditions. They suggest that this may lead to the partial oxidation of peat and the downward migration of natural organic matter-rich leachates that may be responsible for maintaining anoxic conditions in the aquifer below these peat layers, enhancing As release from reductive dissolution of Fe-hydroxides. They also note that the invading oxic conditions may release As from sulfides and suggest As release may occur from both reductive and oxidative mechanisms.

2.3. **Role of micro-organisms in the As release process**

The potential mechanisms implicated in As release discussed above can all proceed in the absence of micro-organisms, with As released by either abiotic desorption or oxidative/reductive processes that are driven purely by changes in the geochemical status of the groundwater. However, consumption of OM in reduced groundwaters suggests a potential role for a microbial contribution to establishing or maintaining the redox environment and associated reactions, which may act to release As to groundwater at a rate which exceeds that driven by purely abiotic processes alone. This lead researchers to assess the role of micro-organisms in the As release process.

Early studies reported how As mobility could be enhanced by the dissimilatory Fe reducing bacteria *Shewanella alga BrY* without the reduction of arsenate (CUMMINGS et al., 1999). Further studies showed that the iron reducing bacteria, *Geobacter Sulfurreducens* and *Geothrix fermentans*, were not able to directly reduce As(V) enzymatically or indirectly through Fe(II) in solution following reduction of Fe(III) phases (ISLAM et al., 2005a; ISLAM et al., 2005b). However,
these studies, as discussed above, highlighted the fact that the reduction of Fe(III) alone was not sufficient to result in As release, with biogenic Fe(II) phases shown to sequester As from solution. Zobrist et al (2000) demonstrated the ability of the dissimilatory arsenate respiring prokaryote (DARP) *Sulfurospirillum barnesii* to reduce both Fe(III) and As(V), with reduction of As(V) to As(III) reported both in solution and when adsorbed to ferrihydrite. Oremland and Stolz (2003) suggested that the ability of such dissimilatory metal reducing microbes to reduce both Fe and As implicates such bacteria in the generation of the As contaminated aquifers of South and South East Asia.

The study of Islam et al (2004) reported the first direct observation for indigenous Fe(III) reducing bacteria facilitating As release from the aquifer sediments of a known As hotspot in West Bengal. As discussed above, they reported a decoupling in the release of Fe and As to solution, and suggest that As reduction may only occur after the majority of available Fe has been consumed. Indeed, at the time of writing this review, no obligate As(V) reducing bacteria have been identified in any sediment taken from an arsenic contaminated aquifer system, with all of the organisms capable of reducing As also able to respire using alternative electron acceptors, including Fe (OREMLAND and STOLZ, 2003). The addition of an electron donor to stimulate microbial metabolism increased both the rate and quantity of As released from the sediment, and suggests that the capacity for As release in these sediments may be restricted by the availability of OM which serves as an electron donor in the process. Van Geen et al (2004) conducted a similar sediment incubation based study and provide further supporting evidence for the requirement of bacteria for significant As release from sediments. They show, through comparison of reduced grey sands and oxidised orange sands sediments taken from Bangladesh, that the addition of an electron donor was required to release any As from oxidised sediments and to release Fe from the reduced sands and that As release was inhibited following the addition of an antibiotic. More recent studies have since further demonstrated the importance of microbial communities on arsenic release (GAULT et al., 2005; GUO et al., 2008; HÉRY et al., 2008; LEAR et al., 2007; PEDERICK et al., 2007; ROWLAND et al., 2007) and sequestration processes (HÉRY et al., 2010) from sediments taken from various regions of South and South East Asia.

Oremland and Stolz (2005) suggest three possible biological processes for As mobilisation from Fe oxide coated sands. In the first of these, As(V) is released to solution following the reduction of Fe oxides by iron reducing bacteria such as *Geobacter*. The second mechanism involves the reduction of sorbed As(V) and release as As(III) via DARPs. In the third mechanisms, both Fe and As are reduced and released via iron reducing DARPs. For the purposes of this review, the
detailed mechanisms by which these bacteria are able to reduce As are not discussed. For a comprehensive description of these mechanisms, genes and enzymes that result in these biotransformations the reader is referred to the reviews of Oremland and Stolz (2003), Oremland and Stolz (2005) and Lloyd and Oremland (2006).

2.4. Role of Organic Matter in arsenic release

The catalytic role of micro-organisms discussed above clearly highlights the importance of organic matter in driving As mobilization in these sediments. However, OM is also implicated in As release through competitive sorption, whilst other studies have demonstrated a further potential role for OM as an electron shuttle between micro-organisms and iron oxide surfaces (LOVLEY et al., 1996; MLADENOV et al., 2010; ROWLAND et al., 2007), suggesting a triple role from OM in As release. Despite the obviously significant role played by OM, the source(s) of OM driving the biogeochemical processes associated with As release remains unknown and is currently a topic of intense debate. This has been identified as one of the key questions remaining that is inhibiting our ability to accurately predict the spatial distribution of As in these groundwaters (FENDORF et al., 2010).

Numerous potential sources of OM have been postulated to be driving As release in South and South East Asia. These can be broadly separated into subsurface, sedimentary sources and surface derived sources. Subsurface sources of OM include the reducing power of peat layers enriched in organic matter (MCARTHUR et al., 2001), the co-deposition of arsenic with organic matter (MEHARG et al., 2006) and the migration of petroleum organics from depth (ROWLAND et al., 2006; VAN DONGEN et al., 2008). Conversely, OM could derive from the entrainment of dissolved organic matter with recharge from surface water (HARVEY et al., 2002).

2.4.1 Subsurface sources of Organic Matter

The first study to postulate a source of OM responsible for driving As release in the groundwaters of South and South East Asia was that of McArthur et al (2001). They suggested that the reductive dissolution of Fe-oxides in Bangladesh is driven by the microbial degradation of buried peat deposits. They postulate that the U-shaped profile of As, Mn and Fe with depth suggests that organic matter must be diffusing upwards from the underlying organic rich clay. This is perhaps supported by the fact that the depth of maximum As of about 30 m also represents the depth (28 – 45) that major peat deposits formed 5000 years ago (MCARTHUR et
al., 2001). Additionally, increases in the DOC content of groundwater with depth have been shown through spectroscopic investigations to be due to a contribution of lignaceous and aromatic DOM indicative of reduced peat soils (MLADENOV et al., 2010). They go on to suggest that the spatial distribution of As concentrations in groundwaters can be largely explained by the distribution of paludal basins where peat deposits are likely to have formed. Indeed, the presence of peat has been identified in other As contaminated aquifer systems, such as in Vietnam (BERG et al., 2001) and Cambodia (TAMURA et al., 2007; TAMURA et al., 2009), which suggests it may play a role in As release regionally.

This suggestion is adapted in a more recent study by McArthur et al (2008) who suggest that the spatial variation of As concentrations regionally is not only controlled by the presence of peat layers within the aquifer, but also an impermeable clay aquiclude that they term the last glacial maximum paleosol (LGMP). This LGMP is present in interfluvial areas but is absent in paleochannels that were eroded during falling sea levels between 120 ka and 20 ka. Where the LGMP is present, the aquifer below it is protected from the influx of water containing OM derived from peat layers in the sediment. However, in the paleochannels where this LGMP is absent, groundwater flow is focussed through these gaps in the aquitard, transporting dissolved organic carbon (DOC) which drives As release. Groundwater flow can then transport this As rich water laterally underneath the LGMP where it may either be sorbed by the aquifer sands, or in areas where the sands are reduced the introduction of available DOC may result in further As release. However, this model does not explain the presence of high groundwater As concentrations in groundwater where no peat is identified in the stratigraphy (HARVEY et al., 2002; MEHARG et al., 2006; NATH et al., 2005; ROWLAND et al., 2006). It is therefore unlikely that peat represents the sole source of OM responsible for driving As release in the groundwater of South and South East Asia.

A second potential subsurface source of OM that may contribute to the groundwater DOC pool was postulated in the study of Meharg et al (2006). They suggest that significant quantities of organic carbon sufficient to drive mobilization of arsenic in Bengal delta aquifers derives from organic matter that was co-deposited alongside As and subsequently buried. This model does not require OM to be leached from sediments and transported, as in the model described above by McArthur et al (2001). Instead, As present as arsenate is concentrated and retained in aerated root zones and animal burrows of vegetated wetland sediments where significant accumulations of Fe(III) oxides are deposited. Upon burial, in-situ degradation of OM establishes the reducing conditions required for dissolution of Fe(III) oxides and the release and/or reduction of As. They suggest that this is responsible for the heterogeneous
groundwater As concentrations observed in this region, which arise as a result of preferential deposition of As in OC-rich sediments which are heterogeneously distributed because of stream / channel paths meandering across the forest. Such a model is consistent with observations of lower As concentrations with depth in these contaminated aquifer systems (BGS and DPHE, 2001; SMEDLEY and KINNIBURGH, 2002).

There are again, however, numerous studies which provide evidence that conflicts with the model postulated by Meharg et al (2006). In their study, Meharg et al (2006) claimed that As concentrations will be higher in vegetated areas compared to paleochannels. This is because OC input is lower to stream / channel beds and eroded and redeposited overbank deposits compared to the highly productive vegetated forest floor where FeOOH and As is concentrated on roots and in burrows. However, more recent studies have shown As concentrations to be greatest in the sediments which directly underlie paleochannels or modern day ponds and wetlands (ACHARYYA and SHAH, 2007; KOCAR et al., 2008; POLIZZOTTO et al., 2008; WEINMAN et al., 2008).

A third potential subsurface source of OM that has been postulated to be driving As release in these groundwaters are thermally mature hydrocarbons. These distributions have been identified in sediments of West Bengal (ROWLAND et al., 2006) and Cambodia (ROWLAND et al., 2007; VAN DONGEN et al., 2008). These hydrocarbons are characterised by abundant high molecular weight n-alkanes and thermally mature distributions of hopanes and steranes. This source of OM is distinct from the other subsurface sources discussed above because it does not originate from the aquifer sediments where As concentrations are highest, but is instead sourced from deep within the subsurface and has migrating up from depth. This source of OM has been shown to be readily biodegradable and linked to, although not directly shown to be the cause of, As release in the sediments of the study sites investigated. In West Bengal, these petroleum derived hydrocarbons were identified in sediments at a location where low concentrations of extractable organic matter in the bulk sediments indicates that the majority of the organic matter present is recalcitrant and hence is less bioavailable than other sources. Interestingly, recent studies have suggested that it is not necessarily the amount of OM present that will control biogeochemical processes in these groundwaters, but is instead how bioavailable the OM is for the microbial communities present (GAULT et al., 2005; MLADENOV et al., 2010; ROWLAND et al., 2007). It is yet to be shown whether or not petroleum derived hydrocarbons are present in other aquifer systems where groundwater As concentrations exceed threshold values. However, even if this is shown to be the case, it is unlikely that they
are present in quantities significant enough to be wholly responsible for driving As release in the regions groundwaters.

2.4.2 Surface sources of Organic Matter

It has, somewhat contentiously, been suggested that the OM responsible for driving As release in these groundwaters has a surface origin, and could be drawn down from surface sources such as rivers, latrines, channels, ponds or irrigated rice fields that are rich in labile organic carbon (HARVEY et al., 2002; McARTHUR et al., 2001). Harvey et al. (2002) suggested that irrigation pumping may draw down DOC transported in these surface waters to the depth where As concentrations are at a maximum. This suggestion is largely based on $^{14}$C ages of DOC and dissolved inorganic carbon (DIC) in groundwater at a well characterised study site in Bangladesh. They show that the radiocarbon ages of DIC are much lower than that of the DOC, which has an age consistent with that of wood fragments from surrounding sediment at similar depths. The authors suggest that the older DOC was mobilized from the sediment following the inflow of water containing young DIC. If this DOC was being consumed in biogeochemical processes associated with the As release process, it would generate DIC with an older signature. The younger DIC signature, they suggest, must therefore derive from the oxidation of young, labile DOC introduced in invading surface waters.

This suggestion is supported by data from a recent study by Neumann et al (2010) who demonstrate that biologically degradable OM in surface ponds is transported in the groundwater as a result of irrigation pumping practices to the depth of peak As concentrations. They further show that OM from paddy rice fields is more recalcitrant and as such is less bioavailable for driving As release processes. This rice paddy water recharges the aquifer through bunds (NEUMANN et al., 2009) and overlies pond derived groundwater in a stratified groundwater flow system, with both sources overlying centuries old groundwater that recharged prior to the installation of the dense network of tubewells. A schematic representation of this model is given in figure 2.6 below. This study also suggests that As contamination of groundwater may be significant where wells are located downstream of recharge zones through ponds, wetlands or permanently saturated water bodies that contain abundant supplies of labile organic carbon. Such a scenario therefore suggests that the observed spatial heterogeneity of As concentrations could be explained by the combined influence of the location of organic rich recharge zones coupled to the direction of groundwater flow.
Conflicting reports of the potential role of ponds to act as sites for recharge are present in the literature however. The study of Sengupta et al. (2008) present isotopic ($\delta^{18}$O and $\delta$D) and geochemical (K, Ca, Mg) tracer data to suggest that pond water is not recharging the groundwater in significant enough volumes to provide sufficient DOC to drive As release processes. In contrast, analogous studies from similar settings in West Bengal and Vietnam show that As rich groundwaters are frequently associated with a contribution of a pond like evaporative signature to the groundwater (Berg et al., 2001; Lawson et al., 2008). This difference perhaps reflects variations in the thickness of the surficial clay aquitard, the depth of ponds within this clay or the age of the ponds between the different sites. It is well known that ponds lose significant volumes of water in the first few years following excavation, after which a gradual accumulation of sediments decreases the permeability of the pond bottom sediments until the pond is essentially sealed from further losses (Harvey et al., 2006).

![Figure 2.6. Schematic of drawdown of surface water from ponds as a result of the excessive abstraction of groundwater as proposed by Harvey et al (2002). Note here that the pond recharge flows beneath the rice field recharge and to the depth of groundwater abstraction as in Neumann et al (2010). Older deep groundwater may also be drawn to the depth of abstraction.](image)

As with the models of subsurface derived OM discussed above, the proposal that surface derived OM is responsible for driving As release contains inconsistencies which suggest it may not be wholly responsible for the contamination of aquifers regionally. It would perhaps be expected that for OM to be derived from the surface, DOC concentrations would be highest in the near surface and decrease with depth as a result of oxidation and microbial metabolism of
the influx and downward migration of labile DOC. However, in general most profiles of DOC in groundwater increase with depth to the As peak and decrease thereafter (Harvey et al., 2002; Kocar et al., 2008; Meharg et al., 2006). Furthermore, an anthropogenic control on the As release process does not account for the hazardously high concentrations of As that are frequently observed in regions such as Cambodia, where little, if any, groundwater abstraction is occurring (Polizzotto et al., 2008).

Whilst each of these models provide compelling arguments as to why a particular source of OM may be responsible for driving As release in the regions groundwaters, the subsequent inconsistencies discussed above suggest that no single source is entirely responsible for the distribution of As contamination in these aquifer systems. To date, As release or the presence of high As groundwaters have only been shown to be associated with the presence of OM in the field (McArthur et al., 2001; Meharg et al., 2006) or to the degradation of OM in microcosm experiments (Rowland et al., 2007; Rowland et al., 2006). It is yet to be shown that oxidation of any of these sources of OM directly results in the release of As to solution in a dynamic system where potentially multiple sources of OM are present. Instead it is more likely that one or more of these sources contribute to the local pool of OM which is driving As release at any given location. Indeed, it has recently been suggested that it is the relative distribution of these various sources of OM in the groundwater DOC reservoir that may govern As release rates in the regions groundwaters. Groundwaters where the DOC reservoir is dominated by younger, fresher contributions of OM may be able to support more rapid As release, whilst groundwaters that have a DOC reservoir that is dominated by older, more recalcitrant sources of OM (such as buried peat deposits) should support a slower rate of As release (Fendorf et al., 2010). This point is particularly important when we consider how As concentrations may change in the future. For example, people who are regularly consuming groundwater with a more labile DOC composition are more vulnerable to increases in the As hazard over short timescales. Resolving what environments and processes are responsible for developing different DOC compositions therefore represents one of the more important issues left to address if we are to more accurately predict how the As hazard will evolve with time, and what locations are most vulnerable to such changes.

2.5. Potential role of anthropogenic interference on arsenic release

The causal link proposed by Harvey et al. (2002) potentially the most troublesome of the models discussed above as this suggests that anthropogenic interference has contributed to
the current As hazard, and may potentially further exacerbate the problem through continued release of As to these groundwaters. This model has been the subject of intense debate (AGGARWAL et al., 2003; HARVEY et al., 2003; VAN GEEEN et al., 2003b); not least because of the implications it holds for agricultural production. This information is critical for policy makers and those responsible for implementing arsenic mitigation in the areas affected because if shown to be the case, more informed drilling programmes and groundwater management practices would play a significant role in future arsenic mitigation strategies.

Numerous studies have been devoted to assessing the efficacy of this model. Most of the studies aimed at elucidating the potential role of groundwater abstraction practices on As mobilisation have utilised isotopic techniques to identify any signature that would support a deviation from that which would be expected under pre-development conditions. Two isotopic systems in particular, namely the isotopes of oxygen ($\delta^{18}O$) and hydrogen ($\delta D$ and $^3H$), have been used by the majority of these studies in an attempt to identify (i) a contribution of an evaporative signature typical of surface waters which have undergone extensive evaporation prior to recharge, and (ii) a contribution of modern (< 60 yrs) water which would be indicative of young water drawn to depth as a result of extensive groundwater abstraction.

The study of Harvey et al (2005) suggest that the isotopic signature of groundwater at their study site is indicative of lighter water present in the upper 30 m mixing with heavier water from below this depth. This mixing is shown to occur at the depth of maximum As concentrations, and likely occurs as a result of convergent groundwater flow driven by irrigation pumping. They suggest that heavier water below 30 m could represent infiltrated pond, river or irrigation water that has been subject to more evaporation than the predominantly precipitation based water above it. This is supported by the presence of a component of tritium active groundwater to a depth of 61 m at this site (HARVEY et al., 2003). Indeed, tritium has been reported at depths of up to 150 m in Bangladesh (AGGARWAL et al., 2000; DOWLING et al., 2003; MCARTHUR et al., 2010; STUTE et al., 2007). This observation of convergent groundwater flow was also reported in a more recent study at the same site by Klump et al. (2006). However, unlike the study of Harvey et al (2005) discussed above, Klump et al. (2006) also report a change in the tritium distribution of the groundwaters at this study site, with no contribution of tritium active water indicative of a recent contribution from surface waters identified below a depth of about 35 m. Indeed, $^4He_{ter}$ accumulation in the groundwater below a depth of 35 m at this site is indicative of groundwater ages in the range of several centuries (KLUMP et al., 2006). Neumann et al (2010) later explained this distribution in the stratified groundwater column model as discussed above.
Several studies report an absence of measurable tritium in wells at or shallower than the depth of the maximum As concentration (AGGARWAL et al., 2003; AGGARWAL et al., 2000; DOWLING et al., 2002). The authors of these studies suggest that this demonstrates that, at least in some locations, As rich groundwater predates the onset of irrigation pumping, and as such groundwater abstraction cannot be responsible for As release processes at these sites. Aggarwal et al. (2003) further argue that the $^3$H distribution with depth did not change between 1979 and 1999, and suggest that hydrologic effects of groundwater abstraction must therefore be negligible. However, Harvey et al. (2003) dispute this and point to the fact that 4 wells below 25 m contain measurable tritium concentrations in 1999 which were not present in 1979, indicative of the migration of young water to extraction depths following the increase in irrigation pumping during this period.

It is of course possible, indeed likely, that both As release and removal processes may be occurring simultaneously as a result of groundwater abstraction practices. The rapid transport of organic carbon from surface waters (HARVEY et al., 2002) or sediments (MCArthur et al., 2001; ROWLAND et al., 2007; ROWLAND et al., 2006) driven by abstraction processes could mobilize arsenic via reductive dissolution of Fe oxides. Alternatively, arsenic may be flushed from the system due to the increased number of pore volumes moving through the aquifer as a result of extensive groundwater abstraction. Indeed, the different flushing histories of sand formations in the Bengal delta has been postulated as a potential hydrogeological control on the observed spatial heterogeneity of dissolved As concentrations in the groundwater there (VAN GEEN et al., 2008). Average As concentrations in irrigation wells were found to be significantly lower than in domestic wells, suggesting that the increased flow through irrigation wells may mobilize As which is then subsequently flushed from the system (HARVEY et al., 2003; MCArthur et al., 2004). Dowling et al (2002) suggest that the largely As free Pleistocene aquifers have been subjected to more than 100 pore volumes of flushing. Conversely, most Holocene sediments have been flushed by perhaps as few as 20 pore volumes. The rate of flushing of these aquifers may have increased as a result of groundwater abstraction, with Harvey et al. (2006) showing a halving of the residence time of groundwater following the advent of pumping for irrigation from 84 to 38 years. This could therefore result in the total flushing of As from the shallow groundwater over the long term. However, the effects of this process over short timescales have yet to be resolved. The potential effects of groundwater abstraction practices on the current As hazard therefore remains a topic of considerable interest, and must be resolved for an improved understanding of how the current As hazard will evolve in the coming years and decades (CHARLET and POLYA, 2006).
Irrespective of the processes occurring, it is difficult to argue that the shallow subsurface groundwater flow regime has not been influenced by groundwater abstraction practices (MICHAEL and VOSS, 2009; MUKHERJEE et al., 2007). Given that the large majority of deep tubewells tap As free groundwater, many have touted the use of this deep reservoir as a sustainable source of safe potable water (AHMED et al., 2006; VAN GEE N et al., 2003a; VAN GEE N et al., 2007; ZHENG et al., 2005). However, recent studies suggest that the deep groundwater exhibits a similar vulnerability as the shallow groundwater to As contamination, with irrigation abstraction of deep groundwater potentially resulting in the draw down As contaminated shallow groundwater (BURGESS et al., 2010; CHARLET et al., 2007; LAWSON et al., 2008; MICHAEL and VOSS, 2008). Indeed, in the Hanoi area of Vietnam, excessive abstraction of groundwater from the deep Pleistocene aquifer for public water supply has resulted in the vertical seepage of reduced groundwater rich in DOC, Fe and ammonia in to the Pleistocene aquifer (BERG et al., 2008), with similar observations reported in nearby Nam Du (NORRMAN et al., 2008). Deeper groundwater, it is suggested, may only represent a sustainable safe source of As-free drinking water if wells are drilled in oxidised sediments, and its utilisation is limited to domestic supply, with irrigation abstraction restricted to shallow groundwaters (BURGESS et al., 2010; MICHAEL and VOSS, 2008). Increases in the deep groundwater As hazard may therefore only become apparent once the finite sorption capacity of deep sediments has been exceeded or once reducing conditions have become established to support As release. Monitoring of As concentrations alone may therefore not be sufficient to identify subtle changes in the water chemistry of deep groundwater. As such, monitoring of the evolution of the mean residence time of deep groundwater over a period of several years should be conducted to identify secular changes in the deep groundwater that may be indicative of an evolution towards conditions which are favourable for the generation of high As groundwater.

It is worth noting at this point that the removal of As from the groundwater through irrigation on to paddy rice fields does not necessarily result in a decrease in the human exposure to As. Recent studies have shown that in West Bengal, as much as 44% of the total exposure to As may come from the rice grown in the fields which are irrigated with As contaminated groundwater (MONDAL and POLYA, 2008). The vulnerability of rice paddy fields to increasing As contents is well established (DITTMAR et al., 2007; MEHARG and RAHMAN, 2003; ROBERTS et al., 2010; ROBERTS et al., 2007), with temporal trends of increasing As content in the soils of paddy rice fields recently reported (DITTMAR et al., 2010). Groundwater As concentrations are inextricably linked to the groundwater flow regime through the transport of As and dissolved
solute that influence As mobility. The coupled effect of groundwater transport and
geochemical reactions has resulted in a very complex spatial distribution of As concentrations
in the groundwaters of South and South East Asia. It is yet to be seen, however, whether these
processes may also result in secular changes to the As hazard in rice, information that is critical
for policy makers whose task it is to reduce exposure to arsenic through groundwaters.

2.6. **Variability in arsenic concentrations**

As discussed and emphasised above, one of the fundamental requirements of policy makers is
that the scientific community develop quantitative models that can predict both the spatial
and temporal changes in As concentrations in the countries affected. Such models require
knowledge of the controls and mechanistic processes involved in developing the current
variations that are observed in the groundwater As concentrations on the spatial scale and the
potential temporal variations which may arise as a result of these processes, both of which are
discussed in more detail below.

2.6.1 **Spatial variability in dissolved arsenic concentrations**

As discussed previously, the majority of As affected aquifers in South and South East Asia are
shallow and of Holocene age (MCARTHUR et al., 2001). The production of risk maps like those
produced in Polya et al. (2005) and the predictive maps produced in Lado et al. (2008) and
Winkel et al. (2008a; 2008b) allow for approximate identification of high As or at risk areas.
However, even within these areas concentrations of groundwater As vary significantly, with
high As (> 10 μg/l) and low As (< 10 μg/l) found within close proximity (MCARTHUR et al., 2004;
VAN GEEN et al., 2003c). Accounting for this high degree of spatial heterogeneity is one of the
key questions vexing researchers at present, and significantly limits our ability to accurately
predict the groundwater As hazard on the scale which can be utilised by those responsible for
the installation of tubewells.

An early study by Pal et al. (2002) found that the aquifers in areas where As concentrations in
groundwater are low are often overlain by a 25- 30 m cap clay aquitard. In the areas where
groundwater As concentrations are high this top layer is either partially preserved or absent.
The only identifiable difference in subsurface lithology in the “safe zones” was the presence of
the clay cap, which Pal et al (2002) suggest helps explain the spatial variability of As
concentrations. They suggest that sediments that have a higher porosity at the top, i.e. where
this clay cap is missing, provide a conduit for the downward transport of OM rich waters which
are capable of driving As release. However, recent studies from different study sites provide conflicting evidence that suggests this observation may not hold true regionally. A study by van Geen et al. (2006) suggest that the aquifers in affected areas are often overlain by a layer of clay or silt which acts as a barrier to oxidants and can lead to the development of reducing conditions. This sediment permeability control on the spatial distribution of redox conditions has been noted elsewhere (ITAI et al., 2008), and is supported by the complimentary studies of Aziz et al. (2008) and Weinman et al. (2008). Aziz et al. (2008) showed that high As groundwaters are associated with fine grained sediments. Where sand deposits reach the surface and the underlying aquifer is unconfined, As levels were found to be uniformly low, with recharge in these locations shown to be an order of magnitude faster than confined aquifers which underlie relatively impermeable fine grained sediment. Weinman et al. (2008) show that the spatial distribution of these fine grain deposits can explained by local river history and floodplain development.

This geomorphic control on As distribution has also been identified in numerous other studies which link high As groundwaters with geomorphologic and surface features such as abandoned or existing channels, swamps and ox bow lakes (ACHARYYA and SHAH, 2007; KOCAR et al., 2008; NATH et al., 2005; POLIZZOTTO et al., 2008). These have been shown to be areas of surface water accumulation where rapid deposition of OM occurs and facilitates the release of As to groundwaters (PAPACOSTAS et al., 2008; QUICKSALL et al., 2008). However, as discussed previously, the groundwater flow regime must also contribute to the observed spatial heterogeneity of As concentrations in these groundwater systems. The complimentary studies of Benner et al. (2008), Kocar et al. (2008) and Polizzotto et al. (2008) combine the sedimentary control on As concentrations with hydrologic transport at a minimally disturbed As rich aquifer system in the Mekong delta of Cambodia. By tracing As contaminated groundwater back to its source, they show that As release is associated with recharge from ponds and wetlands during vertical flow through near surface (< 10 m), river derived sediments. Arsenic is then transported along horizontal flow lines in the aquifer, over hundreds of years, back to the Mekong and Basaac Rivers (Polizzotto et al., 2008). These studies support the requirement for a near surface source of OM to drive reductive processes, which has also been suggested to be driving As release processes in neighbouring Vietnam (BERG et al., 2008; EICHE et al., 2008). This also demonstrates, through the clear contribution of a hydrologic influence to As mobility at this site, the vulnerability of locations that have yet to be affected by massive groundwater abstraction to future changes in the groundwater As hazard. Understanding how As concentrations evolve during transport is therefore of
paramount to providing an improved understanding of the spatial heterogeneity of As concentrations in these groundwater systems and how it will evolve with time.

### 2.6.2 Temporal variability in dissolved arsenic concentrations

In addition to the spatial variability of As which appears to be controlled by surface morphology, biogeochemical release and hydrologic transport processes, temporal variability also appears to be at least partly driven by variations in the timing of aquifer recharge. The study of Polizzotto et al. (2008) report peaks in As concentrations during recharge to the aquifer under periods of strong downward flow at the end of the dry season, with associated low concentrations during the period of river water ingress during the rainy season. Such seasonal variations have also been reported in previous studies (Berg et al., 2001). These seasonal variations however, whilst interesting, are of little interest to policy makers. Of far greater significance is answering the question of whether current As concentrations will change over the coming years, and just as importantly, at what rate. This however remains an area of intense debate and controversy amongst researchers and policy makers in South and South East Asia but is of huge significance when considering mitigation options over both the short and long timescales.

It is not know whether or not the aquifers of the region were contaminated with As prior to increased anthropogenic activity such as the installation of tubewells or excavation of ponds and clay pits. However, evidence from minimally disturbed regions such as Cambodia suggests this is likely to be the case. In the absence of any long term data set following the installation of the tubewells, no temporal trends in arsenic concentrations can be determined. However, in spite of the paucity of monitoring data attempts were made to indirectly infer temporal changes in arsenic concentration by using the age of wells. A study of 6000 tube wells in Bangladesh showed a statistically significant increase in As concentration with well age. A pooled estimate of the increase in As concentration over different well depth ranges determined an increase of $16 \pm 2 \mu g/l$ in well As per decade of well age (Van Geen et al., 2003d). Following this, a study by McArthur et al (2004), using the dataset of DPHE/MMI/BGS (1999), used a similar approach to demonstrate that the proportion of wells which fall above various threshold values for As increase over the first ten year period. After this period the data becomes more scattered making it difficult to draw reliable conclusions, and the observation of low As in relatively young wells may reflect more informed drilling strategies. More direct evidence is provided in the study of Stute et al (2007), who successfully quantified...
a systematic increase in arsenic concentrations of 22 μg/l/yr from a set of 29 monitoring and private tubewells.

To date, however, only two studies report time series data to robustly assess the temporal change in As concentration in any given well. Cheng et al. (2005) showed that, over a 3 year period of monitoring, only one of the 20 tubewells monitored displayed an increase in As concentration from 50 – 70 μg/l. The authors suggest that this demonstrates that groundwater As concentrations typically do not vary over time. However, it has been suggested that the duration that these measurements were taken over is insufficient to draw such conclusions (RAVENSCroFT et al., 2006; SENGUPTA et al., 2006). The study of Dhar et al (2008) report similarly inconclusive results for time series data from 37 monitoring wells over a 2-3 year period. In this study, most wells showed very little variation over the monitoring period. However, 6 wells displayed systematic decreases, with a maximum decrease of 41 μg/l/yr reported at a depth of 11 m from a well containing more than 200 μg/l As, and two wells reported increases over the monitoring period of 14 – 19 μg/l/yr. These studies serve to highlight the fact that, as yet, no study has demonstrated that As concentrations continue to rise over timescales of more than tens of years, and that static studies conducted over a few years are not sufficient to identify any significant change in As concentrations. Moreover, these studies do not adequately account for the current concentrations present in these groundwaters. The potential role of anthropogenic activities in accelerating As release is of particular importance when considering how current As concentrations may change. Future research should be targeted at providing the time series monitoring of As concentrations in groundwaters over decadal timescales, both at locations where massive abstraction is currently taking place, potentially resulting in enhanced As release (i.e. West Bengal and Bangladesh), and at locations that are currently unaffected by human interference (i.e. Cambodia and Vietnam) (POLYA and CHARLET, 2009). Understanding what conditions control As mobility from its initial release to groundwater to its accumulation to concentrations of 100’s μg/l over millennial timescales is crucial when attempting to predict how areas currently not at risk from As contamination may evolve in the future, as well as predicting secular changes in those areas that are already affected.

2.7. Conclusions

It has been more than twenty years since the discovery of elevated As concentrations in the groundwater of the Bengal delta. During this time the large scale effects on the human population consuming excessive As in drinking water has manifested itself in numerous health
effects in the Bengal delta and elsewhere in South and South East Asia. However, in spite of massive screening campaigns and mitigation efforts, tens of millions of people remain exposed to elevated concentrations of As in groundwater. This does not mean to say, however, that progress has not been made in identifying the mechanisms involved in the generation of these As bearing aquifers or on the subsequent controls on the mobility of As in these systems.

The conditions required for As release to groundwater and the biogeochemical processes associated with its release are now well understood, and the role of the hydrological environment in generating the heterogeneous distribution of aqueous As concentrations is now beginning to be acknowledged. However, key questions remain which currently limit our ability to predict the spatial distribution and temporal evolution of the As hazard.

Of the key questions asked by National Governments and policy makers who have been tasked to remove the exposure of the human population in South and South East Asia to elevated concentrations of As in groundwater is where and when will As release occur. Prediction of the spatial distribution of As concentrations has allowed for more informed targeting of “at risk” areas for those responsible with screening and mitigation efforts. However, accurate prediction of As concentrations on a local scale requires a significant improvement in our understanding on the controls of the biogeochemical processes associated with As release. This requires knowledge of the locations associated with the supply and availability of key contributors to As release or sequestration. This must also be combined with an accurate knowledge of local groundwater flow regimes for the transport of dissolved As and its associated constituents. One species in particular has the potential to influence dissolved As concentrations more than any other – organic carbon. A greater understanding on the composition of DOC, the fluxes associated with its contribution, and the controls on its mobility in these groundwater systems is therefore central to any significant improvement in our understanding of the generation of high As groundwaters. It is this kind of stepwise improvement in our understanding of the controls on the As release process that is needed for the development of more sophisticated reactive transport models that are required to accurately predict As concentrations on the local scale.

An additional concern for policy makers is that is it is currently unclear what effect past, present or future anthropogenic disturbance will have on the As content of these groundwaters, with the potential for increases and decreases from the present As concentrations debated. Survey data and isotopic studies suggest a potential for increases in groundwater As concentrations in areas where excessive groundwater abstraction for drinking
and irrigation purposes is occurring. It has also been suggested that the aquifers in currently minimally exploited regions remain vulnerable to changes in the As hazard from human interference, with changes in land uses (from activities such as upstream damming and clay excavation which creates new sites for recharge) and groundwater abstraction practices suggested to have the potential to influence groundwater As concentrations. Given the lack of understanding of temporal trends in As concentrations and the potential for secular increases in the current As hazard, monitoring of As levels over timescales of decades is required to assess the potential for a worsening in the currently observed As hazard. The data from such monitoring schemes, which should incorporate the monitoring of areas where massive groundwater abstraction prevails and those which are relatively unexploited, can then be coupled to models which predict spatial distributions to develop a model which is capable of accurately predicting the evolution of spatial and temporal trends in As concentrations under a range of environmental conditions.

2.8. **References**


Response to comments on "Arsenic mobility and groundwater extraction in Bangladesh". Science 300, 584d.


CHAPTER 3

Use of Isotopic Tracers in Assessing Arsenic Mobilisation
3.1. Introduction

Since the still contentious suggestion that groundwater abstraction practices may play a causal role in As mobilisation in Bengali groundwaters (Harvey et al., 2002), numerous studies have cited the involvement of groundwater flow and interaction with surface waters as one of the likely controls on both the As release process and in developing the spatial heterogeneity we see today in the distribution of As in these groundwaters (Burgess et al., 2010; Kocar et al., 2008; Michael and Voss, 2008; Neumann et al., 2010). An improved knowledge of the role of the hydrological environment is therefore a central requirement in providing a stepwise improvement in our understanding of the As source, release and transport mechanisms which give rise to the generation of the high As groundwaters of South and South East Asia. Chemical and hydrological measurements alone give us indications as to the geochemical and transport processes that have taken place, although these require extrapolations and assumptions regarding aquifer properties and catchment response (as in Benner et al., 2008; Kocar et al., 2008). Isotopic measurements provide the additional information which allows for the provenancing of groundwater and sources of organic carbon implicated in As release, constraining recharge processes, resolving groundwater mixing, monitoring geochemical evolution and in providing a measure of the timescales over which these processes take place. The research presented in this thesis utilises many of the properties discussed above by combining geochemical measurements with those of the isotopic systems of oxygen (δ¹⁸O), hydrogen (δD, ³H) and carbon (δ¹³C, ¹⁴C). The background and application of each of these isotope systems in studying the role of the hydrological environment on As-bearing aquifer systems is discussed in detail below.

3.1.1 Oxygen and Hydrogen isotopes in groundwater studies

The stable isotopes of oxygen (δ¹⁸O) and hydrogen (δD) are used extensively in hydrological studies to provenance groundwaters, assess recharge processes and identify interactions and mixing between different water bodies. Indeed, several studies assessing the mechanisms responsible for As release in the groundwaters investigated in this research have utilised these isotopic systems (Aggarwal et al.,
These isotopes are ideal tracers of groundwater because they are totally conservative in solution, are directly incorporated into the water molecule and exhibit large scale variation in both space and time.

The isotopic composition of water is referred to as the permil deviation from the reference standard Vienna Standard Mean Ocean Water, VSMOW given by:

\[ \delta = \left( \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000 \]  

(3.1)

Where \( R = ^{18}\text{O}/^{16}\text{O} \) and \( ^{2}\text{H}/^{1}\text{H} \) for oxygen and hydrogen respectively.

3.1.2 Isotopic fractionation and partitioning of isotopes through the hydrological cycle

The variation we see in the isotopic signature in natural waters is largely controlled by thermodynamic fractionation which occurs as a result of physical processes such as evaporation and condensation. This fractionation gives rise to water bodies with isotopically distinct fingerprints. It also produces a defined relationship between \( \delta^2\text{H} \) and \( \delta^{18}\text{O} \) in global meteoric precipitation which results from fractionation during condensation of the vapour mass which initially evaporated from ocean water and is defined by the Global Meteoric Water Line (GMWL). This relationship was defined by Craig (1961):

\[ \delta^2\text{H} = 8 \delta^{18}\text{O} + 10 \]  

(3.2)

The slope of 8 is slightly less than the isotopic composition that would be determined from condensation of water under equilibrium conditions based on the ratio of the vapour pressures of HDO and H\textsubscript{2}^{18}O (Ingraham, 1998). Dansgaard (1964) attribute this discrepancy to be due to the fact that condensation of water occurs under conditions close to (but not exactly at) equilibrium whilst evaporation occurs under conditions of nonequilibrium (sometimes referred to as kinetic fractionation). This additional kinetic
fractionation gives rise to the intercept of +10 and is largely the result of local effects of surface temperature, wind speed, salinity and most importantly, humidity, which all contribute to determining the rate of evaporation. This kinetic effect is most pronounced at lower humidities where evaporation becomes an increasingly nonequilibrium process. During this process, the residual surface water becomes enriched in the heavy isotopes as shown by the evaporation line in figure 3.1 below, and will plot below the GMWL. The slopes of water which undergo evaporation are less than 8, with slopes of 4 and 7 reported for low and high humidities respectively (GAT, 1971). Greater deviation from the GMWL along these evaporation lines reflects a greater magnitude of the kinetic effect, driven by more extensive evaporation (CRAIG AND GORDON, 1965).

The relationship between $\delta^{18}$O and $\delta$D serves as a basis for comparison for local and regional meteoric water lines which may differ from the GMWL in both the slope and deuterium intercept as a result of variations in the local climate and geographic considerations. Geographical variations in the isotopic composition of precipitation derive from one or more of four controlling factors, namely the latitude effect, the amount effect, the elevation effect, and the continental effect (DANSGAARD, 1964). The latitude effect arises from the fact that $\delta$ values for oxygen are highly temperature dependent, with increasing isotopic depletion (a shift to lighter, more negative values) observed with progressively lower temperatures, which results in increasingly negative $\delta^{18}$O values at higher latitudes (DANSGAARD, 1964). This is further compounded by the fact that polar regions are located at the end of the Rayleigh rainout process (which is discussed below), which accentuates this effect in the observed $\delta^{18}$O gradient. The amount effect follows a Rayleigh type distillation processes whereby the process of condensation preferentially distils the heavy isotopes from the vapour in to the water phase. As this process continues towards completion, both the water and vapour phases become isotopically depleted with respect to the initial isotopic composition of each phase. The elevation effect, like the latitude effect, arises as a result of the temperature dependence of the isotopic composition of rainfall. Areas of higher elevation force vapour masses to rise and the cooling of the vapour mass by expansion results in orographic precipitation. Precipitation that falls at higher altitudes, where average temperatures are typically cooler, will therefore have a depleted isotopic
signature relative to that which falls at lower altitudes. The continental effect combines the elevation and latitude effects discussed above and is driven by the extreme changes in temperature and topography that are characteristic of large land masses which force rainout from vapour masses. This continental effect is characterised by enriched coastal precipitation and depleted inner continental precipitation (CLARK AND FRITZ, 2000).

In addition to the effects discussed above, temporal variations in the isotopic composition of rainfall have also been reported (INGRAHAM, 1998). In the tropical regions investigated in this research, this temporal variability is apparent from the isotopic depletion which correlates well with the amount of precipitation (ARAGUAS-ARAGUAS ET AL., 2000). The movement of moist air masses, driven by changes in the position of the Intertropical Convergence Zone (ITCZ), results in the onset of the rainy season at set locations and large seasonal variability in the isotopic composition of precipitation. Araguas-Araguas et al (1998) report large scale spatial and temporal variability in the isotopic composition of precipitation in South East Asia which arises from a change in the source of the moisture-producing precipitation over the course of the year. Given these local and temporal variations, any hydrological study should aim to establish a local meteoric water line (LMWL) so comparisons can be made between the isotopic composition of surface waters and groundwater.
Figure 3.1. The relationship between the isotopic compositions of meteoric water, the residual water following evaporation and the vapour phase. The isotopic composition of surface water and atmospheric vapour is defined by the GMWL. The relatively light (isotopically depleted) vapour phase leaves the surface water and the evolution of its isotopic composition is given by the white arrow. The evolution of the isotopic composition of the residual water is given by the evaporation line (black arrow), with increased deviation from the GMWL as a result of more extensive evaporation. This figure was taken and adapted from figure 3.3 in Gat et al (2001). The standard SMOW is presented for reference.

The slope of any given LMWL is controlled by the deuterium excess value, which itself is a function of local conditions related to relative humidity or mixing of differently sourced vapour masses. In the tropical locations typical of the focus of this research, the slope of the LMWL may differ substantially from the GMWL as a result of changes in atmospheric circulation that brings precipitation to the site from two or more different sources that may differ in their isotopic composition and deuterium excess (ARAGUAS-ARAGUAS ET AL., 2000). The deuterium excess, \( d \), for global precipitation was proposed by Daansgard (1964) and is defined for a slope of 8 (and as such is not the same as the deuterium intercept), given by:

\[
d = \delta^2H - 8 \delta^{18}O
\]  

(3.3)
Figure 3.2 below shows the relationship between humidity and $d$ for precipitation. When humidity is low (50 %) the $d$ value is 28.7 ‰. Only at humidities close to 85 % does the $d$ value approach the 10 ‰ observed in the GMWL. Values lower than 10 ‰ may occur as a result of secondary evaporation processes where evaporation takes place after precipitation.

![Figure 3.2. Deuterium excess in precipitation, $d$, which arises from kinetic fractionation at the ocean surface as a function of humidity. Plot based on data in table 1 in Merlivat and Jouzel (1979).](image)

The processes discussed above determine the isotopic composition of precipitation and the evolution of the isotopic composition of surface waters. Both of these water sources may contribute to recharge to groundwater in an aquifer system. Isotope exchange of groundwater with aquifer minerals is assumed to be negligible in these low temperature systems (CLARK AND FRITZ, 2000). For many groundwaters, their isotopic composition will closely resemble that of the mean annual weighted composition of precipitation. In some aquifer systems, recharge from river water is a critical component of recharge, particularly in areas where large scale abstraction of
groundwater is prevalent (Clark and Fritz, 2000). In such instances, the isotopic composition of the river may differ substantially from that of the local precipitation because the water is derived from precipitation at much higher altitudes and as such will isotopically depleted with respect to local precipitation, whilst in arid climates they may be enriched through evaporation (Gonfiantini et al., 1998). In some systems important deviations from the isotopic signature of precipitation may be found in groundwater that are indicative of recharge from surface waters, and this can be used to estimate the relative contribution to recharge from these sources (Krabbenhof et al., 1990). Such small scale variations in the isotopic composition of groundwater are hugely important for groundwater provenance and in identifying the mechanisms of recharge in studies such as the research presented in this thesis.

In groundwater systems where more than one aquifer is present (such as in the multiple aquifer systems of Bengali groundwaters), mixing between different groundwaters should be considered. Deeper groundwaters may have recharged in climatic conditions that are different to that which prevail today. The temperature dependence of the isotopic composition in precipitation under different climates is preserved following recharge in to the groundwater. Older groundwater, such as that which recharged in the Pleistocene in a cooler climate than that of todays (Stute and Deak, 1989), should therefore have an isotopic composition which is more depleted in δD and δ18O relative to groundwater which has recharged in the warmer Holocene period. In a groundwater system such as that of the Bengali aquifer system, deeper groundwater is thought to have recharged maybe several hundreds of kilometres from the location of abstraction, with shallow groundwater thought to recharge much more locally (Burgess et al., 2010; Michael and Voss, 2009; Michael and Voss, 2008). Given that these groundwaters have recharged at different locations, and possibly under different temperature regimes, it should be expected that these groundwaters would have a different isotopic composition. Isotopic techniques, coupled with other chemical measurements such as Cl or electrical conductivity, can be used to identify the presence of different groundwater bodies. In addition, the conservative nature of these isotopes means that mixing ratios are preserved in the isotopic signature of the water body. We can therefore identify and potentially quantify any mixing of these groundwater bodies.
In the case of the field sites investigated in this research, studies have shown that changes in the origin of groundwater recharge occur on a seasonal basis. At the field site in Cambodia, groundwater has been shown to discharge to the Mekong River during the dry season (so recharge must be dominantly from the surface from either surface waters or precipitation), whilst the River Mekong recharges the groundwater following an inversion in the direction of groundwater flow in the rainy season (BENNER ET AL., 2008). Given the seasonally controlled recharge from surface waters (which is inclusive of precipitation, pond and wetland derived recharge); the precipitation based recharge component will not represent the weighted mean annual composition of precipitation discussed above. Precipitation based recharge is more likely to represent the weighted mean isotopic composition of precipitation which falls in the dry season. Similarly, at the field site near Chakdaha in West Bengal, groundwater appears to be recharged, at least at some point of the year, from the River Hooghly (METRAL ET AL., 2008). A less comprehensive assessment of groundwater flow patterns has been conducted here, perhaps because of the difficulties associated with such a study given the convoluted groundwater flow paths which develop as a result of anthropogenic disturbance of the groundwater flow regime through groundwater abstraction. These temporal variations in the sources of recharge, each of which may have a distinct but temporally evolving isotopic composition as discussed above, coupled to the spatial variation in local sources of recharge contribute to the development of a complex evolution of the isotopic composition of groundwater at these sites. This may be additionally complicated by different modes of recharge, with evaporative enrichment during recharge through clay (distributed recharge) contributing to groundwater which may also receive recharge through rapid transport from preferential flow paths that maintained the isotopic composition of the recharging water (localised recharge) (MATHIEU AND BARIAC, 1996).

3.2. **Carbon isotopes in groundwater studies**

The mobilisation of As in to the groundwaters of South and South East Asia is driven by the consumption of organic matter (OM). In spite of the wealth of knowledge on the processes and mechanisms involved in the As release process, the source(s) of OM
critically implicated in these biogeochemical processes has still not yet been constrained. In addition to this, the role of groundwater transport in generating the spatial distribution of As in these groundwater systems is only just beginning to be recognised. An improved understanding of both of these factors requires knowledge of the controls on the biogeochemical processes that occur along different flow paths following recharge and the rate at which groundwater flows along these paths. It also requires isolating and resolving the contribution of any additional interaction between groundwater and surface waters along the flow path. The chemistry and isotopes (both δ¹³C and ¹⁴C) provide a key tool set with which it is possible to trace the origin, transport and fate of OM in groundwater as well as assess the role of the groundwater flow regime in distributing both As and the dissolved constituents that contribute to its release or sequestration.

3.2.1 Carbon isotopes

There are three isotopes of carbon that are useful tracers of the physical and geochemical processes that drive and govern As mobilisation and its spatial distribution. Stable ¹²C is by far the most abundant, constituting 98.89% of all carbon, with stable ¹³C contributing 1.11% (WANG ET AL., 1998). Radioactive ¹⁴C is the third isotope of carbon and has a half life of 5730 years, with a natural abundance in the atmosphere of roughly 1 atom per 10¹² atoms of ¹²C.

The ¹³C/¹²C ratio, like the isotopes of oxygen and hydrogen, is expressed as the difference in permil from a standard, the PeeDee Belemnite (PDB), a Cretaceous mollusc, where:

\[
\delta^{13}C (\text{‰}) = \frac{([^{13}C/^{12}C]_{\text{sample}} - [^{13}C/^{12}C]_{\text{PDB}})}{[^{13}C/^{12}C]_{\text{PDB}}} \times 1000 \quad (3.4)
\]

Soil organic matter has been shown to have a δ¹³C signature comparable to that of the source plant material (FRANCE-LANORD AND DERRY, 1994; SCHWARTZ ET AL., 1986). Plants are generally divided into three categories according to their specific photosynthetic pathway; C₃ plants, C₄ plants and Crassulacean Acid Metabolism (CAM) plants. C₃ plants include all trees, most shrubs and cool season grasses, and use the Calvin photosynthetic pathway. This group have δ¹³C values which range from -20‰ to -35‰.
and often dominate in tropical forests (CLARK AND FRITZ, 2000). C₄ plants include warm season grasses and shrubs which are more prevalent in low latitude and altitude environments with summer monsoonal rainfall, and these use the Hatch-Slack photosynthetic pathway. This group of plants have δ¹³C values between -9‰ to -17‰ and have been shown to be the dominant form of vegetation in hot ecosystems and grasslands (EHLERINGER ET AL., 1991). CAM plants can use both C₃ and C₄ photosynthetic pathways but are only present in significant numbers in desert ecosystems. These have a δ¹³C range of approximately -18‰ to -30‰ (WANG ET AL., 1998).

¹⁴C is a cosmogenic nuclide formed in the atmosphere naturally through nuclear spallation reactions following the bombardment of nitrogen atoms with neutrons:

\[
^{14}N + \text{n} \rightarrow ^{14}C + \text{p}
\]  

(3.5)

The ¹⁴C produced is incorporated in to carbon dioxide molecules following reactions with O₂. This then mixes with living biomass through photosynthesis. This photosynthetically fixed radiocarbon is then released in the soil by decay of dead biomass and root respiration. Radiocarbon in the soil can then be taken into solution as dissolved inorganic carbon (DIC) (CO₂(aq), HCO₃⁻, CO₃²⁻) or as dissolved organic carbon (DOC) at recharge. This ¹⁴C labelled DIC and DOC is then transported in the groundwater along flow paths and can be used as a measure of age. This technique is not without its complications, and interpretation of these ages first requires an assessment of the evolution of the DIC and DOC along the flow path. Contributions of both species can be made from a number of different sources, each of which may have a different but distinct isotopic signature and age.

3.2.2 Sources of carbon in groundwater

The carbon cycle in groundwaters is influenced by many geochemical reactions that combine to produce the signature that is observed in any given sample. Groundwater levels are often maintained through the recharge of meteoric waters. The DIC in these recharging waters is often at equilibrium with atmospheric CO₂, which has a δ¹³C of around -6.4‰ (CLARK AND FRITZ, 2000). The range in δ¹³C for a number of key reservoirs
of carbon is presented in figure 3.3 below. The concentration and isotopic signature of
the DIC then evolves following subsequent organic and inorganic reactions in the
aquifer system. The first of these is the addition of DIC from microbially respired CO₂ in
the soil. This is generated by the aerobic decay of vegetation which has died and
accumulated within the soil, and has a δ¹³C characterstic of the vegetation from which
it derives. As such, the soil CO₂ in C₃ dominated soils is often around -23‰, whilst in C₄
dominated soils it is closer to -9‰ (CLARK AND FRITZ, 2000). Weathering reactions of
carbonate minerals in the soil and aquifer, driven by CO₂ dissolved from the soil zone,
result in further liberation of DIC to the recharging waters and a coupled change in the
δ¹³C signature of the DIC pool. Given that carbonate minerals typically have a heavy
δ¹³C signature, as evidenced by the typical δ¹³C signature of marine carbonates of 0‰,
liberation of DIC from dissolution of these minerals increases the concentration of DIC
in the groundwater and results in a shift in the δ¹³C of to more enriched values. This
chemical evolution often results in the distribution of carbonate species shifting
towards bicarbonate and the groundwater approaching equilibrium with calcite (CLARK
AND FRITZ, 2000).

In addition to the predominantly abiotic inorganic processes associated with carbonate
dissolution and precipitation discussed above, dissolved organic carbon (DOC) may
also be transported by the infiltrating water and is a critical component in the
geochemical evolution of groundwaters by providing a carbon source in microbial
respiration (ARAVENA ET AL., 2004; WASSENAAR ET AL., 1991). Indeed, the microbial
consumption of dissolved organic matter leads redox evolution which may be
accompanied by mineral dissolution and arsenic release in groundwaters. A number of
potential sources of DOC to groundwater exist. High concentrations of DOC can
develop in groundwater following incorporation of surface derived DOC during periods
of high water table, which can happen as a result of monsoonal rainfall (CLARK AND FRITZ,
2000). Conversely, DOC may derive from organic sources from within the aquifer itself.
Buried peat deposits are common in alluvial aquifers of Quaternary deposits such as
those typical in the study areas investigated in this research, and can potentially
contribute DOC to the groundwater (ARAVENA AND WASSENAAR, 1993; ARAVENA ET AL.,
1995). Another potential in-aquifer source of OM potentially contributing to the DOC
pool in groundwater is that which derives from thermally mature hydrocarbons.
Indeed, each of these sources have been suggested to be driving the As release process in South and South East Asian groundwaters (Harvey et al., 2002; McArthur et al., 2001; Rowland et al., 2006).

Figure 3.3. Variations in the $\delta^{13}C$ signature of different carbon reservoirs taken from (Mook, 2000)

Bacteria are isotopically selective (they prefer to break the weaker, light-isotope bonds) and as such the consumption of organic matter is accompanied by a defined isotopic fractionation. The consumption of organic matter may result in a further evolution in groundwater chemistry from an oxic groundwater to an anoxic groundwater when all the $O_2$ is consumed and an alternative electron acceptor is used. These redox reactions may then result in mineral dissolution and precipitation reactions, in particular the reductive dissolution of Fe(III) bearing oxyhydroxides minerals that have been implicated in the As release process. Each reservoir of DOC has a specific $\delta^{13}C_{DOC}$ as shown in figure 3.3 above and the complete oxidation of this
DOC would produce DIC with an isotopic signature equal to that of the $\delta^{13}C$ of the source DOC. Critically, this would generate DIC with an isotopic composition that is much lighter than the $\delta^{13}C_{\text{DIC}}$ produced from mineral dissolution reactions as discussed above. Given this difference, $\delta^{13}C_{\text{DIC}}$ can be used to trace the contribution and involvement of these different sources, and to determine the relative importance of mineral weathering and the oxidation of DOC to the overall DIC pool. Unfortunately, many of the different reservoirs of DOC have $\delta^{13}C_{\text{DOC}}$ that overlap ($C_3$ plants, peat and oil have a signature which overlap around $\delta^{13}C = -30\%o$). As a result, $\delta^{13}C$ alone does not allow for the direct identification of the source of OM driving these processes. However, the additional information gained from knowledge of the $^{14}C$ age of these different sources can be used in conjunction with $\delta^{13}C$ to provide an insight to the origin of the OM.

In the case of the three sources of OM implicated in the As release process, each source will have a characteristic $^{14}C$ signature which should allow for its identification in groundwater. Surface derived DOC will have $^{14}C$ activities that are close to modern levels, with the age increasing along groundwater flow paths following isolation at recharge. Buried organic carbon such as peat that may be present in Quaternary sediments is likely to have a low $^{14}C$ activity that reflects decay since the time in it was deposited. As such, any DOC derived from this material should be correspondingly older. Similarly, carbon which derives from hydrocarbons is likely to be $^{14}C$ free and so the DOC which derives from this source will also be free of $^{14}C$. The presence of this source would result in a dilution in the $^{14}C$ concentration in the groundwater and an apparent increase in the mean DOC age in the groundwater. Despite this, identifying the presence alone of these sources of OM to groundwater is not proof that they are responsible for driving As release mechanisms in these groundwaters. However, the $^{14}C$ age of DIC alongside that of DOC does provide an indication that these sources are at least being consumed in groundwater. As discussed above, DIC can be generated by the oxidation of DOC which drives some of the biogeochemical redox processes that are contributing As to solution. The DIC generated from these processes will therefore have a $^{14}C$ age equal to that of the DOC from which it is sourced. The relationship between numerous carbon sources has been used to infer origins of different carbon species and to constrain the role of transport in groundwater flow systems. Indeed, it
is because DIC was younger than DOC in Bengali groundwaters that it was proposed that it is the drawdown surface derived DOC that is generating the high As groundwaters in that region (Harvey et al., 2002).

A recent study by Clymo and Bryant (2008) showed that DOC was 500 – 1000 years younger than peat present at the same depth, whilst dissolved gases (CO₂ and CH₄) were younger still. This age profile suggests that this material is transported to this depth from above and that neither are released in substantial quantities from the peat. Similarly, Charman et al (1999) found that DOC and dissolved gasses were younger than that of the surrounding peat in a Holocene peat land in South West England at the same depth, and are inferred to be sourced from the vadose zone just below the water table. The identification of tritium in this groundwater is indicative of rapid transport from the surface and collection of these carbon sources en route to these depths. In contrast to this, the study of Aravena et al (1995) used the ¹⁴C age of DOC and CH₄ to show that CH₄ is much older than the groundwater at a site in Southern Ontario, Canada, and derives from buried peat within the Quaternary alluvial aquifer. However, sedimentary organic matter (SOM) found within the aquifer is often high refractory, insoluble and is not thought to contribute significantly to the groundwater DOC pool (Artinger et al., 1995). In general, DOC in shallow groundwaters is thought to dominantly derive from carbon sources in the upper soil zone (Aravena et al., 2004; Wasenaar et al., 1990).

3.2.3 Dating of older groundwaters using ¹⁴C

As well as providing an indication of the source of OM implicated in biogeochemical processes, ¹⁴C also provides a quantitative measure of groundwater age. The dating of older groundwaters should first involve an assessment that they are tritium free and hence have no contribution of modern (< 50 years) recharge, see later section in this chapter for a thorough review of this technique. ¹⁴C dating of groundwaters is by far the most routine, but indirect, dating technique applied to the assessment of groundwater age and both DIC and DOC can be measured to date groundwaters up to 30,000 yrs old (Clark and Fritz, 2000). A thorough description of this technique and the methods of calculating modelled ages are given in chapter 5.
3.3. **Tritium in groundwater studies**

Tritium is perhaps the most commonly used radioisotope used to date modern groundwaters, defined as groundwaters that are recharged within the past 60 years (CLARK AND FRITZ, 2000). Tritium is a short lived isotope of hydrogen with a half life of 12.43 years (LUCAS AND UNTERWEGER, 2000) and is incorporated into the water molecule. As such, it is the only radioisotope that directly dates the groundwater. Furthermore, whilst important in itself in determining the apparent residence time of the groundwater, data from $^3$H-$^3$He dating can also be used for other purposes. A number of studies have used vertical $^3$H-$^3$He to determine hydraulic conductivities (POREDA ET AL., 1988) and groundwater recharge rates (SCHLOSSER ET AL., 1989; SOLOMON ET AL., 1993; SOLOMON AND SUDICKY, 1991). Like $^{14}$C, tritium is produced naturally in the atmosphere by the bombardment of nitrogen atoms by neutrons in cosmic radiation. However, by far the greatest production of tritium released to the atmosphere was as a result of atmospheric testing of thermonuclear bombs during the 1950s and 60s, which resulted in increases in the stratospheric content of tritium of several orders of magnitude (CLARK AND FRITZ, 2000). The test stop treaty in 1963 prevented further atmospheric bomb testing and as such the “bomb peak” observed in groundwaters throughout the world serves as a time marker for use in dating groundwaters (EKWURZEL ET AL., 1994). The levels in the atmosphere have since been flushed out and tritium levels in precipitation are now close to natural levels (CLARK AND FRITZ, 2000).

Tritium concentrations are typically given in terms of tritium units (TU), where 1 TU is equal to 1 $^3$H atom per $10^{18}$ $^1$H atoms. Pre-bomb levels of tritium in precipitation were very low and have been shown to have varied between 3.4 to 15 TU (BROWN, 1961; KAUFFMAN AND LIBBY, 1954). The natural production of tritium varies with respect to geomagnetic latitude, with high concentrations associated with precipitation in higher latitudes. Groundwaters recharged before the onset of atmospheric bomb testing in 1951 can be identified in groundwater as now having concentrations close to the level of detection (approximately 1 TU). Similarly, when groundwater tritium concentrations are high (in excess of approximately 30 TU), thermonuclear bomb $^3$H is present, and suggests recharge during the 1960’s (CLARK AND FRITZ, 2000).
Quantitative estimates of groundwater ages can be determined by the decay of tritium assuming that the tritium input into a groundwater is known and that the measured tritium in a groundwater sample is the result of decay alone, and not influenced by mixing processes or hydrodynamic dispersion. In such a scenario, the age can be calculated from:

\[ t = -17.93 \ln \left( \frac{a_t}{a_o} \right) \]  

(3.6)

Where \( t \) is equal to the estimated age of the groundwater, \( a_t \) is equal to the residual tritium activity of the sample, and \( a_o \) is the initial tritium activity (Clark and Fritz, 2000). The recharge age is then determined by back extrapolation along a decay line from the measured \(^3\text{H}\) concentration to the point at which it intersects the precipitation curve for a given year when infiltration took place. However, the small scale temporal and spatial variability of tritium concentrations in precipitation means that it is often difficult to determine the initial \(^3\text{H}\) for the time of recharge.

A more accurate estimate of the groundwater age can be obtained by accounting for the fact that groundwater at any point is likely to be the product of several years of precipitation which have recharged into the groundwater and have mixed in the unsaturated zone. On entering the saturated or confined zone, this tritium concentration can then decrease by decay. In this case, a multi-year input function should be used to determine the initial \(^3\text{H}\) concentration and can be calculated as the weighted contribution of \(^3\text{H}\) from each year after correcting for the decay of that particular years precipitation contribution during the time it takes to pass through the unsaturated zone. This model assumes that all groundwater along a flow line is made up of equal contributions of precipitation sourced from different years, with the weighting of each year of precipitation following a normal distribution which places the greatest weight on the precipitation from the central years (ie, in a 3 year recharge model, 25 % will be contributed by both the 1\(^{st}\) and 3\(^{rd}\) years, with 50 % contributed from the 2\(^{nd}\) year).
The combined measurement of $^3$H and $^3$He allows quantification of the time since the water was isolated from contact with the atmosphere, and hence the true age of the groundwater (SCHLOSSER ET AL., 1988). $^3$He is produced from the $\beta$-decay of $^3$H in natural waters and so this technique does not require knowledge of the input of tritium through precipitation. However, this technique can only be used when there is a barrier preventing $^3$He$_{tr}$ from escaping into the atmosphere. Under such conditions, such as in groundwaters which undergo recharge but are then isolated from the atmosphere just under the water table, $^3$He can no longer escape (SCHLOSSER ET AL., 1989). As a result, the $^3$He$_{tr}/^3$H ratio increases with time and the $^3$H-$^3$He technique can be used. The apparent water age, $t$, so called because it may have resulted from the mixing of two waters containing different compositions, is obtained from the law of radioactive decay as proposed by Tolstikhin and Kamenskiy (1969) by:

$$
\tau = \frac{1}{\lambda} \cdot \left[ 1 + \frac{^3\text{He}_{tr}}{^3\text{H}} \right] \quad (3.7)
$$

Where $\lambda$ is the decay constant of tritium and is equal to 0.05626 (LUCAS AND UNTERWEGER, 2000). This should be converted to cm$^3$ STP g$^{-1}$ for use in the equation as $^3$He$_{tr}$ is often given in cm$^3$ STP g$^{-1}$. For this 1 cm$^3$ STP g$^{-1} = 4.019 \times 10^{14}$ TU. Other sources of $^3$He, such as excess air and radiogenic production from the decay of U/Th-series elements, must be accounted for and the $^3$He$_{tr}$ concentration determined for this technique to give accurate results. Additions of $^3$He from excess air derives from the fact that He is often present in groundwater at concentrations which exceed solubility equilibrium due to the inclusion of small air bubbles in the groundwater which form during the recharge process (HEATON AND VOGEL, 1981). These additions sources can be accounted for by measuring the concentrations of $^4$He and other noble gases (SCHLOSSER ET AL., 1989; TORGERSEN ET AL., 1977; WEISE AND MOSER, 1987). Furthermore, a certain fraction of $^3$He$_{tr}$ may also be lost by diffusion across the water table, giving rise to ages that are too low (SCHLOSSER ET AL., 1988). Schlosser et al (1988) proposed two different methods to estimate diffusive loss of $^3$He$_{tr}$ across the groundwater table. The first of these compares the total inventories of tritium and ($^3$H + $^3$He) in the groundwater with that of the total tritium if it were a stable isotope. For this the tritium supply function (ST) is required. Deviation of the ratio from 1 is a measure of He loss. The second of these methods uses a numerical
simulation based on the observed peaks of $^3$H and $^3$He. A vertical advection and dispersion value are chosen to fit the bomb tritium peak and the $^3$He loss can then be estimated.

The age resolution of this $^3$H/$^3$He method is dependent on the measurement precision of the $^3$He/$^4$He ratio (SCHLOSSER AND WINCKLER, 2002). For a precision of ±0.2%, age resolution is given in figure 3.4 below. From this it can be seen that for waters with a tritium concentration of 20 TU the resolution is of the order of about 10 days.

This study combines the many applications of the isotope systems of oxygen, hydrogen and carbon discussed above alongside geochemical measurements to robustly assess the role of the hydrological environment on groundwater As concentrations on two model As bearing systems in South and South East Asia with different degrees of anthropogenic disturbance. The multi-isotope approach to the assessment of a groundwater system as conducted in this research allows for a comprehensive and systematic review of the numerous physical and biogeochemical processes operating in these groundwaters and how they contribute to the As release process, and in generating the distribution in As concentrations observed in these aquifer systems. In particular, they will allow for the identification of ground-surface water interactions, elucidation and characterisation of the OM implicated in biogeochemical processes, and in determining groundwater flow rates and rates of As release. This latter point is particularly important for the robust assessment of the role of groundwater abstraction practices on As concentrations in the aquifer systems of this region.
Figure 3.4. The time resolution of the $^3$H/$^3$He method as a function of the tritium concentration based on a typical measurement precision of 0.2% for $^3$He. Based on the figure presented in Schlosser and Winckler (2002).

3.4. References


CHAPTER 4

Analytical Procedures and Experimental Techniques
4.1. Field collection techniques

The field sites investigated in this study are known arsenic (As) hotspots in the Chakdaha block of the Nadia district, West Bengal, India and the Kien Svey region of the Kandal Province, Cambodia. Arsenic concentrations have been reported to range from $<1 - 1340 \mu g/l$ for the Cambodian study site (BUSCHMANN et al., 2007; KOCAR et al., 2008; POLIZZOTTO et al., 2008; POLYA et al., 2005; ROWLAND et al., 2008), whilst As concentrations of $<1 - 562 \mu g/l$ have been reported for the study site in West Bengal (CHARLET et al., 2003; CHARLET et al., 2007; CHATTERJEE et al., 2003; GAULT et al., 2005; LAWSON et al., 2008; NATH et al., 2005; NATH et al., 2008).

Sample collection at West Bengal was undertaken in January 2008. During this period groundwater samples were collected from monitoring piezometers and private tubewells with the use of a MP1 submersible pump (Grundfos) at a discharge rate of approximately 12 litres/minute. Sampling locations were chosen on site to provide a wide range of depths and spatial distribution across the study site. Sample collection in Cambodia was undertaken in April 2009. Groundwater samples were collected from monitoring piezometers with the use of a MP1 submersible pump (Grundfos) for piezometers with a 2.5” internal diameter and discharged at a rate of approximately 12 litres/minute. For piezometers with an internal diameter less than 2.5” a Geopump II peristaltic pump (Geotech Environmental Equipment, Inc) was used to discharge water at a rate of approximately 1 litre/minute. Sample locations were chosen to provide a range of depths over a 3 km transect that is thought to be representative of the groundwater flow direction at this site from the internal wetland basin to the River Mekong (BENNER et al., 2008). At both sites piezometers and tubewells were purged for a minimum of one well volume, with measurements of temperature, pH, Eh and electrical conductivity taken at short intervals until the discharging waters stabilised, at which point measurements were recorded and samples were collected.

Groundwater samples were collected, treated and stored depending on the intended analysis. Samples for major and trace cation and dissolved organic carbon (DOC) analysis were filtered through 0.45 µm cellulose nitrate filters in to 100 ml acid washed glass schott bottles, acidified to pH < 2 using trace element grade HNO₃, and stored at 4°C prior to shipping and analysis. Samples for anion analysis were filtered and stored as above but not acidified. Water samples for stable isotope ($\delta^{18}O$ and $\delta^D$) analysis were collected in 60 ml amber glass bottles with polyeal caps and stored at 4°C. Samples of accumulated monthly rain water for stable isotope analysis were stored in 1 L amber glass bottles with polyeal caps and stored at 4°C. Water samples for $\delta^{13}C$ and $^{14}C$ of dissolved inorganic carbon (DIC) were collected in 500 ml amber
glass bottles and stored at 4°C, while samples for $\delta^{13}$C and $^{14}$C analysis of DOC were collected in 1 L and 2.5 L amber glass bottles respectively and stored at 4°C. Water samples for tritium analysis were collected in 1 L argon filled amber glass bottles and stored with a 4 cm argon head.

4.2. Analytical procedures

4.2.1 Aqueous chemistry analysis

Arsenic and other trace elements were measured using a Plasmaquad 2 inductively coupled plasma – mass spectrometer (ICP-MS, VG Elemental) with a detection limit of < 1 µg/l. Major element concentrations of the water samples were determined by inductively coupled plasma – atomic emission spectroscopy (ICP-AES, Horizon, Fisons). Quality control standards were used throughout the course of analysis to monitor analytical performance. External calibration standards were used to prepare standard calibration curves from which measured concentrations can be corrected for deviation from using weighted ordinary least squares linear regression, with analytical errors calculated using the methods of Miller and Miller (2005). Anion analysis of water samples for Cl$, Br^-$, NO$_2^-$, NO$_3^-$, PO$_4^{3-}$ and SO$_4^{2-}$ was conducted using a Metrohm 761 compact Ion Chromatograph with a Dionex AS9 high capacity column and AG9 high capacity guard column using a flow rate of 1.4 mL/min and a mobile phase of 9mM Na$_2$CO$_3$. NH$_4^+$ was measured using a Camspec M501 uv-vis spectrophotometer following the addition of 0.2mL of Nesslers reagent to 1mL of sample, which is left to react for 10 minutes before analysis. Bicarbonate alkalinity was measured by alkalinity titration with 0.025M HCl. Samples for DOC determination were initially sparged with N$_2$ before analysis on a Shimadzu 5050A TOC analyser.

4.2.2 Stable isotope analysis

Stable isotope analysis was performed at the Isotope Community Support Facility, East Kilbride, Scotland. For $\delta$D determinations, sample and standard waters were directly injected into an on-line chromium furnace at 800°C, with the evolved H$_2$ gas subsequently analysed on a VG 602D (VG Elemental) mass spectrometer with a manual Hg, high gas compression inlet system (DONNELLY et al., 2001). Replicate analyses of water standards (international standards V-SMOW and GISP, and internal standard Lt Std) gave a reproducibility of ±2‰. For $\delta^{18}$O determinations, 200 µl of water sample is transferred into a 10ml exetainer® using an
adjustable pipette with disposable pipette tips. The exetainers® are then placed into the auto-
sampler tray of a Finnegan Delta V mass spectrometer, which is set at 25°C. Each sample is
then over-gassed with a 0.5% CO₂-in-He mixture for 5 minutes and left to equilibrate for a
further 24hrs before mass spectrometric analysis. Oxygen isotopic data were then produced
using the method established by Nelson (2000). Data are reported as permil variations from
the V-SMOW standard. During the analyses of these samples the following standard data
accuracy and precision were obtained for three SUERC internal standards: DSW(2) = -0.3 ±
0.1‰; DW2(2) = -7.4 ± 0.1‰; EKS(2) = -13.1 ± 0.2‰. Accepted values for these standards, as
calibrated by international standards GISP (-24.8‰), V-SMOW (0‰) and SLAP (-55‰), are -0.3,
-7.4 and -12.9‰ respectively. Stable carbon isotopes ratios of total dissolved inorganic carbon
(DIC) were determined after a modified approach of Atekwana and Krishnamurthy (2004).
Water was sampled in triplicate, preserved with 240 µL formaldehyde to inhibit microbial
activity, filled to the top, sealed with parafilm, and stored upside down in the absence of light
at 4°C until analysis. For analysis, 6 mL of sample was transferred via syringe fittings into
helium-purged exetainers. About 200 µL of hot de-aerated concentrated phosphoric acid was
added. After equilibration (~48 h) carbon isotopes were analysed on a Prism3 (Fisons
Instruments) calibrated with marble standards (MAB2, medium marble 85/160, δ¹³C = 2.48‰),
internal sodium bicarbonate (δ¹³C = -4.67‰) and calcium carbonate (δ¹³C = -24.23‰). The
international standards IAEA CO-1 (calcite, δ¹³C = 2.48‰, σ 0.025‰), and NBS 18 (calcite, δ¹³C
= -5.029‰, σ 0.049‰), IAEA CO-8 (δ¹³C = -5.749‰, σ 0.063‰) and IAEA CO-9 (barium
carbonate, δ¹³C = -47.119‰, σ 0.149‰) were used to calibrate the mass spectrometer and
check for accuracy on a monthly basis. By international convention δ¹³C values are expressed
relative to a defined standard Vienna-Pee Dee Belemnite (V-PDB) (COPLEN, 1994).

4.2.3 Carbon – 14 analysis

Samples for carbon-14 measurements of dissolved inorganic carbon (DIC) were stored at 4°C in
a nitrogen atmosphere prior to filtration using 0.45µm PTFE filters. This filtrate was
transferred, minimising exposure to air, to a hydrolysis vessel. CO₂ was recovered from
measured aliquots of groundwater by hydrolysis with H₃PO₄ and purging with nitrogen gas.
The CO₂ was converted to graphite by Fe/Zn reduction and its ¹⁴C/¹³C ratio measured on a
accelerator mass spectrometer (AMS). Samples for carbon-14 DOC determination were also
stored at 4°C prior to filtration in a nitrogen atmosphere using 0.45µm PTFE filters. This filtrate
was then acidified to pH < 4 using 2M HCl, purged with N₂ for 30 minutes and buffered back to
pH = 7 using 1M KOH. These samples were then rotary evaporated from 2.5L to approx 15ml.
The sample was then freeze dried. The total carbon in a known weight of the dried material was recovered as CO₂ by heating with CuO in a sealed quartz tube. The CO₂ was converted to graphite by Fe/Zn reduction and its ¹⁴C/¹³C ratio measured by AMS on either a SMV tandem accelerator mass spectrometer or 250kV single stage accelerator mass spectrometer (both machines by National Electrostatics Corporation, NEC, Wisconsin, US). Stable carbon isotope ratios were measured on sub-samples of CO₂ using a dual-inlet mass spectrometer with a multiple ion beam collection facility (VG OPTIMA). The mass spectrometer was calibrated with international reference materials to a precision of ± 0.1 ‰ for repeat analysis of bottled CO₂.

4.2.4 Tritium analysis

Determination of the tritium content of groundwater samples was achieved using the ³He-ingrowth technique developed by Clarke et al (1976), with measurements of ³He and ⁴He made on a MAP 215 Noble Gas Mass Spectrometer (Mass Analyser Products). Approximately 500 g of the tritium sample is transferred from sample bottles into pre-weighed, one-litre metal canisters. The sample vessel is kept under an argon blanket so that the remaining sample can be re-sealed for further analysis if necessary (see figure 4.1). After sample introduction to the steel canister, a flow-restricting valve is closed and the headspace pumped with a rotary roughing pump through a liquid nitrogen water trap for 5 minutes. The degassed sample is then isolated and shaken for 30 minutes to enhance gas transfer across the water/headscape interface. The pump/shake cycle is then repeated, switching pumping from the rotary pump to a diffusion pump when the pressure surges are low enough. When the pressure is low enough (less than 1x10⁻⁷ Torr) the canister is isolated from the manifold line by locking the stainless steel clamps. The degassed sample is then stored for a minimum of 6 months to allow ingrowth of ³He.

Following this storage period the sample is then analysed by attaching the sample to a second extraction line as shown in figure 4.2. All of the components of this line are made from stainless steel and the line is held at a pressure of less than 1 x 10⁻³ Torr through a series of diffusion pumps. Sample processing is automated and controlled by a PC which opens and closes pneumatic valves operated by solenoid valves through solid state relays, allowing the sample to pass through the extraction line. Once in the line, the extracted gases are passed over three getters to be dried and cleaned of reactive species such as H₂O, N₂, O₂, CH₄ and CO₂. The sample is then allowed to pass over two series of cryostatic cold traps, the second of which, the low temperature cryotrap (LTCT) is held at a temperature of 16 K and sufficient to
trap He (LOTT and JENKINS, 1984). The line in this low temperature cryotrap, along with the magnetic sector and quadrupole mass spectrometers is held at ultra high vacuum using ion pumps. The LTCT is isolated from the line and heated to 40K to release He for analysis. An aliquot of gas released from the LTCT is introduced into the quadrupole mass spectrometer. If the sample is of a suitable size, the remaining He is then expanded into the MAP 215 noble gas mass spectrometer for helium isotope analysis. $^3$He is measured on an electron multiplier while the more abundant $^4$He is measured on a Faraday cup. Calibration is performed between each sample run using aliquots of an air standard. Sample reproducibility was found to be within 2.5% based on duplicate analysis.

Figure 4.1. Schematic diagram of the Manchester Tritium degassing line.

System line blanks were measured throughout the period of analysis to check that there were no leaks in the UHV line and to ensure there is no residual sample remaining prior to the next
sample processing. Manifold line blanks were measured at the start of each day before any samples were run. This was to ensure that the samples have been properly connected to the extraction line, and that there were no leaks at the sample inlet. Manifold line blanks for the period of analysis were less than $4.6 \times 10^{-16}$ cm$^3$STP/cm$^3$ for $^3$He, and less than $1.9 \times 10^{-9}$ cm$^3$STP/cm$^3$ for $^4$He. These represent approximately 0.91% and 78% of typical sample sizes for $^3$He and $^4$He respectively. As discussed above, samples were run against air standards that are processed in an identical way to that of the samples. Air standards were collected from Manchester Airport in stainless steel tanks that are fitted with Nupro valves. The atmospheric abundance of He in dry air is assumed to be $5.24 \times 10^{-6}$ cm$^3$STP/cm$^3$ (Porcelli et al., 2002), which is used to calculate the amount of $^3$He and $^4$He in the standard tanks. The size of each gas will decrease over time as a function of the number of aliquots of standard that are removed from the tank. Knowledge of the size of each air standard is important for calculation of the concentration of He in each sample. This can be determined by equation 4.1 given in Postlethwaite (2002) below. This calculation gave $^3$He and $^4$He abundances of $9.15 \times 10^{-15}$ cm$^3$ and $6.54 \times 10^{-9}$ cm$^3$ respectively for each aliquot volume.

Equation 4.1:

$$S_{o,g} = \frac{P - P_{H_2O}}{1013.25} \cdot \frac{273.15}{273.15 + T} \cdot \frac{V_{col}}{V_{exp}} p_g \cdot (1 - \alpha_L)^m \cdot (1 - \alpha_S)^n$$
where $P = \text{barometric pressure during standard collection} \ (\text{hPa})$, $P_{H_2O} = \text{pressure of atmospheric water vapour during standard collection} \ (\text{hPa})$, $T = \text{ambient temperature during standard collection}$, $V_{col} = \text{total volume of standard tank used to collect standard} \ (\text{equal to 27.251 cm}^3 \ \text{for the collection tank})$, $V_{exp} = \text{total volume during standard expansion} \ (\text{equal to 19776.333 cm}^3 \ \text{for this line})$, $P_g = \text{partial pressure of gas g in air at STP}$, $\alpha_L = \text{ratio of the large aliquot volume to the total volume behind the two aliquots} \ (\text{equal to 3.8 x 10}^{-5})$, $\alpha_S = \text{ratio of the small aliquot volume to the total volume behind the two aliquots} \ (\text{equal to 3.8 x 10}^{-6})$, $m = \text{number of large aliquots removed from the air standard tank}$ and $n = \text{number of large aliquots removed from the air standard tank}$.

The measured $^3\text{He}$ and $^4\text{He}$ of air standards were used to provide an indication of machine stability and reproducibility of the calibration value from which a determination of a sample concentration is made. Figures 4.3a and 4.3b below shows that reproducibility for both $^3\text{He}$ and $^4\text{He}$ was good for a 4 day period of sample analysis, with most data lying within $1\sigma$ of the mean of both isotopes. Only one data point was outside of $2\sigma$ of the mean for $^3\text{He}$ analysis, and as such can be considered unrepresentative of the sample population. The outlier was not considered when determining standard sensitivity from which sample concentrations were calculated.
Figure 4.3. Running standard over a 4 day period of analysis during noble gas analysis for (a) $^3\text{He}$ and (b) $^4\text{He}$. The units are ions per second (ips) for $^3\text{He}$ and Volts (V) for $^4\text{He}$. The dotted lines represent the deviation (1σ) from the mean value for each isotope, which is equal to 2.63ips and 0.0039V for $^3\text{He}$ and $^4\text{He}$ respectively. The 1σ values represent a 2.1% and 8.1% relative error from the mean values of $^3\text{He}$ and $^4\text{He}$ respectively.

4.3. **Calculation of tritium concentrations**

The amount of tritogenic $^3\text{He}$ that has accumulated in the sample during storage following the degassing procedure discussed above has to be corrected for the $^3\text{He}$ present in the sample due to air contamination. With the assumption that all $^4\text{He}$ in the system is air-derived and that there is a proportional amount of associated $^3\text{He}$, the blank-corrected $^3\text{He}$ signal derived from tritium decay is derived (Eqn 4.2 below). This is converted to a sample concentration through multiplication with the $^3\text{He}$ sensitivity determined from measurement of $^3\text{He}$ in manifold line blanks and standards and knowledge of the partial pressure of the isotope in the standard (Eqn 4.3 below).
Equation 4.2:

$$3^\text{He}_{\text{tritiogenic (sample) cc}} = \frac{3^\text{He(standard) cc}}{3^\text{He(standard) ips} - 3^\text{He(blk) ips}} \cdot \left( 3^\text{He(sample) ips} - 4^\text{He(sample)}_Y \times \frac{3^\text{He(standard) ips}}{4^\text{He(standard)}_Y} \right)$$

Equation 4.3:

$$3^\text{He}_{\text{tritiogenic (sample)}} = 3^\text{He sensitivity} \times (3^\text{He(sample)} - 3^\text{He due to air contamination})$$

In these equations, $3^\text{He(standard) ips}$ and $4^\text{He(standard)}_Y$ are the mean $3^\text{He}$ and $4^\text{He}$ signals for the air standard analysed over the period of analysis, $3^\text{He(blk) ips}$ is the $3^\text{He}$ signal for the manifold line blank on the day of the analysis, and $3^\text{He(standard) cc}$ is the abundance of $3^\text{He}$ in the air standard as given above. This value of ingrown $3^\text{He}$ can then be used to determine the amount of $3^\text{H}$ present in the initial sample at the time of sealing on the extraction line (which can subsequently be corrected back to the time of sampling) by equation 4.4 below.

Equation 4.4:

$$3^\text{H} = \frac{3^\text{He}_{\text{tritiogenic}}}{(1 - e^{-\lambda t})}$$

where $t$ is the storage time of the sample, $\lambda$ is the decay constant of tritium and is equal to 0.05626 (LUCAS and UNTERWEGER, 2000). This value in cc’s can then be converted to a tritium unit (TU) concentration by equation 4.5.

Equation 4.5:

$$3^\text{H} = \frac{3^\text{H}_{cc}}{2.5 \times 10^{-15} \cdot W}$$

where $W$ is the weight of the water that has been stored in grams. This value is then subjected correction factors, namely; a drawdown efficiency correction (which accounts for drawdown of the sample to the manifold), a headspace correction (which accounts for the gases present in the water phase that are absent from the headspace), a transfer efficiency correction (which accounts for the efficiency of drawdown of $3^\text{He}$ on to the cryotrap) and a degassing correction (which accounts for fractionation of hydrogen during degassing). These have been determined experimentally in Postlethwaite (2002) and are summarised in table 5.1 below.
Degassing correction  Transfer efficiency correction  Headspace correction  Drawdown correction
0.9995 ± 0.0164  1.6132, σ = 0.0115  1.0045 ± 0.00097  0.9915, σ = 0.06%

| Table 5.1. Summary of correction values given in Postlethwaite (2002) |

4.4. **Estimation of error associated with tritium measurements**

Calculation of the error associated with the $^3$H concentrations (TU) was achieved by first calculating the error associated with each of the component parts that are used in the calculation of the $^3$He$_{tritiogenic(sample)}$ concentration as derived in the equation above and the errors associated with each of the correction factors applied. Below is a breakdown of how each component error was calculated.

Equation 4.6:

$$
\sigma ^{3}\text{He}_{air\text{ contamination}} = \sqrt{\left(\frac{\sigma ^{4}\text{He}_{std}(V)}{x^{4}\text{He}_{std}(V)}\right)^{2} + \left(\frac{\sigma ^{3}\text{He}_{std}/^{4}\text{He}_{std}}{x^{3}\text{He}_{std}/^{4}\text{He}_{std}}\right)^{2}}
$$

The error associated with the $^3$He of the sample is based on Poisson counting statistics of the $^3$He measurement, given by equation 4.7.

Equation 4.7:

$$
\sigma ^{3}\text{He}_{sample} = \left(\frac{\sqrt{N}}{T}\right)^{2} + \left(\frac{\sqrt{n}}{t}\right)^{2}
$$

where $N$ is the total number of $^3$He ions counted during the period analysis, $T$ is the length of time spent counting at the $^3$He peak, $n$ is the number of $^3$He ions counted at baseline and $t$ is the time spent measuring at the baseline.

The fractional error that derives from air contamination corrected for the error that arises from the measurement of $^3$He is therefore given by equation 4.8.

Equation 4.8:

$$
\frac{\sigma ^{3}\text{He}_{air\text{ corrected}}}{^{3}\text{He}_{air\text{ corrected}}} = \frac{\sigma ^{3}\text{He}_{sample} + \sigma ^{3}\text{He}_{air\text{ contamination}}}{^{3}\text{He}_{sample} - \left(\frac{^{4}\text{He}_{sample} \cdot ^{3}\text{He}_{std}}{^{4}\text{He}_{std}}\right)}
$$
The error associated with the stability of the $^3$He measurement, $\sigma_{^3\text{He}}$ is assumed to be 1%. The fractional error associated with the sensitivity of the measurement, which refers to the accuracy at which the standard concentration is determined, is then given by equation 4.9.

Equation 4.9:

$$\frac{\sigma_{^3\text{He corrected standard}}}{^3\text{He corrected standard}} = \frac{\sigma_{^3\text{He std}} + \sigma_{^3\text{He blk}}}{\sigma_{^3\text{He std}} - \sigma_{^3\text{He blk}}}$$

where $^3\text{He std}$ is given by the standard deviation of the $^3$He signal of air standard measurements divided by the mean signal of $^3$He in air standard measurements, and $^3\text{He blk}$ is given as the standard deviation of the $^3$He signal in manifold blank measurements divided by the mean signal of $^3$He in manifold blank measurements. Any measurements shown to lie outside of 2$\sigma$ of the mean signal size are not considered in these calculations.

Errors associated with transfer, degassing, headspace and drawdown inefficiencies are also considered in determination of the total error. Calculation of the errors associated with these corrections is given in equations 4.10 – 4.13 below.

Equation 4.10:

$$\frac{\sigma_{^3\text{He degassing}}}{^3\text{He degassing}} = 0.0164 \quad 0.9995$$

Equation 4.11:

$$\frac{\sigma_{^3\text{He transfer}}}{^3\text{He transfer}} = 0.0115 \quad 1.6132$$

Equation 4.12:

$$\frac{\sigma_{^3\text{He headspace}}}{^3\text{He headspace}} = 0.00097 \quad 1.0045$$

Equation 4.13:

$$\frac{\sigma_{^3\text{He drawdown}}}{^3\text{He drawdown}} = 0.06 \quad 100$$
The total fractional error associated with the $^3\text{He}_\text{tritiogenic}$ concentration can then be given by the square root of the sum of the squares of each of these different contributions given in equation 4.14 below.

Equation 4.14:

$$\sigma_{^3\text{He}_\text{tritiogenic}} = \frac{\sigma_{^3\text{He}_\text{air corrected}}}{^3\text{He}_\text{tritiogenic}} = \sqrt{\left(\frac{\sigma_{^3\text{He}_\text{air corrected}}}{^3\text{He}_\text{aco}}\right)^2 + \left(\frac{1}{100}\right)^2 + \left(\frac{\sigma_{^3\text{He}_\text{corrected standard}}}{^3\text{He}_\text{corrected standard}}\right)^2 + \ldots}$$

This can then be converted to a $^3\text{H}$ in TU by multiplying by the $^3\text{H}$ concentration in that particular sample. The total error is made up of almost 90% of corrections associated with $^3\text{He}$ measurements and air standard corrections, with only approximately 10% deriving from the corrections associated with transfer, degassing, headspace and drawdown inefficiencies.

4.5. Data quality concerns

During the course of this research, $\delta^{13}\text{C}$ measurements were made on the dissolved inorganic carbon (DIC) component in groundwater samples collected from West Bengal from two separate laboratories for 10 samples that underwent $^{14}\text{C}$ analysis; the Natural Environment Research Council (NERC) Isotope Community Support Facility and the NERC Radiocarbon Facility – Environment, both located in East Kilbride, Scotland. The data obtained from the different laboratories is different for these samples, despite them being collected at the same location at the same time. The data for these samples is presented in table 5.2 below.
Table 5.2 shows that the $\delta^{13}$C data obtained from RCF-E is consistently more enriched than the data obtained from ICSF for the same sample, with the difference between the two data sets ranging from 2.26 – 8.07‰. These samples were collected in January 2008. The samples that were analysed at ICSF were received by the laboratory in February 2008, preserved with 240 µL formaldehyde to inhibit microbial activity, filled to the top, sealed with parafilm, and stored until analysis upside down in the absence of light at 4°C. In contrast, the samples analysed at RCL-E were stored in the absence of light at the University of Manchester until February 2010. On receiving the samples at RCF-E, the samples were immediately processed to CO₂ and analysed as per the method discussed in the $^{14}$C analysis section above. Given that both laboratories use international reference standards for sample calibration, it should be assumed that the $\delta^{13}$C data provided by the laboratories are correct. The difference therefore may be explained by the additional storage time that samples analysed at RCF-E were subjected to. A recent study by Taipale and Sonninen (2009) showed that the $\delta^{13}$C signature of samples stored in glass in the absence of any preservation agent increased by 7.7‰ over a period of 183 days. This increase is thought to be a result of diffusive escape of CO₂ from the sample container, and provides an explanation for the difference between the data obtained from the two laboratories. Consequently, the $\delta^{13}$C data obtained from ICSF is used in all interpretations and model calculations for the West Bengal data set described in this thesis. The $\delta^{13}$C data for DIC in Cambodian groundwaters used in model calculations and interpretations is that obtained from the RCF-E in the absence of an independent analysis of this data set. These samples were analysed within 1 year of sample collection, and as such may have a modified $\delta^{13}$C signature relative to their true composition given the potential for diffusive loss of CO₂ as discussed above.
In addition to the potential problems associated with $\delta^{13}C$ data for DIC, interpretation of $\delta^{13}C$ data for dissolved organic carbon (DOC) in Cambodian and Bengali groundwaters suggests this data may also have an abnormal signature. In contrast to DIC, variations in the $\delta^{13}C$ of DOC can only occur as a result of changes in the dominant source of OM to the pool of DOC present in the groundwater. At the time of writing this report there was no published article which reported $\delta^{13}C$ values of DOC as enriched as $+3.5 \%$. Given this, the variations in $\delta^{13}C$ of DOC more likely reflects enrichment in $\delta^{13}C$ imparted on the sample during processing and preparation. Samples that are to be analysed for $\delta^{13}C$ DOC are acidified to pH $< 4$, which is the pH at which all inorganic carbon should be present as carbon dioxide, and sparged with $N_2$ gas to remove all of the DIC from the sample. The $\delta^{13}C$ signature of the sample is therefore assumed to represent the isotopic signature of the remaining DOC. However, if the $CO_2(g)$ is not totally removed from solution, small concentrations of the remaining DIC will impart a significant enrichment on the observed $\delta^{13}C$ signature. Indeed, the process of driving the carbon species to $CO_2(g)$ dominated imparts a fractionation of $8.5 \%$ between $HCO_3^-$ and $CO_2(g)$ at $20^\circ C$ (Mook et al., 1974). Modelled $\delta^{12}C$ for total carbon below (figure 4.4) shows that if as little as $1 – 5 \%$ of the initial DIC remains in solution following the cessation of sparging, the $\delta^{13}C$ can be enriched to a signature that explains the deviation in the $\delta^{13}C$ DOC for these samples. The samples that appear to have been subjected to the greatest amount of enrichment were found to be those which had the lowest DOC to DIC concentration ratio.

However, this process alone cannot explain the enrichment to $+3.5 \%$, which is observed in sample CH18 from the Bengali groundwaters sampled presented in table 5.3 below. The enrichment in this sample is $10.6 \%$, which is greater than the $8.5 \%$ that is imparted on a sample as a result of fractionation between $HCO_3^-$ and $CO_2(g)$. This therefore requires an additional process to impart further enrichment on the sample DOC signature. One possible explanation for this is that the process of sparging could potentially result in a further enrichment of the $\delta^{13}C$ of DIC, with the lighter $^{12}C$ preferentially removed from solution over the heavier $^{13}C$. However, this process cannot be further elucidated with this data. Interpretation of the $\delta^{13}C_{DOC}$ data should therefore be considered in the context of the uncertainty which surrounds the evolution of its isotopic signature and is not recommended for use in mass balance calculations or models.
Table 5.3. Comparison of $\delta^{13}C$ of DOC and DIC of co-existing groundwaters taken from West Bengal in January 2008. The $\delta^{13}C$ DIC data presented here is that obtained from the RCF-E as the DOC samples were also subjected to the same storage time as these DIC samples prior to analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH01</th>
<th>CH02</th>
<th>CH04</th>
<th>CH07</th>
<th>CH09</th>
<th>CH11</th>
<th>CH15</th>
<th>CH18</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{13}C_{\text{DIC}}$</td>
<td>-6.4</td>
<td>-1.4</td>
<td>-3.9</td>
<td>-11.1</td>
<td>-10.0</td>
<td>-6.6</td>
<td>-11.6</td>
<td>-7.1</td>
</tr>
<tr>
<td>$\delta^{13}C_{\text{DOC}}$</td>
<td>-6.0</td>
<td>-6.2</td>
<td>-5.0</td>
<td>-6.5</td>
<td>-6.7</td>
<td>-11.2</td>
<td>-9.8</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Figure 4.4. Modelled enrichment of the $\delta^{13}C$ as a function of increasing contributions of DIC.
4.6. References


CHAPTER 5

Dating of older groundwaters using $^{14}$C: A review of existing models, limitations and a new approach for modelling mean groundwater residence times
5.1. Introduction

The dating of groundwaters remains of paramount importance in physical and chemical hydrology, and is frequently used in groundwater resource management and in determining the rate at which contaminants are transported in the subsurface. Shallow groundwaters are often part of a dynamic groundwater flow regime that has hydraulic connection with the surface and may be subject to contributions of modern recharge and short flow paths. In contrast, deeper groundwater is often not in hydraulic continuity with the shallow groundwater and instead forms part of a regional flow system typically characterised by slower groundwater flow velocities and longer flow paths. The dating of these older groundwaters invariably requires the application of long lived radioisotopes that have either undergone decay or in-growth into the groundwater (CLARK and FRITZ, 2000). These radioisotopes include $^{36}\text{Cl}$, $^4\text{He}$ and $^{81}\text{Kr}$. However, $^{14}\text{C}$ dating of groundwaters is by far the most routine, but indirect, dating technique applied to the assessment of mean groundwater residence time (MRT) and can be measured to date groundwaters up to 30,000 yrs old (CLARK and FRITZ, 2000).

In the application of the $^{14}\text{C}$ technique to dissolved inorganic carbon (DIC) it is assumed that, if the $^{14}\text{C}$ activity of DIC that is gained during aquifer recharge is retained in the groundwater as it flows from recharge along a flow path, without dilution from further contributions of variable $^{14}\text{C}$ activity, its decay can be used as a direct measurement for determination of the MRT. The approach is therefore based on measuring the loss of $^{14}\text{C}$ from radioactive decay in a sample and assumes the initial concentration of $^{14}\text{C}$ is known and has remained constant and that the system is closed to any gains or losses except through radioactive decay. Given these conditions the age of the sample is given by:

$$a_t = a_o \cdot e^{-\lambda t} \quad (5.1)$$

where $a_o$ is the initial activity of $^{14}\text{C}$, $a_t$ is its activity after some time $t$ expressed as percent modern carbon (pmC). In geochemical studies, a half life of 5730 years for $^{14}\text{C}$ (GODWIN, 1962) should be applied, giving rise to a decay constant, $\lambda$, of $1/8267$ (STUIVER and POLACH, 1977).

However, problems in obtaining reliable ages from $^{14}\text{C}$ activities of groundwater derive from the fact that the $^{14}\text{C}/^{12}\text{C}$ isotope ratio of DIC, is not only affected by $^{14}\text{C}$ decay but is in reality often open to gains and losses. The most common reactions which contribute DIC to the groundwater DIC pool are: (i) the dissolution of calcite, which can begin at recharge and continue along a flow path, (ii) dissolution of dolomite, (iii) exchange with the aquifer matrix,
(iv) the oxidation of old organics found within the aquifer and (v) the diffusion of $^{14}$C into the aquifer matrix (CLARK and FRITZ, 2000). The oxidation of dissolved organic carbon in the groundwater has been shown to not significantly impact the inorganic geochemistry or carbon isotopic composition of the dissolved inorganic carbon pool in groundwaters (WASSENAAR et al., 1991). The potential contributions of DIC from the remaining sources are typically $^{14}$C dead and act to dilute the initial activity in DIC. As such uncorrected $^{14}$C groundwater ages often appear too high. This dilution of the $^{14}$C activity must be addressed for correct interpretation of the MRT by the inclusion of a dilution factor, $q$, in the decay equation to obtain a more appropriate initial activity rather than the typically adopted $100$ pmC which represents the natural atmospheric activity of $^{14}$C. This gives rise to the following decay equation:

$$a_{t}^{14}C = q \cdot a_{o}^{14}C \cdot e^{-\lambda t}$$  \hspace{1cm} (5.2)

This can then be simplified to obtain the MRT corrected for additional contributions of DIC to:

$$t = -8267 \cdot ln \left( \frac{a_{t}^{14}C}{q \cdot a_{o}^{14}C} \right)$$  \hspace{1cm} (5.3)

Deriving the value of the dilution factor requires consideration of the various geochemical processes that occur following recharge. This paper discusses existing models and presents an amendment to the conventional Fontes-Garnier (1979) model that considers the potential fractionation between soil CO$_2$ and bicarbonate that may occur in the near neutral pH groundwaters typical of many aquifer systems. We test each of the models discussed by applying them to chemical and isotopic data collected from the groundwaters of a study site in the Kandal Province of Cambodia. We then compare each of the modelled MRTs with measured tritium concentrations from co-existing groundwater. We also discuss the sensitivity of the modelled MRTs derived from the amended Fontes-Garnier model by consideration of the uncertainty associated with the assumption of recharge conditions, the isotopic composition of carbonate minerals and the $^{14}$C activity at recharge.

5.2. **Correction of groundwater DIC $^{14}$C age for carbonate dissolution**

Several models have been proposed to correct measured $^{14}$C activities to obtain more reliable estimates of the MRT. We present below merely a summary of a selection of these models. In each of the correction models for carbonate dissolution discussed below, the diluting contribution of carbonate is $^{14}$C-free, which may represent an oversimplification in younger
aquifers which contain measurable $^{14}$C activities. Nonetheless, these model values still represent a significant improvement on uncorrected ages. A wealth of literature exists on the construction and application of many of these models which is beyond the scope of this paper. However, a more exhaustive review of these can be found in Mook (1976) and Clark and Fritz (CLARK and FRITZ, 2000) and references therein.

5.2.1 Statistical Correction Models

The most primitive models that can be applied to obtain an improved estimate of MRT are statistical models, so called because they apply the same correction factor to all samples to correct for carbonate dissolution. These models assume that after the initial DIC charging of infiltrating surface waters, additional contributions of $^{14}$C free DIC dilute the $^{14}$C activity of the total DIC reservoir. These models apply one dilution factor to the whole data set, which may be practical if it can be assumed that the geochemical and isotopic evolution of the entire groundwater body can be averaged over the area of recharge. One such model employed in numerous investigations is that of Vogel (1970), where a dilution factor of 0.85 is employed for sediments that contain fine grained carbonate (i.e. 85% of the initial $^{14}$C concentration remains in the DIC pool following dilution). However, the application of a single dilution factor to an entire data set only considers carbonate evolution during recharge and discounts any further contributions that take place along groundwater flow paths. As such, these models typically only provide a crude improvement from uncorrected ages and often underestimate the degree of correction that is required.

5.2.2 Geochemical models

In systems where it is unclear where the recharge area is located, or in aquifer systems where additional sources of recharge may occur to groundwater along flow paths, geochemical models provide perhaps a more accurate assessment of the dilution factor that should be applied to measured groundwater ages. These models utilise chemical measurements of the groundwater to quantify contributions of DIC. One such approach is that first suggested by Pearson (1965) who noted that any process which adds, removes or exchanges carbon with the DIC reservoir will alter both the $^{14}$C activity of the groundwater and the $^{13}$C signature. In this model the q value is obtained from a carbon isotope mass balance approach:

$$q = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{carb}}{\delta^{13}C_{soil} - \delta^{13}C_{carb}}$$

(5.4)
where $\delta^{13}\text{C}_{\text{DIC}} =$ measured $^{13}\text{C}$ of sample

$\delta^{13}\text{C}_{\text{soil}} = \delta^{13}\text{C}$ of soil CO$_2$ (generally related to the $\delta^{13}\text{C}$ value of the vegetation cover)

$\delta^{13}\text{C}_{\text{carb}} = \delta^{13}\text{C}$ of prevailing calcite (typically 0‰)

The in-situ measurement or sampling of the soil CO$_2$ that prevails at recharge is often very difficult and may not reflect that which prevailed during recharge of groundwaters in the past. In the absence of a measured value for this parameter, an assumption has to be made for use in the isotope mass balance model first. Similarly, the isotopic signature of carbonate present in the recharge zone that may contribute DIC to the groundwater is also frequently not known. Whilst the $\delta^{13}\text{C}$ of carbonates has been reported to have a range of several permil, a value 0‰ is typically assumed. In Pearson’s model, a soil CO$_2$ $\delta^{13}\text{C}$ of -25‰ is assumed. This assumption frequently leads to this model yielding large q values because the model assumes that contributions of carbonate from the sediment occurs under closed system conditions and as such does not consider isotope exchange with soil gas which can be significant at pHs typical of natural waters. This can give rise to groundwater MRTs that are younger than the true MRT.

To account for the varying degree of openness to the groundwater system a pH dependent fractionation factor, $\varepsilon^{13}\text{C}_{\text{DIC−CO}_2(\text{soil})}$, is introduced and added to the assumed $\delta^{13}\text{C}$ of the soil CO$_2$ to get a more accurate assessment of $\delta^{13}\text{C}$ of recharging waters, given as $\delta^{13}\text{C}_{\text{rech}}$ (CLARK and FRITZ, 2000):

$$\delta^{13}\text{C}_{\text{rech}} = \delta^{13}\text{C}_{\text{soil}} + \varepsilon^{13}\text{C}_{\text{DIC−CO}_2(\text{soil})} \quad (5.5)$$

The pH dependent fractionation factor must first be derived for application in this model. This is calculated from the equation below:

$$\varepsilon^{13}\text{C}_{\text{DIC−CO}_2(\text{soil})} = m\text{CO}_2(\text{aq}) \times \varepsilon^{13}\text{C}_{\text{CO}_2(\text{aq})−\text{CO}_2(\text{g})} + m\text{HCO}_3 \times \varepsilon^{13}\text{C}_{\text{HCO}_3−\text{CO}_2(\text{g})} \quad (5.6)$$

where m is the mole fraction of the two carbon species which are heavily pH dependent. The enrichment factors, $\varepsilon^{13}\text{C}$, are temperature dependent and can be calculated from the equations 5.7 and 5.8 below. Equation 5.7 is that from Vogel (1970) and 5.8 from Mook et al (1974)

$$\varepsilon^{13}\text{C}_{\text{CO}_2(\text{aq})−\text{CO}_2(\text{g})} = \frac{-0.373 \times 10^3}{T} + 0.19 \quad (5.7)$$
The mole fractions of the CO₂ and HCO₃⁻ are determined for any given pH from the following equations:

\[ K_{CO_2} = \frac{[H_2CO_3]}{pCO_2[H_2O]} \]  (5.9)

\[ K_1 = \frac{[H^+[HCO_3^-]]}{[H_2CO_3]} \]  (5.10)

\[ K_2 = \frac{[H^+[CO_3^{2-}]]}{[HCO_3^-]} \]  (5.11)

This first requires knowledge of the thermodynamic reaction constants which are temperature dependent. The following equations provide a means of calculating the pK value (negative log of the thermodynamic equilibrium constant) for each of the equations above. These are presented in Clark and Fritz (2000) and are derived from the regression of data presented in Drever (1997).

\[ pK_{CO_2} = \frac{-7 \times 10^{-5}}{T^2} + 0.016T + 1.11 \]  (5.12)

\[ pK_1 = \frac{1.1 \times 10^{-4}}{T^2} - 0.012T + 6.58 \]  (5.13)

\[ pK_2 = \frac{9 \times 10^{-5}}{T^2} - 0.0137T + 10.62 \]  (5.14)

The value calculated for \( \delta^{13}C_{\text{rech}} \) is then substituted into equation 5.4 in the place of \( \delta^{13}C_{\text{sol}} \) to give:

\[ q = \frac{\delta^{13}C_{\text{DIC}} - \delta^{13}C_{\text{carb}}}{\delta^{13}C_{\text{rech}} - \delta^{13}C_{\text{carb}}} \]  (5.15)

This inclusion of the pH dependent enrichment factor in this model allows for isotope exchange under both open and closed system conditions, and therefore represents a significant improvement on earlier models which only considered closed system isotope exchange. However, an assumption of the prevailing pH and temperature at recharge is
required to calculate the enrichment factor in this model, which can affect the modelled MRT significantly. Indeed, by increasing the assumed pH at recharge by 1 pH unit, the modelled groundwater MRT has been shown to increase by as much as 1785 years (Clark and Fritz, 2000). Furthermore, this model does not account for isotopic fractionation effects during matrix exchange reactions.

The Fontes-Garnier model (Fontes and Garnier, 1979) takes into account all of the previously modelled contributions of DIC, but adds a contribution from matrix exchange in the calculation of the dilution of 14C. This model uses cation concentrations to determine the relative importance of 14C free matrix carbonate and isotope mass balance to determine the relative contribution of 14C from exchange between CO2 gas in the soil and the carbonate matrix. In this model the total matrix derived carbonate contribution (\(mDIC_{\text{carb}}\)) that has exchanged DIC under closed system conditions and the total DIC that has undergone exchange with soil CO2 (\(mDIC_{\text{CO2-exch}}\)) under open system conditions are calculated by:

\[
mDIC_{\text{carb}} = mCa^{2+} + mMg^{2+} - mSO_4^{2-} + \left(\frac{mNa^+ + mK^+ - mCl^- - mNO_3^-}{2}\right)
\]

\[\quad (5.16)\]

\[
mDIC_{\text{CO2-exch}} = \frac{\delta^{13}C_{\text{meas}} \times mDIC_{\text{meas}} - \delta^{13}C_{\text{carb}} \times mDIC_{\text{carb}} - \delta^{13}C_{\text{soil}} \times (mDIC_{\text{meas}} - mDIC_{\text{carb}})}{\delta^{13}C_{\text{soil}} - \delta^{13}C_{\text{CO2-CaCO3}} - \delta^{13}C_{\text{carb}}}
\]

\[\quad (5.17)\]

where \(m\) is the molal concentration of the species, \(\delta^{13}C_{\text{meas}}\) is the isotopic signature measured in the sample, \(\delta^{13}C_{\text{carb}}\) is the isotopic signature of carbonate minerals present in the aquifer system and \(\delta^{13}C_{\text{soil}}\) is the isotopic signature of DIC present in the soil zone. In the equation above, \(SO_4^{2-}\) is used to account for contributions of \(Ca^{2+}\) from gypsum dissolution which would otherwise result in an apparently greater contribution of DIC from calcite dissolution. Similarly, \(Na^+\) and \(K^+\) are used to account for contributions of matrix exchange which would substitute alkaline earth metals for alkali metals with a molar ratio of 1:2, which would otherwise result in a decrease in the contribution of \(Ca^{2+}\) and \(Mg^{2+}\) from carbonate dissolution. Finally, \(Cl^-\) and \(NO_3^-\) are used to act as conservative tracers of contributions from cation exchange processes and Na carbonate dissolution. The fractionation factor between CO2 and solid carbonate is given by Deines et al (1974) by:

\[
\varepsilon^{13}C_{\text{CO2-CaCO3}} = \frac{-3.63 + 1.194 \times 10^6}{T^2}
\]

\[\quad (5.18)\]
The dilution factor for the Fontes and Garnier (1979) model then becomes:

\[
q_{F\rightarrow G} = \frac{mDIC_{\text{meas}} - mDIC_{\text{carb}} + mDIC_{\text{CO}_2 - \text{exch}}}{mDIC_{\text{meas}}} \tag{5.19}
\]

The corrections made for the various processes that contribute DIC discussed above place a series of limitations on the hydrochemical setting to which this model can be applied. Firstly, this model should not be applied to groundwaters where significant silicate weathering, which contributes \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \), is likely to prevail. The \( \text{SO}_4^{2-} \) correction term also suggests that the model should not be applied in settings where leaching of sodium sulphate is likely, or in groundwaters where \( \text{SO}_4^{2-} \) may derive from sulfide oxidation (Fontes and Garnier, 1979). The vegetation type also plays a significant role in how applicable the model is to a groundwater system. This derives from the fact that, as \( \delta^{13}C_{\text{soil}} \approx \delta^{13}C_{\text{CO}_2 - \text{CaCO}_3} \), the denominator tends towards zero and thus the value of \( q \) becomes very large. This problem may arise when \( \text{C}_4 \) plants are the dominant vegetation type in the area of recharge.

This model, like those previously discussed, requires an estimate of \( \delta^{13}C_{\text{soil}} \). In the initial model, it is suggested that this value is equivalent to that which would derive from the oxidation of the local vegetation in purely open system conditions but where rapid flow in to the groundwater ensures this is not subject to fractionation processes. Perhaps a more suitable estimate of \( \delta^{13}C_{\text{soil}} \) for use in this model is to apply the \( \delta^{13}C_{\text{exch}} \) that is derived from assumptions of recharge pH and temperature as discussed above. This allows for recharge under partially open conditions where dissolution of calcite begins under open system conditions in contact with soil \( \text{CO}_2 \), but can continue under the water table under closed system conditions without contact with soil \( \text{CO}_2 \). Given that this value has a correction for fractionation between \( \text{HCO}_3^- \) and \( \text{CO}_2(g) \), the fractionation factor for \( \text{CO}_2(g) \) to \( \text{CaCO}_3 \) in the denominator of the Fontes Garnier (1979) model is no longer appropriate. As such, we apply a temperature independent fractionation factor for \( \text{HCO}_3^- - \text{CaCO}_3 \), \( \epsilon^{13}C_{\text{HCO}_3^- - \text{CaCO}_3} = -1\% \), as determined by Romanek et al (1992) in its place. The amended Fontes-Garnier model for soil gas exchange is therefore given by:

\[
\frac{mDIC_{\text{CO}_2 - \text{exch}}}{\delta^{13}C_{\text{exch}} - \epsilon^{13}C_{\text{HCO}_3^- - \text{CaCO}_3} - \delta^{13}C_{\text{carb}}} = \frac{\delta^{13}C_{\text{meas}} \times mDIC_{\text{meas}} - \delta^{13}C_{\text{carb}} \times mDIC_{\text{carb}} - \delta^{13}C_{\text{exch}} \times (mDIC_{\text{meas}} - mDIC_{\text{carb}})}{\delta^{13}C_{\text{exch}} - \epsilon^{13}C_{\text{HCO}_3^- - \text{CaCO}_3} - \delta^{13}C_{\text{carb}}} \tag{5.20}
\]
5.3. **Application of models to field data**

The field area investigated in this study is situated in the Kandal province of Cambodia and covers an area of approximately 50 km² between the Mekong and Bassac rivers. This area has previously been identified as a region where extensive contamination of the groundwater by As is prevalent (BERG et al., 2007; BUSCHMANN et al., 2007; KOCAR et al., 2008; PAPACOSTAS et al., 2008; POLIZZOTTO et al., 2008; POLYA et al., 2005; ROWLAND et al., 2008). The site is characteristic of the floodplains of the lower Mekong basin, with elevated levees along the banks of the two rivers retreating to a seasonally saturated internal wetland basin which lies between the two rivers. Groundwater flow here is driven by seasonally-variable gradients developed between the Mekong and Bassac rivers and the inland wetland basins (BENNER et al., 2008). In the rainy season, groundwater flows from the rivers towards the wetlands, with groundwater flowing in the opposite direction for the remaining 8 months of the year resulting in net groundwater flow from the wetlands to the rivers (BENNER et al., 2008). The absence of extensive abstraction in the As-rich aquifers of Cambodia means that the subsurface environment remains largely undisturbed.

5.3.1 **Field sampling techniques and analytical procedures**

A set of twenty groundwater samples were collected during January 2009 (dry season) at the study site in Cambodia over a 2.6 km transect perpendicular to the River Mekong and over a depth range of 7.3 – 60 m. A submersible pump (MP1, Grundfos) or a peristaltic pump (Geopump II, Geotech Environmental Equipment, Inc) was used to draw water in wells at a discharge rate of approximately 12 l/min and 1 l/min respectively. Tubewells were purged for a minimum of one well volume, with measurements of temperature, pH, Eh and electrical conductivity taken at short intervals until the discharging waters stabilised, typically within 10 - 40 minutes, at which point measurements were recorded and samples were collected.

Groundwater samples were collected, treated and stored depending on the intended analysis. Samples for major and trace cation analysis were filtered through 0.45 μm cellulose nitrate filters in to 100 ml acid washed glass schott bottles, acidified to pH < 2 using trace element grade HNO₃, and stored at 4°C prior to shipping and analysis. Samples for anion analysis were filtered and stored as above but not acidified. Water samples for δ¹³C and δ¹⁴C of dissolved inorganic carbon (DIC) were collected in 500 ml amber glass bottles and stored at 4°C. Water samples for tritium analysis were collected in 1 L argon filled amber glass bottles and stored with a 4 cm argon head.
Major element concentrations of the water samples were determined by inductively coupled plasma – atomic emission spectroscopy (ICP-AES, Horizon, Fisons). Quality control standards were used throughout the course of analysis to monitor analytical performance. External calibration standards were used to prepare standard calibration curves from which measured concentrations can be corrected for deviation from using weighted ordinary least squares linear regression, with analytical errors calculated using the methods of Miller and Miller (2005). Anion analysis of water samples for Cl\(^{-}\), Br\(^{-}\), NO\(_2\)\(^{-}\), NO\(_3\)\(^{-}\), PO\(_4\)\(_3\)\(^{-}\) and SO\(_4\)\(_2\)\(^{-}\) was conducted using a Metrohm 761 compact Ion Chromatograph with a Dionex AS9 high capacity column and AG9 high capacity guard column using a flow rate of 1.4 mL/min and a mobile phase of 9mM Na\(_2\)CO\(_3\). Bicarbonate alkalinity was measured by alkalinity titration with 0.025M HCl. Stable carbon isotope ratios were measured on sub-samples of CO\(_2\) using a dual-inlet mass spectrometer with a multiple ion beam collection facility (VG OPTIMA). The mass spectrometer was calibrated with international reference materials to a precision of \(\pm 0.1\) ‰ for repeat analysis of bottled CO\(_2\). Carbon-14 measurements for DIC were performed at the Natural Environment Research Council (NERC) Radiocarbon Facility – Environment, East Kilbride, Scotland (allocation number 1411.0409) on either a 5MV tandem accelerator mass spectrometer or 250kV single stage accelerator mass spectrometer (both machines by National Electrostatics Corporation, NEC, Wisconsin, US). Determination of the tritium content of groundwater samples was achieved using the \(^3\)He-ingrowth technique developed by Clarke et al (1976), with \(^3\)He and \(^4\)He measurements made on a MAP-215 noble gas mass spectrometer.

### 5.3.2 Groundwater chemistry

The groundwater of this study area is dominated by Ca\(^{2+}\), Mg\(^{2+}\) and HCO\(_3\)\(^{-}\), which is typical hydrochemistry for the As bearing aquifers of this region (BERG et al., 2001; RAVENSCROFT et al., 2005; ROWLAND et al., 2008). The pH is circum-neutral, with a range from 6.1 – 7.1 (table 5.1 below). An assessment of the degree of electroneutrality showed that groundwaters were generally within 10%,
<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>Alkalinity</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>K⁺</th>
<th>Na⁺</th>
<th>Σ</th>
<th>Σ⁺</th>
<th>EN %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE11 - 12</td>
<td>30</td>
<td>6.4</td>
<td>8.19</td>
<td>2.01</td>
<td>1.16</td>
<td>0.77</td>
<td>6.36</td>
<td>3.42</td>
<td>0.04</td>
<td>1.99</td>
<td>12.14</td>
<td>11.82</td>
<td>1.35</td>
</tr>
<tr>
<td>TE11 - 20</td>
<td>29.6</td>
<td>6.8</td>
<td>9.97</td>
<td>3.20</td>
<td>0.14</td>
<td>1.31</td>
<td>6.75</td>
<td>3.61</td>
<td>0.06</td>
<td>4.35</td>
<td>14.63</td>
<td>14.77</td>
<td>0.47</td>
</tr>
<tr>
<td>TE11 - 55</td>
<td>29.8</td>
<td>6.4</td>
<td>8.37</td>
<td>0.09</td>
<td>0.02</td>
<td>0.00</td>
<td>3.05</td>
<td>1.38</td>
<td>0.07</td>
<td>2.95</td>
<td>8.48</td>
<td>7.45</td>
<td>6.44</td>
</tr>
<tr>
<td>ML01 - 10</td>
<td>28.8</td>
<td>6.1</td>
<td>9.23</td>
<td>1.80</td>
<td>0.00</td>
<td>0.15</td>
<td>4.74</td>
<td>2.44</td>
<td>0.06</td>
<td>2.14</td>
<td>11.19</td>
<td>9.39</td>
<td>8.73</td>
</tr>
<tr>
<td>ML01 - 30</td>
<td>30.2</td>
<td>6.8</td>
<td>6.72</td>
<td>0.19</td>
<td>0.00</td>
<td>0.01</td>
<td>2.27</td>
<td>0.78</td>
<td>0.12</td>
<td>1.20</td>
<td>6.92</td>
<td>4.37</td>
<td>22.64</td>
</tr>
<tr>
<td>ML01 - 40</td>
<td>30.1</td>
<td>7</td>
<td>5.95</td>
<td>0.36</td>
<td>0.00</td>
<td>0.01</td>
<td>2.03</td>
<td>0.69</td>
<td>0.09</td>
<td>0.84</td>
<td>6.32</td>
<td>3.65</td>
<td>26.82</td>
</tr>
<tr>
<td>TE51 - 12</td>
<td>34</td>
<td>6.6</td>
<td>7.62</td>
<td>0.39</td>
<td>0.01</td>
<td>0.01</td>
<td>4.76</td>
<td>2.14</td>
<td>0.08</td>
<td>0.93</td>
<td>8.04</td>
<td>7.92</td>
<td>0.75</td>
</tr>
<tr>
<td>TE51 - 20</td>
<td>30.7</td>
<td>6.9</td>
<td>6.62</td>
<td>0.16</td>
<td>0.00</td>
<td>0.00</td>
<td>2.21</td>
<td>0.88</td>
<td>0.18</td>
<td>1.55</td>
<td>6.78</td>
<td>4.81</td>
<td>16.95</td>
</tr>
<tr>
<td>TC31- 51</td>
<td>30.2</td>
<td>6.8</td>
<td>10.79</td>
<td>0.15</td>
<td>0.11</td>
<td>0.00</td>
<td>4.30</td>
<td>1.68</td>
<td>0.24</td>
<td>2.43</td>
<td>11.06</td>
<td>8.65</td>
<td>12.23</td>
</tr>
<tr>
<td>TE61 - 48</td>
<td>30.2</td>
<td>6.3</td>
<td>12.41</td>
<td>0.14</td>
<td>0.00</td>
<td>0.00</td>
<td>3.82</td>
<td>2.34</td>
<td>0.19</td>
<td>1.30</td>
<td>12.54</td>
<td>7.64</td>
<td>24.27</td>
</tr>
<tr>
<td>ML02 - 8</td>
<td>29.9</td>
<td>6.5</td>
<td>7.27</td>
<td>1.71</td>
<td>0.00</td>
<td>0.26</td>
<td>1.89</td>
<td>0.88</td>
<td>0.04</td>
<td>3.28</td>
<td>9.23</td>
<td>6.10</td>
<td>20.46</td>
</tr>
<tr>
<td>TC45 - 12</td>
<td>31.1</td>
<td>6.3</td>
<td>13.39</td>
<td>9.17</td>
<td>0.01</td>
<td>0.54</td>
<td>9.71</td>
<td>5.64</td>
<td>0.05</td>
<td>6.01</td>
<td>23.10</td>
<td>21.41</td>
<td>3.80</td>
</tr>
<tr>
<td>TC45 - 20</td>
<td>31.1</td>
<td>6.4</td>
<td>10.33</td>
<td>13.51</td>
<td>0.91</td>
<td>3.04</td>
<td>12.02</td>
<td>7.58</td>
<td>0.02</td>
<td>7.20</td>
<td>27.79</td>
<td>26.80</td>
<td>1.81</td>
</tr>
<tr>
<td>ML03 - 10</td>
<td>29.1</td>
<td>6.4</td>
<td>4.79</td>
<td>1.28</td>
<td>0.01</td>
<td>0.55</td>
<td>1.73</td>
<td>1.24</td>
<td>0.03</td>
<td>2.46</td>
<td>6.62</td>
<td>5.46</td>
<td>9.64</td>
</tr>
<tr>
<td>ML03 - 30</td>
<td>29.2</td>
<td>6.1</td>
<td>2.02</td>
<td>0.84</td>
<td>0.92</td>
<td>0.01</td>
<td>1.78</td>
<td>0.83</td>
<td>0.06</td>
<td>1.56</td>
<td>3.79</td>
<td>4.24</td>
<td>5.55</td>
</tr>
<tr>
<td>ML03 - 40</td>
<td>30</td>
<td>6.7</td>
<td>4.98</td>
<td>42.87</td>
<td>0.00</td>
<td>0.07</td>
<td>2.61</td>
<td>1.16</td>
<td>0.08</td>
<td>2.53</td>
<td>47.92</td>
<td>6.39</td>
<td>76.48</td>
</tr>
<tr>
<td>ML04 - 8</td>
<td>30.4</td>
<td>6.4</td>
<td>11.29</td>
<td>1.57</td>
<td>0.17</td>
<td>5.18</td>
<td>6.76</td>
<td>3.48</td>
<td>0.02</td>
<td>8.62</td>
<td>18.21</td>
<td>18.87</td>
<td>1.78</td>
</tr>
<tr>
<td>ML04 - 30</td>
<td>31.4</td>
<td>7.1</td>
<td>3.07</td>
<td>0.60</td>
<td>0.04</td>
<td>0.06</td>
<td>1.87</td>
<td>0.84</td>
<td>0.13</td>
<td>0.93</td>
<td>3.77</td>
<td>3.77</td>
<td>0.01</td>
</tr>
<tr>
<td>ML04 - 44</td>
<td>31.2</td>
<td>6.9</td>
<td>2.77</td>
<td>0.63</td>
<td>0.11</td>
<td>0.10</td>
<td>2.13</td>
<td>0.99</td>
<td>0.13</td>
<td>0.91</td>
<td>3.61</td>
<td>4.15</td>
<td>6.95</td>
</tr>
<tr>
<td>ML05 - 60</td>
<td>33.2</td>
<td>6.5</td>
<td>4.00</td>
<td>0.10</td>
<td>0.33</td>
<td>0.00</td>
<td>2.11</td>
<td>1.23</td>
<td>0.04</td>
<td>1.30</td>
<td>4.43</td>
<td>4.69</td>
<td>2.77</td>
</tr>
</tbody>
</table>

Table 5.1. Hydrochemistry of the groundwaters of the Kandal Province of Cambodia. Values are in milliequivalents per litre. EN is the percentage deviation from electroneutrality. The first 4 characters of each sample represent the well nest, with the final 2 digits equal to the depth the sample was taken from. Anions not used in calculating the MRT for the matrix exchange models [Br, NO₃ and PO₄] are not included here but are presented in Appendix 1.
although some samples did have values which exceeded this, perhaps indicative of large contributions of typically minor species such as Fe(II). However, this explanation cannot be true for sample ML03-40, which has a 76.5% deviation from electroneutrality. This sample contains a significantly elevated Cl⁻ concentration which lies outside of 2σ of the mean of the sample set, and as such should be considered an outlier.

Elevated concentrations of Na⁺ and K⁺ may reflect cation exchange processes which substitute the alkali earth metals, Ca²⁺ and Mg²⁺, for alkali metals, Na⁺ and K⁺. However, the concentrations of these species are typically lower than the alkali-earth metals. This will be further accentuated when the molar correction factor of 0.5 is applied in the models and suggests that, whilst cation exchange processes may be occurring in these groundwaters, the removal of Ca²⁺ and Mg²⁺ is relatively small compared to the contributions of these species from carbonate dissolution. The concentration of SO₄²⁻ is generally very low, although three isolated occurrences of relatively high SO₄²⁻ are present within the groundwaters sampled. These groundwaters were taken from different locations along the transect and likely reflect localised contributions of SO₄²⁻, potentially from gypsum dissolution given the correlation between elevated levels of SO₄²⁻ and Ca²⁺ at these sites.

5.3.3 Isotopic composition and model comparisons

Groundwater tritium concentrations at this study site demonstrate a contribution of recharge that occurred after the onset of atmospheric bomb testing in the 1950s in thirteen of the twenty samples collected over a depth range of 8 – 50 m (table 5.2 below). This is further supported by the presence of ¹⁴C at concentrations that exceed 100 pmC in four samples. However, several samples display ¹⁴C concentrations much lower than one would expect, with ¹⁴C activities as low as 41.51 pmC in groundwaters with co-existing ³H concentrations of 2.01 ± 0.15 TU. This suggests that the ¹⁴C in the DIC pool in the groundwater at this location has been subject to a very large contribution of ¹⁴C-dead DIC at some point since recharge. The ¹⁴C activity does not show any consistent trend along the transect, but does decrease with depth in four of the six well nests, suggesting an increase in age with depth.

The Pearson (1965) and Fontes and Garnier (1979) model dilution factors were calculated using a δ¹³C = -22.9 ‰, which is the average of the δ¹³C of dissolved organic carbon determined for co-existing groundwater. For the Clark and Fritz (2000) and this study model, dilution factors were calculated using a δ¹³C_rech = -18.5 ‰, calculated assuming an average pH at recharge of 6.58 and an
average temperature of 30.5°C (values represent the mean of the sample data). The δ¹³C and δ¹⁴C of carbonate present in the aquifer is assumed to be 0‰ and 0 pmC respectively.

The Pearson model frequently gives the smallest dilution factor of all the models considered. The large range of dilution factors for this model (0.15 – 0.85) suggests that the groundwater DIC pool is subject to variable contributions of carbonate derived ¹⁴C-dead DIC. The large range in the dilution factor for the other models supports this observation. Varying degrees of dilution demonstrates that a fixed statistical dilution factor, such as that applied in the study of Vogel (1970), is not appropriate for these groundwaters, and as such is not modelled here. The additional observation that dilution factors do not consistently increase with depth further suggests that the carbonate content of the aquifer sediments is not homogeneously distributed at this study site. The dilution factors derived from the Clark and Fritz model are typically smaller than those determined in the Pearson model and closer to those determined from the matrix exchange models. This perhaps suggests that the dilution factors determined from the Pearson model, which do not allow for any isotope exchange with the soil gas reservoir under open system conditions, over estimates the contribution of DIC from carbonate minerals. The Clark and Fritz model dilution factors are very similar to those derived from the amended Fontes-Garnier model introduced in this study which applies the same δ¹³C_{ref}. In contrast, the conventional Fontes-Garnier model dilution factors are consistently larger than those derived for these two models. Like the Pearson model, this may reflect the fact that, whilst the conventional Fontes-Garnier approach does allow for open system exchange with the soil reservoir, it assumes that there is not sufficient time for fractionation effects during recharge, which may be significant when the pH is greater than 6.4 (i.e. when HCO₃⁻ becomes the dominant inorganic carbon species in solution). The Clark and Fritz model does not consider cation exchange reactions or mineral dissolution other than that which derives from calcite and potentially dolomite phases. Given the close correlation between dilution factors derived from the amended Fontes-Garnier model, which is consistent with observations of the hydrochemistry discussed above, this suggests that very little contributions are made by cation exchange reactions or from gypsum dissolution, and that the carbon isotope geochemistry of the groundwater evolves only as a function of carbonate dissolution.
<table>
<thead>
<tr>
<th>Tubewell</th>
<th>$\delta^{13}$C %o</th>
<th>A, pmC</th>
<th>$^3$H (TU)</th>
<th>dilution factor, q</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pearson (1965)</td>
</tr>
<tr>
<td>TE11 - 12</td>
<td>-13.1</td>
<td>100.54</td>
<td>2.53</td>
<td>0.57</td>
</tr>
<tr>
<td>TE11 - 20</td>
<td>-15.2</td>
<td>102.62</td>
<td>2.01</td>
<td>0.67</td>
</tr>
<tr>
<td>TE11 - 55</td>
<td>-15.8</td>
<td>60.71</td>
<td>-0.07</td>
<td>0.69</td>
</tr>
<tr>
<td>ML01 - 10</td>
<td>-16.0</td>
<td>101.49</td>
<td>1.35</td>
<td>0.70</td>
</tr>
<tr>
<td>ML01 - 30</td>
<td>-14.1</td>
<td>74.06</td>
<td>-0.05</td>
<td>0.62</td>
</tr>
<tr>
<td>ML01 - 40</td>
<td>-12.3</td>
<td>72.23</td>
<td>-0.14</td>
<td>0.54</td>
</tr>
<tr>
<td>TE51 - 12</td>
<td>-8.7</td>
<td>99.71</td>
<td>2.22</td>
<td>0.38</td>
</tr>
<tr>
<td>TE51 - 20</td>
<td>-11.3</td>
<td>78.26</td>
<td>-0.06</td>
<td>0.49</td>
</tr>
<tr>
<td>TC31 - 51</td>
<td>-17.6</td>
<td>85.70</td>
<td>-0.04</td>
<td>0.77</td>
</tr>
<tr>
<td>TE61 - 48</td>
<td>1.1</td>
<td>89.03</td>
<td>-0.06</td>
<td>-0.05</td>
</tr>
<tr>
<td>ML02 - 8</td>
<td>-17.8</td>
<td>61.03</td>
<td>1.55</td>
<td>0.78</td>
</tr>
<tr>
<td>TC45 - 12</td>
<td>-14.9</td>
<td>84.95</td>
<td>1.91</td>
<td>0.65</td>
</tr>
<tr>
<td>TC45 - 20</td>
<td>-15.0</td>
<td>96.78</td>
<td>1.89</td>
<td>0.66</td>
</tr>
<tr>
<td>ML03 - 10</td>
<td>-14.5</td>
<td>100.77</td>
<td>1.78</td>
<td>0.63</td>
</tr>
<tr>
<td>ML03 - 20</td>
<td>-7.7</td>
<td>66.93</td>
<td>1.63</td>
<td>0.34</td>
</tr>
<tr>
<td>ML03 - 50</td>
<td>-3.4</td>
<td>41.51</td>
<td>2.01</td>
<td>0.15</td>
</tr>
<tr>
<td>ML04 - 8</td>
<td>-16.3</td>
<td>81.59</td>
<td>2.06</td>
<td>0.71</td>
</tr>
<tr>
<td>ML04 - 20</td>
<td>-19.6</td>
<td>93.16</td>
<td>2.65</td>
<td>0.85</td>
</tr>
<tr>
<td>ML04 - 44</td>
<td>-13.3</td>
<td>94.73</td>
<td>2.24</td>
<td>0.58</td>
</tr>
<tr>
<td>ML05 - 60</td>
<td>-14.4</td>
<td>74.63</td>
<td>-0.05</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Table 5.2. Isotopic data and modelled dilution factors for determination of the initial $^{14}$C activity of DIC present in groundwaters of the Kandal Province, Cambodia. The dilution factor of 0.85 as applied in Vogel (1970) is not shown here but is used to model MRT in table 5.3.
The large majority of dilution factors for each of the models lie in the range of 0.3 – 1. However, there are some samples which have dilution factors that are distinct from the others in the sample population. The first of these is sample TE61, which has a dilution factor between -0.05 and -0.56. This sample has a δ¹³C of +1.1‰. This will always result in a negative dilution factor given that the δ¹³C of soil gas, under both open and closed system conditions, is negative. The δ¹³C value of 1.1 for sample TE61 lies outside 2 σ of the mean δ¹³C of the sample set. The δ¹³C signature of some samples was shown in chapter 4 to have been effected by the diffusive escape of CO₂ from some samples during storage, and as such this value should be considered an outlier and not used in the calculation of a MRT. The dilution factors derived for sample ML03-40 are also much lower than the typical values for the sample set, and are negative for the matrix exchange models. The large dilution factor for the δ¹³C models derives from the fact that this sample has an enriched isotopic composition of -3.4‰. Furthermore, as discussed above, this sample contains chloride at a concentration of 42.9 meq/l, which is more than 2 σ from the mean Cl⁻ concentration of the sample set. As with sample TE61, this sample should be considered an outlier. Given that these samples have compositions that do not reflect the typical groundwater chemistry of this aquifer system, both of these samples should be considered as anomalies and discussed no further in the interpretation. Finally, sample ML04-20 has dilution factors greater than 1 for the Clark and Fritz and both matrix exchange models. This sample has a δ¹³C that exceeds that of the recharge conditions once fractionation processes have been considered, which suggests that the groundwater is continuously undergoing exchange with the soil CO₂, which is possible in unconfined aquifers. This will give rise to a modelled MRT that exceeds that of the uncorrected sample. Whilst this process is rare, it cannot be dismissed, and as such these values should still be considered in the interpretation.

Modelled MRTs for each of the models are presented in table 5.3 below, with ages rounded to the nearest year. The larger dilution factors derived for the Pearson model result in younger modelled ages. These values likely reflect the youngest possible MRT for these groundwaters and places an upper limit on the contribution of DIC from carbonate dissolution. The matrix exchange model introduced in this study provides the oldest modelled MRTs. This model gives MRTs of between 0 and 4085 years for the twenty groundwaters analysed and places an upper limit on the MRT of groundwaters following correction for carbonate dissolution. However, each of these models predict MRTs that are contradicted by the measurement of ³H in some groundwater samples. A success rate for the each of the model is given in table 5.3 below and is derived by comparing modelled MRT ages to measurements of ³H in co-existing groundwater.
The Pearson and Fontes-Garnier models both achieved a success rate of 67% following comparison of the MRTs with measured \(^3\)H concentrations. These both contained six discordant results out of the eighteen that were possible to model, one more than both the Clark and Fritz and the amended Fontes-Garnier model suggested here which both achieved a 72% success rate. The Pearson model appears to typically over estimate the correction required for carbonate dissolution, with five of the six discordant ages this model predicts found to be \(^3\)H-dead groundwaters. At locations TC31 and ML05, this overestimation may derive from the fact that this model only considers recharge under closed system conditions, which may not be representative of the recharge environment at these sites. The Pearson and the Fontes-Garnier models also predict a modern signature at site ML01-30, which like those discussed above, is also \(^3\)H-dead. Given that both of these models assume that recharge occurs without significant fractionation between the soil gas and bicarbonate in the recharging water, this probably suggests that the application of this assumption is not appropriate for this location. All models considered give discordant MRTs for samples ML01-40 and TE51-20, predicting modern ages in \(^3\)H-dead groundwaters. This could suggest that all of the models over predict the amount of carbonate derived \(^{14}\)C dead DIC that is contributed to the groundwater at these locations. Alternatively, it could suggest that the carbonate that is undergoing dissolution is not \(^{14}\)C-dead. This may occur when calcite is present as an authigenic phase that has precipitated in the sediment following its deposition. To account for the dilution of DIC from \(^{14}\)C-active carbonate dissolution, the following equation can be used:

\[
q_{\text{activity corrected}} = 1 - q \cdot \left(1 - \frac{\alpha_{\text{carb}}}{100}\right)
\]  

(5.21)

Assuming an initial \(^{14}\)C activity of 102.62 pmC on the initial recharging DIC, this places an upper limit on the age of the dissolving authigenic calcite of approximately 4800 and 3700 years to achieve modern MRTs for the measured \(^{14}\)C activities of 72.2 and 78.26 pmC observed in samples ML01-40 and TE51-20 respectively. This is entirely possible given that these sediments themselves were only deposited since the late Pleistocene (Tamura et al., 2009). The Clark and Fritz and both matrix exchange models provide discordant modelled MRTs for sample ML04-20, estimating relatively old MRT’s in \(^3\)H-active water. As discussed briefly above, the dilution factors derived from these models for this sample suggest the groundwater is frequently undergoing exchange with soil \(\text{CO}_2\). This suggests that, whilst the groundwater at this location may have been transported to this location along a flow path, an additional source of recharge to the groundwater at this location is transporting \(^3\)H and modern \(^{14}\)C from the soil zone in to the aquifer resulting in an apparent increase in the MRT compared to the uncorrected MRT. These models do not have the sophistication
required to account for mixing of differently sourced water bodies and hence are not capable of accurately predicting the MRTs of groundwaters where this is occurring.

The final discordant ages are those predicted for samples ML02, which is predicted by all models to be older than the $^3$H concentration would suggest, and ML04-8 which the Clark and Fritz and both matrix exchange models also predict to be much older than the $^3$H concentration suggests the true MRT to be. This could suggest that the models underestimate the dilution factor required for contributions of DIC from carbonate dissolution at these locations. However, relatively low concentrations of Ca$^{2+}$ and depleted $\delta^{13}$C signatures of the groundwater at these locations suggest this may not be the most likely explanation for this discrepancy. Instead, this could suggest that an alternative source(s) of diluting DIC is made to the groundwater at these sites that is not considered in the models. The measured $^{14}$C activity can be diluted not just by geochemical processes as discussed throughout this study, but also by mixing processes. Bethke and Johnson (2002) show that mixing of old waters that have been trapped in aquitards with younger groundwater occurs at a rate that is controlled only by the ratio of volume fluid in aquitards and aquifers, and is independent of the actual rate of the contribution (a function of permeability). Given that both of these samples are taken from shallow tubewells no more than 8.5 m deep positioned either in or directly below surficial clay deposits at this site, a large contribution of much older water may be made from the extensive clay deposits at these locations. Such a contribution could act to dilute the measured $^{14}$C activity of the groundwater in these locations.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Uncorrected</th>
<th>Pearson (1965)</th>
<th>Clark &amp; Fritz (2000)</th>
<th>Fontes &amp; Garnier (1979)</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE11-12</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>TE11-20</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>TE11-55</td>
<td>4126</td>
<td>1291</td>
<td>3053</td>
<td>2296</td>
<td>3214</td>
</tr>
<tr>
<td>ML01-10</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>ML01-30</td>
<td>2483</td>
<td>&gt; 0</td>
<td>457</td>
<td>&gt; 0</td>
<td>502</td>
</tr>
<tr>
<td>ML01-40</td>
<td>2689</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>TE51-12</td>
<td>24</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>TE51-20</td>
<td>2026</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>TC31-51</td>
<td>1275</td>
<td>&gt; 0</td>
<td>1078</td>
<td>402</td>
<td>1245</td>
</tr>
<tr>
<td>TE61-48</td>
<td>961</td>
<td>DNC</td>
<td>DNC</td>
<td>DNC</td>
<td>DNC</td>
</tr>
<tr>
<td>ML02-8</td>
<td>4082</td>
<td>2204</td>
<td>3966</td>
<td>2635</td>
<td>4085</td>
</tr>
<tr>
<td>TC45-12</td>
<td>1348</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>TC45-20</td>
<td>271</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>ML03-10</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>ML03-20</td>
<td>3319</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>ML03-50</td>
<td>7268</td>
<td>DNC</td>
<td>DNC</td>
<td>DNC</td>
<td>DNC</td>
</tr>
<tr>
<td>ML04-8</td>
<td>1682</td>
<td>&gt; 0</td>
<td>839</td>
<td>801</td>
<td>1056</td>
</tr>
<tr>
<td>ML04-20</td>
<td>586</td>
<td>&gt; 0</td>
<td>1259</td>
<td>1974</td>
<td>1539</td>
</tr>
<tr>
<td>ML04-44</td>
<td>448</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>ML05-60</td>
<td>2419</td>
<td>&gt; 0</td>
<td>581</td>
<td>163</td>
<td>768</td>
</tr>
</tbody>
</table>

Table 5.3. Summary of uncorrected and modelled $^{14}$C MRTs. The Vogel (1970) model applies a dilution factor of 0.85. Values are rounded to the nearest year and calculated according to the models discussed above using an $A_o$ of 102.62 pmC (with $A_o = 100$ pmC used for the uncorrected MRT). > 0 signifies a recharge time that is in the future. DNC signifies the model did not converge on a MRT. Model success is classified as the ratio of concordant ages (between the model in question and $^3$H measurements) to the total number of modelled ages, and is expressed as a percentage.
5.4. Model sensitivities

Estimates and assumptions must be made to allow for a quantitative determination of the size of contributions of $^{14}$C-dead DIC from carbonate dissolution to the groundwater DIC pool. These calculations are critical in the modelling of the MRT following the measurement of the $^{14}$C activity of the bulk DIC pool present in groundwaters. The isotopic and chemical composition of the groundwater is typically the basis on which models are based. Parameters that are less frequently quantified directly are key model constraints that characterise the recharge environment and the aquifer sediment composition, such as the $\delta^{13}$C of soil gas, $\delta^{13}$C of aquifer carbonate minerals and the initial $^{14}$C activity of recharging waters. The correction models are very sensitive to the specified input parameters, and as such the assumptions that are made can have a dramatic effect on the modelled MRT. Each of these parameters will now be discussed in greater detail below, followed by an assessment of the sensitivity of the amended Fontes-Garnier matrix exchange model to variations in these input parameters.

5.4.1 C-13 composition of recharging waters

The isotopic signature of groundwater recharge is a critical parameter in the carbonate dissolution correction models because, when combined with the measured groundwater $\delta^{13}$C, it provides a mass balance approach to calculate the amount of $^{14}$C dilution that the DIC has been subjected to from carbonate dissolution. However, this is a difficult parameter to constrain because it varies from one location to another depending on the dominant vegetation type and the extent of fractionation between CO$_2$(soil) and the dominant carbon species in solution. The vegetation type can often be identified in the field, and measurements of the $\delta^{13}$C of DOC provide a reliable estimate of the potential starting position of the $\delta^{13}$C of DIC. In contrast, the extent of fractionation cannot be measured but can be estimated through reliable assumptions of the temperature and pH of recharge as discussed previously. However, this parameter is extremely sensitive to the assumed pH and temperature, as displayed in figure 5.1 below. Here it can be seen that, as the pH increases from 6 – 7, the fractionation factor undergoes up to a 5 fold increase depending on the temperature of recharge. A further increase of pH from 7 to 8 results in an additional increase in the fractionation factor of up to 3 ‰. The sensitivity of this parameter to temperature is less dramatic, but increases with increasing pH, with a maximum variability of 5 ‰ for an increase in temperature from 0 – 50 °C at a pH of 8. This variability in the fractionation factor translates into variability in the $\delta^{13}$C of DIC of the recharging groundwaters, as can be seen in figure 2 below.
Figure 5.1. Variability in $\varepsilon^{13}\text{C}_{\text{DIC-CO}_2}$ as a function of changes in the pH and temperature at recharge.

Figure 5.7. Variability in $\delta^{13}\text{C}$ of recharging waters as a result of the temperature and pH dependence of $\varepsilon^{13}\text{C}_{\text{DIC-CO}_2}$.
5.4.2 Isotopic composition of carbonate minerals

The isotopic composition of carbonate minerals present in the aquifer matrix also plays a significant role in accounting for the contribution of $^{14}$C-dead DIC from carbonate dissolution. However, unlike the fractionation factor discussed above, only an informed assumption can be made of its $\delta^{13}$C signature in the absence of measured values. Unfortunately, the variation in the isotopic signature of carbonate minerals can be quite large depending on its source. Whilst the range of $\delta^{13}$C in carbonates is frequently between -2 and +2.5 ‰, values typical of marine carbonates (Mook, 2000), the range has been reported to extend from -8 to +3.4 ‰ (Clark and Fritz, 2000).

5.4.3 Initial $^{14}$C Activity

The first key step to any assessment of the MRT of a groundwater is an accurate estimation of the initial $^{14}$C activity at recharge prior to additional contributions from the subsurface. This value will reflect the isotopic signature of atmospheric CO$_2$ that is incorporated into vegetation by photosynthesis and later released in to the soil zone by decay and root respiration. This CO$_2$ is then transported in recharging groundwater giving rise to the initial $^{14}$C of DIC in groundwater. A modelled MRT is then given as a measure of the decrease in $^{14}$C activity by radioactive decay that is preserved in the sample signature relative to this initial activity. An initial $^{14}$C activity of 100pmC may at first thought appear appropriate for groundwaters, but application of this figure should first consider how the $^{14}$C activity has changed over time.

Natural production of $^{14}$C in the upper atmosphere through cosmic-ray spallation reactions has shown considerable variation over time, with approximately a 10% decrease in measured $^{14}$C levels in the atmosphere in the Holocene period alone prior to the onset of atmospheric nuclear bomb testing (Clark and Fritz, 2000). Indeed, extension of the atmospheric $^{14}$C record back over the past 30,000 years shows a systematic decrease in $^{14}$C activity of around 40% that is a result of changes in the earth’s geomagnetic dipole moment (Damon et al., 1989). Superimposed over the top of this long term trend are fine and hyperfine oscillations with a 200 year (Suess wiggles) and 11 year periodicity (Suess, 1980). These short term cyclical variations have been shown to be related to variations in solar output and sunspot activity (Damon et al., 1989; Hoyt et al., 1992; Stuiver and Quay, 1980). Groundwaters that have undergone recharge in the late Pleistocene or early Holocene may therefore have had an initial $^{14}$C activity that is much higher than the 100 pmC that is often assumed to be appropriate. Application of the 100 pmC figure would therefore give rise to MRT of
groundwaters that are significantly younger than the true MRT. Any determination of the MRT of suspected older groundwaters should therefore first consider what an appropriate $^{14}$C activity is, based on complimentary information that may be derived from alternative isotope systems. For example, the O and H isotope system that can be used to derive paleotemperatures that can be used to estimate an approximate time period in which the groundwater underwent recharge, which can then be used to provide an estimate of the $^{14}$C activity of recharging waters.

In addition to cosmogenic and planetary induced changes in the atmospheric $^{14}$C activity, anthropogenic activity has also driven changes in the atmospheric $^{14}$C activity that have took place over the last 150 years. The combustion of fossil fuels during the industrial period introduced $^{14}$C dead CO$_2$ into the atmosphere which resulted in a dilution of atmospheric $^{14}$C of approximately 2% (OESCHGER et al., 1975). Following this, atmospheric bomb testing, which began in 1952 and continued until the early 1960s, introduced a vast quantity of artificial $^{14}$C into the atmosphere which resulted in almost a doubling of the activity of $^{14}$C in the atmosphere by 1963 as displayed in figure 5.3 below. The extent of this enrichment of the $^{14}$C activity varied spatially, with the northern hemisphere experiencing greater enrichment than the southern hemisphere. Indeed, spatial variations have been reported even within the northern hemisphere, with tropical and low latitude regions experience relatively less enrichment compared to polar and mid latitude regions (HUA and BARBETTI, 2004). Attenuation of this $^{14}$C in the oceans and biosphere has since resulted in a decrease in atmospheric $^{14}$C activities, which are now close to natural levels. Groundwater recharge that has occurred during the last 50 years is therefore likely to contain a component of bomb derived $^{14}$C. However, an estimation of the initial $^{14}$C activity is of less importance for these groundwaters because the presence of recharge during the last 50 years, which is approximately the size of the error associated with $^{14}$C measurements, is easily identified through measurement of the $^3$H content of the groundwater.
Figure 5.3. Atmospheric $^{14}$C record for the Northern Hemisphere tropic zone using the data presented in Hua and Barbetti (2004). The atmospheric $^{14}$C records derived for this region is based on measurements from Nydal and Lovseth (1996).

5.5. **Model sensitivity to input parameters**

A sensitivity analysis of the modified Fontes-Garnier model suggested here was conducted to determine the effects of changing input parameters on the calculated MRT. This was carried out by first calculating the MRT based on (i) a mean $\delta^{13}$C for recharging groundwaters of -18.5 ‰ calculated from the mean pH and temperature of groundwaters, (ii) a $\delta^{13}$C of 0 ‰ for the carbonate minerals present in the aquifer, and (iii) assuming an initial $^{14}$C activity at recharge of 100 pmC. Following this the minimum and maximum MRTs were calculated by (i) adding or subtracting 2 $\sigma$ from the mean pH and temperature values to obtain maximum and minimum $\delta^{13}$C signatures of recharging waters (-21.3 and -16.3 ‰ respectively), (ii) varying the $\delta^{13}$C of the dissolving carbonate phase from -2 to +2 ‰ and (iii) varying the initial $^{14}$C activity of recharging waters from 95 to 105 pmC. Table 5.4 below provides a summary (in years) of the variation in the calculated age from the MRT determined initially using the input parameters discussed above. The largest single variation in the modelled
MRT is clearly from the uncertainty which is associated with the temperature and pH that prevail at recharge. Indeed, this variability is more than double that associated with the isotopic signature of carbonate phases and the initial $^{14}C$ activity at recharge. The combined error for all three input parameters of $\pm 1378$ years parameters provides a more accurate estimate of the error associated with modelled MRTs than the measurement error, which is typically no more than $\pm 37$ years for the analysis discussed here.

<table>
<thead>
<tr>
<th></th>
<th>Recharge conditions</th>
<th>Carbonate C-13 signature</th>
<th>Initial C-14 activity</th>
<th>Combined effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>negative error</td>
<td>1232</td>
<td>500</td>
<td>424</td>
<td>1378</td>
</tr>
<tr>
<td>positive error</td>
<td>1098</td>
<td>377</td>
<td>403</td>
<td>1251</td>
</tr>
</tbody>
</table>

Table 5.4. Summary of modelled MRT sensitivity from the mean MRT derived from the input parameters described in the test. The values are given to the nearest year. The negative error is determined by applying a $\delta^{13}C$ at recharge of $-21.3‰$, a $\delta^{13}C$ of carbonate of $-2‰$, and an initial $^{14}C$ activity of 95 pmC. The positive error is determined by applying a $\delta^{13}C$ at recharge of $-16.3‰$, a $\delta^{13}C$ of carbonate of $+2‰$, and an initial $^{14}C$ activity of 105 pmC.

The magnitude of the errors summarised in table 5.4 is constant as a function of the actual modelled MRT. However, the error expressed as a percent of the modelled age will change significantly as the age increases. Figure 5.4 below shows that the percentage error of the modelled MRT is relatively small for old groundwaters, with recharge conditions representing the largest error for a groundwater with a modelled MRT of 35,000 years, with an error of 3.5%. However, as the modelled age becomes younger the size of the error becomes increasingly important, exceeding 10% for all input parameters at modelled MRTs younger than 3900. Indeed, as the modelled MRT approaches zero, the relative size of this error approaches infinity. This demonstrates that, for the amended Fontes-Garnier model suggested here, any modelled MRT below 1378 years may have an error that exceeds the modelled age. Application of the modelled MRTs should therefore be applied with caution in younger groundwater systems, and should consider the potential variability of this estimation in any calculations or models that utilise these ages.
5.6. Conclusions

Three existing geochemical mass balance models that quantify the diluting effect of contributions of \(^{14}\text{C}\)-dead DIC that derives from carbonate dissolution to the total DIC pool in groundwaters have been discussed in detail, and a new model which considers potential fractionation effects during recharge at circum-neutral pH has been proposed. As expected, the Pearson (1965) \(\delta^{13}\text{C}\) model provided the youngest modelled MRTs, which perhaps reflects the somewhat flawed assumption that recharge occurs under open system conditions without any interaction with the soil CO\(_2\). The amended Fontes-Garnier matrix exchange model suggested here gave rise to the oldest modelled MRTs, but was closely followed by the Clark and Fritz (2000) \(\delta^{13}\text{C}\) isotope mass balance model. These models were shown to have the highest success rates following comparison of the MRTs with measured tritium concentrations. This suggests that the amendment made to the conventional Fontes-Garnier (1979) model, which did not previously allow for a pH dependent correction for isotope exchange between CO\(_2\) and DIC during recharge, gives rise to more accurate MRTs than the conventional model provides. However, discordant ages were still obtained for each of the models in both \(^{3}\text{H}\)-active and \(^{3}\text{H}\)-dead groundwaters. These discrepancies may have arisen as a result of

Figure 5.4. Percent error of the modelled MRT as a function of the modelled MRT for the model input parameters. This is calculated based on the minimum error provided in table 5.4. The error approaches infinity as the modelled MRT tends to zero for each of the input parameters considered.
incorrect assumptions or additional processes that are not considered in these models. An overestimation of the dilution factor that is applied could arise if the carbonate phase that is undergoing dissolution is not $^{14}$C free, but is instead present as an authigenic phase that has precipitated following aquifer deposition. This may be particularly important in Holocene aged aquifer systems such as that investigated in this study. Conversely, additional diluting sources, such as that which derives from the mixing of older waters present in low permeability sediments, could also result in the dilution of the initial $^{14}$C activity that is not considered in the correction models.

The uncertainty in the assumptions and estimates that are required to be made for the calculation of MRTs from the amended Fontes-Garnier model described here have been shown to result in large variations in the modelled MRT. A maximum estimate of the combined error associated with the ages derived from this model of 1378 years has been determined assuming a potential $2\sigma$ deviation of recharge parameters, a range from -2 to +2‰ for the $\delta^{13}$C for carbonate phases and an uncertainty of the initial $^{14}$C activity of 5%. This error is far more important for modelled MRTs that have a Holocene age, and becomes less important with increasing modelled age. Whilst direct measurement of the $\delta^{13}$C of carbonate minerals present in the aquifer may improve this error, the largest single variability arises from the uncertainty associated with the pH and temperature that prevailed during groundwater recharge. These values cannot be determined with any measure of confidence given that conditions may have changed since recharge. A $2\sigma$ variability in these values, which represents 99% coverage of the data for a Gaussian distribution, gives rise to an error of the modelled MRT of up to 1232 years. This represents the minimum error for modelled MRTs derived by application of this model.

The comparison of these models highlights the variation in modelled MRTs that can be derived by the application of different models to measured $^{14}$C activities. Comparison of the deviation between models may be useful in providing an improved understanding of the settings under which it may not be appropriate to apply specific models. They also serve to highlight the importance of the comparison between modelled values with data from independent groundwater dating techniques. This can be used to identify erroneous modelled MRTs, and as such may be used to help constrain where model parameters may reasonably be changed to provide a more accurate estimate of the MRT.
5.7. References


CHAPTER 6

Provenancing Organic Matter and tracing ground-surface water interactions in shallow Cambodian groundwaters: Implications for Arsenic Release
6.1. **Introduction**

The extensive contamination of groundwaters by naturally occurring arsenic (As) utilized by millions of people in South and South East Asia as a source of drinking water has long since been recognised as a public health catastrophe (Balgia and Kaiser, 1996; Chakraborty and Saha, 1987; Dhar et al., 1997; Smith et al., 2000). Initially identified in West Bengal in the mid 1980’s (Chakraborty and Saha, 1987) and later in Bangladesh almost a decade later (Nickson et al., 1998a), it was estimated that almost one third of wells tapped groundwater where As exceeded the World Health Organisation (WHO) maximum concentration limit (MCL) of 10 μg/l, with this figure rising to over half of tubewells which exceed the local MCL of 50 μg/l (BGS and DPHE, 2001). Additional surveys prompted by the similar geological, geographical and hydrological settings that prevail elsewhere identified further As contamination of groundwaters in neighbouring Cambodia (Polya et al., 2005; Polya et al., 2003) and Vietnam (Berg et al., 2001) amongst others in the region. It is now feared that as many as 100 million people may be regularly consuming groundwater with hazardous high concentrations of this known carcinogen (Ravenscroft et al., 2009). Consumption of groundwater containing As above the WHO and local MCL has already resulted in numerous deleterious health effects as direct symptoms of arsenicosis in millions of people (Yu et al., 2003), with as many as 100,000 potentially suffering from arsenic induced diseases in Cambodia alone (Sampson et al., 2008). Despite more than a decade of active research, there are still a number of fundamental gaps in our understanding of the As release process that limit our ability to provide key information on how better to predict locations that are at risk of As contamination. Such information is crucial for governments and those responsible for mitigating the effects of the current crisis. These decisions should also be made once the potential for future risk has been considered and quantified so that mitigation strategies put in place now can provide a sustainable source of drinking water for decades to come.

The primary source of As in the groundwaters of this region is the weathering of As-bearing rocks in the upper Himalayas. This As is then transported by the various great rivers and is deposited in the young alluvial deltas which contain an abundance of organic matter (OM). This As is initially sorbed to Fe(III) mineral phases which coat sedimentary grains and which scavenges As from solution under aerobic conditions. It is then thought to be released from the sediments to the groundwater following the reductive dissolution of these secondary Fe oxide phases (Bhattacharya et al., 1997; Charlet and Polya, 2006; Dowling et al., 2002; Horneman et al., 2004; Islam et al., 2004; McArthur et al., 2001; Nickson et al., 1998b; Postma et al., 2007; Stuben et al., 2003; Zheng et al., 2004). This process is catalysed by metal reducing bacteria, with OM shown to be critically implicated as an electron donor in the process (Islam et al., 2004; Van Geen et al., 2004). Additional contributions of
As may occur as a result of oxidative dissolution of As-bearing sulfide minerals (ACHARYYA et al., 1999; AKAI et al., 2004; POLIZZOTTO et al., 2006) or as a result of competitive exchange reactions (APPELO et al., 2002; CHOWDHURY et al., 1999; VAN GEEN et al., 1994), although the magnitude of As release from these processes is unlikely to be as extensive as that which derives from reductive processes. However, whilst the biogeochemical processes that are responsible for liberating As to groundwater are now widely understood, identification of the source of OM that drives these processes remains unresolved, elusive and even controversial (FENDORF et al., 2010).

Several sources of OM have been postulated to be contributing dissolved organic carbon (DOC) to the groundwater which can ultimately be utilised in microbially mediated As release processes. It has been suggested that much of the OM has a surface origin, and could be drawn down from the surface, and in particular from ponds (NEUMANN et al., 2010), with extensive abstraction of groundwater accelerating As release to groundwaters (HARVEY et al., 2002). This particular suggestion is intensely debated (AGGARWAL et al., 2003; HARVEY et al., 2003; SENGUPTA et al., 2008; VAN GEEN et al., 2003), not least because of the implications it holds for future agricultural production. Conversely, the OM may have a sedimentary origin with buried peat (MCARTHUR et al., 2001), aerated root zones and animal burrows (MEHARG et al., 2006) or thermally mature hydrocarbons which have migrated from depth (ROWLAND et al., 2008; ROWLAND et al., 2006) amongst suggested potential sources. However, identification of the source(s) of OM present in the groundwater systems is not trivial given that several studies suggest that it is not necessarily the amount, but the type and reactivity of organic carbon that is important in driving biogeochemical processes (GAULT et al., 2005; MLADENOV et al., 2010; ROWLAND et al., 2007; VAN DONGEN et al., 2008). Indeed, it has been suggested that utilisation of different sources of OM will give rise to different rates of As release to the groundwater (FENDORF et al., 2010). More recalcitrant sources of OM such as older buried peat deposits and sedimentary sources should support a slow rate of As release into the groundwater. In contrast, more reactive, labile sources of OM such as that which may be transported in recharging surface waters will support a much more rapid rate of As release. Distinguishing between the sources of OM present in any groundwater system, and assessing the vulnerability of the system to changes with respect to its dominant OM source, is therefore of critical importance in predicting future changes in the current As hazard.

In this study we apply complimentary isotopic techniques to characterise the hydrological environment and how this influences As mobility at a known As hotspot in Cambodia. The stable isotopes of oxygen ($\delta^{18}$O) and hydrogen ($\delta$D) were used to identify and provide qualitative estimates
of the degree of interaction between ground and surface waters. Radiogenic and stable isotopes of hydrogen (\(^1\text{H}\)) and carbon (\(^{13}\text{C}, ^{14}\text{C}\)) were used to determine groundwater residence times and provenance OM present in the aqueous phase. We have chosen a site in Cambodia where groundwater As concentrations have been shown to exceed 1000 µg/l (KOCAR et al., 2008; POLIZZOTTO et al., 2008). The site has been both hydrogeochemically and hydrogeologically well characterised, with As release shown to occur from near surface, river derived sediments, with most pronounced rates of As release from sediments underlying permanent wetlands and abandoned river channels (BENNEN et al., 2008; KOCAR et al., 2008; POLIZZOTTO et al., 2008; ROWLAND et al., 2008). The site exhibits a relatively simply hydrology, where groundwater is recharged in the internal wetland basin and is transported on centennial timescales to the river Mekong. This simple hydrology reflects natural conditions that would prevail in other As contaminated deltas in the absence of extensive groundwater abstraction which would otherwise result in the development of complex transient flow paths which make provenancing groundwater very difficult (POLYA and CHARLET, 2009; POLYA et al., 2005). This provides us with a unique opportunity to determine the relative contributions of in-aquifer and surface derived OM in the absence of groundwater pumping driven drawdown of surface waters, containing labile OM, distorting the isotopic signature of the groundwater system. This baseline assessment of pre-development conditions will allow for a robust evaluation of the likely release rates of As under natural conditions. From this, an assessment of the vulnerability of these aquifer systems to anthropogenic disturbance, which may act to change the relative contributions of different sources of OM, and as such As release rates to groundwater, can be made.

6.2. Field Area

Like many of the massive As contaminated deltas of South and South East Asia, the Mekong delta in Cambodia is made up almost entirely from the Quaternary deposits of deltaic sediments of the Mekong River and its distributaries and alluvial deposits from the weathering of the Himalayas. Covering an area of almost 63,000 km\(^2\), the lower Mekong delta formation in Cambodia and Vietnam has predominantly occurred within the last 7 ka following the last sea level high stand (NGUYEN et al., 2000; TA et al., 2002). The Mekong River, which carries the tenth largest sediment load of all rivers globally at 160 x 10\(^6\) tonnes of sediment per year (GUPTA, 2004), becomes tidal to the northeast of Phnom Penh, after which it separates in to two major distributaries; the Mekong and Basac rivers. The flow of the Mekong is strongly seasonal, with almost 80 % of its discharge occurring between the months of June and November coincident with the monsoonal rains (JICA, 2002; NGUYEN et al., 2000). The large differences between rainfall in the dry and wet season in the Mekong delta results
in substantial changes in the extent of flooding in the internal wetland basins between the Mekong and Basaac rivers and changes in groundwater levels of up to several metres (JICA, 2002).

The field area investigated in this study is situated in the Kandal province of Cambodia and covers an area of approximately 50 km$^2$ between the Mekong and Basaac rivers and has previously been identified as a region where extensive contamination of the groundwater by As is prevalent (BERG et al., 2007; BUSCHMANN et al., 2007; KOCAR et al., 2008; PAPACOSTAS et al., 2008; POLIZZOTTO et al., 2008; POLYA et al., 2005; ROWLAND et al., 2008). The site is characteristic of the floodplains of the lower Mekong basin, with elevated levees along the banks of the two rivers retreating to a seasonally saturated internal wetland basin which lies between the two rivers. The sedimentary deposits here typically extend to a depth of around 60 m. The sedimentary sequence comprises of young Holocene levee/overbank deposits of orange/grey clay containing laminations of peat and silt which overlay fine grey aquifer sands (KOCAR et al., 2008; TAMURA et al., 2007). These clay deposits range in thickness from 3 to 20 m but typically are between 10 – 14 m thick. The peat here is generally about 5 m thick and typically extends from a depth of approximately 6 m to 11 m. The timing of this peat formation has been shown to be fairly consistent and comparable to that in the Bengal delta at 8.4 – 6.3 ka (MCARTHUR et al., 2004; TAMURA et al., 2009). Solid phase As concentrations in these sediments vary considerably, with concentrations of 12 mg/kg associated with the surficial clay deposits decreasing to 2 mg/kg in the deeper aquifer sands (KOCAR et al., 2008). Older Pleistocene deposits of orange sands and silts occasionally underlie the Holocene sediments, and have been reported at depths as shallow as 20 m in the area of the field site investigated here (TAMURA et al., 2009). Given the almost negligible hydraulic gradients that derive from the flat topography of the study area, groundwater flow is instead driven by seasonally-variable gradients developed between the Mekong and Basaac rivers and the inland wetland basins (BENNER et al., 2008). In the rainy season, groundwater flows from the rivers towards the wetlands, with groundwater flowing in the opposite direction for the remaining 8 months of the year resulting in net groundwater flow from the wetlands to the rivers (BENNER et al., 2008). A total of more than 90 tubewells tapping groundwater at depths from 7 – 60 m have been installed in numerous nests throughout the field area, with several surface water bodies present allowing for characterisation of potential recharge sources (Figure 6.1).
Figure 6.1. Aerial image of the field area located approximately 20 km SE of Phnom Penh, Cambodia. The tubewells sampled in this study are marked with red circles and form a transect 2.6 km long from the River Mekong to the internal wetlands. Locations where surface water samples have been collected during the course of the study are marked by yellow squares. The image was obtained from Google™ Earth.

6.3. Methods

6.3.1 Tubewell installation

The installation of 5 nests of tubewells (ML01 – ML05), comprising 11 wells in total, was conducted during the period of December 2008 – January 2009. Tubewell nest locations were chosen to infill areas of limited spatial resolution in between existing tubewells installed by Stanford University at the site. Installation of the wells was achieved using manual rotation of a 7.6 cm diameter pipe with a 10.2 cm cutting auger. During drilling, water was continuously pumped through the pipe to prevent clogging from cuttings, with sections of pipe 3 m in length progressively added to reach the desired well depth to a maximum of 60 m. Following completion of the well, a 6.4 cm PVC tube was inserted as well casing (with either 1 m or 2 m of screening) and the pipe was retracted, backfilled with the original sediments and sealed with clay. The wells were installed with 1 ft of the PVC well case extending from the surface, capped with a PVC screw cap, and sealed at the surface with
concrete. Shallow wells (7.3 – 9 m in depth) were installed with a 2 m screened interval at the base of the well to allow more rapid recharge from the surrounding clay. In contrast, medium (23.8 – 29.4 m in depth) and deep wells (37 – 60 m in depth) were installed with a 1 m screened depth at the base of the wells. At locations ML01, ML03 and ML04, a combination of one shallow, one medium and one deep well was installed. A shallow well was installed at ML02 and a deep well was installed near the wetlands at ML05.

6.3.2 Groundwater and surface water sampling

A set of twenty groundwater samples were collected over a 2.6 km transect perpendicular to the River Mekong and over a depth range of 7.3 – 60 m as displayed in figure 6.1 above. A further 4 surface water samples were collected from the River Mekong and 3 surface waters (2 ponds and the wetlands) over the course of this transect. A subset of tubewells lying on this transect and all surface waters were collected on a monthly basis for stable isotope analysis.

A submersible pump (MP1, Grundfos) was used to draw water in wells denoted ML at a discharge rate of approximately 12 l/min. In all remaining wells, a peristaltic pump (Geopump II, Geotech Environmental Equipment, Inc) was used to draw water at a discharge rate of approximately 1 l/min. Tubewells were purged for a minimum of one well volume, with measurements of temperature, pH, Eh and electrical conductivity taken at short intervals until the discharging waters stabilised, typically within 10 - 40 minutes, at which point measurements were recorded. Groundwater and surface water samples were collected, treated and stored depending on the intended analysis. Samples for major and trace cation and DOC analysis were filtered through a 0.45 μm cellulose nitrate filter in to 100 ml acid washed glass schott bottles, acidified to pH < 2 using trace element grade HNO₃, and stored at 4°C prior to shipping and analysis. Samples for anion analysis were filtered and stored as above but not acidified. Water samples for stable isotope (δ¹⁸O and δD) analysis were collected in 60 ml amber glass bottles with polyseal caps and stored at 4°C. Samples of accumulated monthly rain water for stable isotope analysis were stored in 1 L amber glass bottles with polyseal caps and stored at 4°C. Water samples for δ¹³C and δ¹⁴C analysis of DIC were collected in 500 ml amber glass bottles and stored at 4°C, while samples for δ¹³C and δ¹⁴C analysis of DOC were collected in 1 L and 2.5 L amber glass bottles respectively and stored at 4°C. Water samples for tritium analysis were collected in 1 L argon filled amber glass bottles and stored with a 4 cm argon head.
6.3.3 Analytical procedures

Arsenic and was measured with inductively coupled plasma – mass spectrometry (ICP-MS) with a detection limit of < 1 µg/l. Major element concentrations of the water samples were determined by inductively coupled plasma – atomic emission spectroscopy (ICP-AES, Horizon, Fisons). Quality control standards were used throughout the course of analysis to monitor analytical performance. External calibration standards were used to prepare standard calibration curves which were used to correct measured concentrations using weighted ordinary least squares linear regression, with analytical errors calculated using the methods of Miller and Miller (2005). Anion analysis of water samples for Cl, Br, NO₂⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻ was conducted using a Metrohm 761 compact Ion Chromatograph with a Dionex AS9 high capacity column and AG9 high capacity guard column using a flow rate of 1.4 mL/min and a mobile phase of 9mM Na₂CO₃. NH₄⁺ was measured using a Camspec M501 uv-vis spectrophotometer following the addition of 0.2mL of Nesslers reagent to 1mL of sample, which is left to react for 10 minutes before analysis. Bicarbonate alkalinity was measured by alkalinity titration with 0.025M HCl. Samples for DOC determinations were initially sparged with N₂ before analysis on a Shimadzu 500 TOC analyser. A complete dataset for each analyte measured is presented in Appendix 1. Calculation of mineral saturation indices was performed in Geochemist’s Workbench® version 6.0 (BETHKE, 2006).

Determination of the tritium content of groundwater samples was achieved using the ³He-ingrowth technique developed by Clarke et al (1976). Stable isotope analysis was performed at the Isotope Community Support Facility, East Kilbride, Scotland. For δD determinations, sample and standard waters were directly injected into an on-line chromium furnace at 800°C (Donnelly et al., 2001), with the evolved H₂ gas subsequently analysed on a VG 602D (VG Elemental) mass spectrometer with a manual Hg, high gas compression inlet system. Replicate analyses of water standards (international standards V-SMOW and GISP, and internal standard Lt Std) gave a reproducibility of ±2‰. For ⁶¹⁸O determinations, 200 µl of water sample is transferred into a 10ml exetainer® using an adjustable pipette with disposable pipette tips. The exetainers® are then placed into the auto-sampler tray of a Finnegan Delta V mass spectrometer, which is set at 25°C. Each sample is then over-gassed with a 0.5% CO₂-in-He mixture for 5 minutes and left to equilibrate for a further 24hrs before mass spectrometric analysis. Oxygen isotopic data were then produced using the method established by Nelson (2000). Data are reported as permil variations from the V-SMOW standard. During the analyses of these samples the following standard data accuracy and precision were obtained for three SUERC internal standards: DSW(2) = -0.3 ± 0.1‰; DW2(2) = -7.4 ± 0.1‰; EKS(2) = -13.1 ± 0.2‰. Accepted values for these standards, as calibrated by international standards GISP (-24.8‰),
V-SMOW (0‰) and SLAP (-55‰), are -0.3, -7.4 and -12.9‰ respectively. δ¹³C analysis was performed on a Prism3 (Fisons Instruments) mass spectrometer and calibrated with marble standards (MAB2, medium marble 85/160, δ¹³C = 2.48‰), internal sodium bicarbonate (δ¹³C - 4.67‰) and calcium carbonate, δ¹³C -24.23‰). Carbon-14 measurements for DIC and DOC were performed at the Natural Environment Research Council (NERC) Radiocarbon Facility – Environment, East Kilbride, Scotland (allocation number 1411.0409) on either a 5MV tandem accelerator mass spectrometer or 250kV single stage accelerator mass spectrometer (both machines by National Electrostatics Corporation, NEC, Wisconsin, US).

6.4. Results:

6.4.1 Aqueous chemistry and aquifer mineral saturation status

Concentrations of dissolved As vary significantly over both lateral and vertical profiles at the study site, with concentrations ranging from 2 to 1100 μg/l and an mean of 209 μg/l (table 6.1 below). Figure 6.2 below shows the distribution of dissolved As concentrations with depth and with distance from the River Mekong. Elevated As concentrations at shallow (< 12 m ) depth are only found in shallow groundwaters within 1 km of the river, with As concentrations equal to or below 10 μg/l in 5 of the 7 shallow tubewells. Arsenic concentrations typically increase with depth in well nests, with the As concentration exceeding the WHO standard of 10 μg/l at depths of greater than 12 m in 8 of the 9 well nests. The high As concentrations found below this depth are all found in the aquifer sands which lie beneath the surficial clay deposits at the site. In contrast, the spatial distribution in the horizontal direction is far less consistent. It appears that there is an area of high As concentrations over the whole depth profile located within 1 km of the river with the exception of the shallow well located closest to the river. After this high As zone dissolved concentrations are consistently lower, with a maximum As concentration of 35 μg/l for samples taken over the next 1.5 km. Following this zone of low groundwater As there is a return to high dissolved As for the sample taken at the edge of the internal wetlands at a distance of 2.6 km from the River Mekong at a depth of 60m. This spatial distribution of As is consistent with that presented in Kocar et al (2008) and Polizzotto et al (2008) for this field site.

The piper diagram in figure 6.3 below presents the distribution of major cations and anions in the groundwater at this site. Groundwater chemistry is typical of most As bearing groundwaters in this region (BERG et al., 2001; MCARTHUR et al., 2001; ROWLAND et al., 2008), with cation chemistry dominated by Ca²⁺ and Mg²⁺, which constitute a maximum of 56.8% and 30.5% of the bulk cationic charge respectively. Site anion chemistry is dominated by HCO₃⁻, which represents a maximum of
93% of the bulk anionic charge. As has previously been reported for groundwaters of this region in Rowland et al (2008), a trend of increasing contributions of Na⁺ and K⁺ may be indicative of the slow accumulation of these species in groundwaters with longer residence times, although this is not supported by the anion chemistry of the same samples which one would expect to have elevated concentrations of Cl⁻ and or SO₄²⁻. The chemical composition of surface waters and Mekong river water falls in the centre of this range for both cations and anions so is unlikely to represent a major control on the chemical composition of groundwaters at this site. An assessment of the degree of electroneutrality showed that groundwaters were typically within 10%, although some samples did have values which exceeded this value, perhaps indicative of large contributions of typically minor species such as Fe(II). There is no consistent trend with As and any other dissolved constituent. With the exception of one well nest (TC45), concentrations of dissolved organic carbon are consistently higher in the intermediate and deep groundwater samples taken from the aquifer sands compared to shallow groundwater in or below the clays, with mean concentrations of 3.4 and 11.2 mg/l of DOC in shallow clay groundwaters and deeper aquifer groundwaters respectively. In contrast, HCO₃⁻ concentrations typically decrease with depth from an mean of 538 mg/l in the shallow groundwater to 413 mg/l in the aquifer sands.

Figure 6.2. Two dimensional plot showing dissolved As concentrations as a function of depth and distance from the River Mekong. The size of the bubble is proportional to the As concentration (in μg/l) with the actual concentration given alongside the marker. Note here the elevated As concentrations at the beginning and end of the profile but the absence of high concentrations in the centre.
The low concentrations of NO$_3^-$ (mean of 0.1 mg/l) and elevated concentrations of redox sensitive species such as Fe, NO$_2^-$ and NH$_4^+$ the first 1 km and last sample site near the boundary of the wetlands (mean concentrations of 5.3, 11.5 and 15.6 mg/l respectively), coupled with typically low Eh values (mean of -26 mV) is consistent with reducing conditions prevailing in the As bearing groundwater at this site. This suggests microbial processes have consumed any initial dissolved O$_2$ and NO$_3$ during recharge, and that redox conditions have evolved to less energetically favourable biogeochemical processes such as Mn(IV) or Fe(III) reduction. Concentrations of SO$_4^{2-}$ of greater than 10 mg/l in 35% of wells sampled suggest that conditions have yet to reach SO$_4^{2-}$ reduction. In contrast, the section of the transect from 1 km to 2.2 km from the Mekong River where concentrations of As are consistently below the local MCL are characterised by more elevated concentrations of NO$_3^-$ and SO$_4^{2-}$, perhaps indicative of an influx of oxidants and the prevalence of aerobic conditions in this section of the transect.

Surface waters at the field site are characterised by low concentrations of all dissolved constituents relative to the groundwater. Concentrations of sulphate in surface waters average 2.6 mg/l. Eleven of the twenty groundwater samples contain concentrations of sulphate that exceed this value. This suggests a possible contribution of sulphate to the groundwater from the dissolution of minerals such as gypsum. Conversely it may represent the presence of connate waters in low permeability sediments that have been incompletely flushed from estuarine sediments as suggested by Ravenscroft (2001) for high Cl groundwater concentrations in Bangladesh. A similar trend of increased concentrations of other dissolved constituents in the groundwater compared to surface waters suggests that a combination of mineral weathering reactions and biogeochemical processes are responsible for generating the elevated concentrations of all dissolved species in the groundwater. The observation that DOC is higher in the groundwater than surface waters, in addition to the fact that it typically increases with depth, suggests that there must be a subsurface contribution of DOC to the groundwater. In contrast, HCO$_3^-$ concentrations in surface waters much lower than those found in shallow groundwater suggests that HCO$_3^-$ is generated, either from the oxidation of DOC or from carbonate mineral dissolution, in the near surface, and either becomes diluted on reaching the aquifer sands, precipitates out of solution or adsorbs to mineral surfaces.
<table>
<thead>
<tr>
<th></th>
<th><strong>Groundwater (n = 20)</strong></th>
<th></th>
<th><strong>Surface waters (n = 4)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
<td>Mean</td>
</tr>
<tr>
<td>Depth</td>
<td>7.3</td>
<td>60.0</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>6.1</td>
<td>7.1</td>
<td>6.6</td>
</tr>
<tr>
<td>EC (µS/cm)</td>
<td>33.0</td>
<td>&gt; 2000</td>
<td>673.0</td>
</tr>
<tr>
<td>ORP (mV)</td>
<td>-163.0</td>
<td>222.0</td>
<td>-26.3</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>28.8</td>
<td>34.0</td>
<td>30.5</td>
</tr>
<tr>
<td>As (µg/l)</td>
<td>2.2</td>
<td>1100.5</td>
<td>209.3</td>
</tr>
<tr>
<td>Cl (mg/l)</td>
<td>3.1</td>
<td>1520.0</td>
<td>139.2</td>
</tr>
<tr>
<td>NO₂⁻ (mg/l)</td>
<td>ND</td>
<td>1.4</td>
<td>0.1</td>
</tr>
<tr>
<td>NO₃⁻ (mg/l)</td>
<td>ND</td>
<td>72.2</td>
<td>11.6</td>
</tr>
<tr>
<td>NH₄⁺ (mg/l)</td>
<td>ND</td>
<td>80.0</td>
<td>15.6</td>
</tr>
<tr>
<td>ΣPO₄³⁻ (mg/l)</td>
<td>ND</td>
<td>3.4</td>
<td>0.6</td>
</tr>
<tr>
<td>ΣSO₄²⁻ (mg/l)</td>
<td>ND</td>
<td>249.0</td>
<td>28.2</td>
</tr>
<tr>
<td>Alkalinity (HCO₃⁻) (mg/l)</td>
<td>123.2</td>
<td>816.8</td>
<td>456.4</td>
</tr>
<tr>
<td>DOC (mg/l)</td>
<td>0.8</td>
<td>63.3</td>
<td>8.4</td>
</tr>
<tr>
<td>Fe (mg/l)</td>
<td>0.0</td>
<td>17.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Sr (µg/l)</td>
<td>112.4</td>
<td>953.8</td>
<td>411.3</td>
</tr>
<tr>
<td>Mn (µg/l)</td>
<td>82.4</td>
<td>1275.7</td>
<td>504.8</td>
</tr>
<tr>
<td>Ca (mg/l)</td>
<td>34.7</td>
<td>240.8</td>
<td>80.9</td>
</tr>
<tr>
<td>K (mg/l)</td>
<td>0.6</td>
<td>9.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Mg (mg)</td>
<td>8.4</td>
<td>92.1</td>
<td>25.5</td>
</tr>
<tr>
<td>Na (mg/l)</td>
<td>19.4</td>
<td>198.2</td>
<td>63.3</td>
</tr>
</tbody>
</table>

Table 6.1. Concentration statistics for aqueous analytes in ground and surface waters collected during April 2009 at study site in Kandal Province, Cambodia. ND denotes not detected. NM denotes not measured.
Figure 6.3. Piper diagram displaying the distribution of major cations and anions in Cambodian groundwaters. Groundwaters are given by black circles, Mekong River water by the blue triangle, and pond waters are given by red squares. Groundwaters tend to cluster around the composition of surface and river waters dominated by Ca, Mg and HCO₃. A possible trend towards more enriched concentration of Na and K may be present.

Mineral saturation indices calculations for two key carbonate hosting minerals considered (siderite and calcite) presented in table 6.2 below suggests that HCO₃ depletion with depth cannot be accounted for by the precipitation of calcite, which is supersaturated in only two of the thirteen deeper groundwater samples. Siderite is supersaturated in six of the thirteen deeper groundwater samples. Whilst mineral precipitation may account for a small amount of the HCO₃⁻ depletion observed with depth, dilution with a larger water mass with a lower concentration represents the most likely process to account for the significant depletion that is observed. Similarly, mineral saturation indices calculations for pyrite (table 6.2) suggest that only one well, ML02, has the necessary concentrations of total Fe and SO₄²⁻, together with sufficiently reducing redox conditions, to support sulphate reduction and pyrite precipitation. This supports the geochemical and redox measurements discussed above that suggest that conditions have not yet evolved to sulphate reduction in these groundwaters. Mineral saturation indices of key Fe(III) and mixed Fe(III)/Fe(II)
phases, which are supersaturated for 75% of the groundwater samples, suggest that there is sufficient Fe available to form pyrite if conditions were favourable. This therefore suggests that the \( \text{Eh} \) of the groundwater, whilst anoxic, remains too high to support sulphate reduction.

<table>
<thead>
<tr>
<th>Tubewell</th>
<th>Hematite</th>
<th>Magnetite</th>
<th>Goethite</th>
<th>Siderite</th>
<th>Calcite</th>
<th>Gypsum</th>
<th>Pyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE11-12</td>
<td>6.61s/sat</td>
<td>2.61s/sat</td>
<td>2.82s/sat</td>
<td>-2.49</td>
<td>-0.39</td>
<td>-2.05</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>TE11-20</td>
<td>6.55s/sat</td>
<td>2.29s/sat</td>
<td>2.79s/sat</td>
<td>1.06s/sat</td>
<td>0.21s/sat</td>
<td>-1.85</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>TE11-55</td>
<td>2.19s/sat</td>
<td>0.88s/sat</td>
<td>0.61s/sat</td>
<td>0.22s/sat</td>
<td>-0.62</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML01-10</td>
<td>2.15s/sat</td>
<td>0.63s/sat</td>
<td>0.59s/sat</td>
<td>0.20s/sat</td>
<td>-0.88</td>
<td>-2.80</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML01-30</td>
<td>4.62s/sat</td>
<td>3.64s/sat</td>
<td>1.82s/sat</td>
<td>0.20s/sat</td>
<td>-0.29</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML01-40</td>
<td>7.29s/sat</td>
<td>7.17s/sat</td>
<td>3.16s/sat</td>
<td>0.85s/sat</td>
<td>-0.15</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>TE51-12</td>
<td>5.37s/sat</td>
<td>4.74s/sat</td>
<td>2.20s/sat</td>
<td>0.73s/sat</td>
<td>-0.22</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>TE51-20</td>
<td>2.82s/sat</td>
<td>2.05s/sat</td>
<td>0.93s/sat</td>
<td>0.32s/sat</td>
<td>-0.19</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>TC31</td>
<td>-2.34</td>
<td>&lt; 3</td>
<td>-1.66</td>
<td>-2.55</td>
<td>0.13s/sat</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>TE61</td>
<td>-2.47</td>
<td>&lt; 3</td>
<td>-1.72</td>
<td>-1.33</td>
<td>-0.51</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML02-10</td>
<td>-1.68</td>
<td>&lt; 3</td>
<td>-1.33</td>
<td>-0.44</td>
<td>-0.75</td>
<td>-2.86</td>
<td>3.72s/sat</td>
</tr>
<tr>
<td>TC45-12</td>
<td>-0.81</td>
<td>&lt; 3</td>
<td>-0.89</td>
<td>-0.21</td>
<td>-0.21</td>
<td>-2.17</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>TC45-20</td>
<td>6.28s/sat</td>
<td>3.56s/sat</td>
<td>2.65s/sat</td>
<td>-1.13</td>
<td>-0.13</td>
<td>-1.40</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML03-10</td>
<td>1.39s/sat</td>
<td>-0.75</td>
<td>0.21s/sat</td>
<td>-0.85</td>
<td>-1.09</td>
<td>-2.51</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML03-20</td>
<td>1.27s/sat</td>
<td>-0.24</td>
<td>0.15s/sat</td>
<td>-0.46</td>
<td>-1.90</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML03-50</td>
<td>-0.88</td>
<td>&lt; 3</td>
<td>-0.93</td>
<td>-2.08</td>
<td>-0.50</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML04-8</td>
<td>4.96s/sat</td>
<td>3.59s/sat</td>
<td>1.99s/sat</td>
<td>0.27s/sat</td>
<td>-0.31</td>
<td>-1.31</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML04-20</td>
<td>7.62s/sat</td>
<td>6.11s/sat</td>
<td>3.32s/sat</td>
<td>-0.91</td>
<td>-0.33</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML04-44</td>
<td>14.29s/sat</td>
<td>14.34s/sat</td>
<td>6.66s/sat</td>
<td>0.77s/sat</td>
<td>-0.57</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>ML05</td>
<td>5.91s/sat</td>
<td>4.54s/sat</td>
<td>2.47s/sat</td>
<td>-0.21</td>
<td>-0.94</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
</tbody>
</table>

Table 6.2. Summary table of the saturation indices of key mineral phases correct to 3 significant figures.

6.4.2 Stable isotopes:

The connectivity and degree of interaction between groundwater and surface waters was investigated by comparing the isotopic signature (\( \delta^D \) and \( \delta^{18}O \)) of groundwater from the study site (\( n = 20 \)) with that of Mekong river water and surface waters located at different points of the transect (\( n = 3 \)). A cumulative monthly sample of precipitation was also analysed to provide a local meteoric water line (LMWL) from which deviations in the isotopic signature of ground and surface water can be measured against. Figure 6.4 below shows the variation in the isotopic composition of local rainwater, groundwater, Mekong river water and surface waters. The local precipitation has a
slope of 8.3 which is similar to that of the global meteoric water line (GMWL) of 8.17 (ROZANSKI et al., 1993). The d excess of the local precipitation of between 8.1 and 17.6 (given here relative to a slope of 8) suggests there is a contribution of a kinetically controlled re-evaporated component of local surface waters to the precipitation characteristic of humid climates (CLARK and FRITZ, 2000). Mekong river water falls on or just below the LMWL for the months of May to November, which largely represents the monsoon season for the study site, and show a trend towards more evaporative signatures in the months of December to April, consistent with the timing of the dry season.

Groundwater samples typically fall on or below the LMWL, with a trend to more enriched values characteristic of the surface waters. This shift towards a more enriched isotopic signature is indicative of a contribution of an evaporated source of recharge to the groundwater at these locations, either from surface waters or as a result of evaporation of meteoric water during recharge. Comparison of the gradients of the regression lines for both the groundwaters (slope = 5.35) and the three surface waters (slopes = 6.06 – 6.1), which all display similar variations in their isotopic signature, suggests that surface waters are the most likely source of recharge to groundwater. These slopes are characteristic of evaporation lines for theoretical evaporation at 70 – 85% which covers the range of average monthly humidities for this location. The groundwater regression line intercepts the LMWL at an isotopic composition of precipitation similar to that which falls around September (intercept: δ¹⁸O = -7.8‰, δD = -48‰). This is very similar to the annual average isotopic composition of rainfall for the samples collected (δ¹⁸O = -7.5‰, δD = -46‰). The regression lines of the isotopic composition of the River Mekong and all three surface waters also intercept the LMWL near this value.

The isotopic composition of groundwater does not show any consistent trend in variation with depth at the same location, which suggests the deep groundwater at this site largely recharged under the same climatic conditions which currently prevail at the site. Similarly, there is no consistent trend in the stable isotopic signature of groundwater with increasing distance from the Mekong along the transect. However, site specific variations with depth can be identified at some locations, namely TE11, TE51 and ML04, all of which lie near surface water bodies. At site TE51 shallow groundwater at 12 m is enriched in δ¹⁸O by 2.85 ‰ compared to the groundwater at 20 m depth. This could reflect a larger contribution of evaporated surface water to the shallow groundwater at this location. The variations observed at sites TE11 and ML04 will be discussed in greater detail below.
Figure 6.4. $\delta^D$ vs $\delta^{18}O$ of groundwaters, surface waters and precipitation at the study site in the Kien Svay region, Kandal Province, Cambodia. Groundwater samples were collected in April 2009, with surface waters collected monthly between February and November 2009 and precipitation collected in the period February to October 2009. The Dixons Q test has shown the groundwater sample that plots to the left of the LMWL to be an outlier at the 99% confidence interval and so has not been considered in deriving the slope of the regression line for groundwater samples.

The three surface waters and the Mekong River show large variations in the isotopic signature of the different water bodies over the course of 11 months from February 2009 – December 2009 (figure 6.5 below). All four water bodies sampled have a broadly similar isotopic composition at the beginning of the monitoring period in February 2009, with $\delta^{18}O$ values of between -3.3‰ and -4.4‰. The Mekong River becomes gradually more depleted in $\delta^{18}O$ in the period of March – October 2009, with the onset of the depletion preceding the beginning of the monsoonal rains at the study site by about 2 months. The isotopic signature of the Mekong is similar to that of the local precipitation during the months of July – September and shows very little effect of evaporation. Instead, it appears to show a depletion in its isotopic signature which may reflect the progressive depletion of precipitation that occurs during a monsoon period, a phenomenon known as the amount effect as discussed previously in chapter 3.

In contrast to the Mekong, the surface ponds and wetlands show an opposite trend of isotopic enrichment in the period from March – August 2009, despite the isotopic composition of
precipitation being much more depleted than that of the ponds in this period. This period of the year represents the period in which both temperature and humidity increases to a peak in August/September and decreases thereafter, and as such reflects the evaporative enrichment of the surface waters at high relative humidities and temperatures at rates that may exceed the input from precipitation. This is supported by water level monitoring of wetlands at this site, which show a decrease in the water table during this period (BENNER et al., 2008). In the period of August – November 2009 the $\delta^{18}$O signature of the wetlands and wetland pond (which are connected) both decrease to more depleted $\delta^{18}$O values before a slight increase in the month of December at which point the two surface water bodies and the Mekong have a similar $\delta^{18}$O signature of -5.4 ‰. This period of the year reflects the point at which temperatures and humidities decrease but rainfall is still at high volumes, and where water levels in the wetlands drastically increase (BENNER et al., 2008). This suggests that dilution of the surface waters from mixing with precipitation is responsible for the depletion in the isotopic signature of these waters. However, the isolated pond does not display the same rapid decrease in $\delta^{18}$O during this period, nor does it display the large variation in $\delta^{18}$O of the other two surface water bodies. This pond is much deeper than the other two surface water bodies and as such may not be as sensitive to evaporation or contributions of precipitation which act to enrich and deplete the pond in $\delta^{18}$O.

Figure 6.5. Temporal variability of $\delta^{18}$O in surface water bodies at the study site in the Kien Svay region, Kandal Province, Cambodia over the period of February 2009 - December 2009.
Monthly monitoring of five tubewells presented in figure 6.6 below shows little consistent temporal variation in the δ¹⁸O signature of the groundwater over the period February 2009 – December 2009. However, large differences exist between different tubewells over the course of the transect. Tubewells TE11-12 and TE11-55 are located only 0.14 km from the Mekong at depths of 12 and 55 m respectively. These wells have the most depleted δ¹⁸O signature of the groundwaters sampled and appear to be unaffected by any contributions of evaporated surface waters. The shallow groundwater at this location may be in the sphere of influence of ingressing river water which recharges the groundwater during the months of July – November (BENNER et al., 2008). Tubewell TE11-55, in contrast, is on average 0.7‰ more depleted than TE11-12 over the course of the year, and as such may tap groundwater that is deeper than this sphere of influence. This depletion therefore perhaps reflects recharge under different climatic conditions than those which prevail today.

Tubewells TC45-12 and TC45-20 have a slightly more enriched δ¹⁸O groundwater signature relative to those at TE11. This may reflect contributions of recharge from surface waters to the groundwater at this location. This is consistent with hydraulic measurements of this well which have also suggested a possible influence of overlying surface waters to the groundwater (BENNER et al., 2008). Ponds in close proximity to this location may act as zones of preferential recharge through thinner or more conductive surficial deposits. Similarly, tubewell ML04-30 is more δ¹⁸O enriched than those at TC45. Indeed, groundwater at ML04-30 at a depth of 30 m is enriched in δ¹⁸O by more than 1‰ on average over the course of the 11 month monitoring period. This suggests that the groundwater at this location has a greater contribution of surface water to the groundwater, perhaps unsurprising given the close proximity (10 m) of this tubewell from the adjacent wetland pond. Further support of this is provided by the peak in the δ¹⁸O isotopic composition of -2.52‰ recorded at ML04-30 in the month of April. Sample collection from this well during this month was done with the use of a Grundfos MP1 submersible pump, which discharges water at a rate approximately 20 times faster than the peristaltic pump which was used for collection of samples from this location in every other month of monitoring. This δ¹⁸O of -2.52‰ is close to that of the nearby wetland pond at a depth of 3 m (-2.35‰) during this month. This suggests that pumping to purge the well and retrieve the sample has resulted in the drawdown of water from the nearby pond to the groundwater at this location.
6.4.3 Tritium

The connectivity of ground and surface water was further investigated through assessment of the tritium content of the groundwater and selected surface waters. The tritium content in precipitation from 1953 to 2004 is presented in figure 6.7 below. Here it can be seen that the present day tritium content at nearby Bangkok is approximately 2-4 TU, and has remained below 6 TU since 1984. The tritium content of the River Mekong of $3.5 \pm 0.18$ TU presented in table 6.3 below is consistent with current levels in precipitation and provides a constraint on the initial tritium content of recharging waters from which estimates of the time that has passed since recharge can be made.

Given that independent sampling of $^3$He and noble gases was not possible for this study site, determination of absolute ages is not possible. However, tritium concentrations in the groundwater of less than 3 TU suggest that infiltration took place following atmospheric bomb testing (the natural decay of tritium in groundwater is significantly slower than the rate of decrease of the thermonuclear tritium input function in precipitation because of massive attenuation in the oceans), which are typically greater than 10 TU in low latitude regions when residual “bomb” tritium is
present (CLARK and FRITZ, 2000). If we assume no hydrodynamic dispersion or mixing then estimates of groundwater age can be made from measured tritium concentrations and assumed tritium input functions. Table 6.3 below presents tritium concentrations for each of the wells and surface waters sampled, and gives mean groundwater residence times based on two tritium input functions.

![Graph](image)


Of the twenty groundwater samples analysed, thirteen were found to be tritium active. These were found over the first 2.2 km of the 2.6 km transect from the river Mekong and over a depth range of 8 – 44 m. Based on the two different tritium input functions used in the derivation of mean groundwater residence times in the table, groundwaters ages for tritium active groundwater range from a minimum of 5 years at site ML04 at a depth of 30 m to a maximum of 55.5 years at site ML01 at a depth of 9 m. All seven tubewells tapping groundwater at depths less than 12 m were found to be tritium active, with $^3$H concentrations found in the range of 1.35 – 2.53 TU. Of the six intermediate depth groundwater samples analysed, four were found to be tritium active with tritium concentrations of 1.63 – 2.65 TU over a depth range of 20 – 30 m. In contrast, only two of the seven deep groundwater samples were found to be tritium active, with concentrations of 2.01 ± 0.1 and 2.24 ± 0.12 TU reported for sites ML03 and ML04 at depths of 42 and 44 m respectively. Tritium dead groundwaters were found from depths of 20 m to the maximum depth of sampling at 60 m.
<table>
<thead>
<tr>
<th>Tubewell</th>
<th>Depth (m)</th>
<th>$^3$H (TU)</th>
<th>± σ (TU)</th>
<th>Mean residence time in years (Ao = 3.5 TU)</th>
<th>± σ years</th>
<th>Mean residence time in years (Ao = 30 TU)</th>
<th>± σ years</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE11 - 12</td>
<td>12.0</td>
<td>2.53</td>
<td>0.14</td>
<td>5.8</td>
<td>0.32</td>
<td>44.3</td>
<td>2.41</td>
</tr>
<tr>
<td>TE11 - 20</td>
<td>20.0</td>
<td>2.01</td>
<td>0.11</td>
<td>9.9</td>
<td>0.55</td>
<td>48.4</td>
<td>2.67</td>
</tr>
<tr>
<td>TE11 - 55</td>
<td>55.0</td>
<td>-0.07</td>
<td>-0.01</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>ML01 - 9</td>
<td>9.0</td>
<td>1.35</td>
<td>0.08</td>
<td>17.0</td>
<td>0.94</td>
<td>55.5</td>
<td>3.08</td>
</tr>
<tr>
<td>ML01 - 29</td>
<td>28.6</td>
<td>-0.05</td>
<td>-0.01</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>ML01 - 37</td>
<td>37.0</td>
<td>-0.14</td>
<td>-0.01</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>TE51 - 12</td>
<td>12.0</td>
<td>2.22</td>
<td>0.12</td>
<td>8.2</td>
<td>0.45</td>
<td>46.7</td>
<td>2.54</td>
</tr>
<tr>
<td>TE51 - 20</td>
<td>20.0</td>
<td>-0.06</td>
<td>-0.01</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>TC31</td>
<td>51.0</td>
<td>-0.04</td>
<td>-0.01</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>TE61</td>
<td>48.0</td>
<td>-0.06</td>
<td>-0.01</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>ML02</td>
<td>8.5</td>
<td>1.55</td>
<td>0.08</td>
<td>14.6</td>
<td>0.79</td>
<td>53.1</td>
<td>2.86</td>
</tr>
<tr>
<td>TC45 - 12</td>
<td>12.0</td>
<td>1.91</td>
<td>0.11</td>
<td>10.9</td>
<td>0.64</td>
<td>49.4</td>
<td>2.90</td>
</tr>
<tr>
<td>TC45 - 20</td>
<td>20.0</td>
<td>1.89</td>
<td>0.10</td>
<td>11.0</td>
<td>0.59</td>
<td>49.5</td>
<td>2.66</td>
</tr>
<tr>
<td>ML03 - 7</td>
<td>7.3</td>
<td>1.78</td>
<td>0.09</td>
<td>12.1</td>
<td>0.63</td>
<td>50.6</td>
<td>2.62</td>
</tr>
<tr>
<td>ML03 - 24</td>
<td>23.8</td>
<td>1.63</td>
<td>0.09</td>
<td>13.7</td>
<td>0.74</td>
<td>52.2</td>
<td>2.82</td>
</tr>
<tr>
<td>ML03 - 42</td>
<td>42.0</td>
<td>2.01</td>
<td>0.10</td>
<td>10.0</td>
<td>0.52</td>
<td>48.5</td>
<td>2.52</td>
</tr>
<tr>
<td>ML04 - 8</td>
<td>8.2</td>
<td>2.06</td>
<td>0.11</td>
<td>9.5</td>
<td>0.51</td>
<td>48.0</td>
<td>2.60</td>
</tr>
<tr>
<td>ML04 - 30</td>
<td>29.1</td>
<td>2.65</td>
<td>0.14</td>
<td>5.0</td>
<td>0.27</td>
<td>43.5</td>
<td>2.33</td>
</tr>
<tr>
<td>ML04 - 44</td>
<td>44.0</td>
<td>2.24</td>
<td>0.12</td>
<td>8.0</td>
<td>0.42</td>
<td>46.5</td>
<td>2.46</td>
</tr>
<tr>
<td>ML05</td>
<td>60.0</td>
<td>-0.05</td>
<td>-0.01</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
<td>&gt; 60</td>
</tr>
<tr>
<td><strong>Surface waters</strong></td>
<td><strong>3H (TU)</strong></td>
<td><strong>± σ (TU)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mekong</td>
<td>3.5</td>
<td>0.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wetlands</td>
<td>1.9</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isolated pond (sampled at surface)</td>
<td>2.1</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isolated pond (sample at 30 m depth)</td>
<td>2.0</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3. $^3$H concentrations for each of the groundwaters and surface waters sampled in April 2009 at the study site in the Kien Sve region, Kandal Province, Cambodia. Errors are given as 1 σ of the tritium concentration. Mean groundwater residence times are given for two tritium input functions. The tritium input function of 3.5 TU represents that in Mekong river water which is assumed to represent the tritium concentration of present day precipitation at the study site. The tritium input function of 30 TU is used to represent the largest possible input function for groundwaters which recharged after the cessation of thermonuclear bomb testing and represents the tritium concentration in precipitation which fell in 1969 based on figure 6.7 above.

The presence of tritium active groundwater suggests an active component of surface water recharge along the entire 2.6 km profile. This recharge is penetrating to depths of up to 44 m at some locations, with depth of $^3$H penetration perhaps dependent on the conductivity of the sediments at these location. The three well nests which report tritium active groundwater over the entire depth profile (TC45, ML03 and ML04) are all located in close proximity to surface water bodies. Including site ML02, which is also tritium active, these groundwaters are all located more than 1.4 km from the river Mekong, much closer to sites of active recharge in the wetlands based on hydrological modelling (BENNER et al., 2008). Similarly, site TE11, which reports tritium active groundwater in both the shallow and intermediate depth groundwaters, is thought to be influenced by ingressing Mekong...
river water based hydraulic head measurements in the rainy season, during which period the Mekong River recharges the groundwater system at this site (BENNER et al., 2008). Tritium concentrations decrease with depth in four of the six well nests, which suggests that groundwater flow is typically from the vertical migration of recharging surface waters over the upper 20 – 30 m, consistent with groundwater flow modelling at the site (BENNER et al., 2008). That tritium concentrations do not always decrease with depth (as observed at sites ML03 and ML04) suggests that there must be rapid flow paths to depth at some locations. At these locations the groundwater at depth is likely to represent a mixture of the vertical migration of water from above and the lateral migration of groundwater through more conductive sediments lateral to the site, potentially infiltrating from the nearby ponds.

Arsenic concentrations were typically quite low in the $^3$H active groundwaters, with only three of the thirteen $^3$H active groundwaters containing As above 35 µg/l (Figure 6.8 below). In contrast, all of the $^3$H dead groundwaters had concentrations of As that exceeded this value, with a range of As concentrations from 44 – 1100 µg/l. This may suggest that the modern component of recharge to the groundwaters provides a supply of oxidants that prevents the onset of the reducing conditions required to support reductive processes. Such a scenario has been noted elsewhere, where the presence of highly conductive sediments can provide recharge at rates of up to an order of magnitude faster than aquifers which underlie relatively impermeable fine grained sediment (AZIZ et al., 2008; ITAI et al., 2008; WEINMAN et al., 2008). In contrast, $^3$H dead groundwaters probably underlie sediments which are relatively impermeable, and which have been shown to act as a barrier to oxidants and lead to the development of reducing conditions (VAN GEEN et al., 2006). This geomorphic control on As distribution has also been identified in numerous other studies which link high As groundwaters with geomorphologic and surface features such as abandoned or existing channels, swamps and ox bow lakes, which are areas of surface water accumulation (ACHARYYA and SHAH, 2007; NATH et al., 2005). These features have been shown to be areas where rapid deposition of OM occurs and facilitates the release of As to groundwaters (PAPACOSTAS et al., 2008; QUICKSALL et al., 2008). The three groundwater samples which are $^3$H active but where As concentrations exceed 100 µg/l can be accounted for based on their location on the profile. Sample TE11-20, which has an As concentration of 346 µg/l, as discussed previously, is located within the sphere of influence of ingressing river water. This would give rise to the modern $^3$H signature that may otherwise be $^3$H dead, and may result in a decrease in the As concentration as a result of dilution. Similarly, locations ML01-10 and TE51-12 are located in the zone of high As but are tritium active. This may either reflect hydrologic transport of As from upstream in to groundwater which has an active component
of modern recharge from above or a rapid removal of oxidants from the system during recharge thus maintaining the reducing conditions that are required for As mobilisation.

Surface water ponds appear to have a tritium concentration that is less than that of the local precipitation (based on the tritium content of Mekong river water). Under normal conditions it would be expected that such surface waters would typically be slightly enriched in tritium relative to the local precipitation because of fractionation during evaporation. This therefore suggests that there is a contribution of water with a smaller tritium concentration than the local precipitation to these surface waters. The only source of water that would not necessarily contain the same concentration of tritium as the local precipitation is groundwater. This observation, alongside the presence of rapid flow paths transporting surface water to groundwater at depths of up to 44 m at site ML04, supports the interpretations based on stable isotopes above that there is significant interaction between surface waters and groundwaters at this site.

![Figure 6.8. Variation in groundwater As concentrations as a function of the $^3$H of the co-existing groundwater.](image)

6.4.4 Carbon – 13 isotope systematics

Carbon-13 is often used in hydrological studies as a tracer of carbonate evolution because of the large variations in the different carbon reservoirs. However, it is typically of limited use in provenancing organic matter (OM) present in the aqueous phase because of the large overlaps in
the isotopic composition of the assumed major sources of DOC to groundwater (i.e. vegetation, peat and wetland OM). In this study carbon-13 measurements were made on both dissolved inorganic carbon (DIC) and DOC for each groundwater sample collected and is presented in figure 6.9 below. Groundwater DIC was found to have a range in δ\(^{13}\)C of -19.6 to +1.1 ‰, whilst DOC was found to have a range in δ\(^{13}\)C of -5.3 to -29.3 ‰. No coherent trend was observed in δ\(^{13}\)C with depth or distance along the transect from the River Mekong for either DIC or DOC and as such these distributions are not presented.

As well as being a useful tracer of carbonate evolution in groundwaters, changes in δ\(^{13}\)C may also be used as an indicator of redox evolution, with certain redox processes producing strong fractionation of the δ\(^{13}\)C of the different carbon species present in both the aqueous and gas phases. The groundwater DIC δ\(^{13}\)C signature appears to show variability over most of its range in a narrow band of δ\(^{13}\)C values of DOC from -24.4 to -29.3 ‰, and otherwise clusters in a narrow δ\(^{13}\)C range from -12 to -17.6 ‰ in DIC. This shift to more enriched values could derive from three different processes. The first potential process is the dissolution of carbonate minerals within the aquifer matrix contributing DIC with a δ\(^{13}\)C equal to that of the dissolving carbonate phase. However, the most enriched groundwater, which likely represents a mixture of DIC from terrestrial sources (which would have a δ\(^{13}\)C signature comparable to the other groundwaters of around -13 ‰) and a more enriched source of δ\(^{13}\)C, has an isotopic composition of 1.1 ‰. This isotopic signature is similar to typical δ\(^{13}\)C values for carbonates which rarely exceed 3.4 ‰ (Clark and Fritz, 2000). Contributions of DIC from carbonates with this signature would have to exceed that from terrestrial and soil sources. This is unlikely given that estimates of carbonate derived DIC contributions to groundwater based on chemical and isotope mass balance calculations in Chapter 5 do not exceed 58% of the total DIC in solution, with carbonate dissolution contributing 48% of the total DIC in this particular sample.

A second potential source of enriched δ\(^{13}\)C values could derive from contributions of DIC which is produced during methanogenesis. Methanogenesis is common in shallow groundwaters and is driven by the bacterial reduction of an organic carbon substrate. The generation of methane occurs only in reducing groundwaters and in the absence of other energy-free electron acceptors such as NO\(_3^-\) and SO\(_4^{2-}\), conditions which are often found in wetlands (Clark and Fritz, 2000). In such settings, methane produced through the acetate fermentation pathway can generate CO\(_2\) with a δ\(^{13}\)C of +10 ‰ (Whiticar et al., 1986). High As groundwaters have been found to be associated with methanogenesis at the site investigated in this study (Buschmann and Berg, 2009). However, as with
the carbonate dissolution driven δ\(^{13}\)C enrichment theory, significant contributions of DIC from methanogenesis are required to generate a δ\(^{13}\)C signature of 1.1 ‰. Such a scenario could only be confirmed by the in-situ measurement of groundwater CH\(_4\) concentrations, supported by determination of the δ\(^{13}\)C of CH\(_4\) in the groundwater. The absence of such data in this study means that this possibility remains unresolved.

The final potential process that could give rise to the enriched δ\(^{13}\)C signature of DIC in some samples is the progressive enrichment of the sample signature following collection but prior to analysis. A recent study by Taipale and Sonninen (2009) showed that the δ\(^{13}\)C signature of samples stored in glass in the absence of any preservation agent increased by 7.7 ‰ over a period of 183 days. This increase is thought to be a result of diffusive escape of CO\(_2\) from the sample container. A difference in the head space between samples could therefore give rise to differing degrees of CO\(_2\) degassing, and could produce the variation in the δ\(^{13}\)C of DIC that we see in these groundwaters.

![Diagram](image)

**Figure 6.9.** Variations in the δ\(^{13}\)C of DIC and DOC in groundwaters collected in April 2009 at the study site in the Kien Svey region, Kandal Province, Cambodia.

The variation in δ\(^{13}\)C of DOC in groundwater is similar to that of the DIC in that it occurs over a narrow band of δ\(^{13}\)C values in DIC from -18 to -13 ‰. However, in contrast to DIC, variations in the δ\(^{13}\)C of DOC can only occur as a result of changes in the dominant source of OM to the pool of DOC present in the groundwater. Values of δ\(^{13}\)C of DOC of around -25 ‰ could derive from any one of the assumed sources of DOC to groundwater, and enrichment in δ\(^{13}\)C could reflect a shift in the
dominant vegetation in the recharging waters from C₃ plants to C₄ plants. However, the isotopic range in δ¹³C of C₄ plants is -10 to -16 ‰ (VOGEL, 1993), and at the time of writing this report there were no published articles which report δ¹³C values of DOC as enriched as -5 ‰. Given this, the variations in δ¹³C of DOC more likely reflects enrichment in δ¹³C imparted on the sample during processing and preparation. Samples that are to be analysed for δ¹³C DOC are acidified to pH < 4, which is the pH at which all inorganic carbon should be present as carbon dioxide, and sparged with N₂ gas to remove all of the DIC from the sample. The δ¹³C signature of the sample is therefore assumed to represent the isotopic signature of the remaining DOC. However, if the CO₂(g) is not totally removed from solution, small concentrations of the remaining DIC will impart a significant enrichment on the observed δ¹³C signature. Furthermore, the process of driving the carbon species to CO₂(g) dominated imparts a fractionation of 8.5‰ between HCO₃⁻ and CO₂(g) at 20°C (MOOK et al., 1974). Modelled δ¹³C for total carbon below (figure 6.10) shows that if as little as 1 – 5 % of the initial DIC remains in solution following the cessation of sparging, the δ¹³C can be enriched to a signature that explains the deviation in the δ¹³C DOC for these samples. The samples that appear to have been subjected to the greatest amount of enrichment were found to be those which had the lowest DOC to DIC concentration ratio.
6.4.5 C-14 of dissolved inorganic carbon

In addition to the use of $^3$H to determine the presence of a young component of recharge to the groundwater system studied here, the $^{14}$C signature of DIC was determined to (i) confirm observations made from $^3$H analysis, and (ii) provide estimates of the mean residence time of groundwaters which are outside the dateable range of the $^3$H technique. These ages are presented in table 6.4 below. The uncorrected age represents that calculated from the actual measured concentration of $^{14}$C in each groundwater sample. The matrix exchange age presented alongside the uncorrected $^{14}$C ages in this table represent $^{14}$C ages which have been corrected using the amended matrix exchange model discussed in chapter 5. This model is based on the Fontes-Garnier model (FONTES and GARNIER, 1979) and uses cation concentrations to correct for contributions of DIC from $^{14}$C-free matrix carbonate. This correction factor also utilises $\delta^{13}$C values obtained from RCF-E to apportion the $^{14}$C in to that which exchanged with CO$_2$ gas in the soil zone under open system
conditions and that which exchanged only with the carbonate matrix under closed system conditions.

Matrix exchange model values presented below are consistent with $^3$H measurements in thirteen of the twenty groundwaters analysed. These concordant age determinations suggest that a major contribution of the groundwater at locations with $^3$H active signatures derives from recharge which has occurred during the last 50 years, whilst there is very little contribution of recent recharge in samples that are $^3$H dead. Interestingly, five of these samples did not require assessment of the dilution of $^{14}$C in DIC through contributions of $^{14}$C-free carbonate, with $^{14}$C values indicative of groundwater that has recharged during the last 50 years at each of these locations. Again, consistent with $^3$H observations, groundwater at depths of 12 and 20 m at site TE11 appears to be influenced by ingressing Mekong river water. The modelled age of 3214 years at a depth of 55 m at site TE11 is of the correct order of magnitude but greater than estimated residence times that has been determined by hydraulic head measurements for groundwater travel times from the internal wetlands to the river Mekong (BENNER et al., 2008). This suggests that groundwater flow in the deep subsurface at this site may be slower than previously thought. However, discordant ages between $^3$H and co-existing $^{14}$C are evident in five of the twenty samples. At tubewells TE61 and ML03-40, input parameters for were shown to contain outliers, and as such modelled ages could not be determined.

The model gives discordant ages for samples ML01-40 and TE51-20, predicting modern ages in $^3$H-dead groundwaters. This could suggest that the models over predicts the amount of carbonate derived $^{14}$C dead DIC that is contributed to the groundwater at these locations. Alternatively, it could suggest that the carbonate that is undergoing dissolution is not $^{14}$C-dead. This may occur when calcite is present as an authigenic phase that has precipitated in the sediment following its deposition. This is entirely possible given that these sediments themselves were only deposited since the late Pleistocene (TAMURA et al., 2009). The matrix exchange model also provides a discordant age for sample ML04-20, estimating a relatively old age in $^3$H-active water. The dilution factor derived discussed in chapter 5 suggests that the groundwater at this location is frequently undergoing exchange with soil CO$_2$, indicative of a contribution of young water from the surface to groundwater which has been transported along a flow path to this location. This would give rise to an older modelled age in water that clearly has a component of $^3$H active recharge.

The final discordant ages are those predicted for samples ML02 and ML04-8, which the matrix exchange model used here predicts to be much older than the $^3$H concentration suggests the true
age to be. The relatively low concentrations of Ca\(^{2+}\) and depleted \(\delta^{13}\)C signatures of the groundwater at these locations suggest that the model has not underestimated the dilution factor required for contributions of \(^{14}\)C-dead DIC from carbonate dissolution at these locations. This suggests that an alternative source(s) of diluting DIC is made to the groundwater at these sites that is not considered in the model. The measured \(^{14}\)C activity can be diluted not just by geochemical processes as discussed throughout this study, but also by mixing processes. Bethke and Johnson (2002) show that mixing of old waters that have been trapped in aquitards with younger groundwater occurs at a rate that is controlled only by the ratio of volume fluid in aquitards and aquifers, and is independent of the actual rate of the contribution (a function of permeability). Given that both of these samples are taken from shallow tubewells no more than 8.5 m deep positioned either in or directly below surficial clay deposits at this site, a large contribution of much older water may be made from the extensive clay deposits at these locations. Such a contribution could act to dilute the measured \(^{14}\)C activity of the groundwater in these locations.

Another point of interest here is the uncorrected \(^{14}\)C ages at sites ML04-30 and 44. Stable isotope and tritium data discussed above are indicative of the presence of evaporated surface waters with a tritium concentration slightly lower than that in present day local precipitation. The stable isotopic composition is characteristic of a large contribution of recharge from the nearby pond. However, the uncorrected \(^{14}\)C signature suggests that there has been sufficient time for dilution of the corrected modern signature from contributions of \(^{14}\)C-free aquifer carbonates. Similarly, the tritium concentration here suggests that it has taken at least 5 – 8 years for the recharging water to reach the groundwater at these locations. It is perhaps therefore more likely that the sampling process, like at ML02, has resulted in the mixing of modern (i.e. present day) recharge from the nearby ponds, which would contain \(^3\)H and \(^{14}\)C concentrations greater than or equal to 100 pmC (or 3.5 TU in the case of \(^3\)H), with groundwater which has a slightly lower \(^3\)H activity and which has had sufficient time to have dilution of \(^{14}\)C in the DIC from contributions of \(^{14}\)C-free matrix carbonate.
<table>
<thead>
<tr>
<th>Tubewell</th>
<th>Uncorrected Age (years)</th>
<th>Matrix Exchange Age (years)</th>
<th>$^3$H (TU)</th>
<th>Model Consistent</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE11 - 12</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>2.53</td>
<td>Yes</td>
</tr>
<tr>
<td>TE11 - 20</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>2.01</td>
<td>Yes</td>
</tr>
<tr>
<td>TE11 - 55</td>
<td>4126</td>
<td>3214</td>
<td>-0.07</td>
<td>Yes</td>
</tr>
<tr>
<td>ML01 - 10</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>1.35</td>
<td>Yes</td>
</tr>
<tr>
<td>ML01 - 30</td>
<td>2483</td>
<td>502</td>
<td>-0.05</td>
<td>Yes</td>
</tr>
<tr>
<td>ML01 - 40</td>
<td>2689</td>
<td>&gt; 0</td>
<td>-0.14</td>
<td>No</td>
</tr>
<tr>
<td>TE51 - 12</td>
<td>24</td>
<td>&gt; 0</td>
<td>2.22</td>
<td>Yes</td>
</tr>
<tr>
<td>TE51 - 20</td>
<td>2026</td>
<td>&gt; 0</td>
<td>-0.06</td>
<td>No</td>
</tr>
<tr>
<td>TC31</td>
<td>1275</td>
<td>1245</td>
<td>-0.04</td>
<td>Yes</td>
</tr>
<tr>
<td>TE61</td>
<td>961</td>
<td>-</td>
<td>-0.06</td>
<td></td>
</tr>
<tr>
<td>ML02 - 10</td>
<td>4082</td>
<td>4085</td>
<td>1.55</td>
<td>No</td>
</tr>
<tr>
<td>TC45 - 12</td>
<td>1348</td>
<td>&gt; 0</td>
<td>1.91</td>
<td>Yes</td>
</tr>
<tr>
<td>TC45 - 20</td>
<td>271</td>
<td>&gt; 0</td>
<td>1.89</td>
<td>Yes</td>
</tr>
<tr>
<td>ML03 - 10</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>1.78</td>
<td>Yes</td>
</tr>
<tr>
<td>ML03 - 20</td>
<td>3319</td>
<td>&gt; 0</td>
<td>1.63</td>
<td>Yes</td>
</tr>
<tr>
<td>ML03 - 50</td>
<td>7268</td>
<td>-</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>ML04 - 8</td>
<td>1682</td>
<td>1056</td>
<td>2.06</td>
<td>No</td>
</tr>
<tr>
<td>ML04 - 30</td>
<td>586</td>
<td>1539</td>
<td>2.65</td>
<td>No</td>
</tr>
<tr>
<td>ML04 - 44</td>
<td>448</td>
<td>&gt; 0</td>
<td>2.24</td>
<td>Yes</td>
</tr>
<tr>
<td>ML05</td>
<td>2419</td>
<td>768</td>
<td>-0.05</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 6.4. Summary of uncorrected and modelled mean groundwater residence times. An internal consistency check is provided by comparing modelled values to measured $^3$H concentrations in co-existing groundwater. Modelled values could not be determined for locations TE61 and ML03-50 because key input parameters were shown to lie more than 2σ from mean values, and as such considered to be outliers.

6.4.6 C-14 ages of dissolved organic carbon

In addition to using $^{14}$C from DIC to determine groundwater residence times, $^{14}$C of DOC can also be used as a provenancing tool to assess the sources of OM that contributes DOC to the groundwater. It can be seen from table 6.5 below that the age of DOC present in the aqueous phase varies significantly, with a range of DOC ages from 4036 years to that which is present at bomb levels and so must have entered the groundwater within the last 50 years. Groundwater DOC increases in age in five of the six well nests, with differences in the DOC ages greater than that of the groundwater age based on the DIC data discussed above. This suggests that contributions of DOC to the groundwater are made by sedimentary sources of OM present within the subsurface consistent with DOC concentration profiles that show an increase with depth. Modern OM is present at depths of 29 and 44 m at ML04. This location was also shown to have a significant contribution of recharge from
modern surface waters based on $^3$H and $^{14}$C$_{DOC}$ measurements discussed above. Stable isotope data is indicative of an evaporative source of recharge, which is likely derived from the nearby pond, and we suggest that pumping of the groundwater for sample collection has drawn this water in through more conductive sediments. The observation of modern OM in groundwater at this depth represents the first occasion that modern DOC has been identified in an As-bearing groundwater system, and demonstrates unequivocally that young, labile surface derived DOC can be transported in recharging waters. That modern DOC is not observed elsewhere along the profile may suggest that the sediments at this site are particularly conductive and thus allow rapid transport of water and its dissolved constituents, including DOC, at rates that exceed that at which it is being consumed in biogeochemical or oxidative processes. This may or may not have been exacerbated by high volume pumping during sample collection. Alternatively, this may suggest that other locations have more significant contributions of sedimentary-derived DOC or that modern DOC is consumed at a faster rate in these locations.

<table>
<thead>
<tr>
<th>Tubewell</th>
<th>Depth (m)</th>
<th>C-14 enrichment (% modern)</th>
<th>+/-</th>
<th>C-14 age (yrs BP)</th>
<th>+/-</th>
<th>$\delta^{13}$C (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE11 - 12</td>
<td>12</td>
<td>99.07</td>
<td>0.46</td>
<td>75</td>
<td>37.01</td>
<td>-5.3</td>
</tr>
<tr>
<td>TE11 - 20</td>
<td>21</td>
<td>87.94</td>
<td>0.41</td>
<td>1032</td>
<td>37.05</td>
<td>-18.3</td>
</tr>
<tr>
<td>TE11 - 55</td>
<td>55</td>
<td>60.50</td>
<td>0.28</td>
<td>4036</td>
<td>38.00</td>
<td>-18.5</td>
</tr>
<tr>
<td>ML01 - 9</td>
<td>9</td>
<td>93.83</td>
<td>0.41</td>
<td>512</td>
<td>35</td>
<td>-13.4</td>
</tr>
<tr>
<td>ML01 - 29</td>
<td>29</td>
<td>71.65</td>
<td>0.31</td>
<td>2679</td>
<td>35</td>
<td>-25.0</td>
</tr>
<tr>
<td>ML01 - 37</td>
<td>37</td>
<td>72.57</td>
<td>0.34</td>
<td>2575</td>
<td>37</td>
<td>-26.5</td>
</tr>
<tr>
<td>TE51 - 12</td>
<td>12</td>
<td>91.08</td>
<td>0.42</td>
<td>751</td>
<td>37.08</td>
<td>-27.3</td>
</tr>
<tr>
<td>TE51 - 20</td>
<td>20</td>
<td>85.47</td>
<td>0.39</td>
<td>1261</td>
<td>37.09</td>
<td>-25.7</td>
</tr>
<tr>
<td>TC31</td>
<td>51</td>
<td>89.99</td>
<td>0.41</td>
<td>847</td>
<td>36.98</td>
<td>-26.6</td>
</tr>
<tr>
<td>TE61</td>
<td>48</td>
<td>89.61</td>
<td>0.39</td>
<td>881</td>
<td>35</td>
<td>-26.6</td>
</tr>
<tr>
<td>ML02</td>
<td>9</td>
<td>75.06</td>
<td>0.33</td>
<td>2304</td>
<td>35</td>
<td>-26.2</td>
</tr>
<tr>
<td>TC45 - 12</td>
<td>12</td>
<td>71.03</td>
<td>0.31</td>
<td>2748</td>
<td>35.44</td>
<td>-19.1</td>
</tr>
<tr>
<td>TC45 - 20</td>
<td>20</td>
<td>93.75</td>
<td>0.41</td>
<td>519</td>
<td>35.13</td>
<td>-21.6</td>
</tr>
<tr>
<td>ML03 - 7</td>
<td>7</td>
<td>91.45</td>
<td>0.42</td>
<td>718</td>
<td>37</td>
<td>-21.6</td>
</tr>
<tr>
<td>ML03 - 24</td>
<td>24</td>
<td>87.88</td>
<td>0.38</td>
<td>1038</td>
<td>35</td>
<td>-26.9</td>
</tr>
<tr>
<td>ML03 -42</td>
<td>42</td>
<td>83.52</td>
<td>0.37</td>
<td>1447</td>
<td>35</td>
<td>-24.4</td>
</tr>
<tr>
<td>ML04 - 8</td>
<td>8</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>ML04 - 30</td>
<td>29</td>
<td>105.38</td>
<td>0.49</td>
<td>&lt; 50</td>
<td>0</td>
<td>-29.3</td>
</tr>
<tr>
<td>ML04 - 44</td>
<td>44</td>
<td>100.71</td>
<td>0.46</td>
<td>&lt; 50</td>
<td>0.00</td>
<td>-26.2</td>
</tr>
<tr>
<td>ML05</td>
<td>60</td>
<td>64.80</td>
<td>0.28</td>
<td>3485</td>
<td>35</td>
<td>-26.2</td>
</tr>
</tbody>
</table>

Table 6.5. C-14 analysis results and derived C-14 ages for dissolved organic carbon. ND for tubewell ML04-8 denotes not determined - insufficient sample material
Figure 6.11. Variations in C-14 ages of DOC and groundwater ages as a function of depth. Groundwater ages are based on modelled $^{14}$C DIC ages where comparison with $^3$H produces concordant ages. Where modelled $^{14}$C DIC ages over predict groundwater age, $^3$H ages assuming a tritium input function of 3.5 TU are used. When modelled $^{14}$C ages are modern alongside co-existing $^3$H dead groundwater, ages of 60 years are used which represent a minimum possible groundwater age.

If it is assumed that the DOC ages presented here represent 100 % of the DOC in solution (i.e. it is not a mixture of different sources), then comparison of these DOC ages with $^{14}$C ages of sediments at this study site presented in Tamura et al (2009) suggest that DOC present in the groundwaters at this site must derive from OM present in the upper 5 m of sediment. However, in reality these ages likely represent a mixture of differently sourced OM that have accumulated during recharge and over the course of the flow path. Indeed, the bulk DOC age is older than the groundwater age (following correction for carbonate dissolution) in every single groundwater (presented in figure 6.11 above) with the exception of two groundwater samples which contain modern DOC in co-existing modern groundwater and one location where groundwater is approximately 400 years older than the co-existing DOC. This demonstrates that a contribution of older OM is required to produce the observed distribution of DOC ages. As discussed previously, $\delta^{13}$C cannot be used to resolve these contributions because of the large overlap in the $\delta^{13}$C of the different OM sources implicated. Given that the OM
sources implicated in As release have a range of ages from modern (in the case of surface derived organic carbon transported during recharge of infiltrating surface waters) to thousands of years old (in the case of buried peat deposits), we calculated model ages of DOC from the mixing of modern OM with sedimentary sourced OM with ages of 1000, 3000, 6000 and 9000 years (figure 6.12) based on two component mixing.

The groundwater DOC data presented in figure 6.12B below is most consistent with mixing between approximately 1 mg/l of modern (age corrected) OM with sedimentary derived OM with ages of 6000 – 1000 years. There is little evidence for mixing of modern OM with sedimentary derived OM that is younger than 1000 years, which is consistent with observed DOC ages that frequently exceed this. Similarly, the data is inconsistent with mixing of modern OM with sedimentary derived OM that is older than 9000 years. C-14 measurements of the sediment from three drill cores at this study site place an upper and lower age limit of 8.4 - 6.3 kyrs on peat deposits present in the subsurface that are typically present at depths of 6 m to a maximum of 14 m (TAMURA et al., 2009). The data presented here suggests that peat deposits contribute very little to the DOC pool present in groundwater at this site, and that the large majority of the DOC that does not derive from the surface is sourced from the upper 5 m of sediments below these peat deposits. This is consistent with observations in Kocar et al (2008) of increases in aqueous concentrations of HCO$_3^-$ to a depth of 5 - 10 m alongside younger $^{14}$C ages of DIC (less than 1200 years) compared to that of the sediment (more than 6000 years old) that they suggest are indicative of a surface or near surface source of OM.

Given that groundwater DOC ages can be explained by mixing of age corrected surface derived OM and sedimentary OM between 1 – 6 kyrs, a maximum estimate of the relative contributions of surface derived OM and sedimentary derived OM can be calculated by simple two component mixing. This is presented in table 6.6 below. From this it can be seen that, as the age of the sedimentary OM end member increases, the contributions of surface derived modern OM must also increase to produce the observed DOC age. Similarly, where modern DOC is present, 100 % of the DOC must derive from modern surface derived OM. Where values are not given the model did not converge on a contribution. This was because the age of the sample was older than the sedimentary OM end member. Older groundwater DOC signatures require that either (i) the groundwater has passed through sediment that is at least as old as the sample, in which case 100 % of the DOC derives from this source, or (ii) that the age of the groundwater is at least as old as the sample, in which case 100 % of the DOC derives from that which has been transported following recharge. It is
unlikely that scenario (i) would occur because it would be expected that the amount of available OM in the sediment would decrease with depth. In contrast, scenario (ii) may be common in groundwaters where significant contributions of modern surface water are present.

In addition to placing limits on the range of ages of sedimentary OM that is mixed with modern OM, we can also constrain the initial concentration of modern OM that is mixed with various additions of sedimentary OM. The data presented in figure 6.12B is consistent with an initial concentration of 1 mg/l of modern DOC mixing with sedimentary OM. Initial concentrations below and above this value provide poor fits to the data, as evidenced by figures 6.12A, C and D above. This suggests that, even with an apparently old DOC signature, a contribution of a surface-derived component of OM must still be present in the groundwater, even if at small concentrations.

The observations and interpretations discussed above are heavily model dependent, and this model likely represents a simplification of the actual processes associated with the liberation of, and

Figure 12. C-14 ages of DOC in groundwater collected in April 2009 at the study site in Kien Svey region, Kandal Province, Cambodia. Lines represent modelled ages of groundwater DOC from mixing of modern OM with sediment derived OM with ages of 1000, 3000, 6000 and 9000 years respectively. Plots A, B, C and D have starting concentrations of 0.1, 1, 2 and 5 mg/l modern organic carbon respectively. Groundwaters that plot to the right of the the 1000 year OM mixing line are composed of a greater contribution of modern OM.
removal of DOC in groundwater. It is more likely that DOC accumulates from different sources over the course of a flow path during which time a fraction of the DOC will be removed following its involvement in biogeochemical processes. In such a scenario, the age of the DOC in the groundwater is actually equivalent to the weighted integrated mean age of the different contributions of DOC along the flow path which remains in the groundwater. As such, these estimates represent the maximum possible contributions of modern OM to the groundwater DOC pool.

<table>
<thead>
<tr>
<th>Tubewell</th>
<th>C-14 enrichment (% modern)</th>
<th>% sedimentary OM</th>
<th>% modern OM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>TE11 - 12</td>
<td>99.07</td>
<td>8.2</td>
<td>3.1</td>
</tr>
<tr>
<td>TE11 - 20</td>
<td>87.94</td>
<td>-</td>
<td>39.6</td>
</tr>
<tr>
<td>TE11 - 55</td>
<td>60.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ML01 - 9</td>
<td>93.83</td>
<td>54.2</td>
<td>20.3</td>
</tr>
<tr>
<td>ML01 - 29</td>
<td>71.65</td>
<td>-</td>
<td>93.0</td>
</tr>
<tr>
<td>ML01 - 37</td>
<td>72.57</td>
<td>-</td>
<td>89.9</td>
</tr>
<tr>
<td>TE51 - 12</td>
<td>91.08</td>
<td>78.3</td>
<td>29.3</td>
</tr>
<tr>
<td>TE51 - 20</td>
<td>85.47</td>
<td>-</td>
<td>46.5</td>
</tr>
<tr>
<td>TC31</td>
<td>89.99</td>
<td>87.0</td>
<td>31.2</td>
</tr>
<tr>
<td>TE61</td>
<td>89.61</td>
<td>90.6</td>
<td>32.5</td>
</tr>
<tr>
<td>ML02</td>
<td>75.06</td>
<td>-</td>
<td>81.9</td>
</tr>
<tr>
<td>TC45 - 12</td>
<td>71.03</td>
<td>-</td>
<td>95.2</td>
</tr>
<tr>
<td>TC45 - 20</td>
<td>93.75</td>
<td>54.9</td>
<td>20.5</td>
</tr>
<tr>
<td>ML03 - 7</td>
<td>91.45</td>
<td>75.1</td>
<td>28.1</td>
</tr>
<tr>
<td>ML03 - 24</td>
<td>87.88</td>
<td>-</td>
<td>39.8</td>
</tr>
<tr>
<td>ML03 - 42</td>
<td>83.52</td>
<td>-</td>
<td>54.2</td>
</tr>
<tr>
<td>ML04 - 8</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>ML04 - 30</td>
<td>105.38</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ML04 - 44</td>
<td>100.71</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ML05</td>
<td>64.80</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.6. Percentage contributions of sedimentary OM and modern surface derived OM (corrected for decay based on $^{14}$C and $^3$H ages of the groundwater). Scenario A, B and C represents mixing of modern OM with sedimentary OM that is 1000, 3000 and 6000 years old respectively. Where values are not given the age of the sedimentary OM that is mixed is younger than the age of the sample and the model does not converge. ND denotes not determined as there was insufficient OC in the sample.

If we now consider the samples which have been shown to be $^3$H dead and those samples which are tritium active but contain elevated concentrations of As (> 100 μg/l) as discussed in 6.4.3. Comparison of As concentrations and the $^{14}$C age of the bulk DOC show a depth dependent variation in the rate of As release (figure 6.13). Arsenic release in the groundwater appears to be more extensive in shallow groundwaters (< 20 m) associated with a younger bulk DOC age compared to deep groundwater (30 – 60 m) containing older DOC. This can be explained by either (i) a depletion
in the amount of available sediment-bound As in deeper sediments as a result of a greater number of volumes of pore water flushing, or (ii) a decrease in the bioavailability of OM to drive the reductive processes associated with As release, or (iii) a combination of the two. This supports the suggestion that different sources of OM can give rise to different rates of As release, which may also be impacted the bioavailability of sediment bound As (Fendorf et al., 2010).

![Figure 6.13. Arsenic concentration as a function of $^{14}$C age of DOC in deep (30 - 60m) and shallow groundwaters (9 - 20m).](image)

Extrapolation of the regression lines back to the y-axis may yield important insights in to the source of OM that is driving As release processes. In both cases, the regression line does not intercept an age of zero for OM. Instead, the regression lines intercept $^{14}$C ages for DOC of 370 and 941 for shallow and deep groundwater respectively. This may suggest that modern OM that is transported in infiltrating surface waters is consumed in aerobic processes during recharge, which supports the observation that $^{3}$H active groundwaters typically have low concentrations of As concentrations at this site. Furthermore, it suggests the OM associated with reductive processes in shallow groundwaters where As release is more extensive more likely derives from the near surface environment and has a minimum mean age of approximately 400 years old (upper 5 m). Similarly, As release in deeper groundwater is less extensive because the OM driving the processes at depth is significantly older, with a minimum age of approximately 1000 years. This also suggests that As is not
only released in the near surface environment but also in the aquifer sediments, and over the entire length of the flow path, with perhaps differing degrees of As release depending on the depth of the flow path and the amount of available As and OM in the sediments.

These observations are further supported by the relationship between concentration and bulk $^{14}$C age of DOC presented in figure 6.14 below. This shows that concentrations of modern DOC are typically low, and concentrations of DOC increase to a maximum of 15.3 mg/l at 51 m depth at site TC31 as a result of contributions from OM with a $^{14}$C age of approximately 847 years. Following this, a decrease in the concentration of groundwater DOC is observed with a concomitant increase in $^{14}$C age of DOC. This increase in age can be explained by contributions of DOC from older sedimentary OM. However, the decrease in concentration requires that a significant proportion of the younger DOC is removed from the groundwater. This is best illustrated at site TE11-55, where DOC is present at 5 mg/l and modelled $^{14}$C ages of the groundwater are 1475 years but $^{14}$C ages of DOC are 4036 years. Assuming the groundwater at TC31 is located on the same flow path as site TE11-55, which is consistent with modelled flow paths in Benner et al (2008), then a decrease in DOC concentration of 10.3 mg/l is associated with an increase in the $^{14}$C age of DOC from 847 years to 4036 years. The DOC would naturally age by 1475 years as a result of decay during transport; giving rise to a DOC age of 2322 years in the absence of any further contributions. A bulk observed age of 4036 years therefore requires that 55% of the remaining 5 mg/l DOC derives from material that is 6000 years old (the upper limit of sediment contributions based on the mixing models discussed above), with only 45% from DOC that has been transported further up the flow path. This corresponds to a loss of the original DOC present in the groundwater of approximately 13.05 mg/l over the course of this flow path and a contribution of 2.75 mg/l DOC from OM that is 6000 years old. This would suggest that the consumption of DOC is not conservative, and that biogeochemical processes preferentially utilise younger, more labile OM over older OM. This is consistent with the results presented in a study by Raymond and Bauer (2001). They showed through measurements of $\delta^{13}$C and $\Delta^{14}$C of DOC and particulate organic matter (POC) that bacterial preferentially utilise a $^{14}$C enriched (young) source of DOC in estuarine and riverine environments. Older OM is typically more recalcitrant and less bioavailable and so $^{14}$C values of DOC may be biologically fractionated and appear more depleted in the absence of the DOC that is utilised by bacteria.
6.5. Discussion

The as yet unresolved debate as to what source of OM is responsible for driving As release in the groundwaters of South and South East Asia remains a topical issue amongst researchers in this field. Site specific variability in the sedimentary profile and the occurrence of high As groundwaters in locations where groundwater abstraction is not common practice have led some to suggest that particular sources of OM cannot be responsible for the generation of high As groundwaters at these sites. However, many of these studies fail to consider the potential for lateral transport of OM from subsurface sources and very few, if any, studies have considered the possibility that modern surface derived OM may be transported in recharge in the absence of groundwater pumping. Such processes could give rise to a groundwater DOC pool that is made up of contributions from a variety of sources of OM, with both surface and subsurface sources present. If this is the case, the relative contributions of these different sources could control As release rates in these groundwaters (FENDORF et al., 2010; GAULT et al., 2005; MLADENOV et al., 2010; ROWLAND et al., 2007; VAN DONGEN et...
al., 2008). The potential for groundwater abstraction practices to change the relative contributions from these different OM reservoirs (viz a viz HARVEY et al., 2002), and thus the rate of As release, must also be considered. This first requires the characterisation of an As bearing aquifer system under pre-development conditions.

6.5.1 Hydrological environment

The data presented and discussed above provides strong evidence to suggest that there is considerable interaction between the groundwater and overlying surface water bodies at this field site. The stable isotopes of oxygen and hydrogen suggest that there is a contribution of an evaporated source of surface waters to the groundwater, particularly in the centre of the transect between 1 km and 2.2 km from the Mekong River. Much of this contribution most likely derives from the large permanently saturated wetland connected natural pond that is located in the centre of the study area. The extent of this interaction appears to be merely a function of the distance from this surface water feature, with the groundwater at ML04 located only 10 m away seemingly receiving a greater contribution of recharge than site TC45 located 40 m away. This is consistent with observations in Benner et al (2008) who report a potential for an influence of surface water contributions to the groundwater at site TC45. This interaction cannot be driven by groundwater abstraction increasing hydraulic gradients within the subsurface. Instead this reflects recharge from surface waters in direct hydraulic continuity with the groundwater along natural rapid flow paths. This demonstrates that, even without groundwater abstraction, natural flow paths have the potential to transport dissolved species from surface water features, such as the wetland connected pond in this study, in to the groundwater. That there are significant contributions from this surface water body in particular suggests that the clay deposits that underlie it may be thinner or nonexistent, and that the sediments that surround it must be highly conductive.

Radiogenic isotope data from $^3$H and $^{14}$C of DIC support the observations made from the stable isotopes and provide a means with which it is possible to place a timescale over which these contributions took place. The groundwater that is located within 100 m of the permanently saturated wetland feature in the centre of the profile was shown to be $^3$H active over its whole depth profile as can be seen from figure 6.15d below. Groundwater located close to the pond, such as that at ML04, appears to have more recent contributions than that located further from the pond at site TC45, although both have recharged within the last 50 years, and perhaps within the last 15 years.
Figure 6.85. Spatial distribution of (a) tubewell locations with associated spatial and depth distributions of the (b) arsenic (μg/l), (c) sulphate (mg/l) and (d) tritium (TU) profiles for the study site in the Kandal province of Cambodia.
The presence of $^3$H active groundwater over the entire depth profile in these locations is inconsistent with modelled groundwater ages at this depth presented in Benner et al (2008) where predicted travel times through the clay are between 248 and 285 years. The travel time of vertical migration of water through the clay cannot be determined by the $^3$H data presented in this study and as such these estimated flow times may be correct. However, this clearly demonstrates that recharge through rapid flow paths from surface water features or clay windows contributes the most significant volume of recharge to the groundwater in this area of the study site and that this dominates the groundwater budget in this aquifer system.

This region of the field site where interaction of the surface water with the underlying groundwater appears to be more extensive is located where concentrations of As are low, consistently below 35 µg/l, and where concentrations of oxidants such as SO$_4^{2-}$ are relatively high, as displayed in figure 6.15 b and c. This suggests that recharge from surface waters, whilst potentially transporting reductants capable of stimulating or enhancing As release, is also capable of transporting oxidants which inhibit the onset of the reducing conditions required for As release. In this particular location it would appear that the supply of oxidants exceeds that of reductants, inhibiting the release of As to the groundwater. However, what is not clear is whether or not these processes consume the entire surface derived DOC component. Any residual DOC that remains in the groundwater after these processes have finished has the potential to be transported along a groundwater flow path to a region where reducing conditions prevail. In such a situation, the residual DOC could then potentially support biogeochemical processes that may result in As release to groundwater.

### 6.5.2 Sources of organic matter present in groundwater

Comparison of the $^{14}$C of different carbon species has been used in numerous hydrological studies, both to provenance different sources of OM present in the aqueous phase and to identify organic carbon sources utilised during microbial processes (ARAVENA and WASSENAAR, 1993; ARAVENA et al., 2004; CHARMAN et al., 1999; CLYMO and BRYANT, 2008; RAYMOND and BAUER, 2001; WASSENAAR et al., 1990; WASSENAAR et al., 1991a; WASSENAAR et al., 1991b). Indeed, it was the observation of younger groundwater $^{14}$C ages of DIC compared to that of the co-existing DOC that provided the basis for the postulation that it could be young, surface derived DOC that was driving As mobilisation in these aquifer systems (HARVEY et al., 2002). In the study of Harvey et al. (2002), $^{14}$C of DIC is used in the absence of $^3$H measurement to identify the presence of a contribution of modern recharge in the groundwater. This recharge is thought to be drawn in as a result of groundwater abstraction.
practises and is assumed to contribute modern organic carbon to the groundwater. However, this
signature is not observed in the bulk $^{14}$C signature of DOC, so the presumption is that this is used
during biogeochemical processes and it is this that is driving As release.

The bulk DOC age in this study is older than the groundwater age (following correction for carbonate
dissolution) in every single groundwater sample with the exception of the three locations. This is
indicative of a subsurface contribution of DOC, consistent with DOC concentration profiles with
depth. Mixing profiles suggest this subsurface source of OM to have an age of between 1000 and
6000 years, consistent with a near surface source of OM as suggested to be driving As release at this
site (KOCAR et al., 2008; POLIZZOTTO et al., 2008). Shallow groundwater often contains a large
component of young surface derived OM with the relative contributions of this young OM typically
decreasing with increasing depth. The data presented here demonstrate the fact that DOC in
groundwater likely derives from numerous sources and that even in pre-development conditions, a
significant amount of the total DOC pool derives from a surface source of OM. Furthermore, the data
suggests that bacteria may utilise a younger, more labile source of OM preferentially over older
more recalcitrant sources of OM, and that this younger source of OM may support more rapid rates
of As release.

The range of bulk DOC ages presented in Harvey et al (2002) of 3000 – 5000 years is smaller than the
range of ages presented in this study of 0 – 4036 years. Only two of the nineteen DOC ages
presented here are older than the minimum DOC age of 3000 years presented in Harvey et al (2002).
This can be explained by either (i) a greater relative contribution of young surface derived DOC to
the total groundwater DOC pool at this site, or (ii) a more complete removal of younger DOC at the
site in Bangladesh. If the redox conditions that prevail in the study site of Harvey et al (2002) are
more reducing, biogeochemical processes may proceed at a faster rate, potentially consuming a
larger portion of the younger surface derived OM. This is perhaps reflected in the high As release
rates of 22 μg/l/yr to groundwater derived from $^3$H/$^3$He dating of Bangladeshi groundwaters (STUTE
et al., 2007).

6.5.3 Vulnerability of groundwater to abstraction practices

The process of groundwater abstraction undeniably results in a change in hydraulic gradients and
the subsurface flow regime in an aquifer system (BURGESS et al., 2010; HARVEY et al., 2003; MICHAEL
and Voss, 2008). An increase in hydraulic gradients could potentially result in a change to the
locations of recharge to the groundwater, and such a change has the capacity to introduce dissolved species that would otherwise not be present in the groundwater at such concentrations. As discussed above, a contribution of more labile OM from the surface could potentially result in more rapid As release to groundwater, and so the vulnerability of the groundwaters to changes in the relative proportions of DOC driven by groundwater abstraction must be considered.

Stable and radiogenic isotope data from the groundwater at site ML04 provides compelling evidence that groundwater abstraction for sampling has resulted in the drawdown of surface water from the nearby pond. The DOC transported in this surface water comprises 100% of the total DOC pool in the groundwater here, and demonstrates unequivocally that surface derived DOC can be transported in recharging waters to the groundwater to depths of 44 m (c.f. SENGUPTA et al., 2008). In this case the drawdown of surface waters rich in labile OM has not resulted in significant As release in this region. This could be due to the fact that the supply of DOC is exceeded by that of oxidants which are capable of consuming the DOC in aerobic processes and prevent the onset of the reducing conditions required for As release. Alternatively, it may reflect the fact that equilibrium has yet to be reached in the groundwater following the introduction and that it may yet lead to extensive As release at this location. This has important implications for regions where groundwater abstraction is common practice because it proves that groundwater abstraction has the potential to introduce dissolved species that are implicated in the As release process.

In Bengal, recent temporal monitoring data shows that there have been negligible changes to groundwater As concentrations over the course of the studies (CHENG et al., 2005; DHAR et al., 2008), which suggests that groundwater abstraction practices are not currently resulting in an increase in the rate of As release. However, this is not to say that they have not done so in the past or may yet do so in the future, or that they are not currently changing at other sites. The sediment at the field site investigated in this study is clearly highly conductive and allows for rapid transport of infiltrating surface waters and their dissolved constituents. Variations in the sedimentary profile give rise to heterogeneous spatial distributions in the hydraulic conductivity of sediments. Such variations may allow rapid transport of surface derived OM at some locations and not at others. The vulnerability of any groundwater to abstraction practices should therefore consider the conductivity of the sediments as a key control in moderating the relative contributions of OM sources, and hence the rate of As release, to the groundwater in this region.
6.6. **Conclusions**

The data presented here demonstrate that extensive surface-groundwater interaction occurs even in the absence of groundwater abstraction, and over very short timescales. Rapid recharge to depths of less than 20 m is common throughout the study site. However, groundwater age appears to increase with increasing depth, characteristic of a stratified groundwater column. In such a setting, groundwater flow is horizontal along natural flow paths, giving rise to groundwater residence times of the order of 3000 years at 60 m depth. Characterisation of the DOC suggests that it comprises a mixture of differently sourced OM, with contributions of young surface or near surface derived OM and older, sedimentary sourced OM clearly present. Mixing profiles suggest this subsurface OM end member to have an upper age limit of 6000 years, consistent with a near surface source of OM driving As release at this site (Kocar et al., 2008; Polizzotto et al., 2008).

We have been able to show a clear association between high As concentrations in shallow groundwaters containing young DOC, and lower concentrations of As associated with older DOC in deeper groundwater. This provides the first direct confirmation that younger, more labile sources of OM are able to support more extensive As release than older, more recalcitrant sedimentary sources. Perhaps more importantly, we are the first to report a purely modern $^{14}$C signature for DOC in groundwaters at two locations. This demonstrates that modern, surface derived OM can be drawn into As contaminated groundwaters. This highlights the vulnerability of groundwaters to rapid changes in its composition from groundwater abstraction practices. Contributions of labile DOC to the groundwater would result in a change in the nature of the bulk DOC to a more bioavailable composition. Such changes clearly have the potential to increase the rate of As release to these groundwaters. However, the relative contributions of different sources of OM alone cannot be used as a proxy for determining As release rates. Any contribution of surface derived OM may also transport oxidants which are capable of consuming the co-transported DOC in aerobic processes and resulting in a change in the groundwater redox conditions to that which results in As sequestration, not release. The vulnerability of a groundwater to changes in As concentration therefore depends on the relative contribution of oxidants and reductants to the groundwater. Furthermore, recharge from surface water bodies may only be possible when the conductivity of the surrounding sediments is sufficient to maintain a hydraulic gradient which supports flow from the surface to the groundwater.

This study provides the most extensive isotopic characterisation of the hydrological environment of an As hotspot under natural conditions to date. This information provides a basis for comparison
with aquifer systems where the extensive abstraction of groundwater has disrupted subsurface flow and natural recharge conditions, potentially altering the distribution of the OM sources implicated in As release. Such information is of critical importance in developing process oriented models which are capable of accurately predicting how the current As hazard will change, and importantly at what rate, so that mitigation strategies can be put in place over the correct timescales to make significant contributions to decreasing the prevalence of As poisoning in the regions affected. The results presented here also suggest that the aquifer systems in largely undeveloped countries such as Cambodia are potentially at risk from anthropogenic interference that may influence the groundwater flow regime. In particular, activities such as groundwater abstraction and the excavation of ponds that creates conduits for focussing water flow have the potentially to significantly change the sources of groundwater recharge and the timescales over which recharge takes place. It is yet to be shown what effects such changes on the hydrological and geochemical environment may have on dissolved As concentrations in these groundwaters.

6.7. References


181


chemistry in shallow and deep aquifers of Araihazar, Bangladesh. J. Contam. Hydrol. 99, 97-111.


CHAPTER 7

Provenancing organic carbon in high arsenic and related shallow and deep groundwaters of West Bengal
7.1. Introduction

Hazardously high concentrations of naturally occurring arsenic (As) in the groundwaters of South and South East Asia has resulted in a humanitarian disaster, with an estimated 100 million people potentially at risk of toxic effects (Balga and Kaiser, 1996; Chakraborty and Saha, 1987; Mandal et al., 1996; Ravenscroft et al., 2009; Sampson et al., 2008; Smith et al., 2000; Van Geen et al., 2003a). Since its initial discovery in West Bengal, a significant amount of research has been conducted to determine the biogeochemical and hydrological controls on As mobility in the groundwaters of the Bengal delta where the greatest number of people are exposed to this toxic metalloid (Akai et al., 2004; Dowling et al., 2002; Harvey et al., 2002; Horneman et al., 2004; Islam et al., 2004; McArthur et al., 2001; Nickson et al., 1998; Van Geen et al., 2003c). These early studies demonstrated that the principle mechanism of As release to the groundwater was from the reductive dissolution of secondary iron oxide phases present within the aquifer matrix on to which As is sorbed (Bhattacharya et al., 1997; Nickson et al., 1998; Stuben et al., 2003; Zheng et al., 2004). This process was later shown to be mediated by metal reducing bacteria that are capable of reducing Fe(III), As(V) or potentially both (Islam et al., 2004; Lloyd and Oremland, 2006; Oremland and Stolz, 2005; Van Geen et al., 2004). These processes require organic matter (OM) as an electron donor for the biogeochemical transformations associated with As release (Islam et al., 2004). However, despite over a decade of research, the dominant source(s) of OM driving the As release process is still unclear and remains a subject of intense debate.

A number of sources of OM have been suggested to be contributing dissolved organic carbon (DOC) to the groundwater in the areas where As contamination is prevalent. These different sources can be split in to subsurface, sedimentary sources and external-surface derived sources. Subsurface sources of OM include that which is co-deposited with the sediments (BGS and DPHE, 2001; Meharg et al., 2006) or buried peat layers which are frequently found in the sedimentary profile throughout this region (McArthur et al., 2001; McArthur et al., 2004; Ravenscroft, 2001). In addition to these, thermally mature distributions of petroleum hydrocarbons have been identified in the shallow groundwaters at the field site investigated here and another known As hotspot in Cambodia, and could potentially contribute to the available DOC pool present in the groundwater at these sites (Rowland et al., 2007; Rowland et al., 2006; Van Dongen et al., 2008). Alternatively, an external source of OM that is transported during recharge from ponds, abandoned or existing channels, swamps or ox bow lakes that are rich in labile OM could represent the dominant source of OM present in the groundwaters of this region (Acharyya and Shah, 2007; Nath et al., 2005; Papacostas et al., 2008; Quicksall et al., 2008). The contributions of DOC from surface waters could potentially
be increased as a result of the extensive abstraction of groundwater which is common in many parts of West Bengal and Bangladesh (Harvey et al., 2002; Neumann et al., 2010). However, the question of whether anthropogenic activity has or will result in significant changes in the supply of DOC, which has the potential to exacerbate the problem of As contamination in the regions where groundwater abstraction is prevalent, remains unanswered (Aggarwal et al., 2003; Charlet and Polya, 2006; Harvey et al., 2003; Klump et al., 2006; Polya and Charlet, 2009; Sengupta et al., 2008; Van Geen et al., 2003b).

It is possible, indeed likely, that all of these sources of OM are capable of supporting As release. Many studies argue that it is not necessarily the amount of OM that is important in determining the extent of As release, but the type and availability of OM that is present that will govern the rates at which it is released to solution (Gault et al., 2005; Mladenov et al., 2010; Rowland et al., 2007; Van Dongen et al., 2008). Internal sedimentary sources of OM may be expected to be more recalcitrant and less available for use in biogeochemical processes given the age of these sources and the potential for them to have been involved in previous reactions which removed the more labile fractions from these OM reservoirs. In this case, such sources may only be capable of supporting a slow rate of As release to the groundwater. In contrast, fresh OM transported during recharge is likely to be more labile and bioavailable and as such may support a much more rapid rate of As release (Fendorf et al., 2010). Determining the relative contributions from these different OM reservoirs is therefore critical for an improved understanding of the As release process that is required to develop models that are capable of making predictions on how the current As hazard will evolve with time. This latter point is a topic of great concern for policy makers and those responsible for mitigating the effects of the current catastrophe, who want to ensure that decisions made now provide a sustainable source of drinking water for decades to come. These decisions first must also consider the potential vulnerability, perhaps on a site specific basis, of the groundwater to changes in the chemical composition of the water arise as a result of anthropogenic activities.

In a comprehensive isotopic study conducted on a known As hotspot in Cambodia presented in chapter 6, we showed that significant ground-surface water interaction occurs in the absence of extensive groundwater abstraction. In the Cambodian system natural flow paths transport surface derived OM in to the groundwater over timescales of less than 50 years. The groundwater DOC pool in Cambodia clearly contains a contribution of differently sourced OM, with data indicative of mixing between modern, surface derived OM and sedimentary OM aged between 1 -6 kyrs. The Cambodian study highlights the vulnerability of groundwaters to increased contributions of surface
derived OM which may be capable of supporting an accelerated rate of As release. In this study we apply isotopic techniques to provenance the OM present in the groundwater at a site in West Bengal where the extensive abstraction of groundwater is prevalent. The stable isotopes of oxygen (δ18O) and hydrogen (δD) are used to characterise the hydrological environment and to identify contributions from surface water bodies to the groundwater at this site. Tritium (3H), δ13C and 14C of dissolved inorganic carbon (DIC) is used in conjunction with these to examine the timescales over which these contributions are made. The contribution of different sources of OM is examined using δ13C and 14C of DOC. These results provide a novel dataset describing the processes and the timescales over which contributions of different sources of OM are made to the groundwater in the presence of groundwater abstraction. This will allow an assessment to be made of the composition of the DOC reservoir present in an As contaminated aquifer which may ultimately influence As release rates to the groundwater in this region.

7.2. Field Area

The As hazard in the Bengal delta is typically restricted to shallow Quaternary sediments of Pleistocene and Holocene age. Pleistocene sediments typically consist of gravels, sands and muds that are coated with iron oxide phases (ACHARYYA et al., 2000; GOODBRED and KUEHL, 2000). Holocene deposits overlay these and were deposited by the Ganges, Brahmaputra and Meghna rivers between 10,000 to 7,000 years BP under the combined influence of the Holocene sea level rise and the erosion of the Himalayas (ACHARYYA and SHAH, 2007). Organic-rich peaty silts, grey muds and clays of the Joypur Alluvium form a surface aquitard, which is found almost exclusively throughout the region, that varies in thickness from 6 to 21 m. Peat is observed in many locations at a depth of about 15 m in this unit and has been reported to have a 14C age of 7.92 ka (MCARTHUR et al., 2008), although this peat layer has not been identified in the sedimentary profile of the field site investigated here (CHARLET et al., 2007; NATH et al., 2005). This is marked in some locations by an impermeable stiff red clay paleosol at a depth of between 21 – 24 m which has been suggested to be a key factor in preventing As contamination of the underlying aquifer, in focussing groundwater flow and hence controlling the observed spatial heterogeneity in As concentrations in the regions groundwaters (MCARTHUR et al., 2004; MCARTHUR et al., 2008). These units overlay 30 to 40 m of grey sands of the Barasat Formation which forms the shallow aquifer. These units are underlain by a 20 m thick clay aquiclude which separates the shallow and the deeper aquifer of yellow/brown Pleistocene sands which is almost always free of As contamination at depths in excess of 100 m (DPHE/MMI/BGS, 1999). The Holocene-Pleistocene contact has been shown to range from depths of
between 30 m to 150 m in these alluvial deposits (VAN GEEN et al., 2003c). Aquifer deposits in the Bengal delta extend to depths in excess of 300 m (BGS and DPHE, 2001).

Figure 7.1. Aerial image of the study site located approximately 65 km N of Kolkata, India. The tubewells sampled in this study are marked with red circles. The image was obtained from Google™ Earth.

The investigated area in this study is situated in the town of Chakdaha in the Nadia district of West Bengal, India, located 65 km north of Kolkata (figure 7.1 above). The site covers an area of approximately 19 km², bound to the west by the Hooghly river, the largest tributary of the River Ganges in West Bengal and has previously been identified as an area where As concentrations are heterogeneously high (CHARLET et al., 2003; CHARLET et al., 2007; CHATTERJEE et al., 2003; GAULT, 2003; GAULT et al., 2005; METRAL et al., 2008; NATH et al., 2005; NATH et al., 2008b; ROWLAND et al., 2006). The site is characterised by the presence of abandoned meanders, oxbow lakes, abandoned river channels, flood plains and natural levees, with high As concentrations frequently associated with abandoned floodplain and meander channel deposits and features indicative of river channel migration (NATH et al., 2005). The town itself is raised relative to the floodplain on natural levee deposits. Numerous excavated ponds are located throughout the village and constitute up to 15% of the land cover. These act as sites of recharge to the groundwater during the wet season when hydraulic gradients between ponds and groundwater are favourable for downward flow (CHARLET et al., 2007). The river Hooghly shows dual behaviour, acting as a source of recharge to the
groundwater during the pre-monsoon period and as a drainage conduit for discharge from the groundwater in the post-monsoon period (NATH et al., 2008b).

7.3. Methods

7.3.1 Groundwater and surface water sampling

A set of twenty two groundwater samples were collected in January 2008 over a 5 km transect perpendicular to the River Hooghly through the village of Chakdaha over a depth range of 12.3 – 123.1 m as displayed in figure 7.1 above. A further pair of samples were obtained from the River Hooghly and a pond that is located in the near vicinity of three of the groundwater samples, with subsequent samples taken in October and November 2008 from each of these locations and a second pond for stable isotope analysis only. Four samples of local precipitation were collected in the period of July to October 2008 for stable isotope analysis. A submersible pump (MP1, Grundfos) was used to draw water in wells at a discharge rate of approximately 12 l/min. Tubewells were purged for a minimum of one well volume, with measurements of temperature, pH, Eh and electrical conductivity taken at short intervals until the discharging waters stabilised, typically within 10 - 40 minutes, at which point measurements were recorded and samples were collected.

Groundwater and surface water samples were collected, treated and stored depending on the intended analysis. Samples for major and trace cation and DOC analysis were filtered through 0.45 μm cellulose nitrate filters in to 100 ml acid washed glass schott bottles, acidified to pH < 2 using trace element grade HNO₃, and stored at 4°C prior to shipping and analysis. Samples for anion analysis were filtered and stored as above but not acidified. Water samples for stable isotope (δ¹⁸O and δD) analysis were collected in 60 ml amber glass bottles with polyseal caps and stored at 4°C. Samples of accumulated monthly rain water for stable isotope analysis were stored in 1 L amber glass bottles with polyseal caps and stored at 4°C. Water samples for δ¹³C and ¹⁴C of dissolved inorganic carbon (DIC) were collected in 500 ml amber glass bottles and stored at 4°C, while samples for δ¹³C and ¹⁴C analysis of DOC were collected in 1 L and 2.5 L amber glass bottles respectively and stored at 4°C. Water samples for tritium analysis were collected in 1 L argon filled amber glass bottles and stored with a 4 cm argon head.

7.3.2 Analytical procedures

Arsenic was measured using a Plasmaquad 2 inductively coupled plasma – mass spectrometry (ICP-MS, VG Elemental) with a typical detection limit of < 1 μg/l. Major element concentrations of the
water samples were determined by inductively coupled plasma – atomic emission spectroscopy (ICP-AES, Horizon, Fisons). Quality control standards were used throughout the course of the analysis to monitor analytical performance. External calibration standards were used to prepare standard calibration curves from which measured concentrations can be corrected for deviation from using weighted ordinary least squares linear regression, with analytical errors calculated using the methods of Miller and Miller (2005). Anion analysis of water samples for Cl⁻, NO₂⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻ was conducted using a Metrohm 761 compact Ion Chromatograph with a Dionex AS9 high capacity column and AG9 high capacity guard column using a flow rate of 1.4 mL/min and a mobile phase of 9mM Na₂CO₃. Bicarbonate alkalinity was measured by alkalinity titration with 0.025M HCl. Samples for DOC determinations were initially sparged with N₂ before analysis on a Shimadzu 5050A TOC analyser. An examination of the degree of electroneutrality was conducted to check that the sum of the charges of the major cations and anions balanced, with all groundwaters shown to be within 6% of electroneutrality.

Determination of the tritium content of groundwater samples was achieved using the ³He-ingrowth technique developed by Clarke et al (1976), with measurements of ³He and ⁴He made on a MAP 215 Noble Gas Mass Spectrometer (Mass Analyser Products). Stable isotope analysis was performed at the Isotope Community Support Facility, SUERC, East Kilbride, Scotland. For δD determinations, sample and standard waters were directly injected into an on-line chromium furnace at 800°C (DONNELLY et al., 2001), with the evolved H₂ gas subsequently analysed on a VG 602D (VG Elemental) mass spectrometer with a manual Hg, high gas compression inlet system. Replicate analyses of water standards (international standards V-SMOW and GISP, and internal standard Lt Std) gave a reproducibility of ±2‰. For δ¹⁸O determinations, 200 ml of water sample is transferred into a 10ml exetainer® using an adjustable pipette with disposable pipette tips. The exetainers® are then placed into the auto-sampler tray of a Finnegan Delta V mass spectrometer, which is set at 25°C. Each sample is then over-gassed with a 0.5% CO₂-in-He mixture for 5 minutes and left to equilibrate for a further 24hrs before mass spectrometric analysis. Oxygen isotopic data were then produced using the method established by Nelson (2000). Data are reported as permil variations from the V-SMOW standard. During the analyses of these samples the following standard data accuracy and precision were obtained for three SUERC internal standards: DSW(2) = -0.3 ± 0.1‰; DW2(2) = -7.4 ± 0.1‰; EKS(2) = -13.1 ± 0.2‰. Accepted values for these standards, as calibrated by international standards GISP (-24.8‰), V-SMOW (0‰) and SLAP (-55‰), are -0.3, -7.4 and -12.9‰ respectively. C-13 analysis was performed on a Prism3 (Fisons Instruments) mass spectrometer and calibrated with marble standards (MAB2, medium marble 85/160, δ¹³C = 2.48‰), internal sodium bicarbonate.
(δ¹³C -4.67‰) and calcium carbonate, δ¹³C -24.23‰). Carbon-14 measurements for DOC were performed at the Natural Environment Research Council (NERC) Radiocarbon Facility – Environment, East Kilbride, Scotland (allocation number 14.68) on both the 5MV tandem accelerator mass spectrometer and 250kV single stage accelerator mass spectrometer (both machines by National Electrostatics Corporation, NEC, Wisconsin, US).

7.4. Results

7.4.1 Aqueous chemistry

The concentration of As varies significantly at this site, with concentrations having a range from 1.6 μg/l to a maximum of 595 μg/l, more than an order of magnitude greater than the local recommended maximum concentration limit (MCL) of 50 μg/l (see table 7.1 for summary statistics and Appendix 2 for the complete analysis of each sampling location). Of the twenty two samples collected, thirteen contain As at concentrations that exceed the local MCL, with this figure rising to eighteen which exceed the World Health Organisation MCL of 10 μg/l. Figure 7.2 below shows the distribution of the As concentrations determined for the wells studied here with depth. Arsenic concentrations show the greatest variation in the shallow (< 40 m) groundwater where 56% of the wells tap groundwater where As exceeds the local MCL. Interestingly, three of the four wells tapped at depths greater than 40 m contain As concentrations that exceed 100 μg/l, with only the deep community well at 123 m tapping groundwater with As concentrations below the WHO limit. The As contamination of deep groundwater at this site has been attributed to the drawdown of As-rich shallow groundwater driven by the over abstraction of deep groundwater (CHARLET et al., 2007). This is consistent with the observations made in recent studies that suggest that the over exploitation of deep groundwater may induce downward flow of As contaminated shallow groundwater in to the previously safe deep groundwater at many locations throughout Bengal (BURGESS et al., 2010; MICHAEL and VOSS, 2008) There is also considerable spatial variation over the course of the site, with areas of low and high As, sometimes in very close proximity to one another (< 10 m), as can be seen in figure 7.3. This patchy spatial distribution of As is consistent with that reported in other studies at this field site (CHARLET et al., 2003; CHARLET et al., 2007; CHATTERJEE et al., 2003; NATH et al., 2005; NATH et al., 2008b). These studies suggest that high As zones are typically associated with finer sediments and sluggish groundwater flow that should be characterised by longer residence times and prolonged sediment-water interaction (CHARLET et al., 2007; NATH et al., 2008a; NATH et al., 2008b).
The major cations and anion chemistry of the groundwaters are presented in figure 7.4 below. As is typical for most of the As bearing aquifer systems of South and South East Asia, the groundwaters of this study site can be characterised as Ca-Mg-HCO₃⁻ type waters (BERG et al., 2001; RAVENSCROFT et al., 2005; ROWLAND et al., 2008). A trend of increasing Cl⁻ concentrations in some samples may be indicative of more extensive water-rock interaction.

<table>
<thead>
<tr>
<th></th>
<th>Minimum</th>
<th>Maximum</th>
<th>Arithmetic Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth</td>
<td>12.3</td>
<td>123.1</td>
<td>38.9</td>
<td>28.6</td>
</tr>
<tr>
<td>pH</td>
<td>6.7</td>
<td>8.1</td>
<td>7.1</td>
<td>0.3</td>
</tr>
<tr>
<td>EC (uS/cm)</td>
<td>110.0</td>
<td>1170.0</td>
<td>534.3</td>
<td>320.8</td>
</tr>
<tr>
<td>Eh (mV)</td>
<td>-245.0</td>
<td>193.0</td>
<td>-150.2</td>
<td>99.2</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>21.5</td>
<td>30.7</td>
<td>26.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Cl⁻ (mg/l)</td>
<td>3.5</td>
<td>155.0</td>
<td>43.0</td>
<td>46.1</td>
</tr>
<tr>
<td>NO₃-N (mg/l)</td>
<td>ND</td>
<td>1.0</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>NO₂-N (mg/l)</td>
<td>ND</td>
<td>24.3</td>
<td>1.1</td>
<td>5.2</td>
</tr>
<tr>
<td>ΣPO₄³⁻(mg/l)</td>
<td>ND</td>
<td>1.0</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>ΣSO₄²⁻(mg/l)</td>
<td>ND</td>
<td>65.0</td>
<td>13.2</td>
<td>20.4</td>
</tr>
<tr>
<td>Alkalinity (HCO₃⁻) (mg/l)</td>
<td>209.5</td>
<td>736.4</td>
<td>531.0</td>
<td>121.7</td>
</tr>
<tr>
<td>As (μg/l)</td>
<td>1.6</td>
<td>595.7</td>
<td>136.2</td>
<td>171.3</td>
</tr>
<tr>
<td>Ca (mg/l)</td>
<td>45.2</td>
<td>178.8</td>
<td>117.4</td>
<td>35.0</td>
</tr>
<tr>
<td>Fe (mg/l)</td>
<td>0.9</td>
<td>12.3</td>
<td>6.1</td>
<td>3.3</td>
</tr>
<tr>
<td>K (mg/l)</td>
<td>1.0</td>
<td>12.9</td>
<td>3.7</td>
<td>2.4</td>
</tr>
<tr>
<td>Mg (mg/l)</td>
<td>9.5</td>
<td>63.8</td>
<td>32.7</td>
<td>11.4</td>
</tr>
<tr>
<td>Mn (mg/l)</td>
<td>0.0</td>
<td>1.0</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Na (mg/l)</td>
<td>11.1</td>
<td>130.8</td>
<td>39.5</td>
<td>32.2</td>
</tr>
<tr>
<td>Sr (mg/l)</td>
<td>0.1</td>
<td>0.6</td>
<td>0.4</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 7.1. Concentration statistics for aqueous analytes in 22 groundwater samples collected from the study site in the Chakdaha block of the Nadia district, West Bengal, in January 2008. A full list of data for each sampling location is provided in Appendix 2.

The low concentrations of NO₃⁻ and SO₄²⁻ alongside elevated concentrations of Fe are consistent with reducing conditions prevailing in the groundwaters of this study site. This is supported by measured Eh values which are highly negative in all but one location, and have an arithmetic mean of -150 mV. The prevalence of reducing conditions in these groundwaters suggests that biogeochemical processes have consumed any initial O₂ and NO₃⁻ that may have been present. Indeed, such negative
values are sufficient to support $\text{SO}_4^{2-}$ reduction (CLARK and FRITZ, 2000), which may explain the typically low concentrations of $\text{SO}_4^{2-}$ in these groundwaters.

Figure 7.2. The distribution of groundwater As concentrations with depth from 22 groundwater samples collected at this study site in January 2008.
Figure 7.3. Spatial distribution of As concentrations in the groundwater at the study site. The size of the red sample location markers are proportional to the As concentration. It appears that high As and low As zones are present at this site, although low As groundwaters can be found in very close proximity (< 10 m) to high As groundwater at the same depth.
7.4.2 Stable isotopes

The stable isotopic signature ($\delta^{18}$O and $\delta$D) of groundwater ($n = 22$) along with local precipitation ($n = 4$), pond water ($n = 5$) and the River Hooghly ($n = 3$) was measured to proveance groundwater at this study site. As can be seen from figure 7.5 below, groundwater samples typically fall above the local meteoric water line developed for Barasat located some 36 km south of this study site (SENGUPTA and SARKAR, 2006). This trend can only be explained by (i) an enrichment in $\delta$D but not $\delta^{18}$O characteristic of significant exchange between water and H2S, or (ii) an enrichment in $\delta$D and depletion in $\delta^{18}$O characteristic of silicate hydration which is only likely to occur in high temperature environments (GEYH, 2000). Two samples of local precipitation and one pond water sample (which likely reflects the isotopic signature of local precipitation) also sit above the LMWL given by Sengupta and Sarkar (2006). Whilst a LMWL for this site cannot be determined based on only 4 samples of precipitation, this suggests that the LMWL here may differ slightly from that presented in...
Sengupta and Sarkar (2006) and may be responsible for the apparent shift in the isotopic signature of the groundwater at this site. The local precipitation does show a progressive depletion in the heavy isotopes from July to October, possibly reflecting the “amount effect” on the isotopic composition of precipitation which has arisen during the monsoon season at this site. That most groundwater appear to have a stable isotopic composition that is similar to that of the precipitation that falls during the months of July and August may suggest that much of the recharge to the groundwater occurs during these months prior to the total flooding of the site which occurs later in the monsoon, during which period groundwater recharge is inhibited by the low hydraulic conductivities that arise as a result of the flooding during this season.

In spite of the uncertainty as to the true LMWL, at least three groundwater samples (CH02, CH17 and CH19) do appear to show a trend towards a more enriched isotopic signature, indicative of a contribution of an evaporated source of recharge to the groundwater at these locations. Indeed, this trend is in the direction of the isotopic composition of the surface ponds that were collected in October and November. Each of these groundwaters was found to contain high concentrations of As, with a range of 115 – 562 µg/l. This suggests that these contributions could derive from local ponds and may transport bioavailable DOC that is capable of supporting extensive As release to the groundwaters at these locations. However, the contribution of pond water recharge to the groundwater is clearly not as significant at this site compared to that which prevails at the study site in Cambodia, possibly suggesting that recharge from precipitation rather than from surface waters dominates at this site.

There does not appear to be any consistent trend in variations in the isotopic composition of groundwater with depth at the study site, nor does there appear to be any consistent variation with location along the transect with the exception of one groundwater sample. This is perhaps not surprising given the complex and transient nature of the flow paths that have developed as a result of the extensive abstraction of groundwater and the widespread excavation of ponds at sites such as this (Harvey et al., 2006). Sample CH04 appears to have an isotopic signature very different to that of the other groundwater samples at this site. The groundwater here is clearly influenced by a contribution from the River Hooghly, which is located less than 100 m from this location, consistent with predictions of groundwater flow. This suggests that the river acts as a source of recharge to the groundwater during the pre-monsoon period (Nath et al., 2008b).
The isotopic composition of the River Hooghly shows significant temporal variation, with the isotopic composition changing in each of the three months samples were collected. The isotopic composition of rivers often reflects the isotopic signature of precipitation that falls at some other location in the catchment (Clark and Fritz, 2000). Variations in the isotopic signature of the river Hooghly likely reflect the variations in the isotopic composition of the numerous tributaries of the River Ganges, which the River Hooghly itself is a distributary of. In contrast, a variation in the isotopic signature of local pond water reflects the variability in the isotopic signature of the local precipitation coupled to the variable isotopic enrichment of the pond as a result of evaporation.

Figure 7.5. δD vs δ18O of groundwater, surface ponds, the River Hooghly and local precipitation at the study site. The LMWL of δD = 7.9δ18O + 8.9 is that which was determined for Barasat, West Bengal, presented in Sengupta and Sarkar (2006), located approximately 36 km south of the study site investigated here. Samples located within the red circle appear to show a contribution from a source of recharge that has an evaporative signature. Monthly accumulated samples of local precipitation are labelled for their month of collection.

7.4.3 Tritium and groundwater dating

The connectivity of ground and surface waters was further investigated through ³H determinations of the groundwater which provide an estimate of the timescales over which contributions from the surface take place. The tritium content in precipitation falling between 1954 and 1994 in Dhaka,
Bangladesh, situated approximately 200 km north east of the field site investigated here, is presented in figure 7.6 below. Here it can be seen that the \(^3\)H content of precipitation has been almost consistently below 10 TU since 1984 and that the \(^3\)H concentration of precipitation was around 4 TU at the end of the monitoring period. The \(^3\)H content of the present day River Hooghly, which should represent that of precipitation, is much higher than these values at 11.7 ± 0.25 TU. This discrepancy between the \(^3\)H content of precipitation and that of the river can either be explained by (i) a more \(^3\)H enriched precipitation falling upstream of the field site, (ii) a significant contribution from groundwater containing residual bomb \(^3\)H (> 20 TU) to the river water, (iii) an increasingly significant contribution of snow melt containing residual bomb \(^3\)H from the source of the river in the Himalayas, or (iv) an external source of \(^3\)H other than that in precipitation to the river. Given the volume of water present in the river it seems unlikely that groundwater would contribute sufficient water mass to result in the observed \(^3\)H concentration. Similarly, given that \(^3\)H concentrations in precipitation are now close to natural, pre-bomb levels, it is unlikely that a source of \(^3\)H enriched precipitation could be giving rise to the \(^3\)H signature of the River Hooghly. The data presented here cannot distinguish which of scenarios (iii) or (iv) is most likely, and as such the high \(^3\)H content of the River Hooghly remains unresolved.

Of the twenty two samples collected, only five samples were found to be \(^3\)H dead, with the remaining 17 samples having a tritium range of 0.77 ± 0.02 – 9.59 ± 0.21 TU (table 7.2 below). The \(^3\)H content of groundwater at this study site is highly variable with a range from \(^3\)H dead waters present at depths of 30 – 123 m to \(^3\)H active waters present at depths of 12 – 63 m (see figure 7.7 below). Groundwaters below 84 m are consistently \(^3\)H dead at this study site, indicating travel times of greater than 60 years to this depth. In contrast, shallow groundwater (< 40 m) at the site has a wide range of \(^3\)H concentrations from 0 to 9.59 ± 0.21 TU. The maximum \(^3\)H concentration of 9.59 ± 0.21 TU reported here at a depth of 22 m is consistent with the maximum value of 9 ± 0.2 TU reported in McArthur et al (2010) for groundwaters in the nearby district of 24-Parganas (North), both of which are similar to those reported for neighbouring Bangladesh where maximum \(^3\)H concentrations of 8.4, 18 and 18.5 TU have been reported in the studies of Dowling et al (2002), Stute et al (STUTE et al., 2007) and Klump et al (2006) respectively. Each of these studies report a maximum \(^3\)H concentration that exceeds the \(^3\)H content of precipitation that has fell since 1984. The presence of \(^3\)H throughout the depth profile confirms the presence of an active hydrologic flow regime in these groundwaters.

Given that present day precipitation typically has \(^3\)H levels of less than 4 TU, \(^3\)H concentrations in the groundwater that exceed this likely represent groundwater that recharged since the cessation of
atmospheric bomb testing but prior to the rapid decrease in $^3$H levels in precipitation which continued until the early 1980s as a result of attenuation in the oceans. An estimate of the residence time of groundwater can be determined by back-extrapolation along a decay line from a measured $^3$H concentration, with the intercept on the $^3$H in precipitation curve representing the time at which this groundwater underwent recharge (see figure 7.6). Indeed, back-extrapolation along a decay curve with a present day $^3$H concentration of 9.6 TU shows that this groundwater must have recharged a minimum of 44 years ago with an initial $^3$H concentration of 111 TU. Similarly, values below 4 TU could represent the decay of older groundwater that recharged a minimum of 35 years ago from precipitation with an initial $^3$H concentration of 28 TU. However, given that the $^3$H level in precipitation is only 4 TU, this may also reflect rapid migration from the surface over very short timescales. The absence of independent $^3$He measurements from un-degassed samples that provide a measure of total groundwater $^3$He means that determination of the absolute mean groundwater residence time is not possible and so a more accurate estimate of the age of groundwaters with $<$ 4 TU cannot be determined. As such the values quoted for decay from an initial $^3$H concentration of 4 TU at recharge represent the minimum mean residence time of the groundwater at these locations. In contrast, the quoted ages of groundwater residence times assuming an initial $^3$H concentration at recharge of 111 TU, which is the maximum possible initial $^3$H concentration assuming no hydrodynamic dispersion, represent the oldest possible residence times of the groundwater.

A possible exception to this is sample CH04 which is located less than 100 m from the River Hooghly. Stable isotope evidence presented above show that the groundwater at this location has a river-like composition, suggesting significant contributions from the river either through lateral recharge to the groundwater during the rainy season or vertically as river water floods the overlying floodplain on which this well is situated. The $^3$H content of the groundwater here of 8.02 ± 0.17 is in the range typical of groundwaters containing residual bomb $^3$H, as discussed above. However, this signature perhaps more likely supports evidence from the stable isotopes that there is a significant contribution from the river Hooghly to the groundwater at this location. The age derived by applying a $^3$H input function that is equal to the river of 11.72 ± 0.25 gives a travel time from the river to the groundwater of 6.81 years at this location, which may be slightly longer than expected given the location in the floodplain. This may suggest that this location also has a contribution of older groundwater which is flowing towards the river. Groundwater here and in other regions has been shown to have seasonally dependent flow both towards and away from the river (BENNER et al., 2008; NATH et al., 2008b). The groundwater at this location could therefore have contributions of
modern, river derived water and older aquifer water which has been transported to this location along a flow path towards the river.

![Graph](image)

Figure 7.6. $^3$H concentrations in precipitation reconstructed for Dhaka, Bangladesh, presented in Stute et al (2001). Dashed and dotted lines represent the decay lines for samples containing 9.6 TU and 4 TU respectively on collection in 2010. These intercept the $^3$H concentration in precipitation profile in 1966 and 1975 respectively.

Applying the lower and upper $^3$H input functions determined above provides estimates of the mean residence time of $^3$H active groundwaters if we assume no hydrodynamic dispersion or mixing, and these are presented in Table 7.2. This may represent an oversimplification at a study site such as this where groundwater pumping will result in the convergence of groundwater from different flow paths, but nonetheless allows an estimate of the relative differences in groundwater residence times and provides an upper boundary of 60 years for travel times to dep.th. The mean groundwater residence times display a range from a minimum of 0.37 years since recharge to 57 years since recharge for those containing residual bomb $^3$H. Seven groundwater samples have travel times to the depth of extraction of less than 10 years, indicative of rapid transport of surface waters to depths of up to 30.8 m. These groundwaters are not restricted to one area, but are spread out over the field site, suggesting the presence of rapid flow paths throughout the area. In contrast, groundwaters which contain residual bomb $^3$H are largely restricted to one area in the eastern section of the study area, with four of the five groundwaters located within 1 km of each other. This
area has previously been identified as an As hotspot, with groundwater flow here shown to be sluggish (NATH et al., 2008b). Whilst $^3$H data still demonstrates an active flow of recharge to this location over timescales of less than 60 years, they also suggest that this location is not as dynamic as other regions of the aquifer which show much more rapid groundwater flow velocities. This may reflect smaller hydraulic gradients in this location or less conductive sediments.

![Figure 7.7. $^3$H distribution with depth in the groundwaters of the study site alongside the $^3$H content of River Hooghly and precipitation in January 2008. Note $^3$H penetration occurs to depths of 63 m, whilst groundwaters below 84 m are $^3$H dead.](image)

There is no clear relationship between the concentrations of $^3$H with that of the co-existing As in the groundwater at this site (figure 7.8 below). High As concentrations are associated with groundwaters that are $^3$H-dead, those that contain residual “bomb” $^3$H and those which contain a recent (< 20 years) contribution of recharge. This suggests that the timescale over which contributions from the surface are made is not a significant control in the generation of high As shallow groundwaters. However, the presence of As at depth in groundwaters that are $^3$H dead, and as such have no contribution of surface recharge since prior to the onset of extensive groundwater abstraction here in the 1960s, is an observation that has important implications. It has previously been suggested that high concentrations of As in the deep groundwater likely derives from the downward migration of As contaminated shallow groundwater driven by deep groundwater abstraction (CHARLET et al., 2007; LAWSON et al., 2008). Most deep tubewells have been installed in the past 10 – 15 years to provide a
source of As free groundwater to the local villages in regions where the contamination of shallow groundwater is pervasive (VAN GEEN et al., 2003a; VAN GEEN et al., 2007). Assuming the \(^3\)H content of shallowgroundwaters in this region has not significantly changed during this 15 year period, which is consistent with observations in Aggarwal et al. (2003), the drawdown of As contaminated shallow groundwater should also introduce a component of \(^3\)H active groundwater to the deep groundwater. The presence of \(^3\)H dead groundwater containing concentrations of As of up to 112 \(\mu g/l\) appears to contradict this hypothesis and suggests instead that this groundwater was contaminated with As prior to its installation.

<table>
<thead>
<tr>
<th>Tubewell</th>
<th>Depth (m)</th>
<th>(^3)H (TU)</th>
<th>(\pm \sigma) (TU)</th>
<th>Mean residence time in years ((A_o = 4) TU)</th>
<th>(\pm \sigma)</th>
<th>Mean residence time in years ((A_o = 111) TU)</th>
<th>(\pm \sigma) years</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH01</td>
<td>30.0</td>
<td>0.01</td>
<td>0.00</td>
<td>&gt; 60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH02</td>
<td>13.8</td>
<td>3.26</td>
<td>0.07</td>
<td>3.67</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH04*</td>
<td>31.4</td>
<td>8.02</td>
<td>0.17</td>
<td>6.81*</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH05</td>
<td>30.8</td>
<td>2.97</td>
<td>0.07</td>
<td>5.36</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH06</td>
<td>21.2</td>
<td>1.37</td>
<td>0.03</td>
<td>19.21</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH07</td>
<td>31.4</td>
<td>0.77</td>
<td>0.02</td>
<td>29.55</td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH08</td>
<td>22.2</td>
<td>2.79</td>
<td>0.07</td>
<td>6.48</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH09</td>
<td>36.6</td>
<td>1.46</td>
<td>0.04</td>
<td>18.04</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH10</td>
<td>21.2</td>
<td>4.62</td>
<td>0.10</td>
<td>&quot;Bomb&quot; tritium</td>
<td>57.00</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>CH11</td>
<td>123.1</td>
<td>-0.01</td>
<td>-0.01</td>
<td>&gt; 60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH12</td>
<td>27.7</td>
<td>1.77</td>
<td>0.04</td>
<td>14.66</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH13</td>
<td>30.8</td>
<td>3.62</td>
<td>0.08</td>
<td>1.78</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH14</td>
<td>33.8</td>
<td>5.66</td>
<td>0.13</td>
<td>&quot;Bomb&quot; tritium</td>
<td>53.37</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>CH15</td>
<td>101.5</td>
<td>-0.01</td>
<td>-0.01</td>
<td>&gt; 60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH16</td>
<td>26.2</td>
<td>7.18</td>
<td>0.16</td>
<td>&quot;Bomb&quot; tritium</td>
<td>49.09</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>CH17</td>
<td>28.3</td>
<td>3.44</td>
<td>0.08</td>
<td>2.71</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH18</td>
<td>84.6</td>
<td>-0.01</td>
<td>-0.01</td>
<td>&gt; 60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH19</td>
<td>63.1</td>
<td>6.35</td>
<td>0.14</td>
<td>&quot;Bomb&quot; tritium</td>
<td>51.3</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>CH20</td>
<td>39.4</td>
<td>0.00</td>
<td>0.00</td>
<td>&gt; 60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH21</td>
<td>22.2</td>
<td>9.59</td>
<td>0.21</td>
<td>&quot;Bomb&quot; tritium</td>
<td>43.9</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>CH22</td>
<td>25.2</td>
<td>3.92</td>
<td>0.09</td>
<td>0.37</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH23</td>
<td>12.3</td>
<td>3.87</td>
<td>0.08</td>
<td>0.59</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Surface waters

River Hooghly 11.72 0.25

Table 7.2. \(^3\)H concentrations for each of the groundwaters and surface waters sampled in January 2008 at the study site. Errors are given as 1 \(\sigma\) of the \(^3\)H concentrations. Mean groundwater residence times are given for two \(^3\)H input functions. The \(^3\)H input function of 4 TU represents that which is present in present day local precipitation. The \(^3\)H input function of 111 represents the maximum possible \(^3\)H concentration at recharge determined by back-extrapolation along a decay line from a present day \(^3\)H of 9.9 TU (see figure 7.6). "Bomb" tritium denotes that the sample contains more \(^3\)H than the \(^3\)H input function used to determine its residence time and therefore clearly contains residual bomb \(^3\)H. In these locations the estimate of groundwater residence time which applies a \(^3\)H input function of 111 TU should be considered appropriate. *Sample CH04 is located in close proximity (< 100 m) from the river, and has been shown by stable isotopes to have a river like signature. The initial \(^3\)H used to calculate the residence time is therefore given as that present in the River Hooghly, 11.72 TU.
7.4.4 C-14 ages of dissolved inorganic carbon

C-14 of DIC was measured in an attempt to provide an accurate measure of the mean residence time of groundwaters which have been shown to be $^3$H dead, as well as to corroborate the findings from $^3$H active groundwater that such waters do have a contribution of modern (< 60 years) recharge. These ages are presented in table 7.3 below. The uncorrected age represents that determined from the measured concentration of $^{14}$C in the groundwater. This value represents the mean weighted contribution from different sources to the DIC pool in the groundwater and is not simply a measure of the decay of the initial DIC present at recharge. Contributions to the DIC pool are made as a result of calcite dissolution, which begins during recharge along a flow path. Further contributions are also made from dolomite dissolution, exchange with the aquifer matrix and from the oxidation of organic material as a result of biogeochemical reactions. This latter source may contain measurable $^{14}$C given that these sediments were deposited during the Holocene period (ARAVENA et al., 1995). However, the oxidation of DOC in groundwater typically does not significantly impact the carbon isotopic composition of DIC in shallow bicarbonate dominated groundwaters because of the relatively small
concentrations of DOC involved (WASSENAAR et al., 1991). The matrix exchange model accounts for contributions of DIC from carbonate and dolomite dissolution, as well as exchange with the aquifer matrix, discussed in greater detail in chapter 5. The modelled results presented in table 7.3 therefore provide an estimate of the mean residence time of the groundwater in the absence of these contributions.

<table>
<thead>
<tr>
<th>Tubewell</th>
<th>Depth (m)</th>
<th>Uncorrected Age (years BP)</th>
<th>Matrix Exchange Age (years BP)</th>
<th>$^3$H (TU)</th>
<th>Model consistent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH01</td>
<td>30</td>
<td>1827</td>
<td>&lt; 60 years</td>
<td>0.01</td>
<td>No</td>
</tr>
<tr>
<td>CH02</td>
<td>13.8</td>
<td>101</td>
<td>&lt; 60 years</td>
<td>3.26</td>
<td>Yes</td>
</tr>
<tr>
<td>CH04</td>
<td>31.4</td>
<td>539</td>
<td>&lt; 60 years</td>
<td>8.02</td>
<td>Yes</td>
</tr>
<tr>
<td>CH07</td>
<td>31.4</td>
<td>1344</td>
<td>&lt; 60 years</td>
<td>0.77</td>
<td>Yes</td>
</tr>
<tr>
<td>CH09</td>
<td>36.6</td>
<td>584</td>
<td>&lt; 60 years</td>
<td>1.46</td>
<td>Yes</td>
</tr>
<tr>
<td>CH11</td>
<td>123.1</td>
<td>2960</td>
<td>&lt; 60 years</td>
<td>-0.01</td>
<td>No</td>
</tr>
<tr>
<td>CH15</td>
<td>101.5</td>
<td>271</td>
<td>&lt; 60 years</td>
<td>-0.01</td>
<td>No</td>
</tr>
<tr>
<td>CH18</td>
<td>84.6</td>
<td>2230</td>
<td>&lt; 60 years</td>
<td>-0.01</td>
<td>No</td>
</tr>
<tr>
<td>CH19</td>
<td>63.1</td>
<td>801</td>
<td>&lt; 60 years</td>
<td>6.35</td>
<td>Yes</td>
</tr>
<tr>
<td>CH20</td>
<td>39.4</td>
<td>1742</td>
<td>&lt; 60 years</td>
<td>0.00</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 7.3. Mean groundwater residence times based on $^{14}$C measurements. Uncorrected ages represent the measured age of the sample. Matrix exchange ages represent modelled results that have accounted for contributions of DIC from $^{14}$C-dead carbonate minerals following dissolution. A consistency check of the modelled ages is provided by comparison with $^3$H concentrations in the co-existing groundwater.

Matrix exchanged modelled ages only produce concordant estimates of the mean residence times of groundwater with $^3$H active groundwaters. Modelled ages suggest a modern (< 60 years) residence time in all of the samples, an observation that is in direct conflict with 5 samples which have no active component of modern recharge from $^3$H concentrations. As such, the model appears to overestimate contributions from sources of DIC other than that present at recharge which results in an under prediction of the mean residence time of groundwaters. This could reflect the large error associated with age estimates of young (60 – 100s of years) groundwater that derives from the assumption of the pH and temperature conditions that prevailed during recharge. This is discussed in greater detail in chapter 5. An interesting point to note here is the uncorrected $^{14}$C age for sample CH04, which has been shown by stable isotope and $^3$H observations to contain a contribution from the nearby River Hooghly. The $^3$H age of 6 years for this location suggests it is unlikely that the groundwater would have sufficient time to accrue sufficient $^{14}$C-dead carbonate from mineral
dissolution to result in the apparent $^{14}$C age of 539 years. This therefore suggests that mixing between older groundwater, which may have a contribution from $^{14}$C-dead carbonate, and ingressing river water has produced this $^{14}$C signature. In the absence of an independent assessment of the mean residence time of $^3$H dead groundwaters, an upper limit of the age of the groundwater is provided in the uncorrected age.

Uncorrected ages for $^3$H dead groundwaters reported here show a general trend of increasing age with depth with the exception of one sample, CH15 (figure 7.9 below). The deepest groundwater at 123 m is shown to have the oldest uncorrected groundwater age of 2960 years, although this may reflect a greater contribution from $^{14}$C dead DIC from carbonate dissolution. Interestingly, $^3$H dead groundwater at CH15 has a $^{14}$C age of DIC of 271 years. It is likely that at least some component of the DIC in this groundwater derives from carbonate dead $^{14}$C, but this nevertheless still places an upper age limit of 271 years for groundwater at this depth. This is much younger than one might expect for deep groundwater which is thought to flow along regional flow paths at these depths. These groundwaters have previously been shown to be thousands of years old based on $^{14}$C dating of the DIC (AGGARWAL et al., 2000; DHAR et al., 2008; MICHAEL and VOSS, 2009).

The presence of a contribution of young groundwater at these depths has been reported for other As contaminated groundwaters, with $^3$H active waters present at depths of up to 150 m in nearby Bangladesh (DOWLING et al., 2003). This suggests that water from a shallower depth is migrating down a flow path to deeper groundwater. The absence of $^3$H in this water suggests that this does not derive from the dynamic shallow groundwater system, but instead must derive from the $^3$H-dead groundwater at depths of 80 m or more. This may contain As that may either sorb to the sediment or begin to accumulate in the deep groundwater. Furthermore, this water may also contain components such as DOC that are used in biogeochemical processes that may result in the onset of reducing conditions in the deep groundwater. If As is present and bioavailable in these sediments, the change in redox conditions in the deep aquifer could result in further As release in the deep groundwater. This process of downward migration of the shallow groundwater may be indicative of the presence of a rapid flow path through very permeable sediments to depth under natural conditions. Alternatively, this process may be driven by the over exploitation of the deep groundwater that has been suggested to be a potentially sustainable source of As free drinking water (BURGESS et al., 2010; MICHAEL and VOSS, 2008; POLYA and CHARLET, 2009; VAN GEEN et al., 2003a; VAN GEEN et al., 2007). The transport of As from shallow groundwaters, coupled to the release of As
in the deep groundwater, could potentially result in very rapid rates of increase in the As concentration in these groundwaters.

Figure 7.9. Uncorrected groundwater C-14 ages as a function of depth for 3H dead groundwaters.

7.4.5 C-14 ages of dissolved organic carbon

The age of the bulk DOC present in the groundwater was determined by measurement of its $^{14}$C concentration and is presented in table 7.4 below. The age of DOC in the groundwaters shows no systematic trend with depth at this study site, with a range from 547 years at 101 m depth to a maximum of 2636 years at 84.6 m depth (figure 7.10). Shallow (< 40 m) groundwater contains DOC with a bulk age that is consistently less than 1500 years. The presence of the youngest DOC of 671 years at a depth of 100 m is again consistent with the drawdown of younger water from above to the deep groundwater. However, this demonstrates unequivocally that this migrating water is also contributing young DOC to the deep groundwater. This has been suggested to be more bioavailable than that of older, more recalcitrant DOC which may be expected to dominate the DOC reservoir in
deep groundwater (Fendorf et al., 2010), and hence capable of supporting more rapid changes in the biogeochemical conditions in the deep groundwater.

<table>
<thead>
<tr>
<th>Tubewell</th>
<th>Depth (m)</th>
<th>C-14 enrichment (pmC)</th>
<th>± σ</th>
<th>C-14 Age (years)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH01</td>
<td>30</td>
<td>82.20</td>
<td>0.39</td>
<td>1574</td>
<td>37</td>
</tr>
<tr>
<td>CH02</td>
<td>13.8</td>
<td>89.52</td>
<td>0.42</td>
<td>890</td>
<td>37</td>
</tr>
<tr>
<td>CH04</td>
<td>31.4</td>
<td>89.10</td>
<td>0.38</td>
<td>927</td>
<td>35</td>
</tr>
<tr>
<td>CH07</td>
<td>31.4</td>
<td>84.39</td>
<td>0.39</td>
<td>1363</td>
<td>35</td>
</tr>
<tr>
<td>CH09</td>
<td>36.6</td>
<td>89.37</td>
<td>0.42</td>
<td>903</td>
<td>37</td>
</tr>
<tr>
<td>CH11</td>
<td>123.1</td>
<td>72.26</td>
<td>0.34</td>
<td>2610</td>
<td>37</td>
</tr>
<tr>
<td>CH15</td>
<td>101.5</td>
<td>91.99</td>
<td>0.43</td>
<td>671</td>
<td>37</td>
</tr>
<tr>
<td>CH18</td>
<td>84.6</td>
<td>72.10</td>
<td>0.32</td>
<td>2628</td>
<td>35</td>
</tr>
</tbody>
</table>

Table 7.4. C-14 analysis results and derived ages of dissolved organic carbon present in the groundwater.

A comparison of groundwater age, determined through either \(^3\)H content or uncorrected \(^{14}\)C age, with the age of DOC is presented in figure 7.11 below. In seven of the eight samples the age of the groundwater is younger than that of the co-existing DOC. The sample in which the groundwater appears to be older than the DOC is likely to have significant contributions of \(^{14}\)C-dead carbonate giving rise to an apparently older groundwater, and so should not be considered in interpretations. Tritium active groundwater in samples CH02 – CH09 suggest that contributions of young DOC could have been made to the groundwater DOC reservoir in these locations. That DOC in the groundwater is older than the age of the groundwater suggests that significant contributions of older DOC have been made to the groundwater DOC reservoir to produce the observed DOC age. This likely derives from an older sedimentary OM source that would result in an apparent increase in the age of the DOC that exceeds that of simple radioactive decay during transport. This is consistent with the data presented in Harvey et al (2002), who show that the DOC is older than the co-existing groundwater based on measurements of the \(^{14}\)C content of both DOC and dissolved inorganic carbon (DIC). They suggest that this is attributed to the release of old aquifer derived carbon as a result of geochemical perturbations driven by the drawdown of young, surface derived recharge waters. In the study of Harvey et al (2002), the young \(^{14}\)C signature of co-existing methane suggests that a young source of
DOC is utilised in biogeochemical processes in preference to the largely older DOC that characterises the bulk DOC.

As discussed above, the bulk age of the DOC presented here likely contains a mixture of DOC sourced from OM of different ages and as such likely represents a weighted mean age of the different contributions of DOC from the different sources of OM. Assuming that the DOC present at recharge is not entirely consumed during the recharge process and migration in to the groundwater, simple two component mixing calculations can be used to determine the relative contributions from a young, surface derived OM source and an older sedimentary OM source. Table 7.5 below presents a summary of the relative contributions of modern, surface derived OM and progressively older sedimentary OM required to produce the observed $^{14}$C age of the bulk DOC. This data suggests that very little contributions, as little as 4.4%, of modern DOC is required to explain bulk DOC ages when a sedimentary source that is 1000 years old is contributing DOC to the groundwater. However, as the age of the contributing OM source increases, the contributions of modern surface derived DOC must also increase to produce the observed bulk DOC age. Indeed, contributions of as much as 87.2 % of the total DOC pool must derive from a modern contribution in sample CH15 if it undergoes mixing with 6000 year old OM. Given that this sample is $^3$H dead, this contribution of DOC must itself be
older than 60 years, and so the contribution of young OM required must therefore increase to produce the observed $^{14}$C age of 547 years.

Figure 7.11. Age of DOC present in the groundwater as a function of the mean groundwater residence time. The regression line intercepts the x-axis at 805 years with an $R^2$ of 0.8392 ($n = 8$).

Of course, the values derived in table 7.5 below assume only two component mixing. In reality, DOC is likely to be contributed over the course of its flow path as it passes through increasingly older sediments. However, it demonstrates the requirement for a presence of young DOC to the groundwaters of this region. If the DOC present in the groundwater largely derived from buried peat deposits in this region for example, which have been shown to be approximately 8 ka (McARTHUR et al., 2008), 55% of the DOC would have to derive from a modern DOC source to produce the oldest $^{14}$C age of 2636 year observed in the bulk DOC in the groundwaters here. This figure represents a minimum value of young material and as the age of the young organic carbon component increases, so too must the contributions from this OM source to produce the observed bulk DOC age. Indeed, regression analysis of the DOC and groundwater age presented in figure 7.11 perhaps suggests that
the bulk DOC age in young groundwaters should be approximately 802 years, perhaps indicative of a large proportion of modern, surface derived DOC being utilised in aerobic processes during recharge. The OM that drives biogeochemical processes is therefore likely to be slightly older than that of the groundwater, and derives from a near surface OM source.

<table>
<thead>
<tr>
<th>Tubewell</th>
<th>Depth (m)</th>
<th>C-14 enrichment (% modern)</th>
<th>% sedimentary OM A</th>
<th>B</th>
<th>C</th>
<th>% modern OM A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH01</td>
<td>30.0</td>
<td>82.20</td>
<td>-</td>
<td>58.5</td>
<td>34.5</td>
<td>-</td>
<td>41.5</td>
<td>65.5</td>
</tr>
<tr>
<td>CH02</td>
<td>13.8</td>
<td>89.52</td>
<td>92.0</td>
<td>34.4</td>
<td>20.3</td>
<td>8.0</td>
<td>65.6</td>
<td>79.7</td>
</tr>
<tr>
<td>CH04</td>
<td>31.40</td>
<td>84.39</td>
<td>95.6</td>
<td>35.8</td>
<td>21.1</td>
<td>4.4</td>
<td>64.2</td>
<td>78.9</td>
</tr>
<tr>
<td>CH07</td>
<td>31.4</td>
<td>89.10</td>
<td>-</td>
<td>51.3</td>
<td>30.2</td>
<td>-</td>
<td>48.7</td>
<td>69.8</td>
</tr>
<tr>
<td>CH09</td>
<td>36.6</td>
<td>89.37</td>
<td>93.3</td>
<td>34.9</td>
<td>20.6</td>
<td>6.7</td>
<td>65.1</td>
<td>79.4</td>
</tr>
<tr>
<td>CH11</td>
<td>123.1</td>
<td>72.26</td>
<td>-</td>
<td>91.2</td>
<td>53.8</td>
<td>-</td>
<td>8.8</td>
<td>46.2</td>
</tr>
<tr>
<td>CH15</td>
<td>101.5</td>
<td>91.99</td>
<td>70.3</td>
<td>26.3</td>
<td>15.5</td>
<td>29.7</td>
<td>73.7</td>
<td>84.5</td>
</tr>
<tr>
<td>CH18</td>
<td>84.6</td>
<td>72.10</td>
<td>-</td>
<td>91.7</td>
<td>54.1</td>
<td>-</td>
<td>8.3</td>
<td>45.9</td>
</tr>
</tbody>
</table>

Table 7.5. Percentage contributions of sedimentary OM and modern surface derived OM (\(^{14}C = 100 \ pmC\)). Scenario A, B and C represent mixing of modern OM with sedimentary OM that is 1000, 3000 and 6000 years old respectively. Where values are not given for a contribution the age of the sedimentary OM was younger than that of the bulk groundwater DOC and as such the model is untenable.

### 7.5. Discussion

#### 7.5.1 Ground-surface water interaction and contributions of DOC

The presence of \(^3\)H active groundwater in all but two of the shallow (< 40 m) samples demonstrates a recent (< 60 years) contribution of recharge to the shallow groundwater throughout the area investigated in this study. However, whilst much of the study site is characterised by recent (< 20 years) contributions of recharge, a small area in the eastern section of the study site has groundwater with higher (> 5 TU) \(^3\)H concentrations that is characteristic of residual “bomb” tritium. This suggests that this location has slightly longer residence time relative to other shallow groundwaters at the site, consistent with previous observations of sluggish groundwater flow in this area of the site (NATH et al., 2008b). Nath et al. (2008) attribute elevated As concentrations in this area of the site to low permeability sediments giving rise to more extensive water rock interaction.
The tritium data presented here clearly demonstrates interaction between groundwaters with recharge from the surface over timescales of a few years to more than 60 years. Complimentary data from the stable isotopes suggest that some of this recharge derives from surface waters with an evaporative signature. Potential sources of surface waters which may contain an evaporative signature include pond water and infiltrating rice field waters. A recent study by Neumann et al. (2010) showed that, whilst water infiltrating into the subsurface from rice fields recharges shallow groundwater with low As concentrations, pond water is the dominant source of recharge to groundwater where As concentrations peak. This pond water was also shown to contain more bioavailable organic carbon compared to the more recalcitrant organic carbon that is transported from rice fields.

Variations in the $^{14}$C age of the DOC with depth, despite showing no coherent trend, are indicative of contributions of DOC from different OM sources to the groundwater and reflect the location specific variability in the distribution of these sources. Ages of DOC that exceed that of the co-existing groundwater provide a clear indication that contributions of DOC are made from sedimentary sources of OM. However, mixing calculations also demonstrate that a contribution of young, surface or near surface derived DOC must also be present in the groundwater to give rise to the bulk DOC ages that are observed in these groundwaters. Such an observation should in part dispel the theory that one particular source of OM is responsible for driving As release in these groundwaters, and instead suggests that different sources of OM contribute organic carbon to groundwater which then may be utilised in biogeochemical processes. Ultimately it is the distribution of these species, which will almost certainly vary from one location to another depending on sediment content, surface morphology and the hydrological environment, that will control the mobility of As in these aquifer systems.

### 7.5.2 Vulnerability of deep groundwater

The presence of $^3$H active groundwater at shallow depths is not surprising and can be readily explained by either natural rapid flow paths from the surface (as observed in Metral et al., 2008) or by invoking a response to extensive groundwater abstraction. In contrast, the presence of younger water at depths of 100 m and more, where groundwater would be expected to derive almost entirely of regional groundwater flow typically of the order of thousands of years old (Aggarwal et al., 2000; Michael and Voss, 2009), suggests that anthropogenic activity has resulted in a disruption
of natural flow paths. Data presented here and elsewhere demonstrates a reduced mean groundwater residence time for deep groundwaters, indicative of a significant contribution from overlying shallow groundwater. The absence of tritium in the deep groundwater here suggests that the contributions at this study site cannot be sourced from water that is shallower than 84 m.

Deep groundwater currently represents the safest source of drinking water in many regions where extensive contamination of shallow groundwater is prevalent. Any indication that this groundwater resource may be subject to contributions of shallow groundwater is therefore of great concern because this downward migrating groundwater may contain high concentrations of As that may result in the contamination of the deep aquifer. What is perhaps of equal concern is that data presented here demonstrates that this migrating water is also contributing young DOC to the deep groundwater. The introduction of reactive DOC has the potential to significantly alter the redox conditions in the deep groundwater, and may ultimately lead to the release of As deep in the aquifer. However, given the numerous biogeochemical processes that occur in groundwater, it is difficult to estimate the timescales over which conditions may evolve to those suitable for As release. Nonetheless, this demonstrates that deep groundwater is vulnerable to changes in its As content and, unless managed properly, may not represent the sustainable source of drinking water it is hoped it would for the millions of people currently exposed to high concentrations of As in the shallow groundwater.

7.6. Conclusions

Shallow groundwater at this known As hotspot in the Chakdaha block of the Nadia district, West Bengal, is characterised by mean groundwater residence times of less than 60 years, with large proportions of the site containing significant contributions of recharge from the last 20 years. Stable isotope data suggests that some of this recharge may derive from contributions of water from surface ponds. Characterisation of the composition of DOC through $^{14}$C measurements suggests that a component of the groundwater DOC reservoir must derive from the surface, and require contributions from surface derived DOC of as little as 4.4% or as much as 84.5% of the total DOC. However, comparison of $^{14}$C ages of the bulk DOC with mean groundwater residence times also demonstrates the requirement for a contribution of DOC from older sedimentary sources of OM.

The relative contribution of different OM sources to the total DOC reservoir may be influenced by anthropogenic activities which have the potential to change natural flow paths and sources of groundwater recharge. Such changes may yet be shown to be associated with secular changes in the As hazard in these groundwater systems.
The data presented here suggests that, whilst deep groundwater currently represents the safest source of potable water in many regions, this groundwater is vulnerable to As contamination from the downward migration of As contaminated shallow groundwater. This invading water may also introduce young DOC that will change the composition of the DOC pool of the deep groundwater that could potentially drive an evolution in the biogeochemical status of the deep groundwater towards the conditions required for As release. However, increases in the deep groundwater As hazard may only become apparent once the finite sorption capacity of deep sediments has been exceeded or once reducing conditions have become established to support As release. Monitoring of As concentrations alone may therefore not be sufficient to identify subtle changes in the water chemistry of deep groundwater. As such, monitoring of the evolution of the mean residence time of deep groundwater over a period of several years may provide a key tool to identify secular changes in the deep groundwater. If identified, such changes may be indicative of an evolution towards conditions which are favourable for the generation of high As groundwater. Such monitoring will also provide an insight in to the effect of groundwater abstraction practices on these groundwaters, information which may be critical for those responsible for providing a sustainable source of drinking water to the millions of people who desperately need it in this region.

7.7. References


Bangladesh. KTH Special Publication, TRITA-AMI REPORT 3084, University of Dhaka, Bangladesh.


CHAPTER 8

The geochemical and isotopic composition of ground waters in West Bengal: tracing ground-surface water interaction and its role in arsenic release
CHAPTER 9

Conclusions
9.1. The generation of high arsenic groundwaters in South and South East Asia

The contamination of groundwater by naturally occurring arsenic (As) in South and South East Asia has resulted in the largest mass poisoning of a human population in history (SMITH et al., 2000). It is now feared that in excess of 100 million people in the rural populations of Bangladesh, India, Cambodia, Vietnam and other neighbouring countries may be exposed to this known carcinogen at concentrations that exceed the World Health Organisation (WHO) standard of 10 μg/l (AHMED et al., 2006; RAVENSCROFT et al., 2009). Early symptoms of this exposure manifest themselves as skin abnormalities and lesions (BALGA and KAISER, 1996; MANDAL et al., 1996; MAZUMDER et al., 1998; SAMPSON et al., 2008), whilst long term exposure can result in cancers of the skin, liver, lungs and other internal organs (CHOWDHURY et al., 2000; POLYA et al., 2010; SMITH et al., 2000; YU et al., 2003). Indeed, exposure to high concentrations of As in drinking waters is estimated to result in a doubling of the cancer burden from liver, bladder and lung cancers in Bangladesh alone (CHEN and AHSAN, 2004).

Groundwaters that contain elevated concentrations of As are largely restricted to the major floodplains of the region, and are almost always associated with rapidly buried organic rich alluvial sediments that have been deposited since the late Pleistocene (CHARLET and POLYA, 2006; POLYA et al., 2005). Groundwater flow in these aquifers is driven by topographically controlled hydraulic gradients, resulting in extremely slow flow velocities and aquifer flushing rates. However, groundwater abstraction has been suggested to have significantly altered the natural hydrological environment in the countries where it is prevalent by developing transient flow paths, changing the location of recharge, and by changing the timescales over which these various processes operate (HARVEY et al., 2006).

It is now widely accepted that As is released to solution following the reductive dissolution of Fe oxides (BHATTACHARYA et al., 1997; NICKSON et al., 1998). This process has been shown to be microbially mediated, and driven by the consumption of organic carbon as an electron donor (ISLAM et al., 2004). Once released to solution, As is then transported in the groundwater along a flow path, during which time it may be subjected to changes in sediment composition, redox conditions, and water chemistry. The spatial distribution of dissolved As concentrations in these groundwaters is therefore the combined result of the biogeochemical processes, which may conspire to release As to or sequester As from solution, which occur during the hydrologic transport of groundwater along a flow path (POLIZZOTTO et al., 2008; POSTMA et al., 2007). What is not clear is how the current
distribution of As in groundwaters has developed and whether anthropogenic activity has contributed to its evolution, either by changing groundwater flow paths, accelerating flow rates, or by exacerbating the problem through the introduction of foreign species which may influence the hydrochemical environment. This information is of critical importance in providing the step wise improvement in our understanding of how the current As hazard has developed that is required to accurately predict how the current As hazard will evolve in the years and decades to come. In this thesis, we have investigated two As-bearing groundwater systems with different groundwater abstraction histories with the aim of assessing the impact of groundwater management practices on the hydrological environment, and how this may influence current and future As release rates.

9.2. Characterisation of a Cambodian aquifer – An insight into pre-development conditions

Our study of a Cambodian aquifer system has shown that, even in the absence of extensive of groundwater abstraction; there is still considerable interaction between the surface and the underlying groundwater. Stable isotope data seems to suggest that a large volume of recharge to the groundwater derives from surface waters such as ponds and wetlands. Data from radiogenic isotopes demonstrates that the recharge to the shallow groundwater (< 12 m) occurs over timescales of less than 50 years. In Cambodia, this interaction cannot be driven by groundwater abstraction increasing hydraulic gradients within the subsurface. Instead this reflects recharge from surface waters in direct hydraulic continuity with the groundwater from natural flow paths. However, only 50% of the groundwaters sampled in the depth range of 20 – 60 m were shown to be tritium active, with $^3$H penetration shown to be less than 48 m. Groundwater at depths greater than that of the $^3$H penetration were shown, through $^{14}$C measurements of dissolved inorganic carbon, to be much older and have mean groundwater residence times of the order of hundreds to thousands of years. This is in contrast to sites in West Bengal and Bangladesh, where $^3$H penetration has been shown to be up to 150 m deep (DOWLING et al., 2002; KLUMP et al., 2006; MCARTHUR et al., 2010; STUTE et al., 2007).

Characterisation of the dissolved organic carbon (DOC) at the Cambodian site suggests that it comprises a mixture of differently sourced organic matter (OM). The radiocarbon age of the bulk DOC requires a contribution of young surface or near surface derived OM, as well as contributions from older, sedimentary sourced OM. Mixing profiles suggest this subsurface OM end member to have an age of between 1000 and 6000 years, consistent with a near surface source of OM as
suggested to be driving As release at this site (KOCAR et al., 2008; POLIZZOTTO et al., 2008). We have been able to show a clear association between high As concentrations in shallow groundwaters containing young DOC, and lower concentrations of As associated with older DOC in deeper groundwater. This provides the first direct confirmation that younger, more labile sources of OM are able to support more extensive As release than older, more recalcitrant sedimentary sources (FENDORF et al., 2010; GAULT et al., 2005; MLADENOV et al., 2010; ROWLAND et al., 2007). Perhaps more importantly, we are the first to demonstrate that modern, surface derived OM can be drawn into As contaminated groundwaters. The combined use of stable and radiogenic isotopes clearly show that this signature has arisen as a direct consequence of rapid transport of recharge waters from a nearby pond following groundwater abstraction during sampling (evidenced by the modern $^{14}$C signature for DOC at depths of 29 and 44 m shown in figure 9.1 below).

This comprehensive isotopic study provides unequivocal evidence to show that water from OM-rich ponds and wetlands can act as a major source of recharge to As bearing groundwaters, and that OM from these water bodies can be transported into these aquifer systems where it may be used in biogeochemical processes associated with As release. Finally, a modern radiogenic signature in both the $^{3}$H and $^{14}$CDOC, in conjunction with a massive contribution of water from a highly evaporated source water as evidenced in the stable isotopic composition of the groundwater, suggests that groundwater pumping as part of the sampling process drew water from a nearby pond into the groundwater at two locations. Together, this demonstrates that, even in the absence of extensive groundwater abstraction, natural flow paths have the potential to transport dissolved species from surface water features in to the groundwater. However, the groundwaters here appear to be highly vulnerable to rapid changes in the water composition brought about by the rapid introduction of surface waters driven by groundwater abstraction.

9.3. **Characterisation of a Bengali aquifer: An insight into Cambodia’s future?**

The aquifer system investigated in West Bengal displays some key differences from that of the groundwater in Cambodia. Firstly, almost all groundwaters up to a depth of approximately 60 m show a significant contribution of modern recharge at this study site. Indeed, much of this groundwater is characterised by mean groundwater residence times of less than 60 years, with large proportions of the site containing significant contributions of recharge from the last 20 years. If we assume that the $^{3}$H profile of the Cambodian groundwater system is characteristic of pre-development conditions, the more extensive presence and deeper penetration of $^{3}$H in these groundwaters suggests that the shallow groundwater flow at this site has been subjected to huge
changes. Pumping of the shallow groundwater has clearly resulted in the drawdown of water from the surface to greater depths over much more rapid timescales. However, unlike in Cambodia, the stable isotopic composition of groundwater in West Bengal is less conclusive, and does not allow for identification of the source of this recharge. Uncorrected $^{14}$C ages of groundwater at 101 m depth in Bengal also appear to be much younger than groundwater at shallower depths in Cambodia. This suggests that younger water from a shallower depth is migrating down a flow path to deep groundwater, as previously suggested for this West Bengal study site (CHARLET et al., 2007). This process may be driven by the over exploitation of the deep groundwater that has been suggested to be a potentially sustainable source of As free drinking water in this region (BURGESS et al., 2010; MICHAEL and VOSS, 2008; POLYA and CHARLET, 2009; VAN GEEN et al., 2003; VAN GEEN et al., 2007).

Based on the typically younger residence times of the groundwater in West Bengal, one might expect the composition of the DOC to reflect a greater contribution of young, surface derived OM in these groundwaters compared to that of Cambodian groundwater. Furthermore, given the presence of modern DOC in Cambodian groundwaters, potentially drawn in by groundwater abstraction, it would not be unreasonable to assume that a similar signature may be observed in a larger proportion of groundwaters in West Bengal. It is perhaps surprising therefore that this modern DOC signature is not observed in any of the groundwaters at the study site in West Bengal (figure 9.1). This is consistent with observations of the DOC signature in neighbouring Bangladesh, where the DOC was reported to have an age range of between approximately 3000 and 5000 years (HARVEY et al., 2002). This likely reflects a difference in the permeability of the sediments at the two sites investigated here, with those at the Cambodian site seemingly able to allow much more rapid flow velocities. This may be further compounded by differences in the source of recharge at these sites, with Bengali groundwaters perhaps receiving a much smaller contribution from surface ponds. This may give rise to a smaller contribution of modern DOC, which, when mixed with older OM at the zone of convergence of numerous flow paths in Bengali groundwaters, does not give rise to the predominantly modern signature we see in some Cambodian groundwaters. This lack of a modern signature of DOC in Bengali groundwaters aside, the composition and depth distribution of DOC appears similar for the two groundwaters investigated, with very little difference in the composition of DOC in the upper 55 m at the two sites. However, the DOC in the deep groundwater between 80 and 125 m in West Bengal has a much younger bulk signature than that of the DOC in groundwater at a shallower depth in Cambodia.
9.4. **The effect of groundwater abstraction on the flow regimes and groundwater chemistry**

This study is the first comprehensive comparison of two As bearing systems with different groundwater abstraction histories. Our data indicates that, even in the absence of extensive groundwater abstraction, there is considerable interaction between surface ponds and wetlands and the underlying shallow (< 20 m) groundwater operating over timescales of less than 50 years. However, the timescales over which this interaction takes place clearly increases with increasing depth, with only 50 % of groundwaters at 20 m or more containing a contribution of recharge from the last 50 years. At depths of 55 m or more, $^{14}$C data of DIC indicate mean groundwater residence times of hundreds to thousands of years. In contrast, groundwaters that have been subjected to massive groundwater abstraction show a clear contribution of modern recharge to depths of up to 63 m in 90% of the samples taken. Groundwater at a depth of 100 m here clearly has a considerably younger mean residence time than that which would exist under natural conditions. The more
extensive presence of recent recharge to the shallow groundwater and younger residence times of the deep groundwater is indicative of a massive change in the natural groundwater flow regime in West Bengal since the onset of extensive groundwater abstraction. That this impact is being seen in deeper groundwater is a worrying observation given that this has been identified as a source of As free drinking water to millions of people in West Bengal and Bangladesh where the contamination of shallow groundwater by As is pervasive.

The $^{14}$C signature of DOC at both of the study sites investigated here clearly demonstrates a requirement for multiple sources of OM to be contributing DOC to the groundwater. Such an observation should help to expel the theory that one particular source of OM is responsible for driving As release in these groundwaters. This instead suggests that different sources of OM may contribute organic carbon to groundwater which then may be utilised in biogeochemical processes, some of which may potentially be associated with As release. However, comparison of this DOC composition suggests that, whilst the distribution of the contributions of different sources of OM appears to be similar for shallow groundwaters at both sites, the typically younger deep groundwaters of West Bengal require a greater contribution of younger OM. This suggests that ground abstraction practices not only result in changes in the groundwater flow regime, but also drive changes in the geochemical composition of the groundwater. It is unclear what effect this is having on the biogeochemical processes which occur in these groundwaters, and whether high concentrations of As at this depth are the result of the downward migration of As contaminated groundwater from above (vis a vis Charlet et al., 2007) or from the release of As from deeper sediments following the introduction of bioavailable DOC. However, a shift towards a younger, more labile bulk DOC pool clearly has the potential to support greater rates of As release.

9.5. Implications for a sustainable source of As free groundwater in South and South East Asia

The investigation of the West Bengal and Cambodia study sites in this research represents the characterisation of end-member environments in terms of the impact generated by anthropogenic disturbance of groundwater systems. Despite the site specific variations in the source, processes and timescales associated with groundwater recharge, our results have important implications for the provision of safe drinking water in this region. Groundwater abstraction clearly changes subsurface flow regimes, and appears to be resulting in the drawdown of groundwater from shallower regions of the aquifer system to the deep groundwater. This invading shallow groundwater may transport As
in to the deep groundwater, contaminating previously As-free groundwater. It also appears to be changing the composition of DOC, giving rise to a more reactive, bioavailable DOC pool which has the potential to further influence As mobility in the deep groundwater. This observation is a cause of great concern in locations such as West Bengal and Bangladesh, where deep groundwater has long been touted as a long term source of safe, As-free drinking water in this region.

The information presented here also has implications for locations such as Cambodia and Vietnam, where the future of groundwater management practices remains unclear. The onset of extensive groundwater abstraction in these locations would clearly result in a change in natural groundwater flow paths, potentially changing sources of recharge or resulting in a greater contribution of recharge from sources where higher permeabilities will support more rapid recharge. It may be expected that the instigation of groundwater abstraction in these locations will result in a shift to a younger bulk DOC composition which has the capacity to support more rapid rates of As release. Such a situation could have potentially devastating effects on these countries because, unlike West Bengal and Bangladesh, the aquifer sediments in these locations do not extend to depths greater than 60 m. As such, these countries do not have the luxury of a deeper, As free source of drinking water. However, whilst an increased contribution of surface water may be expected to result in more extensive As release, it does not necessarily follow that it must do. The introduction of this extra DOC may also be accompanied by contributions of other species which act to consume this additional DOC and which potentially may sequester As from solution. The potential for secular changes in the groundwater As hazard in these regions must therefore not only consider the impact that changes in the DOC composition may have on As concentrations, but also what effect contributions of other species may make to the biogeochemical evolution of these groundwaters.

9.6. References


APPENDIX 1

Cambodia supplementary data
<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC mg/l</th>
<th>As ug/l</th>
<th>Fe mg/l</th>
<th>Mn μg/l</th>
<th>Ca mg/l</th>
<th>K mg/l</th>
<th>Mg mg/l</th>
<th>Na mg/l</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE11 - 12</td>
<td>0.80</td>
<td>6</td>
<td>0.08</td>
<td>0.02</td>
<td>0.04</td>
<td>108.72</td>
<td>1.28</td>
<td>127.44</td>
<td>1.20</td>
</tr>
<tr>
<td>TE11 - 20</td>
<td>1.10</td>
<td>346</td>
<td>4.68</td>
<td>14.59</td>
<td>0.89</td>
<td>295.31</td>
<td>3.49</td>
<td>135.17</td>
<td>1.27</td>
</tr>
<tr>
<td>TE11 - 55</td>
<td>5.06</td>
<td>829</td>
<td>11.21</td>
<td>6.69</td>
<td>0.41</td>
<td>82.43</td>
<td>0.97</td>
<td>61.20</td>
<td>0.57</td>
</tr>
<tr>
<td>ML01 - 9</td>
<td>1.91</td>
<td>212</td>
<td>2.87</td>
<td>17.33</td>
<td>1.06</td>
<td>915.20</td>
<td>10.80</td>
<td>95.07</td>
<td>0.89</td>
</tr>
<tr>
<td>ML01 - 29</td>
<td>6.75</td>
<td>217</td>
<td>2.93</td>
<td>2.20</td>
<td>0.13</td>
<td>799.10</td>
<td>9.43</td>
<td>45.44</td>
<td>0.43</td>
</tr>
<tr>
<td>ML01 - 37</td>
<td>6.48</td>
<td>258</td>
<td>3.49</td>
<td>6.23</td>
<td>0.38</td>
<td>1275.7</td>
<td>15.06</td>
<td>40.63</td>
<td>0.38</td>
</tr>
<tr>
<td>TE51 - 12</td>
<td>3.80</td>
<td>418</td>
<td>5.66</td>
<td>13.11</td>
<td>0.80</td>
<td>676.63</td>
<td>7.99</td>
<td>95.47</td>
<td>0.90</td>
</tr>
<tr>
<td>TE51 - 20</td>
<td>10.89</td>
<td>1100</td>
<td>14.89</td>
<td>2.22</td>
<td>0.14</td>
<td>1018.4</td>
<td>12.02</td>
<td>44.19</td>
<td>0.41</td>
</tr>
<tr>
<td>TC31</td>
<td>15.32</td>
<td>46</td>
<td>0.62</td>
<td>0.00</td>
<td>0.04</td>
<td>468.56</td>
<td>5.53</td>
<td>86.08</td>
<td>0.81</td>
</tr>
<tr>
<td>TE61</td>
<td>11.60</td>
<td>44</td>
<td>0.60</td>
<td>0.18</td>
<td>0.04</td>
<td>106.49</td>
<td>1.26</td>
<td>76.55</td>
<td>0.72</td>
</tr>
<tr>
<td>ML02</td>
<td>6.78</td>
<td>4</td>
<td>0.05</td>
<td>1.21</td>
<td>0.07</td>
<td>474.18</td>
<td>5.60</td>
<td>37.95</td>
<td>0.36</td>
</tr>
<tr>
<td>TC45 - 12</td>
<td>4.88</td>
<td>3</td>
<td>0.04</td>
<td>2.95</td>
<td>0.18</td>
<td>261.92</td>
<td>3.09</td>
<td>194.58</td>
<td>1.83</td>
</tr>
<tr>
<td>TC45 - 20</td>
<td>2.52</td>
<td>2</td>
<td>0.04</td>
<td>0.36</td>
<td>0.04</td>
<td>188.95</td>
<td>2.23</td>
<td>240.80</td>
<td>2.26</td>
</tr>
<tr>
<td>ML03 - 7</td>
<td>3.72</td>
<td>10</td>
<td>0.13</td>
<td>0.93</td>
<td>0.06</td>
<td>1158.1</td>
<td>13.67</td>
<td>34.66</td>
<td>0.32</td>
</tr>
<tr>
<td>ML03 - 24</td>
<td>6.53</td>
<td>35</td>
<td>0.48</td>
<td>15.25</td>
<td>0.93</td>
<td>476.93</td>
<td>5.63</td>
<td>35.73</td>
<td>0.33</td>
</tr>
<tr>
<td>ML03 - 42</td>
<td>63.35</td>
<td>32</td>
<td>0.44</td>
<td>0.02</td>
<td>0.04</td>
<td>510.77</td>
<td>6.03</td>
<td>52.40</td>
<td>0.49</td>
</tr>
<tr>
<td>ML04 - 8</td>
<td>2.20</td>
<td>9</td>
<td>0.12</td>
<td>7.83</td>
<td>0.48</td>
<td>533.04</td>
<td>6.29</td>
<td>35.97</td>
<td>0.71</td>
</tr>
<tr>
<td>ML04 - 30</td>
<td>6.82</td>
<td>13</td>
<td>0.18</td>
<td>0.16</td>
<td>0.04</td>
<td>87.97</td>
<td>1.04</td>
<td>37.51</td>
<td>0.35</td>
</tr>
<tr>
<td>ML04 - 44</td>
<td>6.39</td>
<td>30</td>
<td>0.40</td>
<td>15.85</td>
<td>0.96</td>
<td>365.68</td>
<td>4.32</td>
<td>42.61</td>
<td>0.40</td>
</tr>
<tr>
<td>ML05</td>
<td>3.08</td>
<td>778</td>
<td>10.53</td>
<td>3.52</td>
<td>0.21</td>
<td>322.50</td>
<td>3.81</td>
<td>42.32</td>
<td>0.40</td>
</tr>
</tbody>
</table>

**SURFACE SAMPLES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC mg/l</th>
<th>As ug/l</th>
<th>Fe mg/l</th>
<th>Mn μg/l</th>
<th>Ca mg/l</th>
<th>K mg/l</th>
<th>Mg mg/l</th>
<th>Na mg/l</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetlands</td>
<td>6.72</td>
<td>10.23</td>
<td>0.14</td>
<td>0.24</td>
<td>0.04</td>
<td>206.53</td>
<td>2.44</td>
<td>32.38</td>
<td>0.30</td>
</tr>
<tr>
<td>Wetland connected</td>
<td>6.12</td>
<td>3.27</td>
<td>0.05</td>
<td>0.15</td>
<td>0.04</td>
<td>149.55</td>
<td>1.77</td>
<td>31.92</td>
<td>0.30</td>
</tr>
<tr>
<td>Isolated Pond</td>
<td>4.23</td>
<td>1.99</td>
<td>0.03</td>
<td>0.02</td>
<td>0.04</td>
<td>2.33</td>
<td>0.03</td>
<td>19.53</td>
<td>0.18</td>
</tr>
<tr>
<td>River Mekong</td>
<td>2.39</td>
<td>1.21</td>
<td>0.03</td>
<td>0.11</td>
<td>0.04</td>
<td>0.77</td>
<td>0.01</td>
<td>7.31</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 4. Major and minor cation analysis of groundwater samples collected from study site during April 2009. Error gives the error associated with the measurement at the 95% confidence level.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>pH</th>
<th>EC (µS/cm)</th>
<th>EC (mV)</th>
<th>Tem (°C)</th>
<th>Cl⁻ mg/l</th>
<th>NO₂⁻ mg/l</th>
<th>NO₃⁻ mg/l</th>
<th>NH₄⁺ mg/l</th>
<th>ΣPO₄²⁻ mg/l</th>
<th>ΣSO₄²⁻ mg/l</th>
<th>Br⁻ mg/l</th>
<th>HCO₃⁻ mg/l</th>
<th>Σ⁻</th>
<th>Σ⁺</th>
<th>EN (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE11 - 12</td>
<td>12</td>
<td>6.4</td>
<td>349</td>
<td>222</td>
<td>30</td>
<td>71.4</td>
<td>ND</td>
<td>72.2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>499.6</td>
<td>12.1</td>
<td>11.8</td>
<td>1.35</td>
</tr>
<tr>
<td>TE11 - 20</td>
<td>20</td>
<td>6.8</td>
<td>229</td>
<td>-29</td>
<td>29.6</td>
<td>113.3</td>
<td>ND</td>
<td>8.8</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>62.8</td>
<td>608.6</td>
<td>14.6</td>
<td>14.7</td>
<td>0.47</td>
</tr>
<tr>
<td>TE11 - 55</td>
<td>55</td>
<td>6.4</td>
<td>363</td>
<td>-73</td>
<td>29.8</td>
<td>3.1</td>
<td>ND</td>
<td>1.1</td>
<td>30</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>510.7</td>
<td>8.48</td>
<td>7.45</td>
<td>6.44</td>
</tr>
<tr>
<td>ML01 - 9</td>
<td>9</td>
<td>6.1</td>
<td>137</td>
<td>-44</td>
<td>28.8</td>
<td>63.9</td>
<td>ND</td>
<td>0.08</td>
<td>12</td>
<td>0.87</td>
<td>7.4</td>
<td>0.22</td>
<td>563.4</td>
<td>11.1</td>
<td>9.39</td>
<td>8.73</td>
</tr>
<tr>
<td>ML01 - 29</td>
<td>28.6</td>
<td>6.8</td>
<td>405</td>
<td>-44</td>
<td>30.2</td>
<td>6.8</td>
<td>ND</td>
<td>ND</td>
<td>14.6</td>
<td>0.46</td>
<td>0.4</td>
<td>ND</td>
<td>410.2</td>
<td>6.92</td>
<td>4.37</td>
<td>22.6</td>
</tr>
<tr>
<td>ML01 - 37</td>
<td>37</td>
<td>7</td>
<td>670</td>
<td>-27</td>
<td>30.1</td>
<td>12.8</td>
<td>ND</td>
<td>ND</td>
<td>14.8</td>
<td>0.40</td>
<td>0.5</td>
<td>ND</td>
<td>363.2</td>
<td>6.32</td>
<td>3.65</td>
<td>26.8</td>
</tr>
<tr>
<td>TE51 - 12</td>
<td>12</td>
<td>6.6</td>
<td>478</td>
<td>-30</td>
<td>34</td>
<td>14</td>
<td>ND</td>
<td>0.47</td>
<td>56.7</td>
<td>0.15</td>
<td>0.55</td>
<td>0.19</td>
<td>465.0</td>
<td>8.04</td>
<td>7.92</td>
<td>0.75</td>
</tr>
<tr>
<td>TE51 - 20</td>
<td>20</td>
<td>6.9</td>
<td>876</td>
<td>-116</td>
<td>30.7</td>
<td>5.5</td>
<td>ND</td>
<td>0.09</td>
<td>21.9</td>
<td>1.15</td>
<td>&lt;0.05</td>
<td>0.27</td>
<td>404.0</td>
<td>6.78</td>
<td>4.81</td>
<td>16.9</td>
</tr>
<tr>
<td>TC31</td>
<td>51</td>
<td>6.8</td>
<td>567</td>
<td>-76</td>
<td>30.1</td>
<td>5.2</td>
<td>ND</td>
<td>7</td>
<td>50</td>
<td>0.5</td>
<td>0.08</td>
<td>1.1</td>
<td>658.6</td>
<td>11.0</td>
<td>8.65</td>
<td>12.2</td>
</tr>
<tr>
<td>TE61</td>
<td>48</td>
<td>6.3</td>
<td>1235</td>
<td>-100</td>
<td>30.2</td>
<td>4.8</td>
<td>ND</td>
<td>ND</td>
<td>80</td>
<td>ND</td>
<td>ND</td>
<td>0.7</td>
<td>757.0</td>
<td>12.5</td>
<td>7.64</td>
<td>24.2</td>
</tr>
<tr>
<td>ML02</td>
<td>8.53</td>
<td>6.5</td>
<td>56</td>
<td>-163</td>
<td>29.9</td>
<td>60.5</td>
<td>ND</td>
<td>0.14</td>
<td>0.49</td>
<td>12.4</td>
<td>ND</td>
<td>443.6</td>
<td>9.23</td>
<td>6.10</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td>TC45 - 12</td>
<td>12</td>
<td>6.3</td>
<td>1427</td>
<td>-117</td>
<td>31.1</td>
<td>325</td>
<td>ND</td>
<td>0.4</td>
<td>40</td>
<td>3.4</td>
<td>26.1</td>
<td>0.5</td>
<td>816.7</td>
<td>23.1</td>
<td>21.4</td>
<td>3.80</td>
</tr>
<tr>
<td>TC45 - 20</td>
<td>20</td>
<td>6.4</td>
<td>1439</td>
<td>135</td>
<td>31.1</td>
<td>479</td>
<td>ND</td>
<td>56.2</td>
<td>~0.5</td>
<td>ND</td>
<td>146</td>
<td>0.7</td>
<td>630.6</td>
<td>27.6</td>
<td>26.8</td>
<td>1.81</td>
</tr>
<tr>
<td>ML03 - 7</td>
<td>7.27</td>
<td>6.4</td>
<td>610</td>
<td>-47</td>
<td>29.1</td>
<td>45.4</td>
<td>1.35</td>
<td>0.36</td>
<td>ND</td>
<td>0.25</td>
<td>26.4</td>
<td>ND</td>
<td>292.0</td>
<td>6.62</td>
<td>5.46</td>
<td>9.64</td>
</tr>
<tr>
<td>ML03 - 24</td>
<td>23.8</td>
<td>6.1</td>
<td>569</td>
<td>-70</td>
<td>29.2</td>
<td>29.7</td>
<td>ND</td>
<td>56.9</td>
<td>~0.3</td>
<td>2.4</td>
<td>0.7</td>
<td>ND</td>
<td>123.2</td>
<td>3.79</td>
<td>4.24</td>
<td>5.55</td>
</tr>
<tr>
<td>ML03 -42</td>
<td>42</td>
<td>6.7</td>
<td>ND</td>
<td>ND</td>
<td>30</td>
<td>1520</td>
<td>ND</td>
<td>0.3</td>
<td>7</td>
<td>1.7</td>
<td>3.3</td>
<td>&lt;0.0</td>
<td>303.6</td>
<td>47.9</td>
<td>6.39</td>
<td>76.4</td>
</tr>
<tr>
<td>ML04 - 8</td>
<td>8.19</td>
<td>6.4</td>
<td>&gt;2000</td>
<td>14</td>
<td>30.4</td>
<td>55.7</td>
<td>&lt;0.05</td>
<td>10.7</td>
<td>ND</td>
<td>&lt;0.05</td>
<td>249</td>
<td>0.2</td>
<td>688.6</td>
<td>18.2</td>
<td>18.8</td>
<td>1.78</td>
</tr>
<tr>
<td>ML04 - 30</td>
<td>29.14</td>
<td>7.1</td>
<td>409</td>
<td>60</td>
<td>31.4</td>
<td>21.2</td>
<td>ND</td>
<td>2.4</td>
<td>ND</td>
<td>2.8</td>
<td>&lt;0.0</td>
<td>187.4</td>
<td>3.77</td>
<td>3.77</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>ML04 - 44</td>
<td>44</td>
<td>6.9</td>
<td>33</td>
<td>179</td>
<td>31.2</td>
<td>22.4</td>
<td>ND</td>
<td>7</td>
<td>ND</td>
<td>ND</td>
<td>4.6</td>
<td>ND</td>
<td>169.2</td>
<td>3.61</td>
<td>4.15</td>
<td>6.95</td>
</tr>
<tr>
<td>ML05</td>
<td>60</td>
<td>6.5</td>
<td>1552</td>
<td>-36</td>
<td>33.2</td>
<td>3.7</td>
<td>ND</td>
<td>20.4</td>
<td>ND</td>
<td>0.9</td>
<td>0.2</td>
<td>ND</td>
<td>243.8</td>
<td>4.43</td>
<td>4.69</td>
<td>2.77</td>
</tr>
</tbody>
</table>

**SURFACE SAMPLES**

| Wetlands                        | 26.2 | ND | 0.12 | 1.8 | 0.36 | 3 | ND | 169.7 |
| Wetland connected pond          | 19.8 | ND | 0.5  | ND  | 0.8  | 0.05 | ND | 176.0 |
| Isolated Pond                   | 10.8 | ND | 0.6  | ND  | 1.5  | ND | 115.3 |
| River Mekong                    | 5.4  | ND | 1.1  | 0.15 | 5.1  | ND | 62.28 |

Table 5. Physical and anion composition of groundwaters collected from the study site in April 2009. An assessment of the electroneutrality of each sample is given based on major element concentrations presented in tables 1 and 2.
<table>
<thead>
<tr>
<th>Tubewell</th>
<th>February</th>
<th>March</th>
<th>April</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
<th>October</th>
<th>November</th>
<th>December</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE11 - 12</td>
<td>-6.21</td>
<td>-7.04</td>
<td>-7.00</td>
<td>-6.99</td>
<td>-7.12</td>
<td>-7.18</td>
<td>-7.24</td>
<td>-6.90</td>
<td>-7.06</td>
<td>-6.50</td>
<td>-6.70</td>
</tr>
<tr>
<td>TE11 - 20</td>
<td>-6.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TE11 - 50</td>
<td>-7.70</td>
<td>-7.60</td>
<td>-7.72</td>
<td>-7.68</td>
<td>-7.70</td>
<td>-7.55</td>
<td>-7.53</td>
<td>-7.53</td>
<td>-7.52</td>
<td>-7.56</td>
<td>-7.68</td>
</tr>
<tr>
<td>ML01 - 10</td>
<td>-7.09</td>
<td>-6.94</td>
<td>-7.06</td>
<td>-6.84</td>
<td>-6.72</td>
<td>-6.62</td>
<td>-6.47</td>
<td>-6.31</td>
<td>-6.12</td>
<td>-6.11</td>
<td></td>
</tr>
<tr>
<td>ML01 - 50</td>
<td>-5.81</td>
<td>-6.51</td>
<td>-6.40</td>
<td>-5.81</td>
<td>-5.61</td>
<td>-5.42</td>
<td>-5.25</td>
<td>-5.11</td>
<td>-5.00</td>
<td>-4.90</td>
<td>-4.95</td>
</tr>
<tr>
<td>TE51 - 12</td>
<td>-6.52</td>
<td>-6.50</td>
<td>-6.72</td>
<td>-6.53</td>
<td>-6.47</td>
<td>-6.27</td>
<td>-6.27</td>
<td>-6.31</td>
<td>-6.12</td>
<td>-6.00</td>
<td>-6.11</td>
</tr>
<tr>
<td>TE51 - 20</td>
<td>-6.43</td>
<td>-6.33</td>
<td>-6.61</td>
<td>-6.59</td>
<td>-6.84</td>
<td>-6.47</td>
<td>-7.06</td>
<td>-6.23</td>
<td>-6.20</td>
<td>-6.77</td>
<td>-6.72</td>
</tr>
<tr>
<td>ML02 - 10</td>
<td>-2.52</td>
<td>-5.45</td>
<td>-5.61</td>
<td>-5.64</td>
<td>-5.23</td>
<td>-5.25</td>
<td>-5.29</td>
<td>-5.30</td>
<td>-5.30</td>
<td>-5.18</td>
<td></td>
</tr>
<tr>
<td>TC45 - 12</td>
<td>-6.52</td>
<td>-6.50</td>
<td>-6.61</td>
<td>-6.59</td>
<td>-6.84</td>
<td>-6.47</td>
<td>-7.06</td>
<td>-6.23</td>
<td>-6.20</td>
<td>-6.77</td>
<td>-6.72</td>
</tr>
<tr>
<td>ML03 - 10</td>
<td>-6.43</td>
<td>-6.51</td>
<td>-6.40</td>
<td>-5.81</td>
<td>-5.61</td>
<td>-5.42</td>
<td>-5.25</td>
<td>-5.29</td>
<td>-5.30</td>
<td>-5.30</td>
<td>-5.18</td>
</tr>
<tr>
<td>ML03 - 30</td>
<td>-2.52</td>
<td>-5.45</td>
<td>-5.61</td>
<td>-5.64</td>
<td>-5.23</td>
<td>-5.25</td>
<td>-5.29</td>
<td>-5.30</td>
<td>-5.30</td>
<td>-5.18</td>
<td></td>
</tr>
<tr>
<td>ML03 - 50</td>
<td>-5.61</td>
<td>-6.51</td>
<td>-6.40</td>
<td>-5.81</td>
<td>-5.61</td>
<td>-5.42</td>
<td>-5.25</td>
<td>-5.29</td>
<td>-5.30</td>
<td>-5.30</td>
<td>-5.18</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface waters</th>
<th>February</th>
<th>March</th>
<th>April</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
<th>October</th>
<th>November</th>
<th>December</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mekong River</td>
<td>-4.38</td>
<td>-3.35</td>
<td>-4.22</td>
<td>-6.35</td>
<td>-6.78</td>
<td>-7.4</td>
<td>-6.57</td>
<td>-7.66</td>
<td>-7.66</td>
<td>-6.33</td>
<td>-5.37</td>
</tr>
<tr>
<td>Isolated Pond (surface)</td>
<td>-4.24</td>
<td>-2.94</td>
<td>-2.44</td>
<td>-1.97</td>
<td>-1.96</td>
<td>-1.39</td>
<td>-1.54</td>
<td>-2.16</td>
<td>-2.16</td>
<td>-1.89</td>
<td>-1.78</td>
</tr>
<tr>
<td>Isolated Pond (30 m)</td>
<td>-4.21</td>
<td>-2.68</td>
<td>-2.13</td>
<td>-1.84</td>
<td>-2.05</td>
<td>-0.46</td>
<td>-2.16</td>
<td>-5.31</td>
<td>-6.09</td>
<td>-5.31</td>
<td></td>
</tr>
<tr>
<td>Wetlands (surface)</td>
<td>-3.29</td>
<td>-2.07</td>
<td>-1.85</td>
<td>-2.22</td>
<td>-0.84</td>
<td>-2.34</td>
<td>-5.29</td>
<td>-6.30</td>
<td>-5.43</td>
<td>-5.43</td>
<td></td>
</tr>
<tr>
<td>Wetlands (2 m)</td>
<td>-3.30</td>
<td>-2.90</td>
<td>-1.8</td>
<td>-1.55</td>
<td>-1.35</td>
<td>-0.38</td>
<td>-1.35</td>
<td>-5.41</td>
<td>-6.15</td>
<td>-5.26</td>
<td></td>
</tr>
<tr>
<td>Wetland Pond (surface)</td>
<td>-3.87</td>
<td>-2.35</td>
<td>-1.9</td>
<td>-1.74</td>
<td>-1.1</td>
<td>-0.30</td>
<td>-1.34</td>
<td>-5.54</td>
<td>-6.02</td>
<td>-5.13</td>
<td></td>
</tr>
</tbody>
</table>

| Wetland Pond (3 m) | -3.87 | -2.35 | -1.9  | -1.74 | -1.1  | -0.30 | -1.34  | -5.54 | -6.02 | -5.13 |

Table 6. δ^{18}O isotopic signature of ground and surface waters collected from the study site from February - December 2009. Surface waters are sampled at two depths given in the table.
<table>
<thead>
<tr>
<th>Tubewell</th>
<th>February</th>
<th>March</th>
<th>April</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
<th>October</th>
<th>November</th>
<th>December</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE11 - 12</td>
<td>-38.8</td>
<td>-41.0</td>
<td>-40.8</td>
<td>-43.7</td>
<td>-45.4</td>
<td>-47.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TE11 - 20</td>
<td></td>
<td></td>
<td>-45.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TE11 - 50</td>
<td>-55.0</td>
<td>-50.7</td>
<td>-51.3</td>
<td>-51.3</td>
<td>-50.4</td>
<td>-52.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-53.2</td>
</tr>
<tr>
<td>ML01 - 10</td>
<td></td>
<td></td>
<td>-44.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ML01 - 20</td>
<td></td>
<td></td>
<td>-44.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ML01 - 50</td>
<td></td>
<td></td>
<td>-47.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TE51 - 12</td>
<td></td>
<td></td>
<td>-32.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TE51 - 20</td>
<td></td>
<td></td>
<td>-46.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TC51</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TE61</td>
<td></td>
<td></td>
<td>-46.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ML02</td>
<td></td>
<td></td>
<td>-36.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TC45 - 12</td>
<td>-44.5</td>
<td>-45.8</td>
<td>-36.3</td>
<td>-41.4</td>
<td>-40.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TC45 - 20</td>
<td>-43.9</td>
<td>-44.0</td>
<td>-38.9</td>
<td>-41.4</td>
<td>-43.9</td>
<td>-40.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ML03 - 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-41.3</td>
</tr>
<tr>
<td>ML03 - 30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-40.7</td>
</tr>
<tr>
<td>ML03 - 50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-35.1</td>
</tr>
<tr>
<td>ML04 - 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-37.8</td>
</tr>
<tr>
<td>ML04 - 30</td>
<td>-38.3</td>
<td>-37.7</td>
<td>-19.9</td>
<td>-37.2</td>
<td>-36.8</td>
<td></td>
<td>-34.6</td>
<td></td>
<td></td>
<td></td>
<td>-39.4</td>
</tr>
<tr>
<td>ML04 - 50</td>
<td></td>
<td></td>
<td>-18.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ML05 - 10</td>
<td></td>
<td></td>
<td>-52.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface waters</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mekong River</td>
<td>-30.9</td>
<td>-26.6</td>
<td>-33.3</td>
<td>-36.7</td>
<td>-42.8</td>
<td>-46.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-43.4</td>
</tr>
<tr>
<td>Isolated Pond (surface)</td>
<td>-33.6</td>
<td></td>
<td>-22.8</td>
<td>-17.4</td>
<td>-14.8</td>
<td>-14.8</td>
<td>-13.0</td>
<td>-20.2</td>
<td>-20.0</td>
<td>-20.0</td>
<td>-22.5</td>
</tr>
<tr>
<td>Isolated Pond (30 m)</td>
<td></td>
<td></td>
<td>-29.9</td>
<td>-27.2</td>
<td>-14.5</td>
<td>-16.4</td>
<td>-15.8</td>
<td>-20.7</td>
<td>-21.4</td>
<td>-20.4</td>
<td></td>
</tr>
<tr>
<td>Wetlands (surface)</td>
<td>-25.2</td>
<td></td>
<td>-22.5</td>
<td>-13.3</td>
<td>-10.1</td>
<td>-17.2</td>
<td>-12.5</td>
<td>-26.0</td>
<td>-36.1</td>
<td>-45.3</td>
<td></td>
</tr>
<tr>
<td>Wetlands (2 m)</td>
<td></td>
<td></td>
<td>-13.8</td>
<td>-8.8</td>
<td>-14.8</td>
<td>-12.4</td>
<td>-22.0</td>
<td>-37.0</td>
<td>-45.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wetland Pond (surface)</td>
<td>-25.8</td>
<td></td>
<td>-21.1</td>
<td>-13.7</td>
<td>-16.4</td>
<td>-11.8</td>
<td>-8.2</td>
<td>-16.0</td>
<td>-38.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wetland Pond (3 m)</td>
<td></td>
<td></td>
<td>-29.8</td>
<td>-23.0</td>
<td>-11.6</td>
<td>-16.9</td>
<td>-15.1</td>
<td>-11.7</td>
<td>-17.7</td>
<td>-40.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 7. δD isotopic signature of ground and surface waters collected from the study site from February - December 2009. Surface waters are sampled at two depths given in the table.
APPENDIX 2

West Bengal supplementary data
### Table 8. Major and minor cation analysis of groundwater samples collected from study site during January 2008. Err gives the error associated with the measurement at the 95% confidence level.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As (µg/l)</th>
<th>Ca (mg/l)</th>
<th>Fe (mg/l)</th>
<th>K (mg/l)</th>
<th>Mg (mg/l)</th>
<th>Mn (mg/l)</th>
<th>Na (mg/l)</th>
<th>Sr (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH01</td>
<td>567.91</td>
<td>36.49</td>
<td>89.71</td>
<td>0.66</td>
<td>3.57</td>
<td>0.02</td>
<td>24.60</td>
<td>0.33</td>
</tr>
<tr>
<td>CH02</td>
<td>595.67</td>
<td>38.27</td>
<td>107.80</td>
<td>0.80</td>
<td>3.78</td>
<td>0.02</td>
<td>34.02</td>
<td>0.46</td>
</tr>
<tr>
<td>CH04</td>
<td>120.66</td>
<td>7.75</td>
<td>45.22</td>
<td>0.33</td>
<td>1.67</td>
<td>0.02</td>
<td>9.54</td>
<td>0.13</td>
</tr>
<tr>
<td>CH05</td>
<td>61.50</td>
<td>3.95</td>
<td>174.52</td>
<td>1.29</td>
<td>5.66</td>
<td>0.06</td>
<td>38.37</td>
<td>0.51</td>
</tr>
<tr>
<td>CH06</td>
<td>303.61</td>
<td>19.51</td>
<td>178.85</td>
<td>1.32</td>
<td>8.84</td>
<td>0.10</td>
<td>49.28</td>
<td>0.66</td>
</tr>
<tr>
<td>CH07</td>
<td>113.88</td>
<td>7.32</td>
<td>162.04</td>
<td>1.20</td>
<td>11.35</td>
<td>0.13</td>
<td>12.94</td>
<td>0.08</td>
</tr>
<tr>
<td>CH08</td>
<td>7.31</td>
<td>0.47</td>
<td>109.61</td>
<td>0.81</td>
<td>3.58</td>
<td>0.04</td>
<td>1.95</td>
<td>0.01</td>
</tr>
<tr>
<td>CH09</td>
<td>16.96</td>
<td>1.09</td>
<td>98.31</td>
<td>0.73</td>
<td>4.17</td>
<td>0.05</td>
<td>2.47</td>
<td>0.02</td>
</tr>
<tr>
<td>CH10</td>
<td>1.57</td>
<td>0.10</td>
<td>105.29</td>
<td>0.78</td>
<td>3.25</td>
<td>0.04</td>
<td>2.07</td>
<td>0.01</td>
</tr>
<tr>
<td>CH11</td>
<td>10.60</td>
<td>0.68</td>
<td>99.65</td>
<td>0.74</td>
<td>0.88</td>
<td>0.01</td>
<td>3.15</td>
<td>0.02</td>
</tr>
<tr>
<td>CH12</td>
<td>10.25</td>
<td>0.66</td>
<td>91.54</td>
<td>0.68</td>
<td>3.24</td>
<td>0.04</td>
<td>4.42</td>
<td>0.03</td>
</tr>
<tr>
<td>CH13</td>
<td>54.43</td>
<td>3.50</td>
<td>133.26</td>
<td>0.99</td>
<td>6.15</td>
<td>0.07</td>
<td>3.57</td>
<td>0.02</td>
</tr>
<tr>
<td>CH14</td>
<td>28.17</td>
<td>1.81</td>
<td>112.03</td>
<td>0.83</td>
<td>11.84</td>
<td>0.13</td>
<td>3.09</td>
<td>0.02</td>
</tr>
<tr>
<td>CH15</td>
<td>117.80</td>
<td>7.57</td>
<td>167.78</td>
<td>1.24</td>
<td>6.42</td>
<td>0.07</td>
<td>3.06</td>
<td>0.02</td>
</tr>
<tr>
<td>CH16</td>
<td>58.78</td>
<td>3.78</td>
<td>87.83</td>
<td>0.65</td>
<td>5.87</td>
<td>0.07</td>
<td>2.75</td>
<td>0.02</td>
</tr>
<tr>
<td>CH17</td>
<td>312.40</td>
<td>20.07</td>
<td>98.68</td>
<td>0.73</td>
<td>8.94</td>
<td>0.10</td>
<td>3.29</td>
<td>0.02</td>
</tr>
<tr>
<td>CH18</td>
<td>118.97</td>
<td>7.64</td>
<td>97.43</td>
<td>0.72</td>
<td>5.59</td>
<td>0.06</td>
<td>2.70</td>
<td>0.02</td>
</tr>
<tr>
<td>CH19</td>
<td>121.72</td>
<td>7.82</td>
<td>90.06</td>
<td>0.67</td>
<td>4.79</td>
<td>0.05</td>
<td>2.28</td>
<td>0.02</td>
</tr>
<tr>
<td>CH20</td>
<td>23.12</td>
<td>1.49</td>
<td>108.91</td>
<td>0.81</td>
<td>5.65</td>
<td>0.06</td>
<td>0.96</td>
<td>0.01</td>
</tr>
<tr>
<td>CH21</td>
<td>266.53</td>
<td>17.12</td>
<td>107.30</td>
<td>0.79</td>
<td>8.37</td>
<td>0.09</td>
<td>3.14</td>
<td>0.02</td>
</tr>
<tr>
<td>CH22</td>
<td>38.87</td>
<td>2.50</td>
<td>172.10</td>
<td>1.27</td>
<td>4.87</td>
<td>0.05</td>
<td>4.67</td>
<td>0.03</td>
</tr>
<tr>
<td>CH23</td>
<td>46.35</td>
<td>2.98</td>
<td>144.73</td>
<td>1.07</td>
<td>1.80</td>
<td>0.02</td>
<td>4.38</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Err gives the error associated with the measurement at the 95% confidence level.
<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>EC (μS/cm)</th>
<th>ORP (mV)</th>
<th>Temp (°C)</th>
<th>Cl⁻ (mg/l)</th>
<th>NO₂-N (mg/l)</th>
<th>NO₃-N (mg/l)</th>
<th>ΣPO₄³⁻ (mg/l)</th>
<th>ΣSO₄²⁻ (mg/l)</th>
<th>Alkalinity (HCO₃⁻) (mg/l)</th>
<th>EN (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH01</td>
<td>7.11</td>
<td>0.55</td>
<td>-95</td>
<td>27.2</td>
<td>6.2</td>
<td>ND</td>
<td>0.14</td>
<td>ND</td>
<td>ND</td>
<td>439.33</td>
<td>3.76</td>
</tr>
<tr>
<td>CH02</td>
<td>7.03</td>
<td>0.68</td>
<td>-167</td>
<td>26.8</td>
<td>15.6</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>539.01</td>
<td>3.43</td>
</tr>
<tr>
<td>CH04</td>
<td>7.35</td>
<td>0.22</td>
<td>193</td>
<td>30.7</td>
<td>7.1</td>
<td>ND</td>
<td>ND</td>
<td>0.95</td>
<td>7.5</td>
<td>209.5</td>
<td>2.89</td>
</tr>
<tr>
<td>CH05</td>
<td>6.81</td>
<td>1.1</td>
<td>-113</td>
<td>25.8</td>
<td>149</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>47</td>
<td>703.76</td>
<td>3.33</td>
</tr>
<tr>
<td>CH06</td>
<td>6.97</td>
<td>1.17</td>
<td>-185</td>
<td>26.5</td>
<td>155</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>65</td>
<td>535.45</td>
<td>1.70</td>
</tr>
<tr>
<td>CH07</td>
<td>6.79</td>
<td>1.08</td>
<td>-175</td>
<td>26.4</td>
<td>88</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.4</td>
<td>706.82</td>
<td>1.94</td>
</tr>
<tr>
<td>CH08</td>
<td>6.97</td>
<td>0.69</td>
<td>-150</td>
<td>26.8</td>
<td>31</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>8.3</td>
<td>522.74</td>
<td>1.10</td>
</tr>
<tr>
<td>CH09</td>
<td>7.1</td>
<td>0.5</td>
<td>-165</td>
<td>27.2</td>
<td>18.9</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>7.0</td>
<td>463.75</td>
<td>2.36</td>
</tr>
<tr>
<td>CH10</td>
<td>7.03</td>
<td>0.49</td>
<td>-153</td>
<td>26.4</td>
<td>32</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>2.2</td>
<td>474.43</td>
<td>1.67</td>
</tr>
<tr>
<td>CH11</td>
<td>7.23</td>
<td>0.6</td>
<td>-124</td>
<td>28</td>
<td>5.7</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>2.0</td>
<td>518.98</td>
<td>0.49</td>
</tr>
<tr>
<td>CH12</td>
<td>7.1</td>
<td>0.56</td>
<td>-150</td>
<td>26.3</td>
<td>11.1</td>
<td>ND</td>
<td>1.0</td>
<td>ND</td>
<td>1.0</td>
<td>445.78</td>
<td>2.19</td>
</tr>
<tr>
<td>CH13</td>
<td>7.03</td>
<td>0.35</td>
<td>-191</td>
<td>25.1</td>
<td>45</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>2.8</td>
<td>528.18</td>
<td>1.97</td>
</tr>
<tr>
<td>CH14</td>
<td>7</td>
<td>0.41</td>
<td>-245</td>
<td>29.3</td>
<td>63</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>35</td>
<td>736.39</td>
<td>1.62</td>
</tr>
<tr>
<td>CH15</td>
<td>6.92</td>
<td>0.28</td>
<td>-220</td>
<td>27.6</td>
<td>80</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>41</td>
<td>682.48</td>
<td>2.40</td>
</tr>
<tr>
<td>CH16</td>
<td>7.05</td>
<td>0.35</td>
<td>-222</td>
<td>27.1</td>
<td>6.0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>395.81</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>CH17</td>
<td>6.98</td>
<td>0.16</td>
<td>-226</td>
<td>25.8</td>
<td>18.4</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>528.62</td>
<td>-0.49</td>
<td></td>
</tr>
<tr>
<td>CH18</td>
<td>7.1</td>
<td>0.12</td>
<td>-150</td>
<td>26.5</td>
<td>3.5</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>483.04</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>CH19</td>
<td>7.1</td>
<td>0.11</td>
<td>-182</td>
<td>26.2</td>
<td>22.5</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.4</td>
<td>423.86</td>
<td>-0.80</td>
</tr>
<tr>
<td>CH20</td>
<td>7</td>
<td>0.23</td>
<td>-202</td>
<td>26.7</td>
<td>5.0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>521.61</td>
<td>-0.67</td>
<td></td>
</tr>
<tr>
<td>CH21</td>
<td>6.73</td>
<td>0.63</td>
<td>-220</td>
<td>26.3</td>
<td>29.7</td>
<td>24.3</td>
<td>ND</td>
<td>ND</td>
<td>0.2</td>
<td>531.69</td>
<td>-0.13</td>
</tr>
<tr>
<td>CH22</td>
<td>6.81</td>
<td>0.86</td>
<td>-210</td>
<td>26.4</td>
<td>112</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>52</td>
<td>645.33</td>
<td>0.79</td>
</tr>
<tr>
<td>CH23</td>
<td>7</td>
<td>0.92</td>
<td>-180</td>
<td>26.2</td>
<td>42</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>16.8</td>
<td>645.33</td>
<td>6.04</td>
</tr>
</tbody>
</table>

Table 9. Physical and anion composition of groundwaters collected from the study site in January 2008. ND denotes not detected. An assessment of the electroneutrality of each sample is given based on major element concentrations presented in tables 1 and 2.
<table>
<thead>
<tr>
<th>Sample</th>
<th>δ¹⁸O (%)</th>
<th>δD (%)</th>
<th>δ¹³C DIC ICSF (‰)</th>
<th>δ¹³C DIC (RCF-E) RCF-E (‰)</th>
<th>DIC ¹⁴C enrichment (pmC)</th>
<th>δ¹³C DOC RCF-E (‰)</th>
<th>DOC ¹⁴C enrichment pmC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH01</td>
<td>-5.37</td>
<td>-28.49</td>
<td>-10.56</td>
<td>-6.42</td>
<td>80.18</td>
<td></td>
<td>82.20</td>
</tr>
<tr>
<td>CH02</td>
<td>-4.31</td>
<td>-29.49</td>
<td>-9.49</td>
<td>-1.42</td>
<td>98.78</td>
<td>-6.22</td>
<td>89.52</td>
</tr>
<tr>
<td>CH04</td>
<td>-8.22</td>
<td>-44.86</td>
<td>-10.19</td>
<td>-3.88</td>
<td>93.69</td>
<td>-5.00</td>
<td>89.10</td>
</tr>
<tr>
<td>CH05</td>
<td>-5.20</td>
<td>-23.87</td>
<td>-14.52</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH06</td>
<td>-6.05</td>
<td>-29.82</td>
<td>-10.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH07</td>
<td>-5.58</td>
<td>-32.54</td>
<td>-13.44</td>
<td>-11.13</td>
<td>84.99</td>
<td>-6.51</td>
<td>84.39</td>
</tr>
<tr>
<td>CH08</td>
<td>-6.56</td>
<td>-36.92</td>
<td>-12.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH09</td>
<td>-6.54</td>
<td>-39.24</td>
<td>-12.30</td>
<td>-10.04</td>
<td>93.18</td>
<td>-3.27</td>
<td>89.37</td>
</tr>
<tr>
<td>CH10</td>
<td>-6.29</td>
<td>-33.70</td>
<td>-12.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH11</td>
<td>-5.90</td>
<td>-33.04</td>
<td>-9.76</td>
<td>-6.57</td>
<td>69.90</td>
<td>-11.51</td>
<td>72.26</td>
</tr>
<tr>
<td>CH12</td>
<td>-5.93</td>
<td>-34.44</td>
<td>-12.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH13</td>
<td>-6.81</td>
<td>-39.90</td>
<td>-21.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH14</td>
<td>-6.60</td>
<td>-38.08</td>
<td>-15.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH16</td>
<td>-5.78</td>
<td>-31.47</td>
<td>-12.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH17</td>
<td>-5.06</td>
<td>-33.37</td>
<td>-13.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH18</td>
<td>-5.35</td>
<td>-28.82</td>
<td>-13.69</td>
<td>-7.14</td>
<td>76.36</td>
<td>4.53</td>
<td>72.10</td>
</tr>
<tr>
<td>CH20</td>
<td>-5.29</td>
<td>-28.49</td>
<td>-14.17</td>
<td>-9.85</td>
<td>81.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH21</td>
<td>-6.40</td>
<td>-38.91</td>
<td>-14.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH22</td>
<td>-6.71</td>
<td>-36.59</td>
<td>-14.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH23</td>
<td>-5.76</td>
<td>-32.05</td>
<td>-15.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10. Stable isotopic signature of groundwaters collected from the study site in January 2008. Lab codes are: ICSF = Isotope Community Support Facility, East Kilbride. RCF-E = Radiocarbon Facility – Environment, East Kilbride, Scotland.
<table>
<thead>
<tr>
<th></th>
<th>Precipitation</th>
<th>Pond water 1</th>
<th>Pond water 2</th>
<th>River Hooghly</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{18}$O (‰)</td>
<td>$\delta D$ (‰)</td>
<td>$\delta^{18}$O (‰)</td>
<td>$\delta D$ (‰)</td>
</tr>
<tr>
<td>January</td>
<td>-5.84</td>
<td>-34.0</td>
<td>-8.5</td>
<td>-52</td>
</tr>
<tr>
<td>July</td>
<td>-5.66</td>
<td>-35.8</td>
<td>-3.56</td>
<td>-30.1</td>
</tr>
<tr>
<td>August</td>
<td>-7.39</td>
<td>-48.6</td>
<td>-3.62</td>
<td>-26.5</td>
</tr>
<tr>
<td>October</td>
<td>-9.88</td>
<td>-63.0</td>
<td>-9.88</td>
<td>-63.0</td>
</tr>
<tr>
<td>November</td>
<td>-3.62</td>
<td>-26.5</td>
<td>-3.54</td>
<td>-27.5</td>
</tr>
</tbody>
</table>

Table 11. Variation in stable isotopic composition of surface waters and local precipitation collected from the study site over several months in 2008. Pond water 1 and Pond water 2 represent two pond waters that were sampled by collaborators at the study site. The exact locations of these ponds is uncertain.