Modelling the sources of organic material, processes and timescales leading to arsenic contamination of circum-Himalayan groundwaters

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Daniel Magnone

School of Earth and Environmental Sciences
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Abstract

Arsenic contamination of circum-Himalayan groundwater is leading to one of the greatest humanitarian disasters of modern times, poisoning at least 70 million people who are mostly poor and rural. The groundwater is hosted in Holocene aquifers consisting of Himalayan sediments deposited by the great Asian rivers in deltaic environments. Arsenic is released when organic material (OM) reacts with the iron-oxide minerals co-deposited in the sediments onto which arsenic is adsorbed. The source of OM is one of the most important questions facing researchers and policy makers. There are generally accepted to be three potential sources of OM: 1) sedimentary bound OM (SOM) co-deposited with sediments; 2) thermally mature petroleum upwelled from reservoirs below the aquifers; 3) dissolved organic carbon (DOC) some of which might be drawn in to the aquifer through modern pumping and irrigation.

In this thesis the nature of organic material in the aquifer is researched and the processes and timescales which lead to arsenic release are studied. Here evidence for a new conceptual model of arsenic release is presented. Isotopic tracing combined with a new geochemical model and organic geochemical techniques, shows that OM driving arsenic release pre-dates agriculture in the region and was from natural grasslands in the early Holocene. The geochemical model utilises strontium isotopes to correct the radiocarbon age of dissolved inorganic carbon (DIC) to find only the age and isotopic signature of DIC from oxidation of organic material. This shows that DIC from oxidation of OM was from the early Holocene and had an isotopic signature consistent with the early Holocene SOM in this region. A study of the sediments in the region built upon a geomorphological history shows that the most oxidised SOM is from early Holocene sediments. Thus both techniques separately indicate that pre-agricultural organic material drove arsenic release. This conceptual model however reveals the “arsenic sand paradox”, because whilst release is from early Holocene clays, today highest concentrations of arsenic are in younger sands. Explaining this paradox is the most important next step leading on from this research.
Lay Abstract

In South and South East Asia, from Pakistan at the western periphery, to Cambodia and southern China at the eastern, groundwater, which is commonly used for cooking and drinking, is contaminated with arsenic. This has led to one of the largest natural health catastrophes of modern times. Arsenic poses a huge risk to human health; where the risks associated with this groundwater are similar to the risks from smoking. Researchers have been interested in the causes of these high concentrations of arsenic for about two decades, and it is now widely accepted that the cause of arsenic release is iron oxide minerals onto which arsenic is attached (adsorbed) dissolving into groundwater due to reactions between the minerals and organic material. A major concern for researchers has been that human action might increase arsenic release into these groundwaters; researchers are concerned that pumping water for farming or drinking might draw organic material into the aquifer from the surface and thus increase the number of reactions and amount of iron oxides dissolving, leading to increased levels of arsenic in the groundwater. The results from this research clearly demonstrate that this is not occurring, and that the reactions between iron oxide minerals and organic material occurred before 6,000 years ago, which pre-dates any agricultural activity in the area. Therefore this research has shown that human activity probably does not increase the risk of arsenic contamination to these groundwaters.
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Declaration

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning (except where acknowledged in the main text).
Other Related Published Work

The following publications relate to work conducted for this thesis but are not presented in the thesis.


Presentations

The following presentations were given for work relating to this thesis.


Grants

The following grants were submitted for work relating to this thesis.

**Magnone, D., J. Evans, L. Richards, B. van Dongen, C. Ballentine & D. Polya.** Provenancing dissolved constituents of arsenic-prone Cambodian groundwaters using $^{87}\text{Sr}/^{86}\text{Sr}$ for quantitative corrections of $^{14}\text{C}$ DIC measurements.


The Author

Daniel Magnone graduated from the University of Manchester in June 2013 with a Master of Earth Science Degree (1st Class). His master’s project was research into arsenic contamination in West Bengal for which he was awarded “Best Project for a Master of Earth Science Degree (2013)” by the University of Manchester. He worked at the Diamond Light Source Synchrotron in Oxfordshire researching environmentally friendly solvents. Since September 2013 he has been engaged in the research for this thesis and is the holder of a University of Manchester President’s Doctoral Scholar Award. During this time he has been awarded two prizes for public presentations the Archie Douglas Award for Best Oral Presentation at the British Organic Geochemistry Societies annual conference (2016) and Best oral presentation 2nd prize at the University of Manchester’s post graduate research conference.
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Chapter 1) Introduction

Millions of the poorest inhabitants living in rural areas on the deltas South and South East Asia are undergoing one of the largest mass poisonings in human history. This is due to the exceptionally high concentrations of arsenic in groundwater which is commonly used for drinking and cooking (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002; Smith et al., 2000). In the 1970s and 1980s, before the levels of arsenic became widely known the drinking of groundwater was encouraged due to the high levels of pathogens (including cholera and tuberculosis) present in the surface water (Smith et al., 2000). Yet today it is known that much of the groundwater contains arsenic concentrations far in excess of the World Health Organisation’s (WHO) global limit of 10 µg/L of arsenic in drinking water (WHO, 2011). The effects of arsenic at these concentrations can be severe and daily consumption of water is linked to increased risks of bladder and lung cancers (Marshall et al., 2007), hypertension and diabetes amongst other things (Smith et al., 2000).

The geochemical processes that release arsenic are very well understood. In the natural environment, arsenic exists in two valence states: reduced arsenic, As(III), which is more soluble and more toxic and oxidised arsenic, As(V), which is solid and has a lower toxicity. Within the aquifer sediments arsenic exists as As(V) or as As(III) adsorbed to iron-oxide minerals which were deposited during deltaic sedimentation. Arsenic is released into groundwater by the reductive dissolution of either the iron-oxide mineral or where As(V) is present direct oxidation of As(V). The reduction of arsenic bearing iron minerals is driven by microbial catalysed reactions between the minerals and organic material (OM) (Bhattacharya et al., 1997; Islam et al., 2004; Rowland et al., 2005).

One of the important areas of modern research in this field is what is the source of OM driving arsenic release? In essence three sources of OM have been hypothesised as drivers of arsenic release: 1) sedimentary OM (SOM) co-deposited with the sediments (Eiche et al., 2015; Meharg et al., 2006; Neumann et al., 2014); 2) upwelled thermally mature petroleum from reservoirs deep below the aquifer (Al Lawati et al., 2012; Rowland et al., 2009, 2007, 2006; van Dongen et al., 2008); 3) dissolved organic carbon (DOC) in the water column (Harvey et al., 2002; Lawson et al., 2016, 2013; Neumann et al., 2010). Understanding the source of OM is hugely important to both researchers and to policy makers. This is because there is some evidence young DOC is more bioavailable to the microbial community than other sources of OM and therefore young DOC is driving arsenic release. This is important because it implicates human pumping as a factor potentially increasing the likelihood DOC being drawn into aquifers and therefore increasing the risk of arsenic release (Harvey et al., 2002; Lawson et al., 2016, 2013; Neumann et al., 2011).
Other features have also been cited as important controls on arsenic concentrations and are important to consider in addition to the source of OM. Whilst within Asia alone the arsenic groundwater problem spans a huge area from Pakistan at the western periphery to South East Asia and parts of mainland China in the east (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002) at a local level arsenic concentrations can vary greatly within a relatively short distance (Fendorf et al., 2010; van Geen et al., 2003). One potential reason for this is the associations between geomorphological depositional environments and the concentrations of arsenic in the groundwater, for example at a locality in Cambodia point bar sequences have arsenic concentrations of 253 ± 5.4 µg/L compared with floodplain deposits of 47 ± 1.4 µg/L (Papacostas et al., 2008). It has been suggested that the reason for this is due to higher sorption capacities of the floodplain sediments particularly the iron-sulphides (Quicksall et al., 2008), this has been observed in some deeper Pleistocene aquifers as well (Radloff et al., 2011; van Geen et al., 2013). Furthermore, promotion of iron-sulphide formation as a form of bio-remediation has been researched (Omoregie et al., 2013) therefore the long term security of such minerals is of great importance.

Aims of this thesis and study area

The aim of this research is to better understand the source and age of OM oxidised in an arsenic contaminated aquifer and develop a conceptual geomorphological-organic geochemical model of arsenic release. To this end the specific objectives are: 1) define the source of organic material driving arsenic release in these aquifers; 2) understand what timescale this processes occurs on (i.e. is it human influenced or much longer); 3) relate this to other geochemical or geomorphological processes which control arsenic concentrations.

This research focusses on an area of Cambodia called Kandal Province which contains some of the highest concentrations of arsenic in the country (Polya et al., 2005; Sovann and Polya, 2014). This region is suitable because it has been minimally disturbed by groundwater pumping (Lawson et al., 2013) and is well characterised in terms of water chemistry (Polya et al., 2005; Rowland et al., 2008; Sovann and Polya, 2014), organic material (Quicksall et al., 2008; Rowland et al., 2007; van Dongen et al., 2008), flow patterns (Benner et al., 2008; Kocar et al., 2008; Polizzotto et al., 2008), isotopes (Lawson et al., 2016, 2013) and geomorphology (Papacostas et al., 2008; Tamura et al., 2009, 2007).

Approach of the thesis

This thesis is written in the alternative format and each chapter is intended for publication in a peer review journal. Together the chapters form a coherent dissection of the sources, processes and role of organic material involved in arsenic release.
Chapter 2 sets the geomorphological and sedimentary geochemical framework of the study area, presenting a three dimensional conceptual model of sediment deposition. Bulk and compound specific analysis is used to characterise the organic material and finally oxidation proxies are used to assess the role that OM from different sources and geological periods play in the reduction of iron oxides.

Chapter 3 presents a microcosm study analysing the effects that sedimentary geochemistry has on arsenic release. This includes the roles of sulphides and nitrates present in the sediments and the characteristics of organic material present.

Chapter 4 (like Chapter 2) tackles the issue of identifying the source of OM oxidised in these aquifers but this time uses hydrogeochemical rather than sedimentary techniques. Previous studies from Bangladesh (Harvey et al., 2002) and Cambodia (Lawson et al., 2016) have highlighted a discrepancy between the age of dissolved inorganic carbon (DIC) in groundwater and DOC. It is argued that DIC comes predominantly from the oxidation of OM. Therefore because the oxidised OM is relatively young, young OM is preferentially oxidised over older OM. This is a crucial piece of evidence leading to the hypothesis that human irrigation and pumping is drawing young labile DOC into the aquifer and is increasing arsenic concentrations in groundwater (Harvey et al., 2002; Lawson et al., 2016, 2013; Neumann et al., 2010). In this chapter it is noted that there are multiple sources of DIC in the groundwater and a new radiocarbon is presented to correct the radiocarbon age and $\delta^{13}C$ to DIC from the oxidation of OM only.

Chapter 5 continues on from Chapter 4 and uses the results of the modelling to help build a new conceptual model of arsenic release. This presents analysis of the relationship between the botanical and agricultural history in the Holocene and the source of DOC in the aquifer. It then interprets the relationship between oxidised OM in the aquifer concentrations of arsenic in the aquifer.

Finally Chapter 6 concludes the thesis by drawing together all sections of this thesis into a single conceptual model. This chapter pulls together the results from the sedimentary survey, microcosm experiments and the groundwater modelling presenting answers to the aims raised in this introductory chapter and posing new questions for the future.

Contributions

All research in this thesis was conducted by the author however each chapter, when published in peer reviewed journals, will be authored by multiple co-authors. The contributions of each of the
co-authors are outlined in this section. Where work was contribute by individuals who are not authors it is acknowledged in the acknowledgements section of each chapter.

Chapter 2
The design of this study including research focus and purpose was led by the author with contributions and feedback from Professor David Polya (University of Manchester), Dr Bart van Dongen (University of Manchester) and Dr Laura Richards (University of Manchester). Sample locations, in conjunction with earlier studies, were selected by Professor Polya, Dr van Dongen and Dr Richards. Sediment extraction techniques were agreed upon by the author, Professor Polya, Dr van Dongen and Dr Richards. The fieldwork sampling campaign was undertaken by the author, Dr van Dongen and led by Dr Richards with assistance as acknowledged. All geochemical laboratory work was undertaken by the author under supervision from Dr van Dongen and Professor Polya. Grainsize analysis was undertaken by Dr Richards with help from individuals at the British Geological Survey (BGS) as acknowledged. Proposals for radiocarbon analysis were led by Dr Richards with contributions from the author, Professor Polya, Dr van Dongen and Dr Charlotte Bryant (NERC Radiocarbon Laboratory). Radiocarbon preparation was led by Dr Bryant. All data analysis, presentation of data (including all figures), interpretation and writing was undertaken by the author with supervision and feedback offered by all contributing authors. Sedimentological advice was offered by Dr Merren Jones (University of Manchester).

Chapter 3
The design of this study including research focus and purpose was led by the author with contributions and feedback from all contributing authors. Sample collection was as concurrent with chapter 2. All experiments were undertaken by the author with help as acknowledged. All data analysis, presentation of data (including all figures), interpretation and writing was undertaken by the author with supervision and feedback offered by all contributing authors.

Chapter 4 and Chapter 5
The design of this study including research focus and purpose was led by the author with contributions and feedback from Professor Polya. The model was original designed and built by the author and submitted for a University of Manchester degree in Master of Earth Science supervised by Professor Polya, but has been significantly developed (including changes to fundamental mathematics) and has been coded into R by the author during work for this PhD. Sample locations are the same as chapter 2. Water sampling techniques were presented in a study related to this PhD research (Richards et al., 2015). The fieldwork sampling campaign was undertaken by the author, Dr van Dongen and led by Dr Richards with assistance as acknowledged. Proposals for
radiocarbon analysis were led by Dr Richards with contributions from the author, Professor Polya, Dr van Dongen and Dr Bryant. Strontium isotopic proposals were led by the author in conjunction with Professor Polya, Professor Jane Evans (British Geological Survey), Dr van Dongen, Dr Richards and Dr Bryant. Strontium isotope analysis was led by Professor Evans and radiocarbon analysis was led by Dr Bryant. Geochemical analysis was led by Dr Richards with assistance by the author and is due to published as a separate publication related to this project (Richards et al., n.d.). Sequential extractions were undertaken by the author with assistance as acknowledged. All data analysis, presentation of data (including all figures), interpretation and writing was undertaken by the author with supervision and feedback offered by Professor Polya.

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Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. Nature 430, 68–71. doi:10.1038/nature02638


Chapter 2) Depositional history and geomorphological structure of a Cambodian aquifer in the context of aqueous arsenic and organic matter characterization

Abstract

The mass poisoning of rural populations of South and South East Asia due to high concentrations of arsenic in the groundwater is one of the world’s largest ongoing natural disasters. Geomorphology is an important control on these arsenic concentrations. Sandy particularly scroll bar sediments generally host groundwater with higher concentrations of arsenic than neighbouring floodplains. The reasons for this are multiple, complex and still not fully understood. In this study we research the sediments of a region south of the Cambodian capital Phnom Penh, a well-studied area which is known to have exceptionally high concentrations of arsenic in the groundwater. We show that in this region there are at least three generations of deposition. The first is in the early Holocene (7,000 to 12,000 years before present (BP)) which was deposited during a period of rising sea-levels, the sediments within 10 km of Phnom Penh contain mostly the on-shore deposits. The second occurred between 4,000 to 2,000 years BP and was incision river channels mostly depositing sand, these were caused by a change in monsoon patterns increasing river flow. Finally, the last sequence is the young clay cap which was deposited from a series of flooding events and caused by a change in flow in the Mekong which in turn was caused by the occurrence of the modern flood-pulse at Tonle Sap at about 2000 years BP.

There is a general consensus agreement in the scientific community that arsenic is released from sediments when iron-oxide minerals onto which arsenic is adsorbed reacts with organic carbon (OC). In this process iron-oxides are reduced and organic material is oxidised. There is a strong link between the geomorphology and the source and characteristic of the OC. With the clayey layers containing OC from particulate organic carbon (POC) from rivers and in-situ deposition of C3 plants whilst within the sands it is mostly upwelled petroleum from reservoirs below. Organic oxidation proxies show that amongst plant derived OC the early Holocene sediments contain the highest levels of oxidised OC indicating that arsenic release occurred in the early Holocene rather any later period.

Separately, this study shows that consistent with other similar sediments the when petroleum is present in the sediments the sediment C/N ratio is low. This presents a paradox because the C/N of petroleum is high. We explain this by suggesting that in when OC concentration is low but
dominated by petroleum, nitrogen is from an unrelated source. This is important because a widely used technique to discriminate source of OC are the bulk proxies C/N and δ^{13}C. We suggest that if this technique is employed compound specific proxies should also be used.

1) Introduction

Groundwater arsenic concentrations far in excess of the World Health Organisation’s provisional limit of 10 µg/L (WHO, 2011) blight much of South and South East Asia (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002) and have been linked to cancer rates as high as 10 % of the population (Smith et al., 2000). It is widely accepted that solid arsenic exists sorbed to the surface of iron-oxide minerals within the aquifer sediments, this is released when organic material reacts with the sediments in a microbially facilitated reaction (Bhattacharya et al., 1997; Islam et al., 2004).

The high arsenic groundwater concentrations generally exist in shallow (<50 m) Holocene or Pleistocene aquifers (Polya et al., 2005; Smedley and Kinniburgh, 2002; Sovann and Polya, 2014). Across the region (from West Bengal to Vietnam) geomorphology appears to be an important control on the concentration of arsenic in groundwater. Deltaic deposits; organic-rich deposits; and alluvial deposits have a significantly higher probability of containing high levels of arsenic in the groundwater than floodplain deposits do (Winkel et al., 2008). At sites in Cambodia and Bangladesh lateral accretions; avulsion channels; scroll bar sequences; and point bar sequences have higher levels of arsenic compared to the surrounding floodplain deposits (McArthur et al., 2010; Papacostas et al., 2008).

Several hypotheses attempt to explain the relationship between geomorphology and arsenic groundwater concentrations. Firstly, it is argued that a major control on arsenic distribution is the sorption capacity of the sediments through which groundwater flows. It is suggested that because the clay floodplain sediments contain high levels of sulphide, and have a high surface area, this leads to the sequestration of arsenic from the water column via adsorption (Casanueva-Marenco et al., 2016; Quicksall et al., 2008). This adsorption of arsenic to sulphides has also been observed in sulphide rich Pleistocene aquifers (Radloff et al., 2011; van Geen et al., 2013). However a second hypothesis states that it is the flow patterns that dictate the arsenic distribution. The results of a modelling study built on a simple layer cake sedimentary structure suggest that arsenic is released in the subsurface clays and transported to sandy sediments at depth by the natural groundwater flow (Benner et al., 2008; Polizzotto et al., 2008). Thirdly, geomorphology might affect the bioavailability of organic material. The scroll and point bar sequences tend to be sandy and this might allow for a pathway for young surface derived organic carbon (OC) to penetrate the aquifer to depth and this young OC might be more bioavailable than other OC (Harvey et al., 2002; Lawson
et al., 2016, 2013; Neumann et al., 2010). It is also suggested that upwelled thermally mature petroleum from reservoirs beneath the aquifer might also utilise pathways through the sandy layers (Al Lawati et al., 2013, 2012, Rowland et al., 2007, 2006; van Dongen et al., 2008) and be bioavailable to the microbial community (Rowland et al., 2009). Furthermore, the bioavailability of any OC co-deposited with the sediments (Meharg et al., 2006; Neumann et al., 2014) might be effected by the depositional environments of the sediments (Eiche et al., 2015) particularly as sorption of iron to OC can enhance OC preservation (Lalonde et al., 2012).

Understanding the characteristics and origin of OC in an aquifer is therefore crucial to understanding its bioavailability and its potential to be utilised in the reduction of iron-oxide minerals and thus release arsenic. On a simple concentration level, sandy scroll bar sediments contain lower total organic carbon (TOC) concentrations than surrounding clays (Al Lawati et al., 2012; Eiche et al., 2015; Rowland et al., 2006; van Dongen et al., 2008) but different geomorphological features are also associated with OC with different characteristics and origins.

A recent study at a site in Vietnam used bulk analysis (C/N and δ¹³C) to discriminate between the different sources of OC in the sediments. This found that sedimentary TOC had three major sources: 1) in the clay layers OC from C3-vascular plants dominated, this is probably mostly in-situ deposition due to plant growth; 2) OC from mixing between C3-vascular plants and freshwater POC, 3) mixing between freshwater POC and marine POC in the sandy layers (Eiche et al., 2015). At this site, the OC defined by bulk analysis as being from C3-vascular plants was also defined as being plant derived using HMW n-alkanes (Al Lawati et al., 2012) however, there were discrepancies in interpretation between the two proxies in the apparently POC dominated OC. Compound-specific analysis of OC across the region (like in Taiwan, Cambodia and Vietnam) has found that the deeper sandy sediments contain mature HMW n-alkanes which are indicative of upwelled deep-sourced thermally mature petroleum hydrocarbons (Al Lawati et al., 2012; Rowland et al., 2006; van Dongen et al., 2008). However, hydrocarbons have a very high C/N ratio (Al-Ameri et al., 2015; Killops and Killops, 2005; Leverson, 1967), yet in Vietnam the bulk sedimentary C/N in the sandy sediments where hydrocarbons are present is very low (Al Lawati et al., 2012; Eiche et al., 2015). Thus this presents a “hydrocarbon C/N paradox” which needs to be better understood.

Therefore, present research into OC in circum Himalayan aquifer sediments indicates that different geomorphological features are associated with different relative concentrations of groundwater arsenic. One of the potential reasons for this is the geomorphological which is a dictator of the characteristics of OC which in turn effects its bioavailability. Crucially, two commonly used techniques to study OC in these sediments appear to present contrasting results given that those
with petroleum present also have low C/N ratio. Thus the main aims of this study are: 1) Interpret the sedimentary depositional history and geomorphological framework in this study area which is likely to be representative of the greater region; 2) characterise the TOC in the sediments and link with the depositional history and geomorphological framework has on the TOC characterisation and other geochemical parameters; 3) understand the low sediment C/N ratio where thermally mature OC is present; 4) assess the factors that lead to lower arsenic concentrations in floodplain sediments compared to sandy scroll bar deposits. Finally, previous sedimentary studies of arsenic contaminated aquifers have concentrated on single profile boreholes, in this study we utilise both existing and new data to build the first ever three dimensional geomorphological and sedimentary geochemical model in an arsenic contaminated aquifer.

2) Study site and geological Setting

2.1 Study site and distribution of arsenic in groundwater

The study site is located in Cambodia in an area called Kandal Province. Kandal Province is known to have some of the highest concentrations of groundwater arsenic in the country (Polya et al., 2005; Sovann and Polya, 2014) and as such is one of the most studied regions of the country. A previous study found that arsenic concentrations in groundwater hosted in the sandy geomorphological features such as lateral accretions; avulsion channels; scroll bar sequences; and point bar sequences have arsenic concentrations of 253 ± 5.4 μg/L (mean ± standard error, n = 1977) compared to the surrounding floodplain deposits where concentrations were much lower at 47 ± 1.4 μg/L (n = 6140, p <0.0001) (Papacostas et al., 2008).

2.2 Geological setting

The lowlands of Cambodia are dominated by the Mekong River system, which is one of the great Asian rivers draining from the Himalayas (Hori, 2000). This study focusses on Kandal Province, a region south of Phnom Penh, located between the Mekong River and its distributary the Bassac River. To a depth of at least 30 m, the sediments in this region are Holocene, the early history (7,000 to 10,000 years BP) is dominated by tidal processes due to rising sea-levels during this period (Tamura et al., 2007) which affected much of the Mekong delta (Nguyen et al., 2000; Ta et al., 2002). At about 7,000 years BP sea-level rise ceased and has been falling slowly since at least 4,000 years BP. Over the last 6,000 to 7,000 years the delta has prograded into the South China Sea due to the high sedimentation rate of the Mekong river system (Nguyen et al., 2000; Ta et al., 2002; Tamura et al., 2009, 2007).

Many of the circum-Himalayan rivers are dominated by monsoon processes, where, during the rainy season the monsoon rain causes greater flow in the rivers and increased water levels and
flooding. However, in Cambodia, south of Tonle Sap, this process is less pronounced due to the effects of Tonle Sap. Tonle Sap is a large fluvial lake in the centre of Cambodia, which is connected to the Mekong by the Tonle Sap River. During the rainy season water flow is from the Mekong River into the Tonle Sap with water accumulating in the lake, during the dry season flow reverses flowing into the Mekong from the lake. This means that the seasonal difference in water levels in the Mekong is considerably less than in other circum-Himalayan rivers. This feature results in fewer flooding events and has an important effect on sedimentation downstream of Tonle Sap (Penny, 2006). The seasonal reversal in flow at Tonle Sap is referred to as the flood-pulse. A geochemical and sedimentological study of sedimentary cores from Tonle Sap have determined that the initial flood-pulse occurred 4,000 and 3,600 $^{14}$C years BP due to a change in monsoon intensity (Day et al., 2011). The initial flood-pulse was not like the modern system where the Tonle Sap River joins the lake with the Mekong River but rather a series of flooding events (Penny, 2006). The modern flood pulse, with the connecting river, appears to have started 1,660 $^{14}$C year BP (Day et al., 2011).

Within the study area, land-sat images and interpretation of sedimentary cross-cutting relationships show that at least four generations of scroll bars exist. The oldest of these is perpendicular to the present day Mekong whilst more recent scroll bars run parallel to the modern Mekong and are probably active features (Figure 1). The oldest sediments are most likely the floodplain deposits into which subsequent river channels have eroded and deposited sediment.

![Figure 1 Schematic showing geomorphological features of Kandal Province, Cambodia, based on a land-sat image (Papacostas et al., 2008) and the location of study sites LR01, LR05, LR09, LR10, LR14 (this study), SY (Rowland et al., 2007), KS (Tamura et al., 2007), DS and SR (van Dongen et al., 2008).]
This study has been designed to focus on contrasting sediments to understand the depositional history of sediments just south of Phnom Penh. Within this study sites are labelled LRXX-## where LRXX refers to the location and ## refers to the sample depth in metres. The main focus is on a 4.5 km 2D transect from the Bassac river to the central wetlands running along scroll bars – in other related studies, this transect has been referred to as T-Sand (Richards et al., 2015). In addition, there are two more single sedimentary profiles, LR10 and LR14, located about 6 km east of the transect. The transect (LR01 – LR09) was selected to provide detailed spatial resolution along a vertical and horizontal profile running perpendicular to the major rivers, crucially, here there is a clay cap overlying the sandy aquifer which frequently exists in circum-Asian sediments. LR14 was selected to provide a sample representative of the flood plain and LR10 to study young scroll bars than on the transect (Figure 1). Additional data from other sites (SY, DS, SR and KS) conducted in the same region using similar methods (Rowland et al., 2007; Tamura et al., 2009, 2007; van Dongen et al., 2008) have also been used. Therefore this study compiles a complete and up-to-date repository of organic compositional data and radiocarbon dates for Kandal Province.

3) Methodology

3.1 Sediment collection

Sediments were collected during manual rotary drilling using a cutting auger attached to the end of a hollow steel pipe up to a maximum depth of 30 or 45 m (Richards et al., 2015). Sediments were collected every 3 m through manual hammering of a custom made stainless steel sampler attached to a thinner sampling pole which was lowered through the middle of the hollow drilling pipe. Sediment cores were captured in an internal acrylic sampling tube (25 mm or 50 mm) capped with a one-way valve made from bottled water caps. Samples were removed from the acrylic sampling tube using a purpose built stainless steel sample plunger.

All sediment samples for organic analysis and inorganic analysis were placed in foil bags which had previously been furnaced to 350 °C for 3 hours to remove any organic contaminants. The foil bags were placed in re-sealable polythene bags and flushed with nitrogen to minimise oxidation. A subset of sediment sample for grain size analysis was stored in polythene bags (without a foil bag) and not flushed with nitrogen. All samples were placed in a polystyrene chiller containing ice packs before transport within a few hours of collection to the local laboratory where they were re-flushed with nitrogen and frozen. Samples were transported back to Manchester by non-temperature controlled air freight and once in Manchester samples were stored in a freezer at -20 °C, prior to analysis.
3.2 Inorganic and bulk sediment characterisation

The inorganic composition of the sediments is the total concentration of a given element (in this study iron, sulphur, arsenic) as percentage weight/weight (w/w) of the total sediment – other major and trace elements were calculated but are not reported. The inorganic composition was measured at Manchester Analytical Geochemistry Unit (MAGU), University of Manchester, using X-ray fluorescence (XRF) (Axios Sequential X-ray Fluorescence Spectrometer, PANalytical). Samples for XRF analysis were oven dried at 110 °C for about 8 to 16 hours until constant weight was achieved. Samples were ground in an agate ball mill to a fine powder. Dry, ground sediments (12 g) were mixed with 3 g of wax using the agate ball mill, pelletized and analysed by XRF. This was corrected for loss on ignition at 1000 °C. Data quality was analysed using certified references material (CRM) stream sediment (GBW07311), Quartz Latite (UG-QLO-1), Mica-schist (UG-SDC-1).

Total organic carbon (TOC) and total nitrogen (TN) are the concentrations (% w/w) of these parameters in the sediments. The TOC to TN ratio (C/N) is commonly used as a bulk proxy to assess the origin of OC in the sediments (Eiche et al., 2015; Lamb et al., 2006). TOC and TN were measured in the Faculty of Life Sciences, University of Manchester, using an elemental analyser (Vario EL Cube, Elementar). TOC was measured using the capsule method (Brodie et al., 2011): approximately 20 mg of freeze-dried sample was accurately weighed into silver boats and placed on a hot plate. De-ionised water (DIW) (10 µL, 18 MΩ) was added to the sample with the hot plate gradually heating up to 50 °C. Analysis grade 5 % (w/w) hydrochloric acid (HCl, FisherBrand) was added to the silver boats in steps of 10 µL, 20 µL, 30 µL, 50 µL and 100 µL, not allowing the sample to dry out between each addition. After the addition of the 100 µL of HCl the sample was left to dry out, rolled into a ball and analysed. Three CRMs of: low organic content (C 1.56 ± 0.06 % w/w, N 0.131 ± 0.009 % w/w) soil standard (cert. 242117, Elemental Microanalysis); medium organic content (C 3.19 ± 0.07 % w/w, N 0.27 ± 0.02 % w/w) soil standard (cert. 115255, Elemental Microanalysis); and high organic content (C 7.17 ± 0.09 % w/w, N 0.57 ± 0.02 % w/w) soil standard (cert. 175032, Elemental Microanalysis) were used to check data quality. TN values from the sample capsule method were checked against pure TN values without acidification to check for any errors incurred. For unacidified TN samples were freeze dried ground and approximately 20 mg of sediment accurately weighed into tin sample boats which were rolled into balls for analysis using the elemental analyser. TC, TOC, TN values were checked against an external laboratory for data quality (Elemental Lab, Okehampton, Devon, UK). Both the TOC and TN concentrations were found to have good correlation with the external laboratory, with TOC measured in Manchester equalling 0.97 of the external laboratory’s TOC concentration ($R^2 = 0.99, n = 8$) and TN measured in Manchester equalling 1.10 times that of the laboratory ($R^2 = 0.99, n = 8$) (see supplementary information).
Grain size analysis calculates the size of the diameter of sedimentary particles; it is an important parameter for understanding both sediment surface areas and porosity. Grain size analysis was conducted at the British Geological Survey (Keyworth, UK) using laser diffraction (LS 13 320 Laser Diffraction Particle Size Analyzer, Beckman Coulter, UK), enabled with Polarization Intensity Differential Scattering which accounted for non-spherical, sub-micron particles. Non-standard grain-size cut-offs of (i) clay < 8 µm (φ > 7); (ii) silt 8 µm – 0.063 mm (4 < φ < 7); and (iii) sand 0.063 – 2 mm (-1 < φ < 4) were used to correct for discrepancy between laser ablation and sedimentation methods in the non-spherical particles (Rawlins et al., 2009) – the standard cut off between clay and silt is generally considered to be 2 µm (Vandenberghe et al., 1997). Prior to analysis samples were sonicated for 300 seconds. Data analysis was conducted using Gradistat_v8 (Blott and Pye, 2001).

Radiocarbon analysis provides an estimate of time since a carbon sample lost equilibrium with the atmosphere. All of these samples are bulk sedimentary organic carbon; therefore loss of equilibrium represents burial and lack of disturbance by active plant material. Samples for radiocarbon analysis were pre-treated to remove any carbonate from the sediments but minimising loss of organic carbon. After tests with sediments containing the highest amount of carbonate the following method was used. Samples were placed in pre-cleaned glass beakers, covered by glass fibre filter papers, placed into an evacuated glass container and exposed to concentrated hydrochloric acid fumes at 63 ± 2 °C to hydrolyze any carbonate in the sample. The samples were removed from the desiccator after 24 hours and stirred to ensure full exposure to acid fumes. They were then fumigated for a further 24 hours. Graphite targets for ^14C analysis by AMS were prepared by quantitative recovery of carbon in sealed quartz tubes followed by cryogenic separation of CO₂ (Boutton et al., 1983). Aliquots of CO₂ were converted to an iron/graphite mix by iron/zinc reduction (Slota et al., 1987).

δ¹³C of sedimentary OC is a bulk proxy commonly used to distinguish the source of different plant groups and marine and terrestrial inputs (Eiche et al., 2015; Lamb et al., 2006). A sub-sample of CO₂ (from the radiocarbon analysis) was used to measure δ¹³C using a dual-inlet mass spectrometer with a multiple ion beam collection facility (Thermo Fisher Delta V) in order to correct ^14C data to -25‰ δ¹³C VPDB. The mass spectrometer was calibrated with international reference materials to a precision of ± 0.1 ‰. ^14C analysis was carried out at the SUERC AMS Laboratory, East Kilbride using a 5MV accelerator mass spectrometer, National Electrostatics Corporation, Wisconsin, US (Freeman et al., 2008; Xu et al., 2004) and the data reported in accordance with international practice (Stuiver and Polach, 1977).
Radiocarbon ages do not represent calendar ages and must be calibrated to account for fluctuations in atmospheric $^{14}\text{C}$ concentrations. Within this report $^{14}\text{C}$ years BP refers to the radiocarbon age without calibration and cal years BP refers to the calibrated dates. Calibration of radiocarbon years to calendar age ranges was conducted using OxCal version 4.2 (Bronk Ramsey and Lee, 2013) and IntCal13 calibration curve (Reimer et al., 2013) All sites (including this and previous studies) were calibrated using conventional calibration, except LR05 which also included depth in calibration making use of OxCal’s depositional function to further constrain the calibrated age range. The use of depth can help constrain radiocarbon calibrations but this is only possible at sites that both age with depth and contain at least 5 samples – LR05 was the only site which fit the criteria.

3.3 Organic extraction, separation and analysis

Organic lipid biomarkers are used to analyse organic processes and sources of the sedimentary OC. The concentration of high molecular weight (HMW) $n$-lipids (alkanes, alcohols and alkanoic acids) both as a proportion of gram sediment and gram OC is calculated to show the dominance of these compounds within the sediments and OC. Secondly, the carbon preference index (CPI), the proxy for thermal maturity, is calculated for all lipids. The CPI is the predominance of odd-over-even in case of $n$-alkanes, and even-over-odd in case of $n$-alkanoic acids and $n$-alkanols (Bray and Evans, 1961; Marzi et al., 1993) and is calculated using the same method as van Dongen et al., (2008). For the purposes of this study any value >1.5 is considered to be thermally immature. Thirdly, the average chain length (ACL) calculated using the same method as van Dongen et al., (2008). Finally, the ratio of HMW $n$-alkanoic acids to HMW $n$-alkanes + HMW $n$-alkanoic acids is used to assess the oxidation of OC (van Dongen et al., 2006; Vonk et al., 2008). This is only suitable for those sediments that are dominated by immature OC, e.g. with HMW $n$-alkane CPI values >>1.5. This technique assumes that in any plant derived organic material the ratio of acids to alkanes stays constant and that both have degradation constants, the value of these constants, whilst unknown will be dependant upon the chemistries of the compound (Poynter and Eglinton, 1990). Therefore if OC is oxidised during iron oxide reduction $n$-alkanes are oxidised to alkanoic acids, thus the greater the ratio the more oxidation has occurred.

Extraction of Total lipid extract (TLE) was undertaken in Soxhlet apparatus. Before extraction equipment (including Thimble filter) was cleaned by running a blank extraction for 24 hours. Approximately 30 to 50 g of freeze-dried and powdered sediment was placed within the Thimble filter in the Soxhlet. Unless stated otherwise all solvents were HPLC grade FisherBrand. Approximately 350 ml of a dichloromethane:methanol (DCM:MeOH, 2:1 v/v) mixture was placed in a round-bottomed flask (RBF) at the base of the Soxhlet with anti-bumping granules, and heated to 40 °C with a heating mantle to induce boiling for 24 hours. Solvents were evaporated using rotary
evaporation, the TLE transferred to a vial, blown dry under a stream of nitrogen and frozen before further separation.

Separation of TLE was undertaken on an aliquot of the total sample (about 30 % depending on recovery) using bond elute chromatography with glass solid phase extraction (SPE) columns (Biotage Isolute NH$_2$ 500 mg / 6 ml, 470-0050-L). SPE columns were cleaned by running 12 ml of MeOH, 12 ml of isopropanol:DCM (IPA:DCM, 2:1 v/v) and finally 12 ml of 4% glacial acetic acid (Fluka) in diethyl ether through the column; at no point were the columns permitted to run dry. The TLE was dissolved in IPA:DCM (2:1 v/v), two internal standards, 540 ng of tetracosane-d$_{50}$ (Fluka) and 5400 ng of 2-hexadecanol (Fluka), were added and transferred to toc column. The aliquot was separated by eluting with 12 ml of IPA:DCM (neutral fraction; F1), 12 ml of 4% glacial acetic acid in diethyl ether (acid fraction; F2) and 12 ml MeOH (remaining lipids;F3). F1 and F3 were dried using rotary evaporation whilst F2 was dried under a stream of nitrogen. The sample was frozen, transferred to vials using DCM, dried under nitrogen and frozen before further analysis (whilst F3 was collected it was not used during this study).

Fraction F1 was dissolved in hexane/DCM (9:1 v/v) and passed through a column packed with activated Al$_2$O$_3$. This was eluted into an apolar fraction with 3 ml hexane/DCM, and, a polar fraction with DCM/MeOH (1:1 v/v, 3 ml). The apolar fraction was dried under a flow of nitrogen, dissolved in hexane and analysed using gas chromatography-mass spectrometry (GC-MS, see settings below). The polar fraction was dried using nitrogen and silylated by adding 25 μL bis(trimethylsilyl)trifluoroacetamide (BSTFA), heating at 70 °C for 1 hour in a closed vial, left to cool, dried completely under nitrogen and dissolved in hexane for analysis by GCMS. 540 ng of tetracosane-d$_{50}$ was added to F2 before methylation by adding 100 μL of BF$_3$/MeOH, heating at 70 °C for 1 hour in a closed vial. After cooling 1 mL of (extracted) bi-distilled water was added and the water layer was extracted with DCM. The remaining acid fraction were passed through Na$_2$SO$_4$ to remove any water, dried under nitrogen and silylated using the same method as the polar fraction before analysis by GCMS. These techniques are consistent with earlier studies in the region (Al Lawati et al., 2012; Rowland et al., 2007, 2006; van Dongen et al., 2008).

GCMS was performed using an Agilent 789A GC interfaced to an Agilent 5975C MSD mass spectrometer operated with electron ionisation at 40 eV and scanning from m/z 50 to 650 for all samples and also simultaneous SIM mode of m/z 57 and 66, m/z 75 and 10, and m/z 74 and 100 for alkanes, alcohols and alkanolic acids, respectively. The GC was equipped with an Agilent 7683B auto sampler and a programmable temperature variable (PTV) injector. The samples were injected using a pulsed split-less injection (1 μl inlet pressure of 25 psi for 0.25 mins) and separated on an
Zebron ZB-5MS capillary column (5%-Phenyl Arylene, 95% Dimethyl Polysiloxane: length: 30 m, ID 250 µm, film thickness 0.25 µm). The samples were run at constant flow (1 ml/min) with He as a carrier gas. The heated interface temperature was set to 280 °C, with the main oven temperature at 230 °C and the MS quadrupole at a temperature of 150 °C. The samples were injected at 50 °C and the oven was programmed to 320 °C at 7 °C/min whilst it was held constant for 10 mins. The compounds were identified by comparison of retention times of mass spectra with those present in the literature. Quantitative data were obtained by comparing the individual peaks to that of the known internal standard added.

3.4 Data analysis and presentation

All statistical analysis was conducted using R (R Core Team, 2014). Bulk sedimentary concentrations were kriged to produce geochemical maps using the package geoR (Ribeiro and Diggle, 2015) (variograms shown in supplementary information). All statistical analyses were plotted using the R package ggplot2 (Wickham., 2009).

4) Results

4.1 Bulk sedimentary composition

Grain size analyses of the sediments along the transect indicate that the mean grain size ranges from -0.1 φ for the coarse sand at LR02-27, to 7.47 φ for the fine silt at LR05-45 (Table 1. φ = -log₂ (D/D₀), where D is the diameter of the sample in mm and D₀ is the reference constant 1 mm) (Figure 2). At the bottom centre of the transect (LR05 to LR03, 30 – 45 m) is a clay wedge (>5 φ) which is overlain by sandy sediments (<4 φ, Figure 2, Table 1). The sandy sediments, in turn, are overlain by a clay cap which extends across the top of the entire transect, with the exception of a sandy window, where the sandy scroll bars are exposed to the surface around LR03. At LR09 and LR08 the clay extends to about 21 to 18 m, however across most of the transect it is much shallower and it does not extend far below 9 m (Figure 2, Table 1). LR10 is predominantly fine sand with grain sizes ranging from 2.03 to 4.70 φ, whereas LR14 is more silty and clayey, with grain sizes ranging from 4.13 to 7.33 φ.

TOC concentrations in these sediments are strongly associated with the sedimentary grain size distribution. TOC in the sandy layers is lowest, ranging from <0.05 at multiple locations, to 0.97 % (w/w) at LR02-30 (Figure 2, Table 1). The clay layers have generally higher TOC concentrations, the clay wedge has a range from 0.75 to 1 % (w/w), whilst the shallow clay cap has a medium high TOC content with values between 0.5 and 1.2 % (w/w) with highest values at LR01-6 and LR09-6 (Figure 2, Table 1). Total nitrogen correlates strongly with TOC (TOC = 9.7*TN – 0.01, R² = 0.80, n = 55), one notable outlier is LR02-27 (removed from regression calculation) where TOC is substantially lower.
(0.97 % w/w) than would be predicted based on the high TN concentration of 0.26 % (w/w; Table 1). The C/N ranges from 1.5 (LR03-15) to 16.5 (LR07-30; Table 1). The radiocarbon age of the TOC on the transect ranges from 83 pmc (1,500 $^{14}$C years BP; LR09-6) to 22 pmc (12,100 $^{14}$C years BP; LR05-45) and with $\delta^{13}$C$_{TOC}$ values from -25 to -30 ‰ (Figure 2, Table 1). Generally, the oldest sediments can be found in the deep clay wedge with ages >9,000 $^{14}$C years while the youngest sediments dominate the shallow clay deposits with ages <1,500 $^{14}$C years with intermediate ages for the sandy sediments (Table 2, Figure 1). The shallow samples from the LR10 and LR14 are significantly older than those on the transect with ages of 2,600 $^{14}$C years BP (72 pmc) at LR10-6 and 6,400 $^{14}$C years BP (45 pmc) at LR14-6 (Figure 1). The deeper sediments at 30 m at LR14 are the same age as the deep clay wedge on the transect 9,500 $^{14}$C years BP (31 pmc) (Table 2, Figure 1).

The iron distribution in the transect follows the TOC and grain size distribution closely with moderately-high concentrations near the top of the sediments, 6 m, across the transect (5 – 6 % w/w) and lowest concentrations in the deeper, >15 m, sediments (2 – 3 % w/w; Table 1, Figure 1). The highest concentration on the transect is in the deep clay wedge where the concentration reaches 7 % (w/w). Unlike the TOC and grain size distribution however, there is an additional peak of iron concentration at LR03 extending from 9 m to 21 m (Figure 2). The arsenic concentration in the transect sediments ranges from < 2.9 ppm to 19 ppm (Table 1). However, unlike the iron, there is no consistent pattern of arsenic distribution in these sediments, with most of the sediments < 5 ppm, except for the peak concentration of 19 ppm at LR03 at 21 m (Figure 2).
Figure 2 Kriged results for the distribution of sedimentary median grain size, TOC % (w/w), arsenic % (w/w), iron % (w/w), sulphur % (w/w) and distribution of radiocarbon dates on the transect of this study (Figure 1). Black dots are measured values from which kriging was calculated grey dots are estimate values used for co-kriging.
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<th>S (%)</th>
<th>TOC (%)</th>
<th>TN (%)</th>
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<td>5.75</td>
<td>3.57</td>
</tr>
<tr>
<td>LR09-18</td>
<td>&lt;3</td>
<td>3.74</td>
<td>0.5</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>6.07</td>
</tr>
<tr>
<td>LR09-21</td>
<td>&lt;3</td>
<td>2.72</td>
<td>0.33</td>
<td>0.14</td>
<td>0.02</td>
<td>7.01</td>
<td>3.51</td>
</tr>
<tr>
<td>LR09-24</td>
<td>2.7</td>
<td>3.21</td>
<td>0.27</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2.57</td>
</tr>
<tr>
<td>LR09-27</td>
<td>4.6</td>
<td>3.14</td>
<td>0.89</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>3.18</td>
</tr>
<tr>
<td>LR09-30</td>
<td>3.8</td>
<td>2.27</td>
<td>0.15</td>
<td>0.01</td>
<td>0.00</td>
<td>1.78</td>
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</tr>
<tr>
<td>LR09-39</td>
<td>8.3</td>
<td>3.58</td>
<td>0.14</td>
<td>0.04</td>
<td>0.02</td>
<td>2.23</td>
<td>4.42</td>
</tr>
<tr>
<td>LR09-45</td>
<td>&lt;3.4</td>
<td>1.77</td>
<td>0.24</td>
<td>0.06</td>
<td>0.02</td>
<td>3.83</td>
<td>1.74</td>
</tr>
<tr>
<td>LR10-3</td>
<td>6.2</td>
<td>5.01</td>
<td>0.21</td>
<td>0.22</td>
<td>0.03</td>
<td>6.38</td>
<td>4.70</td>
</tr>
<tr>
<td>LR10-6</td>
<td>&lt;3.7</td>
<td>4.06</td>
<td>0.3</td>
<td>0.17</td>
<td>0.03</td>
<td>5.58</td>
<td>3.62</td>
</tr>
<tr>
<td>LR10-9</td>
<td>&lt;3.6</td>
<td>4.77</td>
<td>0.37</td>
<td>0.19</td>
<td>0.03</td>
<td>6.53</td>
<td>3.44</td>
</tr>
<tr>
<td>LR10-12</td>
<td>&lt;3.6</td>
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<td>0.56</td>
<td>0.42</td>
<td>0.03</td>
<td>13.66</td>
<td>3.53</td>
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</tbody>
</table>

42
<table>
<thead>
<tr>
<th>Sample</th>
<th>δ¹³C_TOC‰ ± 0.1</th>
<th>Conventional Radiocarbon Age</th>
<th>Calibrated age range (Years BP)</th>
<th>Publication code</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>¹⁴C (pmc) ± 1σ</td>
<td>¹⁴C Years BP ± 1σ</td>
<td>From-to</td>
</tr>
<tr>
<td>LR01-6</td>
<td>-25.9</td>
<td>81.4 ± 0.7</td>
<td>1588 ± 37</td>
<td>1555 - 1396</td>
</tr>
<tr>
<td>LR01-30</td>
<td>-25.4</td>
<td>62.6 ± 0.1</td>
<td>3705 ± 36</td>
<td>4150 - 3965</td>
</tr>
<tr>
<td>LR05-6</td>
<td>-25.2</td>
<td>80.5 ± 0.7</td>
<td>1683 ± 35</td>
<td>1695 - 1522</td>
</tr>
</tbody>
</table>

- Samples labelled LRXX-## where LRXX refers to the location (see Figure 1) and ## refers to the depth.
- Total sedimentary arsenic concentration ppm (w/w).
- Total sedimentary iron concentration calculated as Fe₂O₃ % (w/w).
- Total sedimentary sulphur concentration calculated as SO₃ % (w/w).
- Total Organic Carbon % (w/w).
- Total nitrogen % (w/w).
- Carbon to nitrogen ratio.
- Mean grain size reported as $\phi$, $\phi = -\log_2(D/D_0)$. Where D is diameter (mm) and $D_0 = 1$ mm.

n.d. no data.

Table 2 Sedimentary Radiocarbon Data for samples collected in Kandal Province, Cambodia
<table>
<thead>
<tr>
<th>Sample</th>
<th>Value</th>
<th>N</th>
<th>Date</th>
<th>Age</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR05-9</td>
<td>-25.5</td>
<td>78.1 ± 0.3</td>
<td>1923 ± 35</td>
<td>1986 - 1815</td>
<td>0.954</td>
</tr>
<tr>
<td>LR05-15</td>
<td>-25.9</td>
<td>65.3 ± 0.3</td>
<td>3363 ± 35</td>
<td>3696 - 3550</td>
<td>0.887</td>
</tr>
<tr>
<td>LR05-30</td>
<td>-27.9</td>
<td>30.7 ± 0.2</td>
<td>9432 ± 40</td>
<td>10794 - 10498</td>
<td>0.930</td>
</tr>
<tr>
<td>LR05-45</td>
<td>-26</td>
<td>22.2 ± 0.1</td>
<td>12011 ± 45</td>
<td>14031 - 13746</td>
<td>0.954</td>
</tr>
<tr>
<td>LR09-6</td>
<td>-25.7</td>
<td>83.0 ± 0.4</td>
<td>1430 ± 35</td>
<td>1385 - 1290</td>
<td>0.954</td>
</tr>
<tr>
<td>LR09-21</td>
<td>-27.8</td>
<td>61.0 ± 0.3</td>
<td>3911 ± 35</td>
<td>4431 - 4239</td>
<td>0.954</td>
</tr>
<tr>
<td>LR09-30</td>
<td>-27.8</td>
<td>63.4 ± 0.3</td>
<td>3597 ± 35</td>
<td>3987 - 3828</td>
<td>0.940</td>
</tr>
<tr>
<td>LR09-39</td>
<td>-32.3</td>
<td>36.6 ± 0.2</td>
<td>8002 ± 40</td>
<td>9010 - 8719</td>
<td>0.954</td>
</tr>
<tr>
<td>LR09-45</td>
<td>-30.8</td>
<td>68.9 ± 0.3</td>
<td>2930 ± 35</td>
<td>3175 - 2963</td>
<td>0.954</td>
</tr>
<tr>
<td>LR10-6</td>
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<td>72.2 ± 0.3</td>
<td>2555 ± 35</td>
<td>2754 - 2496</td>
<td>0.954</td>
</tr>
<tr>
<td>LR10-27</td>
<td>-27.4</td>
<td>65.0 ± 0.3</td>
<td>3393 ± 37</td>
<td>3724 - 3560</td>
<td>0.933</td>
</tr>
<tr>
<td>LR14-6</td>
<td>-26.2</td>
<td>45.3 ± 0.2</td>
<td>6295 ± 39</td>
<td>7309 - 7161</td>
<td>0.954</td>
</tr>
<tr>
<td>LR14-30</td>
<td>-28.6</td>
<td>30.6 ± 0.2</td>
<td>9450 ± 41</td>
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<td>0.930</td>
</tr>
<tr>
<td>KS-4.07</td>
<td>-26.7</td>
<td>n.r.</td>
<td>700 ± 40</td>
<td>701-558</td>
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</tr>
<tr>
<td>KS-7.08</td>
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<td>n.r.</td>
<td>6250 ± 40</td>
<td>7265-7019</td>
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<tr>
<td>KS-7.9</td>
<td>-27.9</td>
<td>n.r.</td>
<td>6620 ± 40</td>
<td>7570-7440</td>
<td>0.954</td>
</tr>
<tr>
<td>KS-8.33</td>
<td>-29.1</td>
<td>n.r.</td>
<td>6470 ± 40</td>
<td>7458-7293</td>
<td>0.954</td>
</tr>
<tr>
<td>KS-9.08</td>
<td>-28.1</td>
<td>n.r.</td>
<td>7130 ± 40</td>
<td>8020-7922</td>
<td>0.832</td>
</tr>
<tr>
<td>KS-9.6</td>
<td>-30.3</td>
<td>n.r.</td>
<td>7030 ± 40</td>
<td>7954-7786</td>
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</tr>
<tr>
<td>KS-10.48</td>
<td>-28.6</td>
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<td>7150 ± 40</td>
<td>8031-7926</td>
<td>0.911</td>
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</tbody>
</table>

Data from Tamura et al., (2007)
<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth</th>
<th>n.r.</th>
<th>Concentration</th>
<th>Estimated Concentration</th>
<th>Beta-</th>
<th>SUERC-</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS-12.27</td>
<td>-30.0</td>
<td>n.r.</td>
<td>6550 ± 40</td>
<td>7520-7417</td>
<td>0.884</td>
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</tr>
<tr>
<td>KS-12.65</td>
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<td>n.r.</td>
<td>6760 ± 40</td>
<td>7675-7570</td>
<td>0.954</td>
<td>192755</td>
</tr>
<tr>
<td>KS-28.10</td>
<td>-22.0</td>
<td>n.r.</td>
<td>8180 ± 40</td>
<td>9262-9020</td>
<td>0.954</td>
<td>192756</td>
</tr>
</tbody>
</table>

Data from van Dongen et al., (2008)

<table>
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<th>Depth</th>
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<th>Concentration</th>
<th>Estimated Concentration</th>
<th>Beta-</th>
<th>SUERC-</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR-13</td>
<td>-27.1</td>
<td>n.r.</td>
<td>7759 ± 51</td>
<td>8627 - 8425</td>
<td>0.954</td>
<td>9245</td>
</tr>
<tr>
<td>SR-19</td>
<td>-27.5</td>
<td>n.r.</td>
<td>7732 ± 51</td>
<td>8595 - 8417</td>
<td>0.954</td>
<td>9246</td>
</tr>
<tr>
<td>DS-0</td>
<td>-28.1</td>
<td>n.r.</td>
<td>6216 ± 44</td>
<td>7250 - 7004</td>
<td>0.954</td>
<td>9235</td>
</tr>
<tr>
<td>DS-15</td>
<td>-27.0</td>
<td>n.r.</td>
<td>8177 ± 54</td>
<td>9282 - 9009</td>
<td>0.954</td>
<td>9236</td>
</tr>
<tr>
<td>DS-23</td>
<td>-26.6</td>
<td>n.r.</td>
<td>7930 ± 52</td>
<td>8984 - 8610</td>
<td>0.954</td>
<td>9237</td>
</tr>
<tr>
<td>DS-27</td>
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<td>n.r.</td>
<td>9040 ± 61</td>
<td>10300 - 10119</td>
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</tr>
<tr>
<td>DS-40</td>
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<td>n.r.</td>
<td>5370 ± 41</td>
<td>6280 - 6005</td>
<td>0.954</td>
<td>9242</td>
</tr>
<tr>
<td>DS-54</td>
<td>-25.8</td>
<td>n.r.</td>
<td>5293 ± 41</td>
<td>6190 - 5984</td>
<td>0.896</td>
<td>9243</td>
</tr>
<tr>
<td>DS-60</td>
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<td>8241 ± 41</td>
<td>9323 - 9085</td>
<td>0.864</td>
<td>9244</td>
</tr>
<tr>
<td>DS-70</td>
<td>-23.7</td>
<td>n.r.</td>
<td>4937 ± 41</td>
<td>5743 - 5594</td>
<td>0.954</td>
<td>9565</td>
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</table>

Data from Rowland et al., (2007)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth</th>
<th>n.r.</th>
<th>Concentration</th>
<th>Estimated Concentration</th>
<th>Beta-</th>
<th>SUERC-</th>
</tr>
</thead>
<tbody>
<tr>
<td>SY-9</td>
<td>-25.1</td>
<td>n.r.</td>
<td>1532 ± 31</td>
<td>1523 - 1353</td>
<td>0.954</td>
<td>9228</td>
</tr>
<tr>
<td>SY-28</td>
<td>-25.5</td>
<td>n.r.</td>
<td>4218 ± 38</td>
<td>4855 - 4625</td>
<td>0.954</td>
<td>9232</td>
</tr>
</tbody>
</table>

* Samples from this study labelled LRXX-## where LRXX refers to the location (see Figure 1) and ## refers to the depth in metres. Also samples from earlier studies labelled $$-## where $$ is location (see Figure 1) and ## is depth in metres.

n.r. value not reported by original study.

4.2 Lipid analysis

Lipid analyses of the transect sediments indicate the presence of substantial amounts of HMW n-alkanes with concentrations ranging from 6 to 67 ng/g sediment (Table 3) and a distribution that
mostly follows the TOC concentration with highest concentrations predominantly in the clay layers (Table 2, Figure 3). The distribution of HMW \( n \)-alkanes as a proportion of OC ranges from 2 to 62 mg/g OC, with the highest proportions found in the sandy layers and the lowest in the clay sediments (Table 3). Those with a CPI greater than 1.5 are mostly restricted to the clay layers (both the clay wedge and the clay cap) with a notable exceptions of LR05-21 which is a sandy sediment with a relatively high CPI of 2 and LR05-45, which is in the clay wedge but has a relatively low CPI of 1.4 (Table 2, Figure 3). It is also important that LR03-6, a shallow sediment in the sandy window, has a relatively low CPI of 1.5 (Table 2, Figure 3). The ACL ranges from 27.3 to 30.2.

HMW \( n \)-alcohols are also present on the transect, with concentrations approximately 1000 times lower than the HMW \( n \)-alkanes, ranging from below detection limit at two sites to 9.0 pg/g sediment at LR09-6 (Table 2). The distribution follows a broadly similar pattern to the HMW \( n \)-alkanes. As a fraction of OC, the range is from below detection limit to 5.47 ng/g of OC at LR09-30 (Table 2). The CPI of the HMW \( n \)-alcohols ranges from 1.6 at LR01-15, to 12.4 at LR01-6. The ACL ranged from 23.5 to 26.8 (Table 2). The HMW \( n \)-alkanoic acids have a similar magnitude of concentration to the HMW \( n \)-alkanes, ranging from 0.18 ng/g sediment at LR03-6 to 202 ng/g of sediment at LR05-30 or 0.06 mg/g of OC at LR03-6 to 25.4 mg/g of OC at LR05-21 (Table 2). The CPI is consistently high with a range from 3.26 at LR05-45 to 9.96 at LR01-6. The ACL ranges from 22.6 to 27.6. The HMW \( n \)-alkanoic acid to HMW \( n \)-alkane ratio ranges from 0.06 to 0.75.

The polar fractions at LR10 and LR14 are a stark contrast to those on the transect. Firstly, the HMW \( n \)-alcohols have three samples (LR10-9, LR10-15 and LR14-9) with considerably higher concentrations than anything on the transect, at 73.6, 231 and 99.4 pg/g sediment respectively. Concentrations are high, as a proportion of organic carbon, with concentrations of 38.0, 126 and 5.04 mg/kg of OC respectively. Secondly, LR14-15 is notable for having an exceptionally high HMW \( n \)-alkanoic acid concentration of 914 ng/g sediment. Other than this sample the HMW \( n \)-alkanoic concentration on the transect and non-transect sites were similar, with respective mean concentrations of 19 ng/g (n=20) and 18 ng/g sediment (n=6). Finally, at LR14-15 the HMW \( n \)-alkanoic acid to HMW \( n \)-alkane + HMW \( n \)-alkanoic acid ratio is higher than anything on the transect with a value of 0.96. Representative chromatograms for all lipids are presented in supplementary information.
<table>
<thead>
<tr>
<th>Sample Code</th>
<th>HMW n-alkanes (C20-36)</th>
<th>HMW n-alcohols (C20-30)</th>
<th>HMW n-alkanoic acids (C20-C30)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc (ng/g)</td>
<td>Prop (mg/g)</td>
<td>CPI</td>
<td>ACL</td>
</tr>
<tr>
<td>LR01-6</td>
<td>43 3.6 2.8 28.3</td>
<td>0.9 0.1 12.4 25.8</td>
<td>39 3.27 10.0 25.0</td>
<td>0.48</td>
</tr>
<tr>
<td>LR01-15</td>
<td>6.4 6.2 1.0 28.1</td>
<td>0.2 0.2 1.6 21.4</td>
<td>0.3 0.27 4.8 23.5</td>
<td>N/A</td>
</tr>
<tr>
<td>LR01-30</td>
<td>6.6 9.6 1.3 28.0</td>
<td>1.7 2.4 7.9 26.7</td>
<td>1.8 2.63 3.3 23.4</td>
<td>N/A</td>
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<tr>
<td>LR03-6</td>
<td>9.8 3.2 1.5 28.3</td>
<td>1.2 0.4 5.7 26.0</td>
<td>0.2 0.06 5.3 25.2</td>
<td>0.02</td>
</tr>
<tr>
<td>LR03-15</td>
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<td>n.d. n.d. n.d. n.d.</td>
<td>2.3 5.64 5.3 22.6</td>
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<tr>
<td>LR03-30</td>
<td>38 6.1 3.6 29.0</td>
<td>2.1 0.3 7.3 26.4</td>
<td>46 7.53 7.3 27.6</td>
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<tr>
<td>LR05-3</td>
<td>8.3 4.5 1.6 29.3</td>
<td>BDL BDL BDL BDL</td>
<td>3.8 2.06 3.0 26.5</td>
<td>0.31</td>
</tr>
<tr>
<td>LR05-6</td>
<td>33 4.3 3.9 29.6</td>
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<td>5.8 0.76 6.8 25.8</td>
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<td>0.7 0.74 4.2 25.9</td>
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<tr>
<td>LR05-21</td>
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<td>16 25.4 5.9 24.3</td>
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<tr>
<td>LR05-30</td>
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<td>8.4 0.7 5.8 26.5</td>
<td>202 16.9 6.2 27.0</td>
<td>0.75</td>
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<tr>
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<td>13 3.8 1.4 29.9</td>
<td>BDL BDL BDL BDL</td>
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<td>N/A</td>
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<td>2.6 0.50 5.2 24.3</td>
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<tr>
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<td>0.9 0.6 7.2 26.2</td>
<td>11 7.34 6.6 26.6</td>
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</table>

Thi Study
<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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From van Dongen et al., (2008)

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From Rowland et al., (2007)
SY-9 | 3059 | 478 | 7.0 | 29.1 | 3000 | 469 | 7.5 | n.d. | 1583 | 247 | 3.6 | n.d. | 0.34
SY-28 | 419 | 599 | 2.3 | 29.3 | 450 | 643 | 6.6 | n.d. | 620 | 886 | 3.0 | n.d. | 0.60

BDL Below detection limit, n.d. no data, N/A not applicable due to mature CPI.

* Samples from this study labelled LRXX-## where LRXX refers to the location (see Figure 1) and ## refers to the depth in metres. Also samples from earlier studies labled $$-## where $$ is location (see Figure 1) and ## is depth in metres.

** Concentration of aforementioned lipid per mass sediment.

* Proportion of aforementioned lipid per mass organic carbon.

* Carbon preference index of aforementioned lipid.

* Average chain length of aforementioned lipid.

† HMW n-alkanoic acid to HMW n-alkane ratio + HMW n-alkanoic acid.

Figure 3 Distribution of HMW n-alkane ([C<sub>20</sub>-C<sub>36</sub>]) concentration per gram sediment, HMW n-alkane concentration per gram OC and HMW n-alkane CPI along the transect (Figure 1) plotted over grainsize (Figure 2).
5) Discussion

5.1 A sedimentary deposition model

The oldest sediments are in the deep clay wedge (LR05 30 m and 45 m) and range from 9,500 ± 40 14C years BP to 12,000 ± 40 14C years BP. At LR14, the clay dominated profile beneath the floodplain, the radiocarbon date at 30 m is also 9,500 ± 40 14C years BP, however the shallow (6 m) sediments are 6,360 ± 40 14C years BP which is considerably older than anything on the transect at the same depth, which are only about 1,700 ± 40 14C years BP. Given the similarities in ages between the deep clay wedge sediments and the age of the sediments at LR14, it seems likely that the deep clay wedge and the clay at LR14 are a continuous layer of old clay sediments, representing an early Holocene facies (EHF). Provided that little erosion has taken place at LR14 the 6 m sample represents the latter stages of deposition of this EHF, therefore the last sedimentary deposition was shortly after 6,360 ± 40 14C years BP which is equivalent to 7,160 to 7,310 cal years BP. This means sedimentation of EHF ceased simulations with the cessation of sea-level rise in the area at about 7,000 cal years BP (Tamura et al., 2007) and this is likely to be the cause of the cessation.

It is important to understand the depositional environment of the EHF. KS a well-studied high-resolution sedimentary profile (KS) between the Mekong and the Bassac and is located about 20 km east, downstream of the study region. At 30 m at KS the radiocarbon age of sedimentary OC is 8,180 ± 40 14C years BP which is consistent with ages of the EHF at 30 m from this study site. The KS profile also has an unconformity which occurred at about 6,250 ± 40 14C years BP (Tamura et al., 2007) which is consistent with cessation of deposition at this study site. The unconformity exists as far as 70 km further south than KS and is a laterally extensive time-transgressive-surface (Tamura et al., 2009). This means that the EHF sediments in the study site are probably the upstream features of the sediments below the unconformity at KS and thus might be conformable with them. At KS these sediments are intertidal deposits but because EHF sediments at the study site are 20 km further upstream these could be entirely shore zone deposits or offshore deposits – organic proxies can be used to assess this (see below).

The sandy sediments on the transect and also sandy sediments at SY, a site north-west of the transect studied previously (Rowland et al., 2007), are younger than the EHF and range from 2,990 ± 40 14C years BP to 4,260 ± 40 14C years BP. Separately, at LR10, the sandy scroll bar non-transect site near the Mekong, the radiocarbon age of the sediments is 2,620 ± 40 14C years BP at 6 m and 3,460 ± 40 14C years BP at 30 m. This indicates that the sandy sediments are younger than both the clay at LR14 and the sand on the transect, which is in line with the geomorphological history (Figure 1). The contacts between the EHF and the sandy layers (in both the transect and at LR10) represent
unconformities with the appearance of an incision channel at about $4,220 \pm 40$ $^{14}$C years BP (based on the date from SY-27) this is equivalent to 4,855 to 4,625 cal years BP. This timing is consistent with the onset of initial annual flood-pulse (between 4,450 and 3,910 cal years BP) upstream at the Tonle Sapp (Day et al., 2011).

The final depositional sequence on the transect and over SY was the shallow clay cap. Deposition of these sediments started at about $1,900 \pm 40$ $^{14}$C years BP which is equivalent to 1990 to 1820 cal years BP. The dates are consistent with the connection of the Tonle Sapp to the Mekong and the onset modern flood pulse which occurred about 1,660 cal years BP (Day et al., 2011), this is the likely cause of the change in sedimentation. This sedimentary layer does not seem to be present at the non-transect sites LR10 or LR14 or at the transect site LR03 where there is a sandy widow through the clay. This means that modern flooding events do not affect all areas, possibly due to local topography.

Previous studies have noted the unusual aging of some sediments, in that they don’t always age with depth. This is notable at DS where sediment where sediments ages increase with depth down to 27 m but then have younger sandy sediments below 27 m (van Dongen et al., 2008). This also occurs at LR09 (measured by this study) which has a sample of $8,000 \pm 40$ $^{14}$C years BP at 39 m but $2,930 \pm 40$ $^{14}$C years BP at 45 m. Both DS and LR09 are located near rivers and are therefore more likely to be susceptible to incision events. The incising nature of the sands causes the unusual radiocarbon profile ages because they undercut the existing sediments and deposit younger sediments, thus in a single profile they appear to younging down. The depositional history described above is summarised in Figure 4.
5.2 A depositional influence on sediment geochemistry

The TOC concentration is highest in the clay sediments, rapid sedimentation has been associated with the accumulation and preservation of OC in this region (Papacostas et al., 2008). At first, this appears counter-intuitive, given that floodplains are intermittent deposits associated with channel breaches, whilst scroll bar sediments are associated with a constantly flowing channel. However, in fluvial systems it is a long established law that deposition of suspended load will only occur when there is insufficient energy to sustain transportation: this means that larger heavier particles drop out of suspension before smaller lighter particles (Hjulstrom, 1939). Thus clayey sediments are associated with the lower energy deposition than sandy particles. Because most POC in the Mekong is <63 μm (Ellis et al., 2012) this means that it is of clay grain size, and therefore will mostly be deposited with the clay, low energy, floodplain sediments.

High concentrations of sedimentary iron are more associated with clay sediments, which also host high concentrations of OC. At another site within the area, the burial of iron hydroxide minerals is simultaneous with OC burial (Quicksall et al., 2008) thus the preservation of OC and iron
sequestration in clays could be interrelated. Sorption of iron to OC has been observed in other Holocene sediments and is a mechanism for OC preservation (Kaiser and Guggenberger, 2000; Lalonde et al., 2012). However, many clay minerals also contain iron within their structure (e.g. illite, vermiculite) and this is another potential cause of high iron concentration in clay sediments. The similar distribution of sulphur and iron in these sediments indicates that sulphur is mostly from iron sulphide minerals, however, these make up only a small fraction of the total iron concentration. Earlier studies suggested that the presence of sulphides in floodplain deposits reduced arsenic in groundwater in these sediments due to sorption effects (Papacostas et al., 2008).

5.3 Using bulk proxies to constrain the depositional environments

Having established the depositional history a combination of bulk and compound-specific analysis can be used to identify the origin of sedimentary OC. C/N and δ¹³C have been used to discriminate between different OC sources in a Vietnamese arsenic contaminated aquifer (Eiche et al., 2015) and other Holocene estuary sediments from around the world (Lamb et al., 2006 and references therein). By plotting C/N vs δ¹³C different sources of OC from groups (e.g. C₃ vascular plants, freshwater POC, marine POC, etc) can be identified (Lamb et al., 2006). When this is done with the Cambodian sediments from Kandal Province (Figure 5A) initial analysis indicates that the young clay cap sediments have OC sourced from C₃ plants and mixing between freshwater POC and C₃-plants. It also suggests that freshwater POC is an important source of OC in the sandy sediments and the old clay sediments. Crucially, this approach shows that there is no major marine inputs to the sedimentary OC and assuming this reflects the sedimentary depositional environment this is evidence that the EHF are the on-shore features of the prograding delta observed 20 km downstream at KS, where both the sedimentary features and the δ¹³C indicate marine depositional environments (Tamura et al., 2007).

The CPI of the HMW n-alkanes measured by this and previous studies indicate that thermally mature deep-sourced petroleum is present in these aquifers (Al Lawati et al., 2012; Rowland et al., 2007, 2006; van Dongen et al., 2008) however the method of Lamb et al., (2006) cannot identify this source. Furthermore, both this and previous studies show the “hydrocarbon C/N paradox” where sediments with petroleum present have a low C/N. If the HMW n-alkanes are divided into two groups by CPI at 2 (mature vs immature) then sediments also form two groups defined by C/N, those below 8 (the low group) and those above (the high group), as demonstrated in Figure 5C. Thus there appears to be a systematic association between the two proxies and one which makes the bulk proxy potentially unreliable. This relationship between thermal maturity and C/N has been observed before in Vietnam but not properly explained (Al Lawati et al., 2012; Eiche et al., 2015).
The high group is exclusively clay sediments whilst the low group are mostly sandy with the exception of two EHF samples (LR05-45 and LR14-6). In the high group the CPI is indicative of plant derived HMW \( n \)-alkanes whilst the C/N is indicative of C3-plants or mixing between C3-plants and terrestrial POC (Ellis et al., 2012; Lamb et al., 2006). Modern Mekong POC has a high C/N of 12±0.5 (n= 19) (Ellis et al., 2012), which is consistent with other continental rivers South and South East Asia (Ziegler et al., 2016), and this makes it hard to distinguish exactly where the divide between POC and C3-plants is using C/N alone. But these results show that two different proxies indicate that in the young clay cap sediments all of the OC is from C3-plants or from freshwater POC and this also appears to be the case at two of the sites in the EHF (LR05-30 and LR14-30) but not LR05-45 and LR14-6. At KS, which is 20 km downstream and sedimentologically an intertidal deposit the below 15 m, the sample at 28 m has \( \delta^{13}C \) consistent with marine values.

Understanding the origin of OC in the low group is more complex than the high group. The low CPI is indicative of thermally mature petroleum inputs, however petroleum has a very high C/N ratio (>50) (Al-Ameri et al., 2015; Killops and Killops, 2005; Levenson, 1967) and yet, these samples have a low bulk C/N ratio (<8). Of the samples in the low group most plot within the freshwater POC box, however three fall outside (Figure 5A) due to their extremely low C/N. Interestingly these three samples are the samples with the highest proportion of HMW \( n \)-alkanes per gram OC (Figure 5D). Therefore the samples with the lowest C/N ratio are samples that contain the highest proportion of thermally mature HMW \( n \)-alkanes per gram OC. The low C/N groups also contain very low bulk concentrations of TOC which mean slight changes in TOC might have large changes in the C/N. It is possible that the nitrogen is from a source unrelated to the OC and therfore the OC from these sources is likely to be upwelled petroleum but the nitrogen is probably from a different source. Intriguingly evidence is emerging that DOM contains thermally mature HMW \( n \)-alkanes (Ghosh et al., 2015) and given that one potential source of inorganic nitrogen is mineralised nitrogen from the water column this could be the reason for the apparent overlap between the freshwater POC and thermally mature OC. This means that before the bulk approach is used screening for the thermal maturity of OC is essential otherwise the data might be misinterpreted if only the bulk proxy is used. The does not appear to be any systematic effect between \( \delta^{13}C \) and thermally mature HMW \( n \)-alkanes

Finally, this study, consitent with earlier studies has shown that thermally mature HMW \( n \)-alkanes in these aquifers are restricted to the sandy layers. The EHF appears to be a large homogeneous clay block however it has thermally mature HMW \( n \)-alkanes at LR14-6 and LR05-45. This can be explained if the EHF is conformable unit with the intertidal deposits at KS. The intertidal units contain clayey drapes within the sand (Tamura et al., 2007) and it is likely that the onshore
sediments sampled by this study would contain sandy drapes within the clay. These thermally mature sediments add weight to this hypothesis. The apparent clayey block is therefore a function of sampling definition and potential sampling bias given clays caught better in the sample than sands.

![Diagram of sedimentary OC analysis](image)

**Figure 5** Analysis of the origin of sedimentary OC from Kandal Province, Cambodia, using C/N and δ\(^{13}\)C approach of Lamb et al., (2006) (A); comparison of δ\(^{13}\)C to HMW n-alkane CPI (B); comparison of HMW n-alkane CPI to C/N showing division at 2 and 8 respectively (C); comparison of C/N to HMW n-alkane proportion of OC (D). Red circles = young clay sediments, green squares = sandy sediments, blue triangles = early holocene facies.

5.4 Implications on arsenic mobilisation and transport

There are several potential reasons why geomorphology might affect the distribution of arsenic in groundwater. Arsenic distribution is dictated by three key features: 1) the location of arsenic mobilization (Rowland et al., 2007) and transportation of arsenic through the aquifer (Benner et al., 2008; Kocar et al., 2008; Polizzotto et al., 2008); 2) any sequestration through adsorption to the sediments during flow due to higher surface areas in the clays and the presence for arsenic sorbing minerals (Casanueva-Marenco et al., 2016; Papacostas et al., 2008; Radloff et al., 2011; van Geen et al., 2013); 3) the potential for young labile surface derived to enter aquifer and be transported.
to depth i.e. “sandy windows” in the clay (Harvey et al., 2006; Lawson et al., 2016, 2013; Neumann et al., 2010).

Arsenic release is associated with the reduction of iron-oxide minerals by organic material in a process that oxidises organic matter. In this study site the highest concentrations of both iron oxides and OC are in the clay layers (whether young clay sediments or EHF) (Figure 2), therefore these sediments provide the greatest reservoir for potential iron-oxide reduction. The sediments containing the mostly highly oxidised OC are likely to have released more arsenic than the less oxidised. The HMW \( n \)-alkanoic acid ratio to HMW \( n \)-alkane + HMW \( n \)-alkanoic acid ratio is used to assess this in the immature sediments only, the higher the ratio the more oxidation. The results from this approach clearly show that OC in the EHF has undergone more oxidation than either of the two younger facies (Figure 6). This indicates arsenic release might be more associated with the EHF more modern facies.

![Figure 6](image)

*Figure 6 The degradation proxy, HMW \( n \)-alkanoic acid to HMW \( n \)-alkane + HMW \( n \)-alkanoic acid ratio from the thermally immature samples from Kandal Province, Cambodia, grouped by facies.*

Secondly, considering the potential for sorption of arsenic onto sediments. This study clearly demonstrates that the clayey sediments contain much higher concentrations of arseno-phillic minerals. For example the clay layers contain much higher concentrations of elements that have been shown to sequester arsenic from groundwater, these include sulphides and iron oxides (Casanueva-Marenco et al., 2016; Omoregie et al., 2013; Papacostas et al., 2008; Radloff et al., 2011; van Geen et al., 2013) and also higher concentrations of OC which has been shown to sequester iron and trace metals in other environments (Kaiser and Guggenberger, 2000; Lalonde et al., 2012). Furthermore, the clays contain the largest surface area onto which sorption can occur.
In earlier studies of this aquifer and the similar Vietnamese aquifer, researchers have described the possibility that sequestration of iron to OC might be a method of enhanced OC preservation (Eiche et al., 2015; Quicksall et al., 2008). This study shows that iron and OC are strongly related and have highest concentrations in the clay sediments, so this is certainly a possibility, however, this study has not researched the sorption state of these sediments so cannot comment fully on this issue.

A final, important consequence of this study it demonstrates the potential for sandy pathways to exist in the clays to (Figure 4) which would allow young labile surface derived DOM to enter the deeper section of the aquifer. This is important because earlier studies have hypothesised that in this region young surface derived DOC is present in the aquifer and due to its high lability increases arsenic release (Lawson et al., 2016, 2013) this has been hypothesised across South and South-East Asia (Harvey et al., 2002; Neumann et al., 2010). The sandy windows are very evident at LR03 on the transect (Figure 4) but probably also present in the EHF. A second effect of these pathways is that an earlier groundwater modelling study of this region relied on a simple layer cake model of the sediments to show that flow paths could dictate arsenic distribution (Benner et al., 2008; Polizzotto et al., 2008). This study shows that such groundwater flow modelling requires a more complex sedimentary framework, including sandy pathways.

6) Conclusions

6.1 Depositional history

In Kandal Province, in the study site, the oldest sediments are early Holocene deposits (pre 6,200 years $^{14}$C years BP). These are the onshore sediments of a sequence that become intertidal to subtidal 20 km downstream and is a tidal flat 55 km downstream. The end of deposition occurred at about 6,360 $^{14}$C years BP co-insiding with the end of sea-level rise in the region. The next sedimentary phase started at about 4,260 $^{14}$C years BP where the old on shore sediments were incised by a high energy system depositing sands. The $\delta^{13}$C indicates that the OC is from a freshwater terrestrial source rather than marine source, and given the surface geomorphology it is most likely a river system depositing sands in a point bar or scroll bar sequence. Regionally, this phase co-insides with the start of falling sea-levels, delta progradation and the initial onset of the initial flood-pulse at Tonle Sap. The latter two are caused by an increase in monsoon intensity which increased river capacity and energy thus causing the sandy river intrusions into the existing sediment. During this part of Mekong’s history, the river was likely to have large peaks and troughs in its water level and energies driven by the monsoon similar to other circum-Himalayan Rivers. This would have led to the deposition of sandy sediments during the high energy rainy season months. The sandy monsoonal sequence does not occur further downstream at the sites studied.
by Tamura et al., (2009). The final sequence at the study site was the deposition of clay sediments containing OC from C3-plants and freshwater POC deposition which occurred from 1,900 $^{14}$C years BP onwards. This change co-insides with the start of the modern flood-pulse at Tonle Sap. At this point upstream from the study site the Tonle Sap River joined the lake and Mekong together and due to the geometry of the system reduced the difference between the rainy and dry season Mekong water level. The effect of this was to have fewer high energy flooding events downstream of Tonle Sap, thus only low energy flooding events occur leading to the deposition of the shallow clay cap over the sands.

6.2 Organic carbon characterisation

This depositional history has affected the distribution of and nature of the OC in the sediments. Firstly, as indicated by the $\delta^{13}$C and C/N, all clays whether old or young contain high levels of OC from mostly plants or, within the study site only, freshwater POC – which is probably reworked plant material anyway. The sandy sediments contain thermally mature HMW n-alkanes from upwelled petroleum, given that several sites in the EHF have thermally mature HMW n-alkanes it appears that sandy layers exist within this too. These layers allow a pathway for hydrocarbons to flow into the aquifer.

The “hydrocarbon C/N paradox” where sediments with OC from petroleum contain low C/N is explained if the nitrogen is from an unrelated source. A likely source of this nitrogen is mineralised aqueous nitrogen but other inorganic sources or unrelated organic sources like microbes might also be sources. This research shows that the use of C/N in isolation can lead to incomplete conclusions and the use of two proxies (the HMW n-alkane CPI and concentration and the C/N) is advised when using this technique.

6.3 Effect on arsenic in groundwater

Finally, the reasons for the apparent geomorphological control over arsenic concentrations observed by previous studies are likely to be complex. One cause might be the sorption capacity of the sediments, the clay sediments have a higher surface area than the sand and also contain many minerals that readily sorb arsenic including iron-oxide minerals, (iron)-sulphides and OC itself. Therefore if sorption was the overriding factor then sands would have higher concentrations of arsenic than clays. This study also shows that clay pathways exist from the surface to the sandy aquifer allowing for intrusion of young DOC as has previously hypothesised but we find no evidence to support this in the compound specific organic data.

Intriguingly, the organic analysis of this study shows that the highest oxidation of OC to be in the EHF. If this is also used as a proxy for iron reduction and arsenic release then it implies that arsenic
release might be more associated with the EHF than any other facies. This is interesting given that in today arsenic is more associated with the incised sands. One possibility is that arsenic was released in the early Holocene and transported to the sandy intrusions through the sandy layers in the EHF. The potential for arsenic to be a feature of the early Holocene rather than a later feature has not been identified before in these aquifers and is therefore a significant finding.

7) Acknowledgements

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8) References


Omoregie, E.O., Couture, R.M., Van Cappellen, P., Corkhill, C.L., Charnock, J.M., Polya, D.A.,


Chapter 3) Evidence of pyrite oxidation by nitrate, and iron reduction controlled by sedimentary characteristics defined by δ^{13}C and C/N in an Arsenic contaminated aquifer in Cambodia

Highlights

- Pyrite oxidation occurring in an arsenic-contaminated aquifer in Cambodia and can account for up to 19% of the Fe(II) in solution (at one 6 m depth). In this reaction nitrate is the oxidation agent, however in the presence of a labile stimulant nitrate is reduced and thus will not oxidise pyrite.
- Iron-oxide reductive dissolution (but not arsenic release) is preferentially associated with reduction by sediments with a high TOC/N and negative δ^{13}C and this relationship exists and is sometimes stronger in the presence of a labile carbon source.
- The addition of labile carbon increases both iron reduction and arsenic reduction but the underlying sedimentary OM still dictates the amount of iron reduction.
- Iron reduction occurs most readily in the shallow sediments, but arsenic can be released at all depths – particularly in the presence of labile OM – but is usually re-adsorbed to the sediments.
- These findings show the potential vulnerability of low arsenic, sulphide rich aquifers (e.g. floodplains and Pleistocene aquifers) and sulphate utilising bio-remediation techniques if nitrate is introduced to the groundwater.

Abstract

Arsenic contamination of the groundwater of South and South East Asia is one of the world’s largest ongoing international health catastrophes. As is widely accepted to be released by desorption from sedimentary iron-oxide minerals due to redox reactions with organic material (OM). Other forms of Fe minerals such as pyrite have largely been discounted as potential sources of Fe in the system, with sulphate reduction generally being considered a net sink for As and Fe. Here we present a series of microcosm experiments which, as far as the authors are aware, is the first ever observation of pyrite oxidation by nitrate in an As contaminated aquifer. In these experiments at one depth (6 m) pyrite oxidation can account for up to 19% of Fe^{2+} in the system. However in the presence of a labile carbon source nitrate will be reduced and thus will not oxidise pyrite.
A second highly contentious debate is the identification of the controlling source of OM involved in Fe-oxide oxidation. Here we present compelling evidence that the nature of underlying sedimentary OM (as defined by C/N and δ^{13}C) is an important control on the total Fe reduced. The higher the C/N and more negative the negative δ^{13}C the greater the amount of Fe reduced. This is true even when a labile carbon source is present. The amount of As released is not related to either the amount of Fe reduced or the sedimentary C/N or δ^{13}C. As is released more readily than Fe is reduced and Fe reduction is mostly restricted to the high C/N (plant rich) clay cap sediments whilst As release can occur at all depths. Significantly higher masses of both Fe and As are released when a labile carbon source is present. Importantly, in all cases As release tends to re-adsorb to the sediments within a matter of weeks whilst iron stays mobile.

The results from this study have important implications for the long term security of low As aquifers which rely on sulphide minerals to sequester As from the groundwater (such as floodplains and Pleistocene aquifers) and newly developing bio-remediation methods that encourage sulphate reduction to remove As from the groundwater. These results show that introduction of nitrate can dissolve pyrite, however, the effect of this on arsenic concentrations appears to be tempered by re-adsorption arsenic to other minerals.

1) Introduction
On the deltas of South and South East Asia over 100 million people are living in areas where the concentrations of arsenic (As) in groundwater exceeds the World Health Organisation’s (WHO) provisional limit of 10 µg/L. The problem, which spans most deltas of the circum-Himalayan river systems, leads to extreme mass poisoning and high rates of cancer (Smith et al., 2000) if the groundwater is consumed directly (e.g. via drinking) or indirectly (e.g. via rice) (Ravenscroft et al., 2009). One well-studied example of this problem is in Kandal Province, Cambodia, where the groundwater concentrations can exceed 500 µg/L (Polya et al., 2005; Sovann and Polya, 2014).

There is a general consensus that high concentrations of As are derived from iron-oxide minerals onto which As is sorbed. As is released into groundwater due to microbi ally mediated redox reactions with organic material (OM) (e.g. Bhattacharya et al., 1997; Islam et al., 2004). In the late 1990s, Chowdhury et al., (1999) suggested that the oxidation of pyrite could provide additional source iron (Fe) in Bangladeshi aquifers, however several subsequent studies found this process to have a negligible impact on Fe chemistry in the aquifer (McArthur et al., 2001; Nickson et al., 1998; Nickson et al., 2000). Negative correlations between sulphate and Fe suggest that the dominant process which inhibits As release is sulphate reduction (Anawar et al., 2003; Harvey et al., 2002; Kocar et al., 2010) through the formation of pyrite or other Fe-sulphide minerals onto which As can
sequestered (Bostick & Fendorf, 2003; Burton et al., 2014; Kirk et al., 2010). One microcosm study using sediment from West Bengal showed that during Fe reduction and As release sulphate reduction can remove the contaminant (Héry et al., 2010). Some studies have suggested that in certain sulphide-rich sediments such as floodplain deposits (Quicksall et al., 2008) or deeper Pleistocene deposits (Radloff et al., 2011; van Geen et al., 2013) groundwater As concentrations are relatively low because As is adsorbed onto the sediments. This process has even been suggested as a potential method of bio-remediation in these aquifers (Omoregie et al., 2013; Sun et al., 2016; Xie et al., 2016). This means that As security is reliant on the lack of Fe-sulphide dissolution in these sediments.

Another important factor in As release is the source of OM that drives As release. There is significant contention over the source of OM utilised in this process, broadly the potential sources can be divided into three key groups: 1) young labile surface derived dissolved organic carbon (DOC) which is drawn into the aquifer, possibly through pumping for irrigation (Harvey et al., 2002; Lawson et al., 2013; Neumann et al., 2010); 2) sedimentary OM (SOM) that was co-deposited with the sediments (Meharg et al., 2006; Neumann et al., 2014); 3) deep-sourced thermally mature hydrocarbons that have been upwelled from reservoirs existing below the aquifers (Al Lawati et al., 2012; Rowland et al., 2006; van Dongen et al., 2008).

Microcosm experiments have shown that the addition of a labile carbon source in the form of acetate or acetate and lactate can exacerbate the amount of As released (Islam et al., 2004; Rowland et al., 2007). This has been used as evidence for the case that labile DOC drawn into the aquifer from ponds and other surface water can release As and Fe (Harvey et al., 2002; Lawson et al., 2016, 2013; Neumann et al., 2010). Further experiments have shown that the type of OM present might influence the amount of As release, for example at one site in Cambodia, sediments containing OM with thermally mature high molecular weight (HMW) n-alkanes released less As than sediments containing OM with thermally immature plant derived HMW n-alkanes (Rowland et al., 2007). However, in sediments from West Bengal without a labile stimulant, thermally mature HMW n-alkanes are preferentially degraded over the terrestrial sourced n-alkanes (Rowland et al., 2009).

An important caveat to these results is that the experiment in West Bengal was not conducted on sediments from the thermally immature clay cap that pervades much of the circum-Himalayan sediments (Al Lawati et al., 2012; Eiche et al., 2016; van Dongen et al., 2008) so the impact of thermally immature dominated OM on As release is still not fully understood. A microcosm experiment that stimulated sediments from the clay cap in Cambodia using a petroleum proxy released more As and Fe than the same sediments stimulated with a kerogen proxy (Rizoulis et al., 2014) but thermally mature petroleum derived HMW n-alkanes have not been observed in-situ
within the clay cap (Al Lawati et al., 2012; Magnone et al., n.d.; Rowland et al., 2007; van Dongen et al., 2008) therefore it is unclear whether these n-alkanes would be bioavailable in-situ in these shallow clay sediments.

The aims of this study are to use controlled microcosm studies to 1) quantify the effect of sulphur processes on As and Fe release in Cambodian sediments; 2) observe what effect TOC deposited in different environments has on As release and iron reduction; 3) to observe what effect the addition of a labile carbon source has on the system.

2) Methodology

2.1 Study location and sedimentary profile

Kandal Province is a region of Cambodia with some of the highest concentrations of groundwater As in the country (Polya et al., 2005; Sovann and Polya, 2014). The region, which is just south of Phnom Penh has three generations of sediments the earliest are tidal-to shore zone deposits of the early Holocene (7,000 – 12,000 years BP) which are due to early sea-level rise in the region, the second are sandy incision channels (2,000 – 4,000 years BP) which are due to changes in monsoon patterns increasing river flow and finally the most recent sediments are a young clay cap (<2,000 years BP) which are due to a change in Mekong flow patterns caused by the onset of the flood-pulse at the Tonle Sap. Within the groundwater As is highest in the sandy incision channels (Magnone et al., n.d.; Papacostas et al., 2008). Earlier work suggests that this might be due to the in-situ release of As in the clay layers where OM with thermally immature HMW n-alkanes is more bioavailable to the microbial community (Rowland et al., 2007). Groundwater modelling also suggests that As is released from the shallow sediments and transported into the deeper sandy aquifer by the natural flow paths (Benner et al., 2008; Polizzotto et al., 2008). However biomarkers from a comprehensive study of the area indicate that the highest levels of OM degradation are actually in the early Holocene layers (Magnone et al., n.d.). In this study we focus on the younger sediments from the latter half of the Holocene to observe what processes occur that might release arsenic.

The study site is called LR01 (using the nomenclature from earlier studies) (Magnone et al., n.d.; Richards et al., 2015, n.d.) this site was selected because it is at the top of the groundwater flow paths and provides a profile from the young clay, where modelling work (Benner et al., 2008; Polizzotto et al., 2008) and previous experiments (Rowland et al., 2007) predicts As to be released through to the deeper incision sands where high concentrations of As exists.

The sedimentary profile (Figure 7) shows sedimentary data for the site from an earlier study (Magnone et al., n.d.). The site has a clay cap down to about 6 m overlying a sandy aquifer which
extends at least to 39 m. The 6m sample from the clay cap contains the highest concentrations of sedimentary sulphur (S) and TOC whilst the 3 m contains the highest concentration of As and Fe, which is consistent with many profiles of the circum-Himalayan deltaic sediments (e.g. Al Lawati et al., 2012; Eiche et al., 2016; McArthur et al., 2004; Rowland et al., 2007). This means that the largest reservoir of Fe-oxide minerals, Fe-sulphide, and mineral As exists in the clay cap as well as the largest concentration of TOC, however, this is not necessarily bioavailable TOC. The C/N ratio is highest at 6 m and it then becomes lower at its lowest by 21 m before having an increase to a slightly higher ratio at 30 m and deeper. The δ¹³C of is most negative at 6 m and 30 m with 15 m and 21 m being less negative (Figure 7). At 3 m the C/N ratio is lower than at 6 m and at the δ¹³C less negative than at 6 m, this might be because this sample is at the water table and not saturated during the dry season, possibly leading to oxidation.

The previous study undertook organic extractions on three of the sediments (6 m, 15 m and 30 m) from the site. Using the carbon preference index (CPI) of HMW n-alkanes (a proxy for thermal maturity) only the 6 m sample in the clay cap was thermally immature and the two sandy samples (15 m and 30 m) were thermally mature. Over the study site as a whole, a good relationship was found between C/N and the CPI of HMW n-alkanes whereby if the CPI was >2 then the C/N would be >8 and vice versa. This means that all thermally immature samples have a C/N >8 (Magnone et
al., n.d.). $\delta^{13}$C is a proxy for the marine versus terrestrial input to TOC, this shows that all inputs are terrestrial (Magnone et al., n.d.) however 20 km downstream in the early Holocene sediments there is a marine signal which is in keeping with sedimentary structures (Tamura et al., 2007) and this has also been seen at sites in Vietnam (Eiche et al., 2015).

2.2 Sediment collection and characterisation

Sample collection and analysis of inorganic and organic sedimentary geochemistry were undertaken and described by Magnone et al., (n.d.) with differences only where outlined in this article. Sediments for microcosm experiments were extracted with the sediment for geochemical analysis but were not frozen. Instead, these were refrigerated, first in the field laboratory in Cambodia, before transportation to the University of Manchester by non-temperature controlled air freight and stored at 4 °C. C/N, $\delta^{13}$C and $\delta^{15}$N for microcosm samples were measured on the microcosm sediments themselves, however for all inorganic and organic geochemical parameters the values from Magnone et al., (n.d.) were used due to constraints on sediment volume. C/N was measured using the same techniques as Magnone et al., (n.d.), $\delta^{13}$C and $\delta^{15}$N were measured by Elemental Lab (Okehampton, Devon, UK) and checked against values for the same sediments from Magnone et al., (n.d.) to ensure high data quality.

2.3 Study design

The study consists of 5 microcosms from sediments taken from depths of 3 m, 6 m, 15 m, 21 m and 30 m. All have been characterised in terms of inorganic geochemistry, C/N and $\delta^{13}$C (and three have organic data from the earlier study (Magnone et al., n.d.)). The purpose is to observe if these parameters effect release of As from different depths at a site located at the top of the groundwater flow paths and thus a key potential location in terms of As release (Benner et al., 2008; Polizzotto et al., 2008).

The sample from 3 m was selected because it is located in the clay cap and at a depth near the water table, therefore it is only saturated with water during the rainy season when the water table is high. The sample from 6 m was selected because it is located in the centre of the clay cap and very representative of the clay cap: it has high concentrations of sedimentary TOC with thermally immature HMW n-alkanes, high concentrations Fe-oxides and high concentrations of sulphides. Organic work also indicates that degradation is high at this depth. The 15 m and 30 m sample were selected because they are sandy sediments from moderate and deeper depths with thermally mature HMW n-alkanes present and moderate C/N values. The 21 m sample was selected because it was a sandy sediment with a very low C/N ratio and a less negative $\delta^{13}$C than the other sandy sediments. All microcosms were treated in two different ways. Firstly, non-sterile un-stimulated
placed incubated the sediments in artificial groundwater without any other treatment. Secondly, non-sterile un-stimulated placed incubated the sediments in artificial groundwater and stimulated the microcosm with acetate and lactate as a proxy for labile organic carbon.

2.4 Microcosm experiments and analysis

Unless stated otherwise all reagents were reagent grade Fluka (Sigma-Alrich) chemicals. Microcosm experiments were conducted at the University of Manchester, Williamson Research Centre. Unstimulated microcosms were conducted in triplicate and were built from 15 g of sediment and 30 ml of synthetic sterile groundwater (using the recipe of Rowland et al., (2007) - 0.34 mM MgCl$_2$, 0.01 mM KH$_2$PO$_4$, 0.51 mM NaHCO$_3$, 0.025 mM K$_2$CO$_3$, 0.03 mM MgSO$_4$, 0.001 mM KNO$_3$, 1.85 mM CaCO$_3$, with pH adjusted to 7.1 with concentrated HCl (FisherBrand)). Stimulated microcosms were conducted with 10mM lactate and acetate added; Due to limitations in sample volume, these microcosms were built at a size of 10 g of sediment and 20 ml of synthetic sterile groundwater. Microcosms were incubated at 30 °C.

Sampling of the unstimulated microcosms occurred on days 0, 1, 3, 8, 14, 21 and 31. Sampling of the stimulated microcosms occurred on days 0, 8, 14, 21, 31 with fewer sampling sessions due to their smaller size. Fe(II) was measured using a ferrozine method (Riemer et al., 2004). 20 µL of the slurry was digested for one hour in 980 µL of 0.5M HCl. 1960 µL of ferrozine solution (1 g of Ferrozine and 11.96 g of HEPES per 1 L of deionised water the adjusted to pH 7.1 using NaOH), was added to a 40 µL aliquot of digested supernatant and the absorbance (562 nm) measured using a spectrophotometer (Jenway, 6715 UV/Vis) and compared to prepared Fe(II) standards at 1 mM, 5 mM, 10 mM, 20 mM, 50 mM and 100 mM (FeSO$_4$.7H$_2$O in 0.5 M HCl and dilutions thereafter). pH and Eh were measured using Denver Instruments, Ultrabasic probe which was calibrated before each sampling using NIST-approved buffers (pH 2, pH 4, pH 7 and pH 10, Fisher Scientific and 220 mV, Mettler Toledo). Sulphate, nitrate and nitrite were measured using ion chromatography (Dionex IC5S000). Ammonium was measured using Nesslerization/UV-VIS Spec. As speciation was measured using HPLC-ICP-MS (Agilent 7500cx).
3) Results

3.1 As and Fe reduction

All unstimulated microcosms exhibited As release (Figure 8 A) however no more than 0.15 µM and all exhibited As release followed by a decrease after the peak concentration. The addition of acetate and lactate (Figure 8 B) increased the stimulation of sediments particularly at 6 m which had the greatest release of As in the simulated samples (0.23 µM) and at this depth, 3 m and 15 m a decrease in As was also observed. At 21 m and 30 m fluctuation in As concentrations occurred (Figure 8 B). These concentrations and behaviour are consistent with previous microcosms of similar sediments treated in similar ways (Rizoulis et al., 2014; Rowland et al., 2009, 2007) and the decrease in concentration and fluctuations observed probably related to re-adsorption of As to the mineral phase. Re-adsorption and relative prevention of As release due to sulphides has been observed to some extent in Holocene aquifers (Casanueva-Marenco et al., 2016; Héry et al., 2015) in deep-sourced Pleistocene aquifers (Radloff et al., 2011; van Geen et al., 2013).

*Figure 8 Changes in As and Fe$^{2+}$ concentrations with time during microcosm incubation experiments. 3m = yellow small circle; 6m = red diamond; 15m = green triangle; 21m = blue large circle; 30m = pink square.*
In the unstimulated microcosms, the 6 m sample underwent significantly more reduction in Fe than any other depth (Figure 8C). Here Fe increased from 3 mM to a 5 mM plateau with a peak of 10 mM at day 14. 15 m and 30 m microcosms also showed some level of reduction but also a decrease in Fe\(^{2+}\) concentration after the early peak. The addition of a stimulant caused a major increase in Fe reduction with samples increasing from about 3 mM to a peak of about 15 mM by day 14. Increased reduction was also observed in 15 m and 30 m, the latter of which had a peak at day 14 of 6 mM and very small amounts of Fe reduction was observed at 3 m and 21 m (Figure 8D).

Overall, these experiments show that Fe reduction is most dominant at 6 m in both stimulated and unstimulated samples. They demonstrate that As reduction and Fe reduction are not always intrinsically linked with the release of As occurring more readily (particularly in the unstimulated samples) than Fe reduction, therefore significant Fe reduction does not need to occur in order for As to be released. Finally, stimulation by lactate and acetate as a labile organic carbon proxy increases both As reduction and Fe reduction compared to stimulation by sedimentary OM alone.
3.2 Carbonate, ammonium, nitrate and sulphate behaviour

In unstimulated samples carbonate release at all depths is similar with a maximum carbonate concentration of about 1.5 mM (Figure 9A). The most likely source of carbonate in the water column is the oxidation of sedimentary OM. This means that all sites have a similar amount of OM being oxidised. Therefore it is interesting that very different amounts of Fe are reduced, whilst
concentrations in Fe fluctuated even the lowest concentrations sedimentary Fe should provide enough Fe to accept the 1.5 mM of electrons. It might be that the nature of OM or the bioavailability of the Fe-oxide electron acceptor affects the amount of Fe release more than the amount of OM oxidised. In the stimulated microcosm, again, all microcosms showed similar amounts of carbonate released with a maximum concentration of about 3 mM (Figure 9B). The higher concentrations of carbonate in the stimulated microcosms indicates that microbes are consuming more OM, and the most likely candidate is acetate and lactate added to the system. This is consistent with earlier microcosm studies that traced consumption of OM by microbes with labelled δ¹³C acetate and lactate (Héry et al., 2014). In total 10 mM of acetate and lactate was added to the microcosm however only 3 mM of carbonate was released. This might mean that only 30 % of the bioavailable labile carbon was oxidised in the microcosm, however this could also be caused if some of the carbonate precipitated out of solution rather than remaining dissolved.

At 6 m in the unstimulated microcosms ammonium (Figure 9C) and sulphate (Figure 9G) were released into the groundwater and nitrate was lost from the system (Figure 9E). This sulphate behaviour has not been observed before in South East Asian sediments and is therefore unique to this study. Previously sulphate, like nitrate, has been lost during microcosm experiments and this has been interpreted as sulphate precipitation, which to some extent inhibits As release (Héry et al., 2010; Omorogie et al., 2013). The increase of sulphate and ammonium in the pore water, coupled with the loss of nitrate from the water, indicates that some of the Fe release is from the oxidation of pyrite where nitrate acts as the electron acceptor. This is the first time that this has been observed in a South Asian aquifer. The reaction is described in Equation 1.

Equation 1

\[ 5\text{FeS}_2 + 14\text{NO}_3^- + 4\text{H}^+ \rightarrow 7\text{N}_2 + 5\text{Fe}^{2+} + 10\text{SO}_4^{2-} + 2\text{H}_2\text{O} \]

Given that the concentration of nitrate in the artificial groundwater of all samples was 0.001 mM and the day 0 concentration at 6 m was 0.09 mM, the most likely source of the high nitrate concentration in this microcosm is sedimentary nitrate. A farm exists locally, to investigate the source of high sedimentary nitrogen δ¹⁵N was used to infer a potential source of sedimentary nitrogen at this site (only 3 m and 6 m have enough nitrogen to be measured). Sedimentary nitrogen at 3 m and 6 m have δ¹⁵N values of 3.8 ± 0.1 ‰ and 3.2 ± 0.3 ‰ respectively, these are consistent with values for fertilizer or soil organic nitrogen but are too low to be human or animal waste (Aravena et al., 1993) so it is unlikely that effluent is having an effect on Fe-sulphide oxidation in this system.
In the unstimulated samples at depths other than 6 m, nitrate increased during the latter half of the experiment (Figure 9E). This is greatest at 15 m but also observed at 3 m and 21 m. This occurred after a small loss of ammonium and indicates that at these depths ammonium is being oxidised to form nitrate. At 15 m under stimulated conditions, a greater amount of nitrate was released than under unstimulated conditions this is because a greater amount of carbon is available to provide an electron donor (Figure 9F).

When the 6 m microcosm was stimulated with acetate and lactate, sulphate concentrations remained constant throughout the experiment (Figure 9H). The starting nitrate concentrations were far lower than in the unstimulated microcosm (Figure 9F) with no increase observed, this suggests that adding a labile carbon source to the system quickly reduced nitrate removing it from the system. Without nitrate present, there was no source available to oxidise the Fe-sulphide thus explaining the lack of change observed in the sulphate concentrations. This means that all Fe released when the labile carbon source is present is from Fe-oxides rather than pyrite. This reaction is represented by Equation 2.

\[ 8\text{FeOOH} + \text{CH}_3\text{COOH} + 14 \text{H}_2\text{CO}_3 \rightarrow 8\text{Fe}^{2+} + 16\text{HCO}_3^- + 12\text{H}_2\text{O} \]

Using Equations 1 and 2 above and the mass of carbonate and/or sulphate released it is possible to model the theoretical amount of Fe that could be released from carbonate and/or sulphate observed. By comparing these modelled values to the values as measured gives an indication of the importance of the different components. The results of this are shown in Table 4.
Table 4 Measured Fe changes during microcosm experiments vs modelled Fe reduction based changes in anion concentrations.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Carbonate released (mM)</th>
<th>Ammonium loss/gain (+/- mM)</th>
<th>Sulphate loss/gain (+/- mM)</th>
<th>Nitrate loss/gain (+/- mM)</th>
<th>Fe loss/gain (+/- mM)</th>
<th>Fe from carbonate (mM)</th>
<th>Fe from Sulphate (mM)</th>
<th>Fe (from Carbonate)</th>
<th>Fe (from Sulphate)</th>
<th>Total Modelled</th>
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<td>No stimulation</td>
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<tr>
<td>3m</td>
<td>0.60</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.3</td>
<td>0.01</td>
<td>86%</td>
<td>2%</td>
<td>88%</td>
<td></td>
</tr>
<tr>
<td>6m</td>
<td>1.10</td>
<td>0.14</td>
<td>0.62</td>
<td>-0.08</td>
<td>1.6</td>
<td>0.31</td>
<td>34%</td>
<td>19%</td>
<td>54%</td>
<td></td>
</tr>
<tr>
<td>15m</td>
<td>0.72</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>1.0</td>
<td>0.01</td>
<td>36%</td>
<td>1%</td>
<td>37%</td>
<td></td>
</tr>
<tr>
<td>21m</td>
<td>0.70</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.6</td>
<td>0.01</td>
<td>55%</td>
<td>1%</td>
<td>56%</td>
<td></td>
</tr>
<tr>
<td>30m</td>
<td>0.98</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
<td>1.3</td>
<td>0.01</td>
<td>38%</td>
<td>1%</td>
<td>39%</td>
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<td>Stimulation</td>
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<tr>
<td>3m</td>
<td>2.11</td>
<td>-0.01</td>
<td>-0.04</td>
<td>-0.01</td>
<td>0.71</td>
<td>1.1</td>
<td>149%</td>
<td>149%</td>
<td></td>
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<tr>
<td>6m</td>
<td>2.42</td>
<td>-0.10</td>
<td>-0.16</td>
<td>0.00</td>
<td>9.39</td>
<td>1.2</td>
<td>13%</td>
<td>13%</td>
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</tr>
<tr>
<td>15m</td>
<td>1.92</td>
<td>0.02</td>
<td>0.06</td>
<td>0.08</td>
<td>2.70</td>
<td>1.0</td>
<td>36%</td>
<td>36%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21m</td>
<td>2.36</td>
<td>0.04</td>
<td>0.01</td>
<td>-0.03</td>
<td>1.41</td>
<td>1.2</td>
<td>84%</td>
<td>84%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30m</td>
<td>2.78</td>
<td>0.05</td>
<td>-0.05</td>
<td>-0.01</td>
<td>1.43</td>
<td>1.4</td>
<td>97%</td>
<td>97%</td>
<td></td>
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</tr>
</tbody>
</table>

These results show that with the exception of one sample (3 m stimulated), the modelled values underestimate the amount of Fe reduced by about 50%. This could relate to potential remineralisation of carbonate and sulphate leading to underestimation of the concentration of carbonate or sulphate reacted, or it could indicate that another reaction of Fe release is occurring which hasn’t been accounted for. Either way, the most important finding is that at 6 m at least 19% of the Fe in the system could be released from pyrite oxidation.
3.4 OM source and As & Fe reduction

![Figure 10](image_url)

*Figure 10* Fe and As released during microcosm experiments vs sedimentary C/N and δ^{13}C. Blue circles = unstimulated; green triangles = stimulated.

In the unstimulated samples there is a strong relationship between both C/N and Fe reduced (Figure 10A) but no relationship between As release (Figure 10B), the Fe relationships are lessened when the sample is stimulated (Figure 10A). In the unstimulated samples, there is no relationship between the δ^{13}C and Fe released (Figure 10C) or As released (Figure 10D). However, upon stimulation, a relationship between the underlying sedimentary δ^{13}C and amount of Fe released exists (Figure 10C). Generally, higher C/N ratios and less negative δ^{13}C are associated with more Fe release, when samples are stimulated the general pattern remains the same, however, more Fe is reduced and this is despite the C/N and δ^{13}C being sedimentary parameters. Thus it shows that even in the presence of labile stimulant sedimentary parameters do have important associations with Fe reduction. The addition of acetate and lactate to the system increases the amount of As released but still does not show any relationship with the underlying sedimentary composition. Therefore an underlying sedimentary control on Fe reduction exists but there is not one for As reduction. This control is represented by the C/N or δ^{13}C ratios. This has been observed before in microcosms stimulated with fresh plant material of varying C/N ratios (Solaiman et al., 2009). The high C/N is associated with thermally immature HMW n-alkanes, this means that this study finds
that sediments containing thermally immature plant OM releases more Fe than the thermally mature. These findings concur with an earlier study from nearby sediments which showed the highest concentration of As and Fe to be released from the thermally immature layers as well (Rowland et al., 2007).

3.3 Eh and pH behaviour

Redox (Eh) and pH are two of the most important parameters that dictate the solubility of Fe and As (Al-Abed et al., 2007; Lu and Zhu, 2011; Masscheleyn and Delaune, 1991). The redox pathway gives important information about the speciation of Fe and As, and therefore the likelihood of either entering the water column or reducing. In the unstimulated samples at 15 m, 21 m and 30 m there was no major change in Eh (Figure 11 15 m, 21 m and 30 m), but at 3 m, 15 m and 21 m an increase in pH from neutral to mildly alkali did occur, this was greatest on the first day and then remained relatively constant (Figure 11 3 m, 15 m and 21 m). This means that the Eh-pH pathway for unstimulated 3 m, 15 m, 21 m and 30 m never crossed either of the speciation boundaries. In the microcosms these samples showed little Fe reduction therefore the Eh-pH reaction path is consistent with the chemical behaviour.
At 6 m, during the first day an increase in pH occurred (Figure 11 6 m), which is consistent with the carbonate released, but there is also a large change in Eh towards more reducing conditions. By the end of the microcosm experiment only this depth had crossed a speciation pathway. That only 6 m moved towards more reducing conditions is consistent with it having the only significant Fe reduction, it is also consistent with nitrate being reduced (Appelo and Postma, 2005). The increase in pH is consistent with consumption of hydrogen ions which is required for pyrite oxidation in Equation 1.

At 3 m, in the stimulated samples, a steady decrease of Eh occurs coupled with an initial increase in pH followed by a gradual decrease. This gradual change in Eh is consistent with the very slow Fe reduction observed (Figure 11 3 m). At 6 m there is a very quick decrease in Eh to more reducing conditions, whilst the conditions remain significantly reduced Eh starts to increase at a very slow rate and pH starts to decrease, broadly flowing the \( \text{Fe}^{2+}/\text{Fe(OH)}_3 \) transition boundary. The large change in Eh is consistent with the dramatic reduction of Fe between day 0 and day 8. At 15 m the Eh-pH does not vary much from the unstimulated pathway (Figure 11 15 m). The 21 m and 30 m microcosms both quickly become more reducing with a lower Eh from day 0 to day 8 but then become less by days 21 and 31 (Figure 11 21 m and 30 m). The lack of sustained or continuing reduction in the 21 m and 30 m microcosms explain the lower levels of Fe reduction in the stimulated samples at these depths.

The Eh-pH pathways show that the only depth at which significant reduction took place was at 6 m; at all other sites any change in chemistry was driven by changes in pH. They also show that under the stimulation by lactate and acetate only 6 m could sustain reducing conditions, at all other depths where conditions became reducing there was a quick return to less reducing conditions. Finally, speciation boundaries for arsenic and iron (Lu and Zhu, 2011; Masscheleyn and Delaune, 1991) clearly show arsenic more readily reduces and becomes soluble than iron, which is borne out by the microcosm results.

3.6 Wider implications
Earlier work has shown that the sequestration of As to sulphides exists through weak bonds (O’Day et al., 2004) and this experiment illustrates the vulnerability of As contaminated aquifers to pyrite oxidation under the correct circumstances, notably in the presence of nitrates and absence of labile OM. Not only has pyrite been observed to be dissolved during this experiment but sulphate remains in solution after dissolution and does not precipitate out as has been observed elsewhere (Héry et al., 2010). This vulnerability is of particular concern for two reasons: firstly, some studies have considered deeper Pleistocene aquifers (Radloff et al., 2011; van Geen et al., 2013) and floodplain
deposits (Quicksall et al., 2008) to have low As concentrations because the sulphide-rich sediments sequester As; secondly, new methods of bioremediation are utilising sulphide as a way of reducing As concentrations in the aquifers (Omoregie et al., 2013; Sun et al., 2016; Xie et al., 2016). The results from this study show that a change in chemical composition of the water, notably the addition of nitrate, can cause the dissolution of pyrite which risks the security of water. The effect of pyrite oxidation might however be tempered by re-adsorption of As to other minerals as appears to happen in this study.

These results also play into the debate on the OM source involved in As release. Firstly, it demonstrates that sedimentary OM alone can release As without the addition of labile carbon, but that the addition of a labile carbon source clearly elevates the amount of As released and Fe reduced. The amount of Fe reduction (although not As released) is clearly strongly related to the underlying source of sedimentary OM, even when labile carbon is present. Finally, these results show that Fe release is most dominant at 6 m depth however As release can exist at all depths suggesting that Fe at least is released in the near surface and transported to depth (Polizzotto et al., 2008) but As is released more readily at all depths.

4) Conclusions

For the first time in sediments from an arsenic contaminated aquifer in South and South East Asia, pyrite oxidation has been observed. In one of our samples from a depth of 6 m, it could account for a 19% of total reduced iron. The oxidation agent is nitrate, most likely from a sedimentary source – probably soil but possibly fertilizer. However, this process only occurs in the absence of a labile carbon source. The addition of acetate and lactate prevents pyrite oxidation because it causes the fast reduction of nitrate removing it from the system before it has the opportunity to oxidise pyrite. The full effect of pyrite oxidation is however diminished due to re-adsorbance of As to other minerals within the clays.

The most important source of Fe$^{2+}$ in the system for either a stimulated or unstimulated microcosm is the oxidation of Fe-oxides by organic material. This experiment has shown that C/N and $\delta^{13}$C of the sedimentary organic material, regardless of whether or not a labile carbon source is present, is an important factor as to the amount of Fe that will be reduced. The higher the C/N or the more negative the $\delta^{13}$C, the more Fe$^{2+}$ will be released. The concentration of arsenic released is not related to the amount of Fe reduced or related to the source of sedimentary OM, however, the addition of a labile carbon source will encourage both Fe reduction and arsenic release. These findings are of particular importance due to the recent bioremediation methods being developed which use sulphate sequestration, and well switching to Pleistocene aquifers due to their high
sulphate concentrations leading to sequestration of arsenic. These results demonstrate the potential impact of nitrate contamination on arsenic release in these sites.

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6) References


Chapter 4) A new $^{14}$C correction model using $^{87}$Sr/$^{86}$Sr to attribute the age of dissolved inorganic carbon from the degradation of organic material - application to a Holocene aquifer, Cambodia

Abstract

The radiocarbon age for dissolved inorganic carbon (DIC) in groundwater is a key parameter for understanding groundwater history and processes. Historically, this parameter has been used to calculate the age of recharge of the aquifer and several models have been developed to provide corrections of bulk DIC age to recharge DIC age. These models work on the premise that DIC in an aquifer has multiple sources (carbonate dissolution, rainwater, soil zone, etc.) and calculate the effect of carbonate from soil and carbonate mineral dissolution on the radiocarbon age of DIC to correct to an estimate of recharge age. These models have two key weaknesses: 1) many are not effective in silicate-dominated aquifers; 2) most only correct to the age of recharge.

In this study, we present a new model that corrects to find the age of organic material oxidised to form inorganic carbon in groundwater and present a successful application of the model in a Holocene silicate-dominated aquifer in Cambodia. This model first calculates the mixing of solutes from different sources utilising a new $^{87}$Sr/$^{86}$Sr mixing model, then calculates the absolute concentration of inorganic carbon from the oxidation of organic material and finally applies a correction to $\Delta^{14}$C and $\delta^{13}$C.

1) Introduction

1.1) Background and existing models

A key parameter in the study of groundwater resources and dynamics is the radiocarbon age of dissolved inorganic carbon (DIC). Natural $^{14}$C is constantly produced in the upper atmosphere through reactions between cosmogenic radiation and $^{14}$N (Anderson et al., 1947). $^{14}$C oxidises to form $^{14}$CO$_2$ which can enter the carbon cycle through a range of methods, including precipitation and photosynthesis by plants. Once equilibrium with atmospheric $^{14}$C is broken (e.g. through plant death and burial or precipitation entering groundwater recharge) $^{14}$C will decay at a half-life of 5730±40 years but $^{12}$C will not (Godwin, 1962). Thus, by comparing the initial $^{12}$C/$^{13}$C ratio (called time zero, $A_0$) and the $^{14}$C/$^{13}$C ratio of the sample today ($A_t$) an estimated of the time since
equilibrium with the atmosphere was broken can be established. This is the radiocarbon age and is calculated by the following equation.

\[ t = \frac{\tau}{\log(2)} \log \left( \frac{A_t}{A_0} \right) \]

Where: \( \tau \) is half-life; \( A_t \) is the specific activity (ratio of \( ^{14}C/^{12}C \)) as measured; \( A_0 \) is the specific activity (ratio of \( ^{14}C/^{12}C \)) at time zero and it is the time since time zero. By convention, the specific activity (\( A_0/A_0 \)) is reported as a percentage of modern carbon activity (pmc). 100 pmc is considered to be the \( ^{14}C/^{12}C \) ratio at 1950 before widespread atomic bomb testing, this date is reported as radiocarbon years (Stuiver and Polach, 1977). However, because in reality, \( A_0 \) has varied naturally over geological time calibration curves (Reimer et al., 2013, 2004; Stuiver and Reimer, 1993) in combination with calibration software (e.g. OxCal (Bronk Ramsey and Lee, 2013)) can be used to calculate the age in calendar years.

If DIC from rainwater is the only source of DIC in groundwater then the radiocarbon age of DIC will represent the age of aquifer recharge. However, atmospheric CO\(_2\) is not the only source of DIC in most groundwater systems. A range of sources including seawater infiltration, dissolution of carbonates and oxidation of organic matter, organic material (OM) can all add to the DIC in the system (Plummer and Glynn, 2013). Given each these sources will have a different \( ^{14}C \) age the \( ^{14}C \) age of the bulk DIC will record an average of all the different sources and not merely that of atmospheric DIC at recharge. To account for this several correction models have been developed to calculate the \( ^{14}C \) from atmospheric carbon only and thus provide an estimate of atmospheric recharge. A quick summary of these models is provided below, however, a full review was recently published by Plummer and Glynn (2013) for the International Atomic Energy Agency.

**Vogel’s Model**

One of the oldest and simplest models is Vogel’s model. It is based on a study of about 100 \( ^{14}C \) measurements of dissolved carbon in groundwaters of north-west Europe this model assumes that 85\( \pm \)5\% of DIC in the system came from dissolved atmospheric carbon and therefore considers \( A_0 = 85\pm5\% \) modern carbon (Vogel, 1970, 1967).
Tamer’s Model, Pearson’s Model and Related Models

Tamer’s model calculates $A_0$ by assuming the $^{14}$CO$_2$ in the soil zone has been diluted by carbonate dissolution, which is radiocarbon dead (Tamers, 1970, 1967; Tamers and Scharpenseel, 1970). It is expressed thus:

$$A_0 = \frac{(m\text{CO}_2 + 0.5m\text{HCO}_3^-)A_g + (0.5m\text{HCO}_3^-)A_c}{m\text{CO}_2 + m\text{HCO}_3^-}$$

Where $m$ is the molalities; $A_c$ is the activity of carbonate and $A_g$ is the activity of soil gas. In many circumstances, $A_c$ may be considered 0 (where carbonate is radiocarbon dead) and $A_g$ considered 100% (where the soil is modern).

Pearson’s Model uses the same assumptions of soil and carbonate mixing as Tamer’s model, but here isotope mass balance of $^{13}$C is used to calculate the initial activity instead (Ingerson and Pearson, F, 1964; Pearson and Hanshaw, 1970).

$$A_0 = \frac{\delta_T - \delta_c}{\delta_g - \delta_c}(A_g - A_c) + A_c$$

Where $\delta_T$ is the $\delta^{13}$C of total dissolved carbon, $\delta_g$ is the $\delta^{13}$C of gaseous CO$_2$ from the soil and $\delta_c$ is the $\delta^{13}$C of carbonates. Very often it may be considered that $\delta_g = -25‰$ and $\delta_c = 0‰$ with $A_c$ and $A_g$ being the same as in Tamer’s Model. Thus $\delta_T$ is the only significant variable.

$$A_0 = \frac{\delta_T}{-25‰} \times 100pmc$$

Many models have been developed on similar principles to these, but with subtle variations. Evan’s Model, though not developed from Pearson’s Model, has similarities to it (Plummer and Glynn, 2013) it considers the fractionation of isotopes up the recrystallization of carbonate by assuming that calcite is in equilibrium with HCO$_3^-$ (Evans et al., 1979). Eichinger (1983) contains gas exchange and Salem et al., (1980) divides the model into a two-step approach first considering the equilibrium of HCO$_3^-$ with the gas phase and secondly the dissolution of solid carbonate. Finally, Mook’s model is a step by step approach which considers the isotopic equilibrium of CO$_2$ gas with all other carbonate species. The model is considered most appropriate in carbonate dominated
groundwater (Mook, 1980, 1976, 1972) and can be considered to be like Tamer’s Model but with an additional correction term (Fontes, 1992; Plummer and Glynn, 2013).

**Fontes and Garnier’s Model**

Fontes and Garnier (1979) considered closed system mixing between two end-members: CO₂ from the soil zone and dissolved carbonate minerals. The approach produces estimations for the amount of active and radiocarbon dead carbon in the system (this approach attempts to overcome problems such as pre-analytical mineralisation in sample bottles). The first section of the model is an isotopic exchange between mineral carbon and soil zone carbon and works on the principle that δ^{13}C of DIC fractionates up speciation.

\[
\delta_T C_T = (C_M - q)\delta_M + (C_T - C_M)\delta_g - q(\delta_M - \varepsilon)
\]

\[
\delta_T C_T = C_M\delta_M + (C_T - C_M - q')\delta_g + q'(\delta_M + \varepsilon)
\]

Where δ refers to δ^{13}C content (‰); C refers to carbon; T, M and g refer to total, solid carbonate and gas respectively; ε refers to the isotopic enrichment factor; q refers to the number of moles of solid carbonate in equilibrium with part of the soil CO₂ whilst q’ refers to the number of moles of soil CO₂ in equilibrium with solid carbonate. Therefore q = -q’ and when written in the form of the equation below indicates the direction of isotopic exchange. A positive q indicates gaseous CO₂ is dominating the system whilst a negative q indicates that solid carbonate is dominating the system.

\[
q = q' = \frac{C_T\delta_T - C_M\delta_M - (C_T - C_M)\delta_g}{\delta_g - \varepsilon - \delta_M}
\]

\(A_0\) is solved below.

\[
A_0 C_T = C_M A_M + (C_T - C_M) A_g + q(A_g + 0.2\varepsilon - A_M)
\]

\[
A_0 (f-g) = \left(1 - \frac{C_M}{C_T}\right) A_g + \frac{C_M}{C_T} A_M + k
\]

Where k is calculated through an amended version of Tamer’s model.
\[ k = (A_g + 0.2\varepsilon - A_M) \left( \frac{C_T\delta_T - C_M C_M \delta_M - (1 - C_M C_T) C_g \delta_g}{C_g \delta_g - \varepsilon_{i-j} - C_M \delta_M} \right) \]

In their review, Plummer and Glynn (2013) describe Fontes and Garnier (1979)’s model as arguably the most comprehensive model for the determination of \(A_0\), however, it is easily affected by the \(\delta^{13}C\) of soil gas and this data is not always available. The model is also considered of limited use in silicate-dominated aquifers and aquifers where significant proportions of \(SO_4^{2-}\) has come from oxidation of sulphides or the leaching of sodium sulphate (e.g. tropical aquifers). This is due to the calculation of \(C_M\) become more complex.

**Coetsiers and Walraevens Model**

More recently Coetsiers and Walraevens (2009) attempted to identify the impact of calcite dissolution, oxidation of organic matter and \(CH_4\) formation. Unlike earlier models, this utilised analysis of independent parameters to the radiocarbon by using the concentrations of Ca\(^{2+}\), Fe\(^{2+}\), \(SO_4^{2-}\) and \(HCO_3^-\) concentrations as a method of quantifying the originates from calcite dissolution, reduction of Fe oxides, reduction of \(SO_4^{2-}\) and \(CH_4\) production respectively. This, they argue, makes the model applicable in a wider range of aquifers.

1.2) Philosophy behind this model

With the exception of Coetsiers and Walraevens (2009)’s all models outlined above correct by assuming only two main factors: soil and carbonate mixing and fractionation. Therefore, in silicate-dominated or sulphate rich aquifers, many are not applicable (e.g. Fontes and Garnier, 1979). This means they are of limited use in many tropical regions. Furthermore, all the existing models are designed to correct to rainwater and because (with the exception of Coetsiers and Walraevens (2009)) they use knowledge of rainwater \(\delta^{13}C\) and correct back to that they are inflexible and do not allow for correction to another source (e.g. DIC from oxidation of organic matter). The aim of this study is to provide a model that can correct the radiocarbon age of DIC from the oxidation of OM and is applicable in a silicate rich tropical aquifer.

The approach of this model is similar to Coetsiers and Walraevens (2009)’s model and uses the concentration of calcium and magnesium to correct for the input of calcite and dolomite minerals, however unlike Coetsiers and Walraevens (2009) who assume bulk calcium to come from dissolution of calcite this model use the \(^{87}Sr/^{86}Sr\) to quantify the dissolution of carbonates and
silicates and calculates the DIC inputs from these sources. $^{87}\text{Sr}/^{86}\text{Sr}$ has been used to study the weathering of rocks by river systems in circum-Himalayan rivers (Bickle et al., 2005, 2003, 2001; Colin et al., 2006; Jacobson and Blum, 2000; Jin et al., 2011; Liu et al., 2007; Oliver et al., 2003; Tipper et al., 2006a, 2006b), the Congo (Negrel et al., 1993), the Amazon (Allègre et al., 1996) and in central Europe (Négre, 1999; Négre et al., 1997; Négre and Deschamps, 1996). The strontium approach has also has proven to be effective in groundwater research (Négre and Petelet-Giraud, 2005).

One of the advantages of this model over other models is that it robustly calculates the concentration of inorganic carbon (IC) from the oxidation of OM and, separately, from the weathering of silicates and of carbonates. The calculation of the concentrations of IC (independant to the radiocarbon correction) from different inputs means that this model could be utilised in research regarding the carbon budgets of the great rivers where strontium has already been used to quantify weathering budgets (Bickle et al., 2005; Colin et al., 2006; France-Lanord and Derry, 1999; Liu et al., 2007; Negrel et al., 1993; Oliver et al., 2003; Tipper et al., 2006a; Tripathy and Singh, 2010) and thus could contribute into important debates surrounding the Raymo Hypothesis and natural climate change forcings (Raymo and Ruddiman, 1992).

In this study, we produce a new mixing model utilising $^{87}\text{Sr}/^{86}\text{Sr}$ to quantify the mixing of solutes from silicates, carbonates and rainwater. This is used to quantify the proportion of DIC formed from the oxidation of OM. Having calculated this the model can be used to constrain either DIC from re-charge or to find the radiocarbon date of DIC from the oxidation of OM. In this example, we correct the radiocarbon age and $\delta^{13}\text{C}$ of DIC formed from the oxidation of OM. To achieve this requires knowledge of groundwater recharge from an independent source (e.g. tritium dating, CFC analysis, $^{85}\text{Kr}$) – if the model were used to correct to find re-charge and estimate of the age of OM would be required. The model should be effective across the spectrum of silicate and carbonate aquifers and at a range of temperatures.

1.3) Assumptions of the new mixing model

The mixing model is derived from three basic assumptions about conservative groundwater mixing: 1) the water chemistry and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a water sample is the product of the proportional mixing of different sources’ chemical inputs (Borg and Banner, 1996; Negrel et al., 1993); 2) every source is known and has an end-member which is chemically and isotopically definable; 3) each end-member has a distinct chemical composition and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is ideal for these purposes because it doesn’t fractionate upon weathering and Na can be used as a conservative tracer (Negrel et al., 1993; Stewart et al., 1998).
Given these assumptions, if a groundwater only has three sources, the chemistry of the sample can be entirely accounted for by the three sources: dubbed source “a”, source “b” and source “c”. This assumption is described algebraically in Equation 3 where “X” is the fractional proportion of water from source “a”, “b” or “c”.

Equation 3

\[ X_a + X_b + X_c = 1 \]

Secondly, the amount of any given element, “Y”, from a specific source (“Y_{src-spl}”) is equal to the proportional input of water from a given source (“X_{src}”) and the concentration of “Y” in the end-member (“Y_{src-en}”) of said source (Equation 4). Then, like with Equation 3, if all have Y has come from the three sources then the concentration of total “Y” in the sample (“Y_{spl}”) is equivalent to the sum of “Y” from the three sources (Equation 5):

Equation 4

\[ Y_{src-spl} = Y_{src-en} \times X_{src} \]

Equation 5

\[ Y_{spl} = Y_{a-spl} + Y_{b-spl} + Y_{c-spl} \]

By considering Equation 3, Equation 4, Equation 5 as simultaneous equations gives the equations which may be used to calculate the proportional inputs of the test ions from the specific different sources (“a”, “b” and “c”), Equation 6 and Equation 7. Equation 6 and Equation 7 are the fundamental equations on which the mixing model is based. The concentrations of \(^{86}\)Sr at the end-members (required for Equation 7) can be calculated to be 9.86% of the total strontium concentration at the end-member (de Laeter et al., 2003) and the concentration of \(^{87}\)Sr is calculated from this and the measured ratio.

Equation 6

\[
X_{EMA} = \frac{\alpha_a \cdot \beta_{a,1} - \alpha_a \cdot \beta_{a,3}}{\alpha_{a,1} \cdot \beta_{a,2} - \alpha_{a,2} \cdot \beta_{a,1}}
\]

\[
X_{EMB} = \frac{\alpha_b \cdot \beta_{b,1} - \alpha_b \cdot \beta_{b,3}}{\alpha_{b,1} \cdot \beta_{b,2} - \alpha_{b,2} \cdot \beta_{b,1}}
\]

\[
X_{EMC} = \frac{\alpha_c \cdot \beta_{c,1} - \alpha_c \cdot \beta_{c,3}}{\alpha_{c,1} \cdot \beta_{c,2} - \alpha_{c,2} \cdot \beta_{c,1}}
\]
Where:

**Equation 7**

\[
\begin{align*}
\alpha_a &= \left( [^{18}S_{a}]-[^{16}S_{a}] \right) \cdot \frac{^{18}Sr}{^{87}Sr_{\text{Sr}}} \ + \ \left( [^{18}S_{b}]-[^{16}S_{b}] \right) \\
\beta_a &= \left( [^{18}S_{a}]-[^{16}S_{a}] \right) \cdot \frac{^{18}Sr}{^{87}Sr_{\text{Sr}}} \\
\gamma_a &= \left( [^{18}S_{a}]-[^{16}S_{a}] \right) \\
\alpha_b &= \left( [^{18}S_{b}]-[^{16}S_{b}] \right) \cdot \frac{^{18}Sr}{^{87}Sr_{\text{Sr}}} \ + \ \left( [^{18}S_{c}]-[^{16}S_{c}] \right) \\
\beta_b &= \left( [^{18}S_{b}]-[^{16}S_{b}] \right) \cdot \frac{^{18}Sr}{^{87}Sr_{\text{Sr}}} \ + \ \left( [^{18}S_{c}]-[^{16}S_{c}] \right) \\
\gamma_b &= \left( [^{18}S_{b}]-[^{16}S_{b}] \right) \\
\alpha_c &= \left( [^{18}S_{c}]-[^{16}S_{c}] \right) \cdot \frac{^{18}Sr}{^{87}Sr_{\text{Sr}}} \ + \ \left( [^{18}S_{T}]-[^{16}S_{T}] \right) \\
\beta_c &= \left( [^{18}S_{c}]-[^{16}S_{c}] \right) \cdot \frac{^{18}Sr}{^{87}Sr_{\text{Sr}}} \ + \ \left( [^{18}S_{T}]-[^{16}S_{T}] \right) \\
\gamma_c &= \left( [^{18}S_{c}]-[^{16}S_{c}] \right)
\end{align*}
\]

For Equation 7, square brackets denote that the concentration is required, subscript letters “a, b, c and T” denote values at EM\textsubscript{a}, EM\textsubscript{b}, EM\textsubscript{c} and in the total sample respectively. Y represents the concentration of an element e.g. Ca or Mg. Na represents sodium which is used as the conservative tracer in this study but Na can be replaced by another conservative tracer, for example, Lithium, if it is deemed more suitable. A version of this equation is published as an R script to allow easy use of the equation and simple plotting. This is in the supplementary information where there is also a worked example. Having calculated the proportion of element Y in the system, using the mixing model (Equation 6 and Equation 7), the absolute concentrations of element Y from the individual components can be calculated (x = given end-member, T = total):

**Equation 8**

\[
[Y]_x = [Y]_T \cdot X_x
\]

1.4) Defining end-members for the new mixing model

Within geological systems the main inorganic end-members are divided into two broad groups: firstly hydrological end-members and secondly lithological end-members. Hydrological end-members include rainwater and seawater whilst lithological end-members include silicate rocks, carbonate rocks and evaporites. Crucially surface water is not a hydrological end-member as chemically this is, in reality, a mixture of both rainwater and the rocks through which the rivers have flown.

In order to use this model accurately, the lithological end-members must be converted into hydrological end-members. The composition of the lithological end-member is considered to be the entirety of the mineral phase composition (e.g. silicate might consist of talc and anorthite and carbonate might be calcite and dolomite). Different mineral phases are extracted using appropriate sequential extractions, measured and converted in to mineral phases through stoichiometric assumptions. The entire mineral phase is considered during the modelling and not simply individual
minerals. Whilst carbonate phase is might be mostly dolomite and calcite, strontium carbonate and sodium carbonate are also important trace minerals for the model. Similarly, appropriate strontium and sodium minerals in the silicate phase are important for the model. Having measured the composition using sequential extractions, the mineral assemblage is described by using the stoichiometry (Equation 9 to Equation 12).

\[ \text{Equation 9} \]
\[ \text{MgCa(CO}_3\text{)}_2 \text{ (mM, Dolomite) = Mg (mM)} \]

\[ \text{Equation 10} \]
\[ \text{CaCO}_3 = \text{Ca (mM, Calcite) – Mg (mM)} \]

\[ \text{Equation 11} \]
\[ \text{CaAl}_2\text{Si}_2\text{O}_8 \text{ (mM, Anorthite) = Ca (mM)} \]

\[ \text{Equation 12} \]
\[ \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \text{ (mM, Talc) = Mg (mM)}/3 \]

Note that whilst Equation 9 to Equation 12 demonstrate the application to dolomite, calcite, anorthite and talc only this same approach can be used with any mineral assemblage. The full mineral compositional make-up of each lithological end-member (e.g. carbonate and silicate) is modelled using PHREEQ-C (Parkhurst and Appelo, 2013), or other appropriate software, by dissolving the different lithological end-members into a water solution to calculate the hydrological end-member. $^{87}\text{Sr}/^{86}\text{Sr}$ in water is assumed to be the same as that measured in the lithological end-member during sequential extraction given it does not fractionate upon weathering.

During geochemical modelling the composition of an end-member is selected by the following rules: 1) the end-member is reached when all minerals become saturated; 2) if minerals do not become saturated, then the end-member is achieved when saturation plateaus; 3) if saturation never plateaus, then the end-member is achieved at peak or trough Ca/Na, Mg/Na or other appropriate ion to tracer ratio. Having calculated end-members all sample data points within the system should fall between all end-members if they do not then this means 1) an end-member has been miscalculated/ not properly defined; 2) an unaccounted end-member is a significant source in the system; 3) the samples are not all from the same geochemical system. End-member values must also be attributed to radiocarbon dates and $\delta^{13}$C of each end-member source. These can be measured using other parameters (e.g. Tritium dating for rainwater) or derived from general principles (e.g. most carbonate rocks are radiocarbon dead).
1.5) Quantifying sources of DIC

1.5.1 Carbonate quantification

The rest of this example is a silicate-carbonate-rainwater system however this can be adapted for other geological settings. From the absolute concentrations of calcium and magnesium and from carbonate calculated using Equation 8, it is possible to calculate the DIC from carbonate. Assuming that the predominant minerals are Dolomite \((\text{MgCa(CO}_3)_2)\) and Calcite \((\text{CaCO}_3)\) this means all magnesium comes from dolomite and the concentration of calcium from dolomite is the same as the concentration of magnesium from dolomite thus the calcium from calcite is the total calcium concentration minus the magnesium concentration. From these rules and the stoichiometry of carbonate mineral dissolution, the concentration of bicarbonate from each mineral phase can be calculated. The reaction takes place due to the processes of acid rain, therefore, each mole of mineral dissolved bicarbonate will also be accompanied by a mole of rain derived bicarbonate hence the stoichiometric calculation is doubled. The bicarbonate, as calculated, is equal to the entirety of the DIC from carbonate dissolution, this is because although post-dissolution bicarbonate will undergo changes in speciation (dictated by pH) as long as no precipitation occurs it will remain as part of the DIC. All of this is represented in Equation 13, Equation 14 and Equation 15.

**Equation 13**

\[
[\text{DIC}]_{\text{Dol}} = ([\text{Mg}]_{\text{Cb}} \times 2) \times 2
\]

**Equation 14**

\[
[\text{DIC}]_{\text{Cal}} = ([\text{Ca}]_{\text{Cb}} - [\text{Mg}]_{\text{Cb}}) \times 2
\]

**Equation 15**

\[
[\text{DIC}]_{\text{Cb}} = [\text{HCO}_3]^+_{\text{Cal}} + [\text{HCO}_3]^+_{\text{Dol}}
\]

1.5.2 Silicate quantification

The absolute concentrations of Calcium and Magnesium dissolution can be calculated from in the same approach as the carbonate quantification, but using the silicate proportions instead (Equation 8). Having calculated the absolute concentrations of calcium and magnesium from silicates it is possible to use the stoichiometric relationships of silicate dissolution in acid rain to calculate the concentration of DIC introduced into the system from this weathering reaction. For this, simple mineral phases are assumed, for example, Magnesium is assumed to be all from Forsterite \((\text{Mg}_2\text{SiO}_4)\) and Calcium from Larnite \((\text{Ca}_2\text{SiO}_4)\). Like with carbonate, DIC is equal to bicarbonate. For
other sites, it may be important to assume other mineral phases are present. This calculation is shown in Equation 16.

\[ [\text{DIC}]_{\text{SIL}} = [\text{Ca}]_{\text{SIL}} \times 2 + [\text{Mg}]_{\text{SIL}} \times 2 \]

1.5.3 Rainwater quantification

It is not possible to calculate the proportion of DIC from rainwater from any stoichiometric principle because by definition it does not come from any dissolution. Instead, a tracing method is used. It is assumed that the ratio of calcium and magnesium to DIC in rainwater is the same as the ratio of calcium and magnesium to DIC in rainwater when it is a constituent of groundwater. Therefore, the concentration of calcium and magnesium from rainwater in groundwater is calculated using Equation 8 and the ratio of DIC to magnesium and calcium from the end-member is used to calculate the DIC from rainwater in the groundwater (Equation 17).

\[ [\text{DIC}]_{\text{RW}} = \frac{[\text{DIC}]_{\text{RW}-EM}}{[\text{Ca}]_{\text{RW}-EM} + [\text{Mg}]_{\text{RW}-EM}} \times ([\text{Ca}]_{\text{RW}} + [\text{Mg}]_{\text{RW}}) \]

1.5.4 Organic Matter quantification

Having quantified the concentration from all sources of the geological inputs of DIC all remaining DIC is assumed to be from the oxidation of OM. Therefore, by subtracting the concentrations from the geological sources (rainwater, carbonate, and silicate) the concentration of DIC from OM oxidation is calculated (Equation 18).

\[ [\text{DIC}]_{\text{OM}} = [\text{DIC}]_{\text{T}} - [\text{DIC}]_{\text{cb}} - [\text{DIC}]_{\text{rw}} - [\text{DIC}]_{\text{sil}} \]

1.6) Radiocarbon and $\delta^{13}$C correction

$\Delta^{14}$C is used in the radiocarbon correction (consistent with Tamers’ and Pearson’s models which are also mass balance models). The correction works using age-concentration (AgeConc), an amended version of the established term “age-mass”. In age-mass, it is assumed that that age itself is not conserved in the aquifer, but the product of mass and age is (Bethke and Johnson, 2002; Goode, 1996). With AgeConc, the age and $\delta^{13}$C of total DIC in groundwater is the product of the averaged sum of inputs (i.e. carbonate, silicate, rainwater and organic matter oxidation), given that each input has an individual radiocarbon age and $\delta^{13}$C changes in the proportion of DIC from a given input will change the total DIC age or $\delta^{13}$C. Therefore to calculate the age of DIC from a source with
an unknown age (in this case OM) all sources with a known age must be subtracted from the total AgeConc. AgeConc is calculated in Equation 19. In Equation 19 x can be an end-member (with known radiocarbon age) or the total DIC concentration and bulk radiocarbon age.

Equation 19

\[ \text{AgeConc}_x = [\text{DIC}]_x \cdot \Delta^{14}C_x \]

By subtracting the sum of AgeConc of source specific DIC (Equation 19) from the AgeConc of bulk DIC leaves the AgeConc of DIC from oxidised OM (Equation 20). By dividing the AgeConc of the DIC from OM by the concentration of DIC from OM the corrected age for OM is calculated (Equation 21).

Equation 20

\[ \text{AgeConc}_{\text{OM}} = \text{AgeConc}_T - \sum \text{AgeConc}_x \]

Equation 21

\[ \Delta^{14}C_{\text{OM}} = \frac{\text{AgeConc}_{\text{OM}}}{[\text{DIC}]_{\text{OM}}} \]

The correction of $\delta^{13}C$ is almost identical to the radiocarbon age correction except that AgeConc is replaced with C13Conc. The process is outlined in Equation 22 to Equation 25 this reveals the concentration $\delta^{13}C$ of DIC from the oxidation of OM (in Equation 25 as DIC-OM). To calculate the value of OM from which DIC was oxidised fractionation of carbonate species must be accounted for using Equation 26 (the speciation proportions are calculated from the pH of the groundwater sample) (Cerling, 1984; Doerr and Münnich, 1980).

Equation 22

\[ \text{C13Conc}_x = [\text{DIC}]_x \cdot \delta^{13}C_x \]

Equation 23

\[ \text{C13Conc}_T = [\text{DIC}]_T \cdot \delta^{13}C_T \]

Equation 24

\[ \text{C13Conc}_{\text{OM}} = \text{C13Conc}_T - \sum \text{C13Conc}_x \]

Equation 25

\[ \delta^{13}C_{\text{DIC-OM}} = \frac{\text{C13Conc}_{\text{OM}}}{[\text{DIC}]_{\text{OM}}} \]

Equation 26
\[
\delta^{13}C_{CO_2(aq)} = \delta^{13}C_{TIC} - \epsilon^{13}C_{HCO_3^- (aq)} \times \%HCO_3^- (aq) - \epsilon^{13}C_{HCO_3^- (aq)} \times \%CO_2(aq) + 4.4
\]

2) Methodology

2.1 Locality, sample collection and groundwater measurements

The study site is located in Cambodia about 10 km south of the capital Phnom Penh in an area called Kandal Province. It is divided into two localities the first a predominantly sandy transect running perpendicular to the Bassac river for about 4.5 km (T-Sand) and another transect about 6 km due west, extending for 3 km from the Mekong with mixed sand and clay sediments (T-Clay). Geomorphologically, T-Sand consists of recent shallow clay sediments, overlying older sandy sediments, whilst T-Clay consists of early Holocene sediments at LR14 and younger sandy sediments incised into the early Holocene sediments (Magnone et al., n.d.). Samples were collected both pre and post Monsoon. The groundwater has high levels of modern rainwater (Lawson et al., 2016, 2013; Richards et al., 2016). The sites are labelled LRXX-#-PRE/POST where LRXX refers to the site, # states the depth and PRE/POST refers to the season of collection, e.g. LR01-6-PRE was from site LR01 from 6 m deep and was collected before the monsoon.

Groundwater wells were constructed using manual rotatory drilling and flushed several months after drilling to remove contaminant drilling fluid (surface water). This was quantified using a Lithium tracer, full details of the methods can be found in Richards et al., (2015). $^{87}$Sr/$^{86}$Sr and cation samples were filtered to µm 0.45 (cellulose and polypropylene syringe filters, Minisart RC, UK) and acidified in the field to pH 2 with nitric acid (trace grade nitric acid, BDH Aristar, UK). 2.5 L was collected for $^{14}$C DOC analysis. All above samples were stored in fridges at first in Cambodia and then in Manchester, UK at -20 °C before analysis. 500 ml of water was collected for $^{14}$C DIC samples which were collected in 1L FlexFoil Plus bags which had been pre-flushed with nitrogen at the University of Manchester. These were frozen for storage before analysis. This is consistent with earlier methods (Bryant et al., 2013).

2. 2 Defining end-members (rainwater)

Rainwater composition is from the World Data Center for Precipitation Chemistry (WDCPC) from stations in Thailand and Malaysia collected between 1996 – 2016 and 1987 – 2016 respectively (“World Data Centre for Precipitation Chemistry,” 2016). Additional DIC data were taken from a site in Western Thailand (Panyakapo and Onchang, 2008). A strontium isotopic sample was collected from a rainwater collection tank located at the field laboratory and prepared in the same way as the groundwater samples.
3.3 Sequential extractions

Sequential extractions were undertaken to obtain the composition of the carbonate and silicate fractions of sediments. The processes were adapted from previous studies of similar sediments and is suitable for $^{87}\text{Sr}/^{86}\text{Sr}$ analysis as well as compositional analysis (Colin et al., 2006; Jacobson and Blum, 2000; Kamenov et al., 2009; Liu et al., 2007; Mossop and Davidson, 2003). Samples were selected to cover a range of localities, depths and chemical compositions based on an XRF study of 100 sediments from the area (presented in Chapter 1 of this thesis). Sites selected were LR01-6, LR05-6, LR09-6, LR09-30 and LR14-30.

Oven dried samples were heated to 550 °C to remove any OM, second the carbonate phase was extracted with 5M acetic acid (Fluka) at approximately 25 °C for 24 hours and stored for further analysis, the iron oxide phase was removed using 5 % (w/w) analysis grade hydrochloric acid (FisherBrand) and finally the silicate phase was digested in a microwave oven using concentrated hydrofluoric-HCl mix. After the carbonate and Fe-oxide extraction the supernatant was removed and stored for further preparation and the sample washed five times using a centrifuge. Silicate and carbonate samples were evaporated to incipient dryness before being re-dissolved in 5% HCl for analysis.

3.4 Analytical techniques

pH was measured in the field, along with DO, ORP and temperature using a multiprobe (YSI, Professional Plus). Alkalinity ($\text{HCO}_3^- + \text{CO}_3^{2-}$) was measured in the field using a field titration kit (Aquamerck 111109, Merck, Germany) and corroborated using Gran Titration method within 24 hours, all reported as $\text{HCO}_3^-$. $\text{H}_2\text{CO}_3$ was calculated from pH and log K ($\log[\text{HCO}_3^-] = -6.3 + \log(\text{H}_2\text{CO}_3) + \text{pH}$) for both groundwater and rainwater samples (Appelo and Postma, 2005). Cation elemental composition of water samples and sediment extracts were measured at the University of Manchester in Manchester Analytical Geochemical Unit (MAGU) using ICP-AES (Perkin-Elmer Optima 5300 dual view) with strontium concentrations determined by ICP-MS (Agilent 7500cx). The rainwater sample from the water tank was also measured for comparison to the WDCPC data.

Strontium isotopic ratios were measured at the NERC Isotope Geosciences Laboratory (NIGL) and determined by Thermal Ionisation Mass Spectrometry (TIMS) (Thermo Triton multi-collector mass spectrometer). Birck (1986)’s method was followed for loading prepared samples onto a single Re filament. All radiocarbon samples were prepared to graphite (Slota et al., 1987) at the NERC Radiocarbon Facility (East Kilbride) and analysed at the SUERC AMS (Freeman et al., 2008; Xu et al., 2004). All $\delta^{13}\text{C}$ values were measured using a dual inlet stable isotope mass spectrometer (Thermo Fisher Delta V) and are reported to the VPD. $^{14}\text{C}$ of DOC were prepared by rotary evaporating an
aliquot of the sample to a few millilitres before quantitative transfer to pre-weighed acid washed beakers. Samples were covered with glass fibre filters and freeze dried before placing in a desiccant free glass desiccator with a beaker of concentrated hydrochloric acid in order to hydrolyse any inorganic carbon present. The desiccator was placed in a water bath at 67 °C (making the internal temperature of the desiccator 63 ± 2 °C) and the air evacuated using a vacuum pump. Total carbon was recovered as CO₂, which was cryogenically isolated and graphitised with Fe/Zn reduction (Slota et al., 1987). ¹⁴C TIC samples were prepared from defrosted samples by liberating carbon as CO₂ using hydrolysis by H₃PO₄. As with DOC samples were graphitised using Fe/Zn reduction (Slota et al., 1987). All samples are normalised to δ¹³C values of the sample to account for fractionation.

3.5 PHREEQC modelling carbonate and silicate dissolution concentrations
A mineral composition of the carbonate sedimentary phase was built from the chemical composition of the extracts assuming four key minerals Calcite, Dolomite, SrCO₃ and Na₂CO₃. Appropriate water end-members were modelled in PHREEQC using dissolution into the rainwater end-member. A mineral composition of the silicate sedimentary phase was built from the chemical composition of the extract based on appropriate plagioclase (Albite, Anorthite and K-Feldspar) minerals and Talc as an Mg-silicate which are all suitable minerals in the circum-Himalayan sediments (Galy and France-Lanord, 2001, 1999; Rowland et al., 2007; Uddin and Lundberg, 1998). Appropriate water end-members were modelled in PHREEQC using dissolution into rainwater. The accompanying PHREEQC scripts for both end-members are presented in the supplementary information.

3) Results
3.1 Groundwater concentration and radiocarbon dates
pH of this groundwater covers a neutral range with pH from 6.60 to 7.53 and a mean of 6.97, generally, the shallower groundwaters are slightly more acidic and the deeper waters slightly more alkaline. DIC (the sum of the inorganic carbonate species) ranges from 4.77 mM to 20.56 mM and a has a mean of 9.09 mM, due to the neutral pH most of this is dominated by the HCO₃⁻ which ranges from 67 to 94 % of DIC. The most dominant of the geologically sourced elements (i.e. no organic component only lithological and rainwater) is sodium, which ranges from 0.30 to 3.96 mM with a mean of 1.33 mM and calcium, which ranges from 0.78 to 2.82 mM and has a mean of 1.67 mM. Magnesium has a lower concentration than the other geologically sourced elements ranging from 0.45 to 1.94 mM and has a mean of 0.95 mM. This means that the Ca/Na ratios are higher than Mg/Na with a maximum of 4.72 (mM/mM) and a mean of 1.87 (mM/mM) whilst Mg/Na has a maximum of only 2.53 (mM/mM) and a mean of 1.03 (mM/mM) both have low minimums of 0.40
(mM/mM) and 0.25 (mM/mM) respectively. These ranges mark minimum and maximum values for the end-member concentrations as outlined in the rules in section 1.4 i.e. the end-members must encapsulate these ranges. Those with a higher Ca/Na ratio and Mg/Na ratio are generally from T-Sand and the lower ratios generally from T-Clay. Strontium is only a trace element in these groundwaters, like in most others, with a range from 2.05 µM to 6.85 µM and a mean of 3.84 µM. Isotopically they range from 0.71055 to 0.71250. Generally, higher ratios are found in T-Clay than T-Sand this is described in Table 5.

Table 5 Geochemistry of the Groundwaters of Kandal Province, Cambodia (all data from Richards et al., (n.d.) except $^{87}$Sr/$^{86}$Sr and carbonate speciation calculations this study).

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<th>H$_2$CO$_3$ (mM)</th>
<th>Mg (mM)</th>
<th>Ca (mM)</th>
<th>Na (mM)</th>
<th>Sr (µM)</th>
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<td>LR14-6-PRE</td>
<td>6.95</td>
<td>7.5</td>
<td>1.68</td>
<td>1.05</td>
<td>1.75</td>
<td>3.63</td>
<td>2.75</td>
</tr>
<tr>
<td>LR14-15-PRE</td>
<td>6.64</td>
<td>11</td>
<td>5.03</td>
<td>0.98</td>
<td>1.89</td>
<td>3.96</td>
<td>3.95</td>
</tr>
<tr>
<td>LR14-21-PRE</td>
<td>6.61</td>
<td>14</td>
<td>6.76</td>
<td>1.0</td>
<td>1.93</td>
<td>1.80</td>
<td>5.16</td>
</tr>
<tr>
<td>LR14-30-PRE</td>
<td>6.78</td>
<td>8.7</td>
<td>2.88</td>
<td>1.17</td>
<td>1.56</td>
<td>1.49</td>
<td>4.48</td>
</tr>
</tbody>
</table>

Max 7.53 14.50 6.76 1.94 2.82 3.96 6.85 0.71250
Min 6.60 3.30 0.56 0.45 0.78 0.30 2.05 0.71055
Mean 6.97 7.24 1.86 0.95 1.67 1.32 3.84 0.71123
St. Dev. 0.25 3.21 1.64 0.41 0.57 0.94 1.24 0.00046
skew 0.50 0.89 1.88 0.97 0.53 1.23 0.64 0.8
n 34 34 34 33 34 34 34 30

a Sample identification LRXX-#-PRE/POST where XX denotes the site, # denotes the depth and PRE/POST denotes the season of collection.

b pH of groundwater samples

c Bicarbonate concentration in mM.

d Carbonic acid concentration in mM.

e Magnesium concentration in mM.

f Calcium concentration in mM.

g Strontium concentration in µM.

h Strontium isotopic ratio (87Sr/86Sr)

n.d. = No data.
TIC in this groundwater is relatively young ranging from the post-bomb carbon of 95 $\Delta^{14}$C ‰ to considerably older -535 $\Delta^{14}$C ‰ with a mean -91 $\Delta^{14}$C ‰. DOC has a much broader and predominantly older range of ages than the DIC. The youngest DOC is modern carbon with a $\Delta^{14}$C ‰ of -8.96 and the oldest has a $\Delta^{14}$C ‰ of -728 the mean $\Delta^{14}$C ‰ is -333. The $\delta^{13}$C of the DOC covers, very broadly the C3 plant range with a mean of -31.4 ‰ and a range -16.2 to -43.52 ‰ however the $\delta^{13}$C of the DIC is much less negative with a range of 3.44 to -20.78 ‰ and a mean of -12.95 ‰ which is more indicative of a range of mixed sources. These values are presented in Table 6.

_Table 6 Radiocarbon dates of DIC and DOC of the groundwaters of Kandal Province, Cambodia_

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\delta^{13}$C ‰ (DIC)</th>
<th>$\Delta^{14}$C ‰ (DIC)</th>
<th>Publication code (DIC)</th>
<th>$\delta^{12}$C ‰ ± 0.1 (DOC)</th>
<th>$\Delta^{14}$C ‰ (DOC)</th>
<th>Publication code (DOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR01-6-POST</td>
<td>-12.4</td>
<td>-18.2 ± 4.53</td>
<td>SUERC-62509</td>
<td>-24.1</td>
<td>-207 ± 3.69</td>
<td>SUERC-56905</td>
</tr>
<tr>
<td>LR01-15-POST</td>
<td>-17.5</td>
<td>95.7 ± 5.05</td>
<td>SUERC-62510</td>
<td>-30.3</td>
<td>-143 ± 3.78</td>
<td>SUERC-56895</td>
</tr>
<tr>
<td>LR01-30-POST</td>
<td>-17.5</td>
<td>27.3 ± 4.74</td>
<td>SUERC-62511</td>
<td>-16.2</td>
<td>-8.96 ± 4.58</td>
<td>SUERC-58889</td>
</tr>
<tr>
<td>LR01-45-POST</td>
<td>-19.7</td>
<td>-197 ± 3.72</td>
<td>SUERC-62512</td>
<td>-25.3</td>
<td>-257 ± 3.5</td>
<td>SUERC-57670</td>
</tr>
<tr>
<td>LR05-15-POST</td>
<td>-8.8</td>
<td>79.6 ± 4.99</td>
<td>SUERC-62514</td>
<td>-31.2</td>
<td>-24.7 ± 4.52</td>
<td>SUERC-56900</td>
</tr>
<tr>
<td>LR05-30-POST</td>
<td>n.d.</td>
<td>n.d.</td>
<td>N/A</td>
<td>-42.3</td>
<td>-467 ± 2.49</td>
<td>SUERC-64798</td>
</tr>
<tr>
<td>LR09-9-POST</td>
<td>-8.9</td>
<td>-67.2 ± 4.31</td>
<td>SUERC-62518</td>
<td>-32.9</td>
<td>-372 ± 2.96</td>
<td>SUERC-64799</td>
</tr>
<tr>
<td>LR09-30-POST</td>
<td>-14.4</td>
<td>-74.4 ± 4.3</td>
<td>SUERC-62520</td>
<td>n.d.</td>
<td>n.d.</td>
<td>N/A</td>
</tr>
<tr>
<td>LR01-6-PRE</td>
<td>-8.4</td>
<td>-26.6 ± 4.27</td>
<td>SUERC-55302</td>
<td>-38.9</td>
<td>-637 ± 1.79</td>
<td>SUERC-64788</td>
</tr>
<tr>
<td>LR01-9-PRE</td>
<td>-6.5</td>
<td>17.2 ± 4.47</td>
<td>SUERC-56190</td>
<td>-26.7</td>
<td>-146 ± 3.77</td>
<td>SUERC-57669</td>
</tr>
<tr>
<td>LR01-15-PRE</td>
<td>-15.8</td>
<td>83.7 ± 5.12</td>
<td>SUERC-55292</td>
<td>-35.4</td>
<td>-528 ± 2.22</td>
<td>SUERC-64790</td>
</tr>
<tr>
<td>LR01-30-PRE</td>
<td>-18</td>
<td>30.3 ± 4.52</td>
<td>SUERC-56184</td>
<td>-38.1</td>
<td>-435 ± 2.62</td>
<td>SUERC-64791</td>
</tr>
<tr>
<td>LR01-45-PRE</td>
<td>-20.8</td>
<td>-186 ± 3.58</td>
<td>SUERC-56191</td>
<td>-37.8</td>
<td>-604 ± 1.87</td>
<td>SUERC-64795</td>
</tr>
<tr>
<td>LR02-30-PRE</td>
<td>n.d.</td>
<td>n.d.</td>
<td>N/A</td>
<td>n.d.</td>
<td>n.d.</td>
<td>N/A</td>
</tr>
<tr>
<td>LR05-6-PRE</td>
<td>-17.3</td>
<td>49.5 ± 4.84</td>
<td>SUERC-62513</td>
<td>-43.5</td>
<td>-728 ± 1.46</td>
<td>SUERC-64796</td>
</tr>
<tr>
<td>LR05-15-PRE</td>
<td>-7.8</td>
<td>80.2 ± 4.74</td>
<td>SUERC-55299</td>
<td>-36.8</td>
<td>-293 ± 3.27</td>
<td>SUERC-64797</td>
</tr>
<tr>
<td>LR09-6-PRE</td>
<td>-16.5</td>
<td>16.6 ± 4.46</td>
<td>SUERC-56185</td>
<td>-41.3</td>
<td>-638 ± 1.77</td>
<td>SUERC-64801</td>
</tr>
<tr>
<td>Sample identification LRXX-#-PRE/POST where XX denotes the site, # denotes the depth and PRE/POST denotes the season of collection.</td>
<td>δ¹³C of dissolved inorganic carbon (DIC).</td>
<td>Δ¹⁴C of DIC.</td>
<td>Radiocarbon Publication Code for DIC.</td>
<td>δ¹³C of dissolved inorganic carbon (DOC).</td>
<td>Δ¹⁴C of DOC.</td>
<td>Radiocarbon Publication Code for DOC.</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>LR09-9-PRE</td>
<td>-3</td>
<td>-29.2 ± 4.47</td>
<td>SUERC-62519</td>
<td>-39.5</td>
<td>-446 ± 2.43</td>
<td>SUERC-64800</td>
</tr>
<tr>
<td>LR09-30-PRE</td>
<td>-11.2</td>
<td>-80.4 ± 4.36</td>
<td>SUERC-55293</td>
<td>-27.6</td>
<td>-116 ± 4.11</td>
<td>SUERC-56896</td>
</tr>
<tr>
<td>LR09-45-PRE</td>
<td>-20</td>
<td>-102 ± 3.94</td>
<td>SUERC-55812</td>
<td>-26.2</td>
<td>-172 ± 3.92</td>
<td>SUERC-57673</td>
</tr>
<tr>
<td>LR10-15-POST</td>
<td>-14.7</td>
<td>-54 ± 4.2</td>
<td>SUERC-63013</td>
<td>-27.7</td>
<td>-232 ± 3.58</td>
<td>SUERC-56903</td>
</tr>
<tr>
<td>LR10-30-POST</td>
<td>-16.3</td>
<td>-268 ± 3.2</td>
<td>SUERC-63014</td>
<td>n.d.</td>
<td>n.d.</td>
<td>N/A</td>
</tr>
<tr>
<td>LR14-30-POST</td>
<td>3.4</td>
<td>-505 ± 2.4</td>
<td>SUERC-63016</td>
<td>-29.1</td>
<td>-447 ± 2.67</td>
<td>SUERC-57666</td>
</tr>
<tr>
<td>LR10-9-PRE</td>
<td>-14.3</td>
<td>-4.7 ± 4.6</td>
<td>SUERC-63012</td>
<td>n.d.</td>
<td>n.d.</td>
<td>N/A</td>
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<tr>
<td>LR10-15-PRE</td>
<td>-18.4</td>
<td>-6.7 ± 4.68</td>
<td>SUERC-55300</td>
<td>n.d.</td>
<td>n.d.</td>
<td>N/A</td>
</tr>
<tr>
<td>LR10-21-PRE</td>
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<td>-280 ± 3.37</td>
<td>SUERC-57686</td>
<td>-23.6</td>
<td>-267 ± 3.22</td>
<td>SUERC-57690</td>
</tr>
<tr>
<td>LR10-30-PRE</td>
<td>-17.5</td>
<td>-266 ± 3.45</td>
<td>SUERC-55811</td>
<td>n.d.</td>
<td>n.d.</td>
<td>N/A</td>
</tr>
<tr>
<td>LR14-6-PRE</td>
<td>-14.9</td>
<td>15 ± 4.5</td>
<td>SUERC-63015</td>
<td>n.d.</td>
<td>n.d.</td>
<td>N/A</td>
</tr>
<tr>
<td>LR14-15-PRE</td>
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<td>-389 ± 2.7</td>
<td>SUERC-55303</td>
<td>-31.3</td>
<td>-524 ± 2.2</td>
<td>SUERC-56906</td>
</tr>
<tr>
<td>LR14-30-PRE</td>
<td>-1.6</td>
<td>-535 ± 2.04</td>
<td>SUERC-56189</td>
<td>n.d.</td>
<td>n.d.</td>
<td>N/A</td>
</tr>
</tbody>
</table>

3.2 Sediment extraction results

The \(^{87}\text{Sr}/^{86}\text{Sr}\) of the silicate and carbonate fraction are each distinct from each other with the former having a value of 0.72033 ± 0.00022 and the latter a value of 0.71223 ± 0.00020. The silicate value is in keeping with previous studies in the region conducted north of this study site in the Tonle Sapp (Day et al., 2011) and across the Mekong (Liu et al., 2007) as far as the authors are aware no measurement of the carbonate fraction has been undertaken in the Mekong drainage basin.
The composition of the sediments is dominated by the silicate phase, which has very high concentrations of potassium and sodium, and which have means of 220 mmol/Kg and 161 mmol/Kg respectively, with lower concentrations of magnesium (73.6 mmol/Kg) and the lowest concentration of Calcium at 26.3 mmol/Kg. The carbonate phase has high concentrations of calcium (41.9 mmol/Kg) and magnesium (16.4 mmol/Kg) and much lower concentrations of potassium and sodium (5.8 mmol/Kg and 2.7 mmol/Kg respectively). In both the silicate and carbonate phase strontium concentrations are low with a concentration of 345 ± 116 µmol/kg in the silicate and 43.4 ± 9.3 µmol/kg in the carbonate phase. This equates to a carbonate mineral phase of 59.0 ± % Calcite, 37.8 ± % Dolomite, 3.1 ± % Na₂CO₃ and a 0.1 % SrCO₃ with a total composition of 43.4 mmol/Kg. The silicate phase consists of 37.2 % Albite, 6.1 % Anorthite, 51.0 % K-Feldspar, 5.7 % Talc and 0.04% of SrSiO₄ with a total of 431 mmol/Kg. This is all defined in Table 7.
Table 7 Sedimentary composition as defined by carbonate and silicate fractions from sequential extractions for selected sites from Kandal Province, Cambodia.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>87Sr/86Sr</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
<th>Na</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample ID</td>
<td>(mmol/Kg)</td>
<td>(mmol/Kg)</td>
<td>(mmol/Kg)</td>
<td>(mmol/Kg)</td>
<td>(µmol/Kg)</td>
<td>(µmol/Kg)</td>
</tr>
<tr>
<td>LR01-6</td>
<td>0.72031</td>
<td>39.6</td>
<td>130</td>
<td>320</td>
<td>229</td>
<td>720</td>
</tr>
<tr>
<td>LR05-6</td>
<td>0.72056</td>
<td>13.0</td>
<td>24.0</td>
<td>210</td>
<td>160</td>
<td>79.8</td>
</tr>
<tr>
<td>LR09-6</td>
<td>0.72083</td>
<td>32.3</td>
<td>114</td>
<td>248</td>
<td>168</td>
<td>364</td>
</tr>
<tr>
<td>LR09-30</td>
<td>0.71954</td>
<td>7.60</td>
<td>5.10</td>
<td>89.7</td>
<td>40.9</td>
<td>125</td>
</tr>
<tr>
<td>LR14-30</td>
<td>0.72042</td>
<td>39.1</td>
<td>93.9</td>
<td>232</td>
<td>204</td>
<td>436</td>
</tr>
<tr>
<td>Mean</td>
<td>0.72033 ± 0.00022</td>
<td>26.3 ± 6.72</td>
<td>73.6 ± 25.0</td>
<td>220 ± 37.4</td>
<td>161 ± 32.5</td>
<td>345 ± 116</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>87Sr/86Sr</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
<th>Na</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample ID</td>
<td>(mmol/Kg)</td>
<td>(mmol/Kg)</td>
<td>(mmol/Kg)</td>
<td>(mmol/Kg)</td>
<td>(µmol/Kg)</td>
<td>(µmol/Kg)</td>
</tr>
<tr>
<td>LR01-6</td>
<td>0.71158</td>
<td>71.1</td>
<td>32.0</td>
<td>9.1</td>
<td>3.9</td>
<td>79.6</td>
</tr>
<tr>
<td>LR05-6</td>
<td>0.71216</td>
<td>43.4</td>
<td>15.6</td>
<td>7.5</td>
<td>3.3</td>
<td>39.9</td>
</tr>
<tr>
<td>LR09-6</td>
<td>0.71212</td>
<td>46.2</td>
<td>16.4</td>
<td>6.6</td>
<td>3.1</td>
<td>37.5</td>
</tr>
<tr>
<td>LR09-30</td>
<td>0.71275</td>
<td>10.5</td>
<td>1.30</td>
<td>1.3</td>
<td>0.8</td>
<td>29.4</td>
</tr>
<tr>
<td>LR14-30</td>
<td>0.71257</td>
<td>38.4</td>
<td>16.6</td>
<td>4.7</td>
<td>2.2</td>
<td>30.8</td>
</tr>
<tr>
<td>Mean</td>
<td>0.71223 ± 0.00020</td>
<td>41.9 ± 9.67</td>
<td>16.4 ± 4.85</td>
<td>5.84 ± 1.33</td>
<td>2.66 ± 0.54</td>
<td>43.4 ± 9.25</td>
</tr>
</tbody>
</table>

**Lithological Mineral End-member Compositions**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>mmol/kg</th>
<th>%</th>
<th>Mineral</th>
<th>mmol/kg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>25.6 ± 10.8</td>
<td>59 ± 25</td>
<td>NaAlSi₃O₈</td>
<td>161 ± 32.5</td>
<td>37 ± 8</td>
</tr>
<tr>
<td>MgCa(CO₃)₂</td>
<td>16.4 ± 4.8</td>
<td>38 ± 11</td>
<td>CaAl₂Si₂O₈</td>
<td>26.3 ± 6.72</td>
<td>6.1 ± 1.6</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>1.3 ± 0.3</td>
<td>3.1 ± 0.6</td>
<td>KaSi₃O₈</td>
<td>220 ± 37.4</td>
<td>51 ± 8.7</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>0.04 ± 0.01</td>
<td>0.10 ± 0.02</td>
<td>Mg₃Si₄O₁₀(OH)₂</td>
<td>24.5 ± 8.33</td>
<td>5.7 ± 1.9</td>
</tr>
<tr>
<td>Total</td>
<td>43.3 ± 16.0</td>
<td>Total</td>
<td>432 ± 84.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Sample identification LRXX-#-PRE/POST where XX denotes the site, # denotes the depth and PRE/POST denotes the season of collection.

b 87Sr/86Sr ratio of given lithological phase (carbonate or silicate).
Calcium concentration of lithological phase (carbonate or silicate) in mmol/Kg.

Magnesium concentration of lithological phase (carbonate or silicate) in mmol/Kg.

Potassium concentration of lithological phase (carbonate or silicate) in mmol/Kg.

Sodium concentration of lithological phase (carbonate or silicate) in mmol/Kg.

Strontium concentration of lithological phase (carbonate or silicate) in µmol/Kg.

Mineral composition of the lithological end-members using Equation 9 to Equation 12.

Mineral in given phase.

Concentration of mineral in given phase (mmol/kg).

Percentage of mineral in given phase.

3.3 End-member results from PHREEQ-C modelling

Dissolution of mineral compositions for the carbonate and silicate phases as defined in Table 7 were modelled in PHREEQ-C to calculate the corresponding hydrological end-member waters for the model. PHREEQ-C modelling (Figure 12) shows that in the carbonate minerals Na$_2$CO$_3$ never reach a saturation index (SI) of 0 and the SI never plateaus therefore the peak Ca/Na and peak Mg/Na are selected following the rules from section 1.5. This is the water composition after the dissolution of 0.2 mili-moles of the carbonate assemblage. All of the silicate minerals reach saturation, therefore at 0.15 mili-moles of silicate dissolution, when Talc has an SI of 0) the water composition is selected. These compositions are presented in Table 8.

![Figure 12 PHREEQ-C results for the calculation of carbonate and silicate groundwater end-members for utilisation by the model presented in this study.](image-url)
The calcium, magnesium and sodium concentrations in the rainwater end-members are between one and two magnitudes lower than the silicate and carbonate hydrological end-members. The Ca/Na and Mg/Na of carbonate are calculated to be $6.12 \pm 0.81$ and $3.02 \pm 0.33$ respectively, both of which are greater than the highest groundwater ratio and therefore fulfil the criteria of the model. The lowest Ca/Na ratio is from the silicate end-member which has a value of $0.19 \pm 0.01$ whilst rainwater has a value of $0.25 \pm 0.02$. The lowest Mg/Na ratio is the rainwater end-member which has a value of $0.13 \pm 0.01$ whilst the silicate ratio is $0.37 \pm 0.08$. In both cases, the lowest ratio is less than the lowest groundwater ratio and therefore fulfils the criteria of the model.

Rainwater has an $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.70929, this is close to the modern seawater value of 0.7092 (McArthur et al., 2001) and which is as expected given that seawater is the primary source of rainwater. This value is far lower than any of the groundwater samples so fulfils the criteria for minimum end-member whilst the high silicate value ($0.72033 \pm 0.00022$) far exceeds the maximum groundwater concentration of 0.71250 therefore together the end-member compositions (Table 8) fulfil the criteria of the model.

Tritium dating from previous studies at this site has found high levels of post-1960s tritium present (Lawson et al., 2016, 2013; Richards et al., 2016) therefore the $\Delta^{14}\text{C}$ ‰ of DIC from rainwater is assumed to be dominated by bomb carbon and will have a composition of 600 ‰. Based on the pH the DIC split is 44.3 % HCO$_3^-$ and 55.7 % H$_2$CO$_3^-$ therefore based on fractionation principles the $\delta^{13}\text{C}$ of DIC in this rainwater is -3.6 ‰ (Appelo and Postma, 2005). Carbonate dissolution contains DIC in equal proportions from rainwater and carbonate dissolution. Carbonate minerals are assumed to be carbon dead and rainwater is assumed to be bomb-carbon, therefore, an age of -200 ‰ is assumed for this end-member. The $\delta^{13}\text{C}$ of DIC from carbonate dissolution been studied and due to fractionation is assumed to be -16 ‰ in closed systems (i.e. T-Sand deep sands) and between -12 ‰ and -5 ‰ in open systems depending on plant material present, therefore in the shallow clays in T-Sand -5 ‰ is assumed (Appelo and Postma, 2005). Carbonate from silicate dissolution entirely comes from rainwater, therefore, the $\Delta^{14}\text{C}$ ‰ is assumed to be 600 ‰ and the $\delta^{13}\text{C}$ to be +2 ‰ because only the HCO$_3^-$ is considered.
Table 8 End-member compositions calculated from sequential extractions and PHREEQC modelling for utilisation in the model presented by this study.

<table>
<thead>
<tr>
<th>End-Member</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>Sr (µM)</th>
<th>DIC **</th>
<th>pH **</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rainwater (µM)*</td>
<td>6.97 ± 0.34</td>
<td>3.72 ± 0.20</td>
<td>27.88 ± 1.91</td>
<td>0.67 ± n.d.</td>
<td>16.40 ± n.d.</td>
<td>6.00 ± n.d.</td>
</tr>
<tr>
<td>Carbonate (mM)</td>
<td>0.44 ± 0.04</td>
<td>0.22 ± 0.01</td>
<td>0.07 ± 0.01</td>
<td>0.59 ± 0.10</td>
<td>N.C.</td>
<td>N.C.</td>
</tr>
<tr>
<td>Silicate (mM)</td>
<td>0.02 ± 0.00</td>
<td>0.03 ± 0.01</td>
<td>0.09 ± 0.00</td>
<td>0.13 ± 0.01</td>
<td>N.C.</td>
<td>N.C.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ca/Na</th>
<th>Mg/Na</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>$\Delta^{14}$C ‰</th>
<th>$\delta^{13}$C ‰</th>
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</thead>
<tbody>
<tr>
<td>Rainwater</td>
<td>0.25 ± 0.02</td>
<td>0.13 ± 0.01</td>
<td>0.709290</td>
<td>600</td>
<td>-3.6</td>
</tr>
<tr>
<td>Carbonate (Deep)</td>
<td>6.12 ± 0.81</td>
<td>3.02 ± 0.33</td>
<td>0.71223 ±</td>
<td>-200</td>
<td>-12</td>
</tr>
<tr>
<td>Carbonate (Shallow)</td>
<td>0.81</td>
<td>0.33</td>
<td>0.00020</td>
<td>-5</td>
<td></td>
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<tr>
<td>Silicate</td>
<td>0.19 ± 0.01</td>
<td>0.37 ± 0.08</td>
<td>0.72033 ±</td>
<td>600</td>
<td>2</td>
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</tbody>
</table>

3.4 Mixing model and $^{14}$C and $\delta^{13}$C correction model results

Figure 13A and Figure 13B are the visual representations of the mixing model analysis. These plots show that the three end-members can represent all of the solute input from calcium and magnesium for all sites. The interpretation of the mixing model outputs in conventional ternary diagrams is shown in Figure 13C and Figure 13D with raw values available in Table 9. This shows that on T-Clay carbonate dissolution is of limited importance to the total amount of calcium and magnesium with it rarely has an input greater than 20%. On T-Sand the proportion of carbonate to calcium and magnesium changes from <20% to ≈80%. On both transects, depth, and not the distance from the rivers, is the most important predictor of the proportion of carbonate in the system. The shallower the water the greater the proportion of calcium or magnesium from carbonate. In the calcium model % carbonate = -0.009depth (m) + 0.46 ($R^2 = 0.59$) whilst in the magnesium model % carbonate = -0.010depth (m) + 0.49 ($R^2 = 0.81$).
Figure 13 Mixing model analysis for calcium (A) and magnesium (B) and interpretation in conventional ternary diagrams (C, D respectively).
Table 9 Mixing model output results for calcium and magnesium from different end-members for the groundwaters of Kandal Province, Cambodia.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ca from silicate</th>
<th>Ca from Carbonate</th>
<th>Ca from rainwater</th>
<th>Mg from silicate</th>
<th>Mg from carbonate</th>
<th>Mg from rainwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-Sand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LR01-6-POST</td>
<td>25 ± 1.4%</td>
<td>42 ± 3.5%</td>
<td>33 ± 3.7%</td>
<td>24 ± 2.3%</td>
<td>44 ± 4.3%</td>
<td>32 ± 3.8%</td>
</tr>
<tr>
<td>LR01-30-POST</td>
<td>47 ± 1.9%</td>
<td>18 ± 1.6%</td>
<td>36 ± 3.3%</td>
<td>50 ± 4.0%</td>
<td>13 ± 3.3%</td>
<td>37 ± 2.6%</td>
</tr>
<tr>
<td>LR01-45-POST</td>
<td>45 ± 1.7%</td>
<td>7 ± 0.6%</td>
<td>48 ± 2.8%</td>
<td>50 ± 3.9%</td>
<td>1 ± 2.9%</td>
<td>49 ± 3.0%</td>
</tr>
<tr>
<td>LR05-15-POST</td>
<td>1 ± 0.7%</td>
<td>48 ± 4.0%</td>
<td>51 ± 3.2%</td>
<td>15 ± 1.3%</td>
<td>32 ± 3.5%</td>
<td>53 ± 3.9%</td>
</tr>
<tr>
<td>LR09-9-POST</td>
<td>29 ± 1.3%</td>
<td>25 ± 2.1%</td>
<td>46 ± 3.0%</td>
<td>21 ± 1.9%</td>
<td>36 ± 3.8%</td>
<td>43 ± 3.7%</td>
</tr>
<tr>
<td>LR01-6-PRE</td>
<td>23 ± 1.3%</td>
<td>43 ± 3.6%</td>
<td>33 ± 3.8%</td>
<td>24 ± 2.3%</td>
<td>42 ± 4.2%</td>
<td>33 ± 3.7%</td>
</tr>
<tr>
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<td>39 ± 3.2%</td>
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<td>-5 ± 0.4%</td>
<td>55 ± 4.5%</td>
<td>50 ± 4.3%</td>
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<tr>
<td>LR01-15-PRE</td>
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<td>37 ± 4.1%</td>
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<tr>
<td>LR01-30-PRE</td>
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<td>15 ± 1.3%</td>
<td>46 ± 2.9%</td>
<td>43 ± 3.4%</td>
<td>11 ± 3.1%</td>
<td>46 ± 3.1%</td>
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<tr>
<td>LR01-45-PRE</td>
<td>44 ± 1.7%</td>
<td>8 ± 0.8%</td>
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<td>49 ± 3.0%</td>
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<tr>
<td>LR02-15-PRE</td>
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<td>37 ± 3.3%</td>
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<tr>
<td>LR02-30-PRE</td>
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<td>45 ± 3.6%</td>
<td>15 ± 3.2%</td>
<td>40 ± 2.9%</td>
</tr>
<tr>
<td>LR05-6-PRE</td>
<td>23 ± 1.3%</td>
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<td>37 ± 3.2%</td>
<td>27 ± 3.6%</td>
<td>36 ± 3.2%</td>
</tr>
<tr>
<td>LR05-15-PRE</td>
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<td>27 ± 4.5%</td>
<td>27 ± 2.5%</td>
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<td>33 ± 3.6%</td>
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<td>35 ± 2.8%</td>
<td>17 ± 3.1%</td>
<td>48 ± 3.4%</td>
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<td>20 ± 1.8%</td>
<td>38 ± 3.9%</td>
<td>42 ± 3.8%</td>
</tr>
<tr>
<td>LR09-6-PRE</td>
<td>34 ± 1.7%</td>
<td>32 ± 2.7%</td>
<td>34 ± 3.5%</td>
<td>22 ± 2.2%</td>
<td>49 ± 4.6%</td>
<td>29 ± 3.9%</td>
</tr>
<tr>
<td>LR09-9-PRE</td>
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<td>20 ± 1.8%</td>
<td>50 ± 2.8%</td>
<td>23 ± 2.0%</td>
<td>28 ± 3.4%</td>
<td>49 ± 3.7%</td>
</tr>
<tr>
<td>LR09-30-PRE</td>
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<td>22 ± 1.9%</td>
<td>57 ± 2.7%</td>
<td>20 ± 1.6%</td>
<td>23 ± 3.1%</td>
<td>56 ± 4.0%</td>
</tr>
<tr>
<td>LR09-45-PRE</td>
<td>51 ± 1.9%</td>
<td>3 ± 0.3%</td>
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<td>50 ± 3.9%</td>
<td>4 ± 3.0%</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T-Clay</th>
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<tbody>
<tr>
<td>LR10-30-POST</td>
<td>34 ± 1.2%</td>
<td>8 ± 0.7%</td>
<td>57 ± 2.6%</td>
<td>39 ± 3.1%</td>
<td>3 ± 2.8%</td>
<td>58 ± 3.8%</td>
</tr>
<tr>
<td>LR14-30-POST</td>
<td>46 ± 1.8%</td>
<td>12 ± 1.0%</td>
<td>42 ± 3.0%</td>
<td>45 ± 3.6%</td>
<td>14 ± 3.2%</td>
<td>41 ± 2.9%</td>
</tr>
<tr>
<td>LR10-9-PRE</td>
<td>41 ± 1.6%</td>
<td>10 ± 0.9%</td>
<td>49 ± 2.8%</td>
<td>41 ± 3.3%</td>
<td>10 ± 3.0%</td>
<td>49 ± 3.2%</td>
</tr>
<tr>
<td>Site</td>
<td>Calcium Silicate</td>
<td>Calcium Carbonate</td>
<td>Calcium Rainwater</td>
<td>Magnesium Silicate</td>
<td>Magnesium Carbonate</td>
<td>Magnesium Rainwater</td>
</tr>
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<td>-------------------</td>
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<td>LR10-15-PRE</td>
<td>41 ± 1.6%</td>
<td>10 ± 0.9%</td>
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<td>41 ± 3.3%</td>
<td>10 ± 3.0%</td>
<td>49 ± 3.2%</td>
</tr>
<tr>
<td>LR10-21-PRE</td>
<td>35 ± 1.3%</td>
<td>6 ± 0.5%</td>
<td>59 ± 2.6%</td>
<td>39 ± 3.0%</td>
<td>2 ± 2.8%</td>
<td>59 ± 3.9%</td>
</tr>
<tr>
<td>LR10-30-PRE</td>
<td>58 ± 2.3%</td>
<td>12 ± 1.2%</td>
<td>30 ± 3.4%</td>
<td>64 ± 5.0%</td>
<td>3 ± 3.2%</td>
<td>33 ± 2.0%</td>
</tr>
<tr>
<td>LR14-6-PRE</td>
<td>52 ± 1.9%</td>
<td>4 ± 0.4%</td>
<td>44 ± 2.9%</td>
<td>55 ± 4.3%</td>
<td>-1 ± 3.0%</td>
<td>46 ± 2.7%</td>
</tr>
<tr>
<td>LR14-15-PRE</td>
<td>52 ± 1.9%</td>
<td>4 ± 0.4%</td>
<td>44 ± 2.9%</td>
<td>56 ± 4.3%</td>
<td>-2 ± 3.0%</td>
<td>46 ± 2.7%</td>
</tr>
<tr>
<td>LR14-21-PRE</td>
<td>38 ± 1.5%</td>
<td>11 ± 1.1%</td>
<td>51 ± 2.8%</td>
<td>40 ± 3.1%</td>
<td>9 ± 2.9%</td>
<td>51 ± 3.4%</td>
</tr>
<tr>
<td>LR14-30-PRE</td>
<td>60 ± 2.3%</td>
<td>14 ± 1.2%</td>
<td>27 ± 3.5%</td>
<td>59 ± 4.8%</td>
<td>15 ± 3.5%</td>
<td>26 ± 2.2%</td>
</tr>
</tbody>
</table>

*a* Sample identification LRXX-#-PRE/POST where XX denotes the site, # denotes the depth and PRE/POST denotes the season of collection.

*percentage of groundwater calcium from silicate as modelled by this study.*

*percentage of groundwater calcium from carbonate as modelled by this study.*

*percentage of groundwater calcium from rainwater as modelled by this study.*

*percentage of groundwater magnesium from silicate as modelled by this study.*

*percentage of groundwater magnesium from carbonate as modelled by this study.*

*percentage of groundwater magnesium from rainwater as modelled by this study.*

*n.d. = no data.*

DIC from the oxidation of OM as modelled by this study ranges from 1.32 ± 0.92 mM to 16.27 ± 1.06 mM and has a range of between 28 % and 80 % of the DIC. T-Clay has consistently greater concentrations of DIC from OM than T-Sand and this also represents greater proportions of DIC derived from OM in the DIC. Within T-Clay the greatest concentration of DIC from OM is in the clayey site LR14 located near a pond where DIC from OM have a mean concentration of 11.01 mM. T-Clay and LR10 have a mean concentration of 4.07 mM with the only major exception at LR09-9 in both the pre and post monsoon samples were the mean concentration is 12.57 mM. Like LR14 this depth at LR09 is clayey and it is located near the Bassac River another source of surface water. Two sites, LR01-6-PRE and LR05-6-PRE, have negative values of DIC from OM. At LR05-6-PRE this is within the model error and it is assumed that no DIC came from the oxidation of OM, however at LR01-6-PRE the negative value is outside the range of modelled error, but only by 0.72 mM, therefore, it is also assumed that no DIC came from the oxidation of OM at this site. For both of these sites, no radiocarbon calculation was undertaken.

The modelled Δ14C has a range from modern 53 ± 63.1 ‰ to radiocarbon dead of -1172 ± 183 ‰ with a mean of -479. These values are considerably older than the un-modelled DIC values. Eligible
values must be between 600 ‰ (bomb carbon) and -1000 ‰ (radiocarbon dead) and all samples are within these limits when modelled error is considered. The modelled δ¹³C ranged from -41.2 ± 6.82 to 3.56 ± 0.65 ‰. The samples are broadly divided into three key groups: group one has a very negative isotopic value with a median of -36.25 ‰ and contains about 58%; group two has a less negative isotopic median value of -16.4 ‰ and contains 21% of the samples; and finally group 3 has an isotopic value that is both positive and slightly negative this contains 21% of the samples and has a median of -3.1 ‰.

Table 10 Modelled concentrations of DIC from different geological source and that from the oxidation of OM and the corrected ages of Δ¹⁴C and δ¹³C for the groundwater of Kandal Province, Cambodia.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>DIC from Carbonate mM b</th>
<th>DIC from Silicate mM c</th>
<th>DIC Rainwater mM d</th>
<th>DIC from Organic Material mM e</th>
<th>Δ¹⁴C %o (Mod) f</th>
<th>δ¹³C %o (Mod) g</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR01-6-POST</td>
<td>3.03 ± 0.22</td>
<td>1.71 ± 0.09</td>
<td>0.97 ± 0.29</td>
<td>5.75 ± 0.47</td>
<td>-211 ± 37.7</td>
<td>-24.35 ± 1.83</td>
</tr>
<tr>
<td>LR01-15-POST</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
</tr>
<tr>
<td>LR01-30-POST</td>
<td>0.53 ± 0.06</td>
<td>1.64 ± 0.06</td>
<td>0.50 ± 0.19</td>
<td>3.46 ± 0.35</td>
<td>-292 ± 46.7</td>
<td>-31.91 ± 2.86</td>
</tr>
<tr>
<td>LR01-45-POST</td>
<td>0.14 ± 0.04</td>
<td>1.34 ± 0.05</td>
<td>0.55 ± 0.20</td>
<td>3.67 ± 0.37</td>
<td>-608 ± 71.2</td>
<td>-33.72 ± 2.91</td>
</tr>
<tr>
<td>LR05-15-POST</td>
<td>1.55 ± 0.11</td>
<td>0.54 ± 0.02</td>
<td>0.86 ± 0.24</td>
<td>3.65 ± 0.63</td>
<td>-0.77 ± 42.3</td>
<td>-11.5 ± 0.87</td>
</tr>
<tr>
<td>LR09-9-POST</td>
<td>2.50 ± 0.22</td>
<td>1.77 ± 0.09</td>
<td>1.39 ± 0.34</td>
<td>12.10 ± 0.55</td>
<td>-214 ± 22</td>
<td>-14.39 ± 0.58</td>
</tr>
<tr>
<td>LR09-30-POST</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
</tr>
<tr>
<td>LR01-6-PRE</td>
<td>3.37 ± 0.24</td>
<td>1.90 ± 0.09</td>
<td>1.12 ± 0.30</td>
<td>-0.47 ± 0.49</td>
<td>d.n.m</td>
<td>d.n.m</td>
</tr>
<tr>
<td>LR01-9-PRE</td>
<td>2.95 ± 0.21</td>
<td>-0.33 ± 0.03</td>
<td>1.24 ± 0.32</td>
<td>3.22 ± 0.49</td>
<td>53 ± 63.1</td>
<td>-10.63 ± 0.83</td>
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<tr>
<td>LR01-15-PRE</td>
<td>1.59 ± 0.12</td>
<td>1.33 ± 0.06</td>
<td>0.53 ± 0.21</td>
<td>1.32 ± 0.92</td>
<td>-303 ± 235</td>
<td>-40.76 ± 23.91</td>
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<tr>
<td>Sample</td>
<td>Effect</td>
<td>Value 1</td>
<td>Value 2</td>
<td>Value 3</td>
<td>Value 4</td>
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<td>---------</td>
<td>---------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>LR01-30-</td>
<td>PRE</td>
<td>0.46 ± 0.06</td>
<td>1.47 ± 0.05</td>
<td>0.66 ± 0.22</td>
<td>2.37 ± 0.33</td>
<td>-437 ± 84</td>
</tr>
<tr>
<td>LR01-45-</td>
<td>PRE</td>
<td>0.19 ± 0.05</td>
<td>1.54 ± 0.05</td>
<td>0.64 ± 0.21</td>
<td>3.14 ± 0.33</td>
<td>-732 ± 90.1</td>
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<tr>
<td>LR02-15-</td>
<td>PRE</td>
<td>0.89 ± 0.08</td>
<td>1.09 ± 0.05</td>
<td>0.48 ± 0.20</td>
<td>2.66 ± 0.41</td>
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</tr>
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<td>LR02-30-</td>
<td>PRE</td>
<td>0.69 ± 0.07</td>
<td>1.54 ± 0.06</td>
<td>0.59 ± 0.20</td>
<td>2.13 ± 0.34</td>
<td>N.C.</td>
</tr>
<tr>
<td>LR05-6-</td>
<td>PRE</td>
<td>2.66 ± 0.20</td>
<td>2.36 ± 0.08</td>
<td>1.07 ± 0.27</td>
<td>-1.20 ± 0.48</td>
<td>d.n.m</td>
</tr>
<tr>
<td>LR05-15-</td>
<td>PRE</td>
<td>2.20 ± 0.16</td>
<td>1.04 ± 0.03</td>
<td>0.60 ± 0.21</td>
<td>1.63 ± 0.36</td>
<td>-66.6 ± 84.1</td>
</tr>
<tr>
<td>LR05-30-</td>
<td>PRE</td>
<td>0.61 ± 0.08</td>
<td>1.36 ± 0.06</td>
<td>0.71 ± 0.23</td>
<td>3.78 ± 0.37</td>
<td>-370 ± 53.3</td>
</tr>
<tr>
<td>LR07-15-</td>
<td>PRE</td>
<td>1.77 ± 0.14</td>
<td>1.05 ± 0.06</td>
<td>0.87 ± 0.27</td>
<td>2.91 ± 0.39</td>
<td>N.C.</td>
</tr>
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<td>PRE</td>
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<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
</tr>
<tr>
<td>LR09-6-</td>
<td>PRE</td>
<td>3.52 ± 0.29</td>
<td>1.93 ± 0.12</td>
<td>1.03 ± 0.33</td>
<td>3.16 ± 0.56</td>
<td>-288 ± 87.5</td>
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<tr>
<td>LR09-9-</td>
<td>PRE</td>
<td>2.32 ± 0.22</td>
<td>2.28 ± 0.11</td>
<td>1.78 ± 0.38</td>
<td>13.04 ± 0.66</td>
<td>-195 ± 22.2</td>
</tr>
<tr>
<td>LR09-30-</td>
<td>PRE</td>
<td>0.91 ± 0.08</td>
<td>0.80 ± 0.03</td>
<td>0.90 ± 0.26</td>
<td>4.33 ± 0.40</td>
<td>-324 ± 47.8</td>
</tr>
<tr>
<td>LR09-45-</td>
<td>PRE</td>
<td>0.12 ± 0.08</td>
<td>1.67 ± 0.08</td>
<td>0.48 ± 0.20</td>
<td>4.38 ± 0.42</td>
<td>-445 ± 52.7</td>
</tr>
<tr>
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<td>POST</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
<td>N.C.</td>
</tr>
<tr>
<td>LR10-30-</td>
<td>POST</td>
<td>0.34 ± 0.07</td>
<td>2.00 ± 0.06</td>
<td>1.27 ± 0.30</td>
<td>7.09 ± 0.67</td>
<td>-671 ± 71</td>
</tr>
<tr>
<td>LR14-30-</td>
<td>POST</td>
<td>0.66 ± 0.11</td>
<td>2.31 ± 0.10</td>
<td>0.79 ± 0.25</td>
<td>15.16 ± 0.61</td>
<td>-743 ± 44.7</td>
</tr>
<tr>
<td>LR10-9-</td>
<td>PRE</td>
<td>0.79 ± 0.15</td>
<td>3.33 ± 0.13</td>
<td>1.49 ± 0.34</td>
<td>3.42 ± 0.59</td>
<td>-811 ± 154</td>
</tr>
</tbody>
</table>
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LR10-15-
PRE 0.88 ± 0.17 3.81 ± 0.15 1.71 ± 0.36 5.34 ± 1.04 -603 ± 126 -41.16 ± 6.82
LR10-21-
PRE 0.24 ± 0.07 1.91 ± 0.06 1.22 ± 0.30 6.77 ± 0.66 -691 ± 76 -26.83 ± 2.06
LR10-30-
PRE 0.48 ± 0.08 3.45 ± 0.12 0.77 ± 0.23 4.16 ± 0.58 -1154 ± 167 -40.41 ± 4.75
LR14-6-
PRE 0.12 ± 0.09 3.10 ± 0.11 1.00 ± 0.27 4.96 ± 0.65 -463 ± 71.1 -30.75 ± 3.33
LR14-15-
PRE 0.11 ± 0.08 3.24 ± 0.11 1.07 ± 0.28 11.61 ± 0.55 -758 ± 47 -8.72 ± 0.21
LR14-21-
PRE 0.62 ± 0.10 2.43 ± 0.09 1.25 ± 0.30 16.27 ± 0.87 N.C. N.C.
LR14-30-
PRE 0.79 ± 0.12 3.20 ± 0.13 0.53 ± 0.21 7.06 ± 1.06 -1172 ± 183 -3.59 ± 0.85

Sample identification LRXX-#-PRE/POST where XX denotes the site, # denotes the depth and PRE/POST denotes the season of collection.

Concentration of dissolved inorganic carbon (DIC) from carbonate dissolution as modelled by this study.

Concentration of DIC from carbonate dissolution as modelled by this study.

Concentration of DIC from silicate dissolution as modelled by this study.

Concentration of DIC from rainwater as modelled by this study.

Concentration of DIC from organic material oxidation as modelled by this study.

Δ14C oxidised OM as modelled by this study.

δ13C oxidised OM as modelled by this study.

N.C. = Not calculated
d.n.m. = did not model.

Discussion

4. 1 Establishing the origin of modelled DIC

The bulk DIC and bulk DOC have very different radiocarbon and δ13C values (Figure 14A) with DIC being considerably younger and less negative than DOC. However, when rainwater, carbonate and
silicate derived DIC are removed from the bulk DIC composition the age of the modelled DIC is systematically older than the bulk DIC and more δ¹³C negative. This means that the on Figure 14A the modelled DIC is similar in age and δ¹³C to the DOC. The similarity between the two ages suggests that the modelled DIC comes from the oxidation of DOC, however, robust critique is required to validate this hypothesis.

The radiocarbon date of OM, DOC in this study, can exist in two ways. Firstly DOC could be from a point source and therefore contain a single date (e.g. like plant fragments) however, it is more likely that DOC has multiple sources and therefore the radiocarbon date of DOC is actually the average of multiple sources each in proportion. This is important when assessing the outputs of the model because in the first situation, if DOC comes from a point source and thus has only one date, then DIC from the oxidation of DOC will have the same radiocarbon age as the DOC. However, in the second case, where DOC has multiple sources of different ages (which is more likely), then the dynamics of DOC oxidation affect the age of both DIC and DOC when sampled. DOC can be oxidised in three ways: 1) all DOC is oxidised evenly i.e. old and young DOC are oxidised at the same rate (equal rate oxidation); 2) young DOC is oxidised first and old DOC is oxidised last once all young DOC has been oxidised (dynamic oxidation); 3) old DOC is oxidised first and young DOC is oxidised last (reverse dynamic oxidation). In Equal rate oxidation, like with DOC from a point source, DIC and DOC will have the same ages. However, in dynamic oxidation and reverse dynamic oxidation, the value of the DIC and the DOC will change depending on the percentage of DOC oxidised and the range of ages within the DOC. If DOC is assumed to have a Gaussian distribution around the median age, then the ages of DIC and DOC at different steps of consumption can be modelled. For dynamic oxidation as the first proportion of DOC is oxidised the DIC is young and the mean DOC age remains close to the median age, however, as the oxidation continues the fraction of DOC being oxidised gets progressively older and thus the mean DIC age gets older, also as the younger fractions of DOC are oxidised so the mean DOC becomes progressively older. If DOC becomes completely oxidised then the at the end of DOC oxidation with have the same Gaussian distribution as the original DOC and DOC will no longer be present. The same is true for reverse dynamic oxidation, however, the changes in ages of DIC and DOC will be opposite.

Figure 14C shows the modelled results of how the radiocarbon ages of DIC and DOC change during the oxidation of DOC to DIC for both dynamic oxidation (closed arrows) and reverse dynamic oxidation (open arrows). DOC is assumed to have a median age of 0, -250 and -500 ‰ and the standard deviation is assumed to be 100 ‰. The tangents of the oxidation paths form straight lines at y = x ± 175 these two lines form the limits of equal rate oxidation. The end points of the oxidation
paths form straight lines along $y = x \pm 500$ and this forms the regions of dynamic and reverse dynamic oxidation.

Figure 14D shows that all samples fall either within the dynamic, reverse dynamic or equal rate oxidation zones. Within model error 61% of the samples measured fall into the equal rate oxidation zone of this 3 samples (LR01-30, LR01-6 and LR05-15) plot along equal oxidation line. The two samples in the dynamic oxidation zone are LR09-6-PRE and LR09-9-PRE and the two samples from T-Sand in the reverse dynamic oxidation zone are LR09-45-PRE and LR01-45-POST this indicates that in the deeper samples a large amount of DIC is from the oxidation of OM older than bulk DOC whilst in the shallow samples oxidation of OM younger than bulk DOC is preferential. The second group of samples that exhibit preferential degradation of OM older than bulk DOC (reverse dynamic oxidation) are the three sites from T-Clay – LR14-30-POST, LR10-21-PRE and to a lesser extend LR14-15-PRE – this indicates that on T-Clay significantly different oxidation behaviour is occurring compared to T-Sand. This can be observed in Figure 14A where all of the young modelled DIC with less negative $\delta^{13}C$ is from T-Sand whilst all of the T-Clay samples have old modelled ages.

Finally, like with radiocarbon age, a comparison of $\delta^{13}C$ DOC to modelled $\delta^{13}C$ can help establish the origin of modelled DIC. Figure 14C shows the distribution of two main plant groups as categorised by $\delta^{13}C$, C3-plants (rice, grass, wheat etc) and C4 plants (e.g. corn), there is a third group in some locations which is crassulacean acid metabolism (CAM) (e.g. pineapple) which has values between C3 and C4 plants (Deines, 1980; Hoefs, 2015). On Figure 14B 61 % of the samples plot within or around the margins of the C3 box suggesting that both the modelled DIC and the DOC box are from C3 sources. Of these LR01-45-POST, LR05-30-PRE, LR09-45-PRE and LR14-21-PRE are within the box; LR09-6-PRE, LR01-30-PRE, LR01-45-PRE, LR01-15-PRE all have $\delta^{13}C$ values for DOC and DIC, which are significantly more negative than C3 plants and this could be indicative of methanogenic processes or mixing between methanogenic processes and C3 plants (Panchuk et al., 2008). The DOC of LR09-30-PRE and LR01-6-POST have $\delta^{13}C$ values of C3 plants, but modelled DIC has $\delta^{13}C$ values of CAM plants, this could be an example of preferential oxidation of OM derived from CAM over C3 plants whilst the opposite is seen at LR01-30-POST which has a CAM value of DOC but a C3 value for modelled DIC. Finally, there is a group of samples where the $\delta^{13}C$ values of the modelled DIC are significantly less negative than the DOC. The DOC has $\delta^{13}C$ values relating to C3 plants or mixing of C3 plants and methanogenic processes, but the modelled DIC is that of C4 plants or less negative. Three samples (LR14-15-PRE, LR05-15-POST and LR09-9-POST) have modelled DIC values closer to C4 plants, however, four other samples (LR01-9-POST, LR09-9-PRE, LR05-15-PRE and LR14-30-POST) contain modelled DIC with values which are less negative than C4 plants. There appears to be no relation between $\delta^{13}C$ and the age of modelled DIC or DOC.
In summary, a comparison of Δ^{14}C ages of modelled DIC and DOC in the groundwater (Figure 14D) shows that the modelled DIC is mostly from the oxidation of DOC. Some samples fall into dynamic oxidation and reverse dynamic oxidation groups. Comparison of δ^{13}C of modelled DIC and DOC in the groundwater (Figure 14B) shows that at some localities DIC comes from DOC, however, at other localities where modelled DIC is less negative than DOC the picture is more complex. Either C4 and CAM plant OM is preferentially oxidised over bulk OM or the model fails to fully account for all the sources of DIC at these sites. C4 plants in the region include sugarcane, corn and banana plants all of which contain high energy sugars and offer a mechanism for preferential oxidation, whilst CAM includes pineapples which are also present (Chikaraishi et al., 2004; Chikaraishi and Naraoka, 2007).

Figure 14 A) distribution of Δ^{14}C and δ^{13}C of bulk DIC, bulk DOC and modelled DIC values arrows show the relationship between bulk DIC and modelled DIC; B) δ^{13}C comparison of bulk DOC modelled and modelled DIC with C3 and C4 groups defined (Deines, 1980; Hoefs, 2015); C) reaction paths of DOC and modelled DIC for dynamic (preferential young DOC oxidation) and reverse dynamic (preferential old DOC oxidation); D) Δ^{14}C comparison of bulk DOC modelled and modelled IC with dynamic and reverse dynamic oxidation groups shown.

4.1 Mixing model discussion

The mixing model clearly shows that there is a strong relationship between depth and proportion of calcium and/or magnesium from carbonates. These groundwaters contain strongly stratified water by pH and Eh (Richards et al., in prep.), it is in the shallow, slightly acidic and less reducing water that the high proportion of calcium and magnesium from carbonate dissolution occurs. The
relationship between pH and DIC from carbonates has an envelope relationship, however, it is likely that the strong relationship between depth and proportion of calcium or magnesium from carbonate is due to these bulk parameters.

Two samples (LR01-6m-PRE and LR05-6m-PRE) calculated negative concentrations from the oxidation of OM. This is due to comparatively high concentrations of calcium and magnesium and calcium in the groundwater and comparatively low concentrations of DIC. One possible reason for this is the re-precipitation of carbonate minerals, however, this seems unlikely to be the case given that the waters here have some of the lowest pH in the study. This shows one aspect of the limitations of this model and that caution must be taken to ensure correct interpretation. It is likely that in this case, the groundwater contained negligible concentrations of DIC from OM oxidation and that these two samples were slightly out of the range of the model.

5) Conclusions
This study has demonstrated the successful application of a new radiocarbon correction model for accounting different sources of DIC and other elements. It shows that the use of a new mixing model based on $^{87}$Sr/$^{86}$Sr and solute ratios coupled with PHREEQ-C can quantify the mixing of geologically sourced solutes. From this quantification it is possible to quantify the proportion of inorganic carbon (DIC) from geological sources and that from the oxidation of organic matter, therefore facilitating the correction of radiocarbon dates and δ$^{13}$C provided a priori knowledge of the end-member values.

In this study, we demonstrated the application to correct for the age of DIC from the oxidation of OM. The closeness of the Δ$^{14}$C of DOC in the groundwater and modelled DIC showed suggests the modelled DIC is from the oxidation of DOC at depth. Furthermore, the study identifies that, on the whole, the DOC is oxidised as a bulk rather than with a preference for young or old OM. It is suggested however that where DOC has a mixed plant source (C3 and C4) C4 is preferentially oxidised over DOC.

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has structural similarities to ML’s manuscript. We thank Chansopheaktra Sovann (Royal University of Phnom Penh) and Chivuth Kong (Royal University of Agriculture, Phnom Penh) for their assistance and invaluable local knowledge. Hok Meas (Kandal Province, Cambodia) and his team of local drillers are thanked for their hard work on this project. We are grateful to Pheary Meas and Yut Yann (Royal University of Agriculture, Phnom Penh) and Dina Kuy (Resources Development International – Cambodia) for their hard working during fieldwork. We thank Lori Frees whose support of and laboratory co-ordination was invaluable during the field work (Resources Development International – Cambodia) and we thank Resources, Development International – Cambodia for allowing us to use their laboratory and other local assistance. Paul Lythgoe (The University of Manchester) is gratefully thanked for conducting ICP-MS analysis. Last, thanks are due to Dr Karen Thesis (The University of Manchester) for help with undertaking sequential extractions particularly carrying out digestions with hydrofluoric acid.

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Chapter 5) High arsenic groundwater concentrations associated with pre-agricultural oxidised organic material in a Cambodian aquifer

Extremely high groundwater arsenic concentrations far in excess of the world health organisation’s provisional limit are leading to excess cancer rates akin to that of smoking across large areas of South and South East Asia \(^1,2\). The source of aqueous arsenic is widely accepted to be solid arsenic adsorbed to the surface of iron oxide minerals deposited in aquifer sediments, which is released due to redox reactions between the minerals and organic material (OM) \(^3\). The age and isotopic signature of dissolved inorganic carbon (DIC) in the groundwater has been used in previous studies as a proxy to understand the source and age of oxidised OM. This has been used to help build models of arsenic release, in circum-Himalayan aquifers DIC is consistently younger than DOC indicating that young OM is preferentially oxidised over older DOC \(^4,5\). An important implication of this is that irrigation might be increasing the arsenic risk in the region by drawing young DOC into the aquifers and encouraging arsenic release, but this hypothesis is highly contentious \(^6,7\). Resolving this hypothesis is of great importance to arsenic research but also has significant wider policy implications. One of the major problems with using bulk DIC as a proxy for oxidised OM is that bulk DIC contains multiple other sources which all contribute to the radiocarbon and isotopic signature \(^8\). In this study we utilise a new model developed to account for multiple sources \(^9\) and show that DIC from oxidised OM is not young, as has been previously suggested but consistent with the age and \(\delta^{13}C\) of bulk DOC in the aquifer. Furthermore, the age and \(\delta^{13}C\) of oxidised OM in the aquifer appears to pre-date any human activity in the region and is more associated with natural pre-agricultural grasslands in the earlier Holocene, thus indicating that arsenic is an intrinsic feature of these aquifers and not significantly driven by any human activity.

Across South and South East Asia connectivity between surface water and groundwater has been demonstrated. Isotopically light stable isotopes (\(\delta^{18}O\) and \(\delta D\)), indicative of the presence of surface water, are present in groundwater in aquifers in regions with high levels of irrigation, for example in Bangladesh \(^10\) and West Bengal, and aquifers with low levels of irrigation for example in Cambodia \(^5,11\). Tritium dating has demonstrated that the infiltrating surface water is young (< 50 years) \(^5,11\) but the exact effect of this infiltration on arsenic concentrations is still being debated. On the one hand it is argued that young surface water flushes high-arsenic groundwater from the
aquifer to replace it with surface water which is lower in arsenic \textsuperscript{6,12}, but on the other hand it is also argued that the infiltration draws in particularly labile young surface derived DOC which increases the risk of arsenic release \textsuperscript{4,5,10,11,13}.

In their widely cited paper Harvey \textit{et al.}, \textsuperscript{4} demonstrated that DIC in an arsenic contaminated aquifer in Bangladesh is far younger than DOC at the same site. By assuming that DIC came entirely from the oxidation of OM they concluded that young DOC is preferentially oxidised over old DOC. One of the most important implications of this study is that irrigation might exacerbate the problem by drawing young DOC into the aquifer leading to an increase in arsenic release. However, this conclusion has been questioned due a discrepancy between the depth of “bomb-carbon” in the aquifer and peak arsenic concentrations \textsuperscript{7}. “Bomb-carbon” is the elevated concentration of \textsuperscript{14}C in the atmosphere caused by atmospheric atomic bomb tests in the 1950s. Therefore the presence of bomb-carbon traces water entering the aquifer in or since the 1950s. Widespread irrigation and pumping did not start until the 1970s in Bangladesh, bomb carbon at the site extends no further than 19 m in the aquifer, therefore the maximum depth of irrigation effect on the aquifer is about 19 m, yet the high concentrations of arsenic extend much deeper (30 – 40 m). Thus other researchers argue that arsenic concentrations pre-date the onset of modern pumping in the 1970s \textsuperscript{7} and even go so far as to argue that the younger infiltrated water is more associated with lower concentrations of arsenic and thus might be flushing out or diluting down groundwater with pre-existing high concentrations of arsenic \textsuperscript{6,12}.

Regardless of the debate surrounding arsenic flushing versus increased concentrations of labile DOC increasing arsenic concentrations, the use of DIC as proxy for oxidised OM is flawed. DIC in groundwater consists of multiple sources including carbonate dissolution, silicate dissolution, seawater infiltration, rainwater and the oxidation of OM. Each of these sources contributes to the bulk radiocarbon age of DIC \textsuperscript{8}. Since the 1960s multiple different models have been developed to correct DIC radiocarbon ages to the age of DIC from rainwater, so as to constrain re-charge of the aquifer (see \textsuperscript{8} for detailed summary). Recently however, a new model was developed which first calculates the concentration of DIC from the different sources (including the oxidation of OM) and then applies a radiocarbon and \textsuperscript{δ13}C correction to assess the origin and age of DIC from a specific source \textsuperscript{9}. In this study we demonstrate its application along a transect of an arsenic contaminated aquifer in Cambodia.
The study site

Hydrogeology

The study site is located in Kandal Province, an area of Cambodia on the Mekong delta south of the capital Phnom Penh. Here arsenic groundwater concentrations can be as high as 500 µg/L. Groundwater flow in the province is strongly dictated by the annual monsoon, during the dry season groundwater flow is from the central wetlands to the rivers, however during the rainy season flow is reversed and flows from the rivers to the wetlands. Over the course of a year there is a net-flow from the wetlands to the river and it is argued that this flow pattern leads to an accumulation of arsenic at the base of the net flow paths. In this study we present data from a transect running perpendicular to the rivers, starting at the Bassac river and running to the central wetlands (LR09 to LR01) and two single profiles, one located in sands near the Mekong River (LR10) and one located in clay floodplain sediments about 3 km from the Mekong (LR14) (Figure 15). Tritium dating indicates that high levels of recent (post 1950s) rainwater is present, this means any DIC present from rainwater and recent silicate or carbonate dissolution will have high levels of bomb-carbon present skewing the radiocarbon age of bulk DIC.

Agricultural and botanical history

Plants have evolved different pathways of fixing CO₂ during photosynthesis, these pathways have resulted in two main plant groups: C3 plants (most common e.g. wheat, rice etc.) and C4 plants (less common e.g. millets, sugarcane etc.) . The different pathways contain different isotopic signatures with C3 plants having a δ¹³C range from about -20 to -35 ‰ whilst C4 ranges from -18 to -9 ‰. The δ¹³C of OM in the environment (sedimentary and water) can provide a record of botanical-agricultural change. The botano-archaeological record of crop farming in Cambodia throughout the Holocene is sparse, though there are details from the last 2000 years at the Temples of Angkor in the North of Cambodia and a site and a 3500 year record at an archaeological site called Angkor Borei located 20 km south of the study site. A more detailed Holocene picture exists in neighbouring Thailand, here and most likely in Cambodia, prior to agricultural practices most of the vegetation would have been natural forests and grasslands. In modern day Cambodia on the Mekong delta, unlike many other tropical countries (including Thailand), the natural grassland and forestland are mostly C4 plants and it is likely that this been the case throughout the Holocene. The earliest farming in Thailand started after 5000 years BP and was predominantly the C4 plant millets however by 3000 years BP rice, a C3 plant, had become the most dominant crop in the region. This timing is consistent with a period of dam building at Angkor Borei which might be indicative of changing farming practices here as well. Whilst widespread irrigation is commonly
thought of as a 20th century feature of these groundwaters it is important to remember that during the Angkorian Empire (1200 years BP to 500 years BP) large irrigation projects were undertaken at major settlements 18,19, though the extent of this on the deltas is unknown 20.

Sources of DIC

In this study the highest concentrations of arsenic in groundwater (in sample taken pre-monsoon) is in the deeper section of the aquifer (Figure 15), part of what dictates this is the pH and Eh of the system (data not shown, see 27), which makes the aquifer highly chemically stratified 27. The new geochemical model has assumes there are four key sources of DIC in the aquifer: carbonate dissolution, silicate dissolution, rainwater and oxidised organic material. On all sites, depth is an important dictator of the amount of DIC from a given source. The shallow samples contain the lowest percentages of DIC from oxidation of OM, but oxidised OM is frequently the major contributor to DIC in the deeper aquifer (>9 – 15 m, 25 – 30 % DIC) (Figure 15).

The model corrects the δ13C of oxidised OM, thus defining oxidised OM sources, these are: C3 plants, C4 plants 16, C4? plants (which have a δ13C which is slightly lighter than typical for C4 plants) and methane. The stratification is reflected in the source of oxidised OM in the aquifer (Figure 15). The deeper section of the aquifer is dominated by C3 oxidised OM, the moderate depth by C4 oxidised OM, the shallow waters near the river with apparent methanogenic processes and nearer the wetlands with negligible OM oxidation (Figure 15). Finally, unsurprisingly the highest concentration of DIC from rainwater is in the shallow section of the aquifer. This is also the location of lowest concentrations of arsenic within the aquifer (Figure 15). Previous studies have indicated that low arsenic concentrations might be due to the higher sorption capacities of shallow clay sediments compared to deeper clays 24, however it could also be due to rainwater flushing or diluting arsenic concentrations in this region 6,12,15.
Figure 15 Geomorphological map of Kandal Province, Cambodia (the study area), a series of transects showing arsenic groundwater concentrations $^{27}$, DIC groundwater concentrations from oxidised OM and rainwater with oxidised OM source groups defined through colours. Percentage distribution of DIC from different sources in different profiles $^9$.

**Source of OM driving arsenic release**

In terms of $\delta^{13}$C and radiocarbon age of bulk DOC there is a clear relationship between the botanical and agricultural history at this site and the DOC in the groundwater. The oldest, pre-agricultural, DOC in the groundwater is associated with C3 plants and is therefore in keeping with the natural Cambodian grasslands present during this section of the history (Figure 16A). The appearance of agricultural millet production between 5000 years BP and 3000 years BP, is recorded with in a small number of samples in the DOC (Figure 16A), however more dramatically the highest proportion of DOC is concurrent with the onset of rice farming in the region from 3000 years BP to the present day (Figure 16A).
At this site, like with the site from Bangladesh, there is a discrepancy between the $\Delta^{14}C$ and $\delta^{13}C$ of DOC and DIC. DIC is younger and isotopically lighter than DOC (Figure 16A). However, by correcting the DIC radiocarbon ages and $\delta^{13}C$ of DIC by removing the young rainwater DIC, and DIC from dissolution of silicates and carbonates the modelled DIC from oxidation of OM is actually similar to that of DOC present at depth (Figure 16A). The higher concentrations of arsenic are exclusively associated with the older, oxidised OM which is mostly from C3 plants (Figure 16C) whilst, those with C4 derived OM have considerably lower concentrations of arsenic (Figure 16B).

Crucially, regarding drivers of arsenic in groundwater DIC from the oxidation of OM is associated with the oxidation of pre-agricultural DOC from natural grassland (Figure 16A). Whilst there is some young oxidised DIC from C4 plants these are associated with lower concentrations of arsenic in groundwater (Figure 16C). Two of the older C4 derived DIC samples might be related to millets farming in the mid-Holocene, however the rest are < 1200 years BP and if there is any anthropogenic influence are more likely to be associated with Angkorian practices or modern practises but it impossible to state with any certainty.

![Figure 16A](image1.png) $\Delta^{14}C$ and $\delta^{13}C$ distribution of DOC density (green line contours), DIC density (grey dashed contours) and modelled DIC from oxidation of OM with corresponding arsenic concentrations represented in the dot size. Also showing the two historical eras of farming (C4 millets followed by C3 rice) in the region brown squares. B) Arsenic concentrations vs modelled oxidised OM $\Delta^{14}C$. C) Modelled oxidised OM $\delta^{13}C$ vs Arsenic concentrations.
The results from this study show that the DIC from oxidised OM comes from pre-agricultural, natural grassland derived OM, this is consistent with an earlier sedimentary study which showed that the highest concentration of oxidised SOM at this site was from the early Holocene. This implies that arsenic is an intrinsic feature of Cambodian aquifers and not driven by any anthropogenic activity. Later changes in Holocene agriculture are reflected in the bulk DOC in the aquifer but not in the DIC from oxidation of OM. We have also shown that those localities associated with higher proportions of rainwater and younger oxidised DIC contain lower concentrations of arsenic, adding weight to the hypothesis that younger intrusions of surface water are actually diluting or flushing higher concentrations of arsenic from the aquifer (though this could also be a function of sorption capacities of clay sediments). Finally, we have clearly demonstrated that the use of DIC as a proxy for oxidised OM is flawed unless corrected so that it only accounts for the DIC from the oxidation of OM and not additional geological sources.

**Method Summary**

Sample collection, analysis, and modelling techniques are outlined in previous papers which are all available through open access. Samples were collected from purpose built sampling wells both pre and post monsoon. Wells were drilled using manual rotary drilling and used a lithium tracer to minimise and quantify contamination. Groundwater chemistry was measured using ICP-MS, ICP-AES and Ion Chromatography at University of Manchester’s Manchester Analytical Geochemical Unit, radiocarbon was prepared at the NERC Radiocarbon Laboratory and SUERC Isotope AMS, strontium isotope measurements for the correction model were conducted at the NERC isotope geochemistry laboratories.

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Chapter 6) Conclusions

The research for this thesis has robustly analysed the organic material driving arsenic release in a Cambodian aquifer. The approach taken has been to divide each of the potential sources of organic material (OM) (sedimentary organic material (SOM); upwell ed petroleum and dissolved organic carbon (DOC) in the water column) into their respective groups and study them in relative isolation. In these concluding remarks I intend to draw together the different sources into a coherent model of arsenic relating to the OM.

The geomorphology and organic geochemistry survey (chapter 2) demonstrated that the characterisation of SOM is dictated by the geomorphology which in turn has been controlled by major regional climatic and geological controls in the region. There are three generations sedimentary deposition in the region firstly the old early Holocene sediments deposited during a period of rising sea-level (6,000 to 10,000 years BP), followed by incising sandy sediments due to a change in monsoon patterns and finally a much more recent (<2000 years) layer of young clays which are deposited due to changing river flow patterns caused by the appearance Tonle Sap lake upstream of the study site. The early Holocene sediments are probably interbedded sand and clays as is observed in the same facies further downstream rather than a homogenous clay block (Tamura et al., 2009, 2007).

If the early Holocene sediments do have heterogeneous grain size distribution then the sandy layers within the clays provide a pathway for the thermally upwelled petroleum to enter the sandy aquifer. Like in other circum-Himalayan aquifer sediments in Vietnam, West Bengal and Bangladesh, in Kandal Province almost all of the sandy sedimentary layers consist of thermally mature petroleum derived OM which is not present in the clay layers. The clay layers consist of OM from plant deposition either in situ or from the deposition of riverine particulate organic carbon (POC). Sandy windows are also present within the young clay sediments and this provides a pathway for young surface derived DOC to travel to much deeper in the aquifer, even into the early Holocene sediments previous studies showed (Lawson et al., 2016, 2013) however no significant evidence is found for this in the SOM. The most significant finding from the sedimentary survey, however, is that the most oxidised OM is OM in the early Holocene facies. This facies contains OM which has an isotopic signature consistent with C3-plants and given that modern natural Cambodian grassland is also C3 (Edwards et al., 2010) it seems likely that this has been the case throughout the Holocene. Thus the sedimentary survey indicates that oxidation of OM which could potentially be linked to arsenic release which occurred in the early Holocene.
The results of the microcosm experiments (chapter 3) clearly demonstrate that iron-oxide reduction is linked to the type of SOM present, these results were consistent with earlier experiments from other local sediments (Rowland et al., 2007). Iron-oxide reduction is most prevalent in the thermally immature plant derived SOM, this might be a function of bioavailability or the energy available in different types of SOM, interestingly even with the addition of the labile stimulant the underlying SOM appears to control much of the reduction. Arsenic is less strongly linked to the source of SOM but does react strongly to the addition of a labile stimulant. Fundamentally this is not surprising as earlier work has shown that whilst arsenic release and iron reduction are somewhat linked they are not intrinsically coupled (Islam et al., 2004). What is interesting is that arsenic appears to be more readily liberated from sediments than iron and this is not what previous experiments revealed (Islam et al., 2004; Rowland et al., 2007). Crucially however, once liberated arsenic appears to re-adsorb to the sediments within a matter of weeks, this is not a unique finding (Héry et al., 2015, 2010) and it indicates that the extent of arsenic release from late Holocene sediments on general groundwater arsenic concentrations might in fact be limited by sorption.

Separately, the new radiocarbon correction model (chapter 4) corrects radiocarbon ages of bulk dissolved inorganic carbon (DIC) to find the radiocarbon age of DIC from the oxidation of OM. The results pose serious questions about the interpretation of data from previous studies in both Cambodia and other circum-Himalayan groundwaters (Harvey et al., 2002; Lawson et al., 2016, 2013). The strontium isotope mixing method clearly shows that there are multiple sources of DIC in the aquifer and not just DIC from the oxidation of OM. Because DIC from other sources contains high levels of “bomb-carbon” (Lawson et al., 2016, 2013; Richards et al., 2016) this skews the radiocarbon date of bulk DIC, younging it dramatically. Once the bomb carbon has been removed from the radiocarbon date of bulk DIC, the DIC formed from the oxidation of OM has radiocarbon date consistent with that of the early Holocene and the δ^{13}C of the DIC from oxidised OM is akin to that of C3-plants. This is likely to be a concern for similar previous high profile studies of Bangladeshi groundwater (Harvey et al., 2002; Neumann et al., 2010) which also has high levels of bomb carbon (McArthur et al., 2011, 2010; van Geen et al., 2003).

This means that independently the sedimentary study and the new hydrogeochemical model both indicate that the OM oxidised and presumably that which drove arsenic release was from the early Holocene. Together these studies fundamentally change the way that arsenic release can be thought of in this region. The results of the correction model not only show the oxidation of OM from the early Holocene but also that oxidation was mostly from C3 plants. Given that the sedimentary study showed that Cambodia contained C3 grasslands at this stage of the Holocene it appears likely that the OM oxidised during arsenic release is natural early Holocene C3 grasslands.
Later anthropogenic changes in agriculture are observed in the radiocarbon and $\delta^{13}$C of DOC, with first the farming of millets (C4 plant) and then the change to rice (C3 plant), but none of these are associated with high levels of arsenic. This means that arsenic is an intrinsic feature of these aquifers and not related to anthropogenic drivers, in fact the strontium isotopes appear to show that areas with high rainwater are associated with lower arsenic thus indicating that arsenic might be flushed by pumping as suggested by previous studies (McArthur et al., 2011, 2010).

The early Holocene oxidation model leaves one problem unexplained however, and that is why the highest concentrations of arsenic are associated with the sandy layers from the late Holocene whilst release appears to be associated early Holocene clayey sediments. This might be described as the “arsenic sand paradox” and must be properly explained if arsenic in this groundwater is to be fully understood, one reason indicated by the sedimentary survey and other work related to this project (Casanueva-Marenco et al., 2016) indicates that sorption might be the controlling factor but transportation of arsenic from older clay sediments to younger sands must be explained. Nevertheless, the early Holocene oxidation model is validated by two independent geochemical studies (one sedimentological and one hydrogeological) conducted by research for this thesis and represents an important development in arsenic-groundwater research in the region.

**Future Work**

The most important future work relating to this study is in understanding the arsenic sand paradox. To do this several approaches might be taken. Firstly, as of yet, no microcosm studies have been undertaken using sediments from the early Holocene facies so know real understanding of the chemical processes that might have been involved in releasing arsenic from these sediments can be known. Undertaking this is an important first step. Furthermore, studies should also be undertaken downstream in the sediments from the intertidal zone (Tamura et al., 2009, 2007) as this would also reveal if high arsenic concentrations are restricted to onshore sediments or are also at risk in the tidal sediments. National surveys suggest that these areas are lower in arsenic (Sovann and Polya, 2014) but no significant work has yet been undertaken on the finer detail in this area. Groundwater modelling of diffusions and flow should be undertaken to look at the timescales for arsenic to be transported from the early Holocene facies to the younger sands. The effect of pre-agricultural OM on arsenic release has only been identified in Cambodia, future work should focus on conducting similar studies in Bangladesh and West Bengal to see if the correction method provides the same findings across the circum-Himalayan groundwater. If so then this will indicate that high arsenic concentrations are an intrinsic and long term feature of these groundwaters and have little anthropogenic influence. Finally and separately, this study has shown that sulphide
minerals in this aquifer is potentially vulnerable to oxidation by nitrates and work should be undertaken check long term security issues from this.

References


Supplementary Information for Chapter 2: Depositional history and geomorphological structure of a Cambodian aquifer and the effect on arsenic concentrations and organic matter characterisation

Introduction

In the supplementary information detail is given about the data quality assurances of this study for the carbon and nitrogen measurements. It also shows variograms from the kriging undertaken for this study and the radiocarbon calibration code for OxCal and the OxCal plots. Example chromatograms are also presented, these represent samples for both thermally mature and immature n-alkanes as well as n-alkanoic acids and n-alcohols.

Carbon/Nitrogen Data quality

An external laboratory (Elemental Microanalysis, Devon, UK) was used to check the data quality of the in-house measurements. These produced high levels of correlation between analysis conducted at the University of Manchester and the laboratory with R\(^2\) values of 0.998, 0.998 and 1 for total carbon, total nitrogen and total organic carbon respectively. These all had relationships close to 1 to 1 with coefficients of 0.957, 0.911 and 1.03 respectively (Figure 17).

![Total Carbon, Total Nitrogen and Total Organic Carbon as measured at the University of Manchester and at an external laboratory for data quality purposes.](image)

Figure 17 Total carbon, Total Nitrogen and Total Organic Carbon as measured at the University of Manchester and at an external laboratory for data quality purposes.
Kriging

Ordinary kriging was undertaken in GeoR (Ribeiro and Diggle, 2015). Kriging was undertaken on grain-size distribution using omnidirectional kriging the variogram for which is presented in Figure 18. Both exponential and spherical models were attempted to fit to the in all cases spherical models provided the best fit and only this is shown. Grainsize data proved to have strongly stratified grainsize horizontal to the surface.

![Figure 18](image)

*Figure 18 Omnidirectional variogram of grainsize data for study shown with lines (line styles and colours representing different directions) and uni-directional kriging shown with points. Spherical models shown with smooth fitted orange lines.*

Due to the lower number of data points, geochemical kriging was undertaken using unidirectional variograms only. All with the exception of sulphur were fitted with both spherical and exponential curves and in all cases spherical curves provided the best fit. Sulphur was the poorest fit and this required a circular fitting model to provide an accurate best fit. TOC Kriging was undertaken on the natural log of TOC values and then calculated out at a later stage as this provided a better fit.

![Figure 19](image)

*Figure 19 Variograms of geochemical data plotted for this study with corresponding models (all spherical apart from sulfur which is circular).*
Radiocarbon Calibrations

Radiocarbon calibrations were undertaken using OxCal software (Bronk Ramsey and Lee, 2013) using the IntCal13 curve (Reimer et al., 2013). This section provides the code used for all calibrations presented in this study and provides the OxCal plots for the data collected by this study but not the earlier studies (Rowland et al., 2007; Tamura et al., 2007; van Dongen et al., 2008). For all samples except LR05, simple single radiocarbon calibration was undertaken (Figure 20 and Figure 21). For LR05 a P_Sequence was also used (Figure 22) this applies Bayesian logic to a depth profile assume that all samples age with depth this provides a more accurate calibration where this technique is suitable.

```
Plot()
{
    R_Date("LR01-6m-SED", 1588, 37);
    R_Date("LR01-30m-SED", 3705, 36);
    R_Date("LR10-6m-SED", 2555, 35);
    R_Date("LR10-27m-SED", 3393, 37);
    R_Date("LR14-6m-SED", 6295, 39);
    R_Date("LR14-30m-SED", 9450, 41);
    R_Date("LR09-6m-SED", 1430, 35);
    R_Date("LR09-21m-SED", 3911, 35);
    R_Date("LR09-30m-SED", 3597, 35);
    R_Date("LR09-39m-SED", 8002, 40);
    R_Date("LR09-45m-SED", 2930, 35);
}
```

*Figure 20 OxCal code for radiocarbon calibration of the sedimentary data collected for this study.*

```
Plot()
{
    R_Date("SR-13", 7759, 51);
    R_Date("SR-19", 7732, 51);
    R_Date("DS-0", 6216, 44);
    R_Date("DS-15", 8177, 54);
    R_Date("DS-23", 7930, 52);
    R_Date("DS-27", 9040, 61);
    R_Date("DS-40", 5370, 41);
    R_Date("DS-54", 5293, 41);
    R_Date("DS-60", 8241, 41);
    R_Date("DS-70", 4937, 41);
    R_Date("SY-9", 1532, 31);
    R_Date("SY-28", 4218, 38);
    R_Date("KS-4.07", 700, 40);
    R_Date("KS-7.08", 6250, 40);
    R_Date("KS-7.9", 6620, 40);
    R_Date("KS-8.33", 6470, 40);
    R_Date("KS-9.08", 7130, 40);
    R_Date("KS-9.6", 7030, 40);
    R_Date("KS-10.48", 7150, 40);
}
```

*Figure 21 OxCal code for radiocarbon calibration of the sedimentary data collected for this study.*
OxCal code for radiocarbon calibration of the sedimentary data collected by previous studies (Rowland et al., 2007; Tamura et al., 2007; van Dongen et al., 2008).

Figure 21

Where possible all samples were reported to a 95.4% probability confidence, however, a small number of sites (LR01-30, LR10-27, LR09-30 and LR14-30) were reported to lower probabilities because where a lower probability outlier increased the calibration ages significantly (Figure 23).
At LR05 the Bayesian approach had high levels of agreement with the simple calibration approach in all samples. Where possible all samples were reported to a 95.4% probability confidence, however, at LR05-6, LR05-15 and LR05-30 lower probabilities were used to provide a more accurate calibration (Figure 24).
Figure 24 OxCal plots showing conventional simple calibration in light grey and Bayesian calibration in darker grey. Red distribution is measured data and the blue line is the calibration curve.

Chromatography

For completeness a selection of representative scanned (not SIM) chromatograms are shown in Figure 25. The \(n\)-alkanes from LR05-6m represent the immature (i.e. high CPI) \(n\)-alkanes whilst the \(n\)-alkanes from LR05-45m show the immature (i.e. low CPI) \(n\)-alkanes. LR09-6m shows typical \(n\)-alkanoic acids and LR14-9m shows typical \(n\)-alcohols.
Figure 25: Representative chromatograms for different compounds and maturities for data collected by this study. The internal standard in the alkane phases occurs at about 17 mins and at 19 mins for the alkanoic acids and is not shown in the alcohols.

References


Supplementary Information for Chapter 4: A new 14C correction model using 87Sr/86Sr to attribute the age of dissolved inorganic carbon from the degradation of organic material - application to a Holocene Aquifer, Cambodia

Introduction
This supplementary information gives the R code for the a priori strontium isotope mixing model (APSIMM) described mathematically in the article, instructions on usage and an example code for using the model with the data from this article. It is recommended that APSIMM is run in RStudio and the instructions are given assuming RStudio is used. This information starts with an explanation of how to load the model into R, a breakdown of each function (purpose and usage) and a annotated worked example. Finally, it also gives an example of PHREEQ-C code to calculate end-members for the model.

Instructions on loading APSIMM:
1) Open RStudio and start a new file.
2) Copy all of Figure 26 into a newly opened tab in RStudio and save this as a new file called APSIMM-R_Functions.R – do not edit the code in anyway. Detailed reading of Figure 26 is not required for usage.
3) Ensure that the global environment is clear by pressing “clear”.
4) Click anywhere on the APSIMM code and press ctrl + A followed by ctrl + Enter. All APSIMM functions are now loaded (this means that provided “clear” is not pressed APSIMM will work like a conventional R package – if you do press “clear” simply reload the functions using step 4).
5) Open a new tab to start your calculations.

```r
#Set-up Sr.Split function
Sr.Split <- function(Sr, Sr.Ratio) {
    Sr86 <- Sr*0.0986
    Sr87 <- Sr86*Sr.Ratio
    t(data.frame(Sr86, Sr87))
}
```
# Set up AP.plot function
AP.plot <- function(ion, Na = Na, ion.Na.Ratio, Sr86 = Sr86, Sr87 = Sr87, Sr.Ratio, xlab = "Set xlab", ylab = expression(bold("^87*Sr/^86*Sr")), EM = c("EM1","EM2","EM3"), P = 1000, yfit = 0.01, xfit = 10, text.pos = 2, log = "x"){
  GT <- c(rep(0, P), rep(0.1, P), rep(0.2, P), rep(0.3, P), rep(0.4, P), rep(0.5, P), rep(0.6, P), rep(0.7, P), rep(0.8, P), rep(0.9, P))

  # Set up background code for EM1
  XEM1.3 <- rep(rev(seq(0, 1, by = 1/(P-1))), 10)
  XEM1.1 <- GT*(1 - XEM1.3)
  XEM1.2 <- 1 - XEM1.3 - XEM1.1
  ion.Na.GT.EM1 <- (ion[1]*XEM1.1 + ion[2]*XEM1.2 + ion[3]*XEM1.3)/(Na[1]*XEM1.1 + Na[2]*XEM1.2 + Na[3]*XEM1.3)
  Sr87.Sr86.GT.EM1 <- (Sr87[1]*XEM1.1 + Sr87[2]*XEM1.2 + Sr87[3]*XEM1.3)/(Sr86[1]*XEM1.1 + Sr86[2]*XEM1.2 + Sr86[3]*XEM1.3)
  ion.Na.GT.EM1 <- matrix(ion.Na.GT.EM1, nrow = P, ncol = 10)
  Sr87.Sr86.GT.EM1 <- matrix(Sr87.Sr86.GT.EM1, nrow = P, ncol = 10)

  # Set up background code for EM2
  XEM2.1 <- rep(rev(seq(0, 1, by = 1/(P-1))), 10)
  XEM2.2 <- GT*(1 - XEM2.1)
  XEM2.3 <- 1 - XEM2.2 - XEM2.1
  ion.Na.GT.EM2 <- (ion[1]*XEM2.1 + ion[2]*XEM2.2 + ion[3]*XEM2.3)/(Na[1]*XEM2.1 + Na[2]*XEM2.2 + Na[3]*XEM2.3)
  Sr87.Sr86.GT.EM2 <- (Sr87[1]*XEM2.1 + Sr87[2]*XEM2.2 + Sr87[3]*XEM2.3)/(Sr86[1]*XEM2.1 + Sr86[2]*XEM2.2 + Sr86[3]*XEM2.3)
  Sr87.Sr86.GT.EM2 <- matrix(Sr87.Sr86.GT.EM2, nrow = P, ncol = 10)

  # Set up background code for EM3
  XEM3.2 <- rep(rev(seq(0, 1, by = 1/(P-1))), 10))
  XEM3.3 <- GT*(1 - XEM3.2)
  XEM3.1 <- 1 - XEM3.3 - XEM3.2
  ion.Na.GT.EM3 <- (ion[1]*XEM3.1 + ion[2]*XEM3.2 + ion[3]*XEM3.3)/
(Na[1]*XEM3.1 + Na[2]*XEM3.2 + Na[3]*XEM3.3)

Sr87.Sr86.GT.EM3 <- (Sr87[1]*XEM3.1 + Sr87[2]*XEM3.2 + Sr87[3]*XEM3.3)/
(Sr86[1]*XEM3.1 + Sr86[2]*XEM3.2 + Sr86[3]*XEM3.3)

Sr87.Sr86.GT.EM3 <- matrix(Sr87.Sr86.GT.EM3, nrow = P, ncol = 10)

#Plot Graph
par(mar=c(5.1, 5.1, 2.1, 2.1)+0.1)
plot(ion.Na.Ratio, Sr.Ratio, xlab = xlab, ylab = ylab,
log = "x", pch = 16, col = "Blue", font.lab = 2,
xlim = range(min(ion.Na.Ratio)*(xfit/xfit^2),
max(ion.Na.Ratio)*xfit),
ylim = range (min(Sr.Ratio) - yfit, max(Sr.Ratio) + yfit))
text(ion.Na.Ratio, Sr.Ratio, EM, pos = text.pos, offset = 0.5)

#EM1 Lines
lines(ion.Na.GT.EM1[,1], Sr87.Sr86.GT.EM1[,1], col = "red3", lwd =2)
# This is a zero line.
lines(ion.Na.GT.EM1[,2], Sr87.Sr86.GT.EM1[,2], lty = 2, col = "gray")
lines(ion.Na.GT.EM1[,3], Sr87.Sr86.GT.EM1[,3], lty = 2, col = "gray")
lines(ion.Na.GT.EM1[,4], Sr87.Sr86.GT.EM1[,4], lty = 2, col = "gray")
lines(ion.Na.GT.EM1[,5], Sr87.Sr86.GT.EM1[,5], lty = 2, col = "gray")
lines(ion.Na.GT.EM1[,6], Sr87.Sr86.GT.EM1[,6], lty = 2, col="green4")
lines(ion.Na.GT.EM1[,7], Sr87.Sr86.GT.EM1[,7], lty = 2, col = "gray")
lines(ion.Na.GT.EM1[,8], Sr87.Sr86.GT.EM1[,8], lty = 2, col = "gray")
lines(ion.Na.GT.EM1[,9], Sr87.Sr86.GT.EM1[,9], lty = 2, col = "gray")
lines(ion.Na.GT.EM1[,10], Sr87.Sr86.GT.EM1[,10], lty = 2, col = "gray")

#EM2 Lines
lines(ion.Na.GT.EM2[,1], Sr87.Sr86.GT.EM2[,1], col = "royalblue4", lwd =2) # This is a zero line.
lines(ion.Na.GT.EM2[,2], Sr87.Sr86.GT.EM2[,2], lty = 2, col = "gray")
lines(ion.Na.GT.EM2[,3], Sr87.Sr86.GT.EM2[,3],lty = 2, col = "gray")
lines(ion.Na.GT.EM2[,4], Sr87.Sr86.GT.EM2[,4],lty = 2, col = "gray")
lines(ion.Na.GT.EM2[,5], Sr87.Sr86.GT.EM2[,5], lty = 2, col = "gray")
lines(ion.Na.GT.EM2[,6], Sr87.Sr86.GT.EM2[,6],lty = 2, col="green4")
lines(ion.Na.GT.EM2[,7], Sr87.Sr86.GT.EM2[,7], lty = 2, col = "gray")
lines(ion.Na.GT.EM2[,8], Sr87.Sr86.GT.EM2[,8], lty = 2, col = "gray")
lines(ion.Na.GT.EM2[,9], Sr87.Sr86.GT.EM2[,9], lty = 2, col = "gray")
lines(ion.Na.GT.EM2[,10], Sr87.Sr86.GT.EM2[,10], lty = 2, col = "gray")

#EM3 Lines
lines(ion.Na.GT.EM3[,1], Sr87.Sr86.GT.EM3[,1], col = "sandybrown", lwd = 2)  # This is a zero line.
lines(ion.Na.GT.EM3[,2], Sr87.Sr86.GT.EM3[,2], lty = 2, col = "gray")
lines(ion.Na.GT.EM3[,3], Sr87.Sr86.GT.EM3[,3], lty = 2, col = "gray")
lines(ion.Na.GT.EM3[,4], Sr87.Sr86.GT.EM3[,4], lty = 2, col = "gray")
lines(ion.Na.GT.EM3[,5], Sr87.Sr86.GT.EM3[,5], lty = 2, col = "gray")
lines(ion.Na.GT.EM3[,6], Sr87.Sr86.GT.EM3[,6], lty = 2, col = "green4")
lines(ion.Na.GT.EM3[,7], Sr87.Sr86.GT.EM3[,7], lty = 2, col = "gray")
lines(ion.Na.GT.EM3[,8], Sr87.Sr86.GT.EM3[,8], lty = 2, col = "gray")
lines(ion.Na.GT.EM3[,9], Sr87.Sr86.GT.EM3[,9], lty = 2, col = "gray")
lines(ion.Na.GT.EM3[,10], Sr87.Sr86.GT.EM3[,10], lty = 2, col = "gray")

rm(ion.Na.GT.EM3,Sr87.Sr86.GT.EM3,ion.Na.GT.EM2,Sr87.Sr86.GT.EM2,ion.Na.GT.EM1,
   Sr87.Sr86.GT.EM1,XEM1.1,XEM1.2, XEM1.3, XEM2.1, XEM2.2,
   XEM2.3,XEM3.1,XEM3.2,XEM3.3)

#Set up the AP.calc function

AP.calc <- function(Sr.Ratio.spl, ion.Na.Ratio.spl, Sr87 = Sr87, Sr86 = Sr86, ion, Na,
   EM.names = C("EM1", "EM2", "EM3"))
{
  a1.1 <- (Sr86[2]-Sr86[3])*Sr.Ratio.spl-(Sr87[2]-Sr87[3])
a1.2 <- (Sr86[1]-Sr86[3])*Sr.Ratio.spl-(Sr87[1]-Sr87[3])
a1.3 <- (Sr86[3]*Sr.Ratio.spl)-Sr87[3]
B1.2 <- (Na[1]-Na[3])*ion.Na.Ratio.spl-(ion[1]-ion[3])

a2.1 <- (Sr86[3]-Sr86[1])*Sr.Ratio.spl-(Sr87[3]-Sr87[1])
a2.2 <- (Sr86[2]-Sr86[1])*Sr.Ratio.spl-(Sr87[2]-Sr87[1])
a2.3 <- (Sr86[1]*Sr.Ratio.spl)-Sr87[1]
B2.1 <- (Na[3]-Na[1])*ion.Na.Ratio.spl-(ion[3]-ion[1])
B2.2 <- (Na[2]-Na[1])*ion.Na.Ratio.spl-(ion[2]-ion[1])
B2.3 <- (Na[1]*ion.Na.Ratio.spl)-ion[1]

a3.1 <- (Sr86[1]-Sr86[2])*Sr.Ratio.spl-(Sr87[1]-Sr87[2])
a3.2 <- (Sr86[3]-Sr86[2])*Sr.Ratio.spl-(Sr87[3]-Sr87[2])
a3.3 <- (Sr86[2]*Sr.Ratio.spl)-Sr87[2]
B3.1 <- (Na[1]-Na[2])*ion.Na.Ratio.spl-(ion[1]-ion[2])
B3.2 <- (Na[3]-Na[2])*ion.Na.Ratio.spl-(ion[3]-ion[2])
B3.3 <- (Na[2]*ion.Na.Ratio.spl)-ion[2]
X.EM1 <- (a1.3*B1.1 - a1.1*B1.3) / (a1.1*B1.2 - a1.2*B1.1)
X.EM2 <- (a2.3*B2.1 - a2.1*B2.3) / (a2.1*B2.2 - a2.2*B2.1)
X.EM3 <- (a3.3*B3.1 - a3.1*B3.3) / (a3.1*B3.2 - a3.2*B3.1)

AP.df <- data.frame(X.EM1, X.EM2, X.EM3)
names(AP.df) <- EM.names
AP.df

# Set up the AP.err function

AP.err <- function(Sr.Ratio.spl, ion.Na.Ratio.spl, Sr87 = Sr87, Sr86 = Sr86, ion, Na,
                   ion.Na.Ratio.spl.err, ion.err, Na.err,
                   EM.names = C("EM1", "EM2", "EM3")){

  a1.1 <- (Sr86[2] - Sr86[3]) * Sr.Ratio.spl1 - (Sr87[2] - Sr87[3])
  a1.2 <- (Sr86[1] - Sr86[3]) * Sr.Ratio.spl1 - (Sr87[1] - Sr87[3])
  a1.3 <- (Sr86[3] * Sr.Ratio.spl1) - Sr87[3]

  a2.1 <- (Sr86[3] - Sr86[1]) * Sr.Ratio.spl1 - (Sr87[3] - Sr87[1])
  a2.2 <- (Sr86[2] - Sr86[1]) * Sr.Ratio.spl1 - (Sr87[2] - Sr87[1])
  a2.3 <- (Sr86[1] * Sr.Ratio.spl1) - Sr87[1]

  a3.1 <- (Sr86[1] - Sr86[2]) * Sr.Ratio.spl1 - (Sr87[1] - Sr87[2])
  a3.2 <- (Sr86[3] - Sr86[2]) * Sr.Ratio.spl1 - (Sr87[3] - Sr87[2])
  a3.3 <- (Sr86[2] * Sr.Ratio.spl1) - Sr87[2]

  X.EM1 <- (a1.3*B1.1 - a1.1*B1.3) / (a1.1*B1.2 - a1.2*B1.1)
  X.EM2 <- (a2.3*B2.1 - a2.1*B2.3) / (a2.1*B2.2 - a2.2*B2.1)
  X.EM3 <- (a3.3*B3.1 - a3.1*B3.3) / (a3.1*B3.2 - a3.2*B3.1)


  B1.2.err <- ...
  B1.3.err <- ...
  B2.1.err <- ...
  B2.2.err <- ...
  B2.3.err <- ...
  B3.1.err <- ...
  B3.2.err <- ...
  B3.3.err <- ...

  # Further calculations...
}

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B2.3.err <- sqrt((ion.Na.Ratio.spl*Na[1]*sqrt((Na.err[1]/Na[1])^2 +

N1.1 <- a1.3*B1.1 - a1.1*B1.3
D1.1 <- a1.1*B1.2 - a1.2*B1.1
N1.1.err <- a1.3*B1.1.err + a1.1*B1.3.err
D1.1.err <- a1.1*B1.2.err + a1.2*B1.1.err
X.EM1.err <- sqrt((X.EM1*sqrt((N1.1.err/N1.1)^2 +
                      (D1.1.err/D1.1)^2))^2)
F2.1 <- a2.3*B2.1 - a2.1*B2.3
D2.1 <- a2.1*B2.2 - a2.2*B2.1
N2.1.err <- a2.3*B2.1.err + a2.1*B2.3.err
D2.1.err <- a2.1*B2.2.err + a2.2*B2.1.err
X.EM2.err <- sqrt((X.EM2^2 + (N2.1.err/N2.1)^2) + (D2.1.err/D2.1)^2))
N3.1 <- a3.3*B3.1 - a3.1*B3.3
D3.1 <- a3.1*B3.2 - a3.2*B3.1
N3.1.err <- a3.3*B3.1.err + a3.1*B3.3.err
D3.1.err <- a3.1*B3.2.err + a3.2*B3.1.err
X.EM3.err <- sqrt((X.EM3^2 + (N3.1.err/N3.1)^2) + (D3.1.err/D3.1)^2))

AP.df <- data.frame(X.EM, X.EM2, X.EM3,
                     X.EM1.err, X.EM2.err, X.EM3.err)
names(AP.df)[1] <- EM.names[1]
names(AP.df)[2] <- EM.names[2]
names(AP.df)[3] <- EM.names[3]
AP.df

Figure 26 R code for a-priori strontium isotope mixing model (APSMM) presented in this study.

Functions

**Strontium Isotope Splitting (Sr.Split)**

*Description*

Splits the strontium isotopic ratio (\(^{87}\text{Sr}/^{86}\text{Sr}\)) into its component parts by assuming that a constant percentage of strontium is \(^{86}\text{Sr}\) therefore any changes in the ratio relate to \(^{87}\text{Sr}\). Within APSIMM this is used to help prepare end-members for calculations.

*Usage*

Sr.Split(Sr,Sr.Ratio)

*Arguments*

Sr The bulk strontium concentration in (µ or m)moles/L.
Sr.Ratio The strontium isotopic ratio (\(^{87}\text{Sr}/^{86}\text{Sr}\)).
**APSIMM Plotting Function (AP.plot)**

*Description*

Plots the ternary style diagrams to display the APSIMM calculations. This plots like a conventional `plot`. Data is plotted after running `AP.plot` using the `points` function.

*Usage*

`AP.plot(ion, Na, ion.Na.Ratio, Sr86, Sr87, Sr.Ratio, xlab, ylab, EM, P, yfit, xfit, text.pos)`

*Arguments*

- **ion**: The concentration of the ion at the end-member.
- **Na**: The concentration of the tracer ion (normally sodium) at the end-member.
- **ion.Na.Ratio**: The ratio of the ion to the tracer at the end-member.
- **Sr86**: The concentration of the $^{86}$Sr at the end-member (usually calculated using `Sr.Split`).
- **Sr87**: The concentration of the $^{87}$Sr at the end-member (usually calculated using `Sr.Split`).
- **Sr.Ratio**: The $^{87}$Sr/$^{86}$Sr ratio at the end-members.
- **xlab**: Set label for the x-axis defaults to "set xlab".
- **ylab**: Set label for the y-axis defaults to "$^{87}$Sr/$^{86}$Sr".
- **EM**: The names of the end-members, defaults to "EM1","EM2","EM3".
- **P**: Pixels used to draw the lines, greater pixels smooths the curve but uses more processing power. Defaults to 1000.
- **yfit**: Sets margins between the plot and the edge of the plotting area in y direction. Defaults to 0.01.
- **xfit**: Sets margins between the plot and the edge of the plotting area in x direction. Defaults to 10.
- **text.pos**: Sets the text position. Defaults to 2.
**APSIMM Calculation Functions (AP.calc and AP.err)**

*Description*

AP.calc calculates the proportion mixing from different sources in a solution but does not return an error estimate. AP.err calculates the proportion mixing from different sources in a solution and returns an error estimate.

*Usage*

AP.calc(Sr.Ratio.spl, ion.Na.Ratio.spl, Sr87, Sr86, ion, Na, EM.names = C("EM1", "EM2", "EM3"))

AP.err(Sr.Ratio.spl, ion.Na.Ratio.spl, Sr87, Sr86, Sr86, ion, Na, ion.Na.Ratio.spl.err, ion.err, Na.err, EM.names)

*Arguments*

Sr.Ratio.spl  The strontium $^{87}$Sr/$^{86}$Sr ratio in the sample being analysed.

ion.Na.Ratio.spl  The ion to tracer ratio in the sample being analysed.

Ion  The concentration of the ion at the end-member.

Na  The concentration of the tracer ion (normally sodium) at the end-member.

Sr86  The concentration of the $^{86}$Sr at the end-member (usually calculated using Sr.Split).

Sr87  The concentration of the $^{87}$Sr at the end-member (usually calculated using Sr.Split).

ion.Na.Ratio.spl.err  The error of the ion to tracer ratio in the sample being analysed.

ion.err  The error of the concentration of the ion at the end-member.

Na.err  The error of the concentration of the tracer ion (normally sodium) at the end-member.

**APSIMM R Example**

*Data Preparation*

It is advised that the user use the data provided in this study and follow the worked example when using APSIMM for the first time. The data should be arranged as described below. The minimum requirement for data loaded to calculate is sample strontium isotope ratio ($^{87}$Sr/$^{86}$Sr) and ion to tracer ratio (in this example Ca/Na). It is advised that an ion to tracer ratio error is also added to added. All data should be in columns and must be presented in wide format. For this example data is loaded as a csv file. Figure 27 shows the correct layout for data to be calculated by APSIMM with
sample names in column A, the calcium to sodium ratio of the sample in column B, the error of the Ca/Na ratio in column C and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in column D.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ca/Na</th>
<th>Ca/Na.err</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR01-30-POST</td>
<td>1.39</td>
<td>0.1</td>
<td>0.71169</td>
</tr>
<tr>
<td>LR01-45-POST</td>
<td>0.72</td>
<td>0.05</td>
<td>0.7111</td>
</tr>
<tr>
<td>LR01-6-POST</td>
<td>3.15</td>
<td>0.22</td>
<td>0.71147</td>
</tr>
<tr>
<td>LR05-15-POST</td>
<td>4.43</td>
<td>0.31</td>
<td>0.71065</td>
</tr>
<tr>
<td>LR09-30-POST</td>
<td>2.29</td>
<td>0.16</td>
<td>0.71102</td>
</tr>
<tr>
<td>LR09-9-POST</td>
<td>2.13</td>
<td>0.15</td>
<td>0.71102</td>
</tr>
<tr>
<td>LR01-15-PRE</td>
<td>2.89</td>
<td>0.2</td>
<td>0.71168</td>
</tr>
<tr>
<td>LR01-30-PRE</td>
<td>1.29</td>
<td>0.09</td>
<td>0.71113</td>
</tr>
<tr>
<td>LR01-45-PRE</td>
<td>0.8</td>
<td>0.06</td>
<td>0.71109</td>
</tr>
<tr>
<td>LR01-6-PRE</td>
<td>3.29</td>
<td>0.23</td>
<td>0.71142</td>
</tr>
</tbody>
</table>

*Figure 27 Correct layout of data for APSIMM calculations in the worked example.*

**Calculations**

Figure 28 presents a worked example for calculating the proportional input to groundwater using calcium against a sodium tracer. This example is based on the data from this study (a section of which is in Figure 27). This example should be copied into a new R studio tab and followed line by line to ensure comprehension of the method.

*N.B. Any text after a “#” is for annotation purposes only and is not used in the calculation.*

```r
#APSIMM For Ca for Cambodia

#Import Data in Correct format
setwd("C:\documents\mystrontiumdata")#Set working directory
data<-read.table(file="mydata.csv", #load datasheet
header=TRUE, sep=" ", stringsAsFactors=F)

#Define End-members
EM <- c("Silicate","Carbonate","Rainwater")#Set names of end-members
Sr.Ratio <- c(0.720329, 0.712235, 0.70929) #Set $^{87}\text{Sr}/^{86}\text{Sr}$ end-member values
Sr.Rat.Err <- c(0.00022, 0.00020, 0.00021) #Set $^{87}\text{Sr}/^{86}\text{Sr}$ end-member errors (for plotting only)
Sr <- c(0.127, 0.59, 0.67) #Set Sr Concentrations (umol/kg)
```
Sr <- Sr/1000 #Convert to mmol/kg

Srconcs <- Sr.Split(Sr = Sr, Sr.Ratio = Sr.Ratio) #calculate Sr split
Sr87 <- Srconcs[2,] #split 87Sr into component
Sr86 <- Srconcs[1,] #split 86Sr into component

Na <- c(0.087, 0.07, 27.88/1000) #Set Na Concentrations (mmol/L)
Na.err <- c(0.002, 0.01, 1.910/1000) #Set Na errors (mmol/L)

Ca <- c(0.0165, 0.44, 6.97/1000) #set Ca Concentrations (mmol/L)
Ca.err <- c(0.001, 0.04, 0.340/1000) #set Ca errors (mmol/L)

Ca.Na.Ratio <- Ca/Na #Calculate ion/Na ratio
Ca.Na.Err <- c(0.012, 0.812, 0.021) #set or calculate ion/Na errors

#Create the APSIMM Ternary Style Diagram
AP.plot(ion = Ca, Na = Na, ion.Na.Ratio = Ca.Na.Ratio, xlab = "Ca/Na", EM = EM, text.pos = c(2,3,1), yfit = 0.001, xfit = 10, Sr86 = Sr86, Sr87 = Sr87, Sr.Ratio = Sr.Ratio)

#add data points to the AP.plot
points(data$Ca.Na, data$X87Sr.86Sr, pch = 16, col = "firebrick2")

#add error bars to the figure at the end-members

#Conduct a basic APSIMM calculation without errors calculated
AP.dat.Ca<-AP.calc(Sr.Ratio.spl = data$X87Sr.86Sr, ion.Na.Ratio.spl = data$Ca.Na, ion = Ca, Na = Na, Sr87 = Sr87, Sr86= Sr86, EM.names = EM)

#Conduct an APSIMM calculation with errors calculated
AP.err.Ca <- cbind(data[1],AP.err.Ca)#Add row names to the data output

Figure 28 worked example of APSIMM using calcium data from this study
PHREEQ-C Modelling Codes

Below in Figure 29 and Error! Reference source not found. are the PHREEQ-C codes used for calculating the end member composition of carbonate and silicate end-members. PHREEQ-C should be utilising the llnl database for this modelling.

```plaintext
SOLUTION 1
  temp     30
  pH       4.6
  pe       4
  redox    pe
  units    mg/kgw
  density  1
  Ca       0.28
  Cl(-1)   1.05
  K        0.16 charge
  Mg       0.09
  N(-3)    0.48
  N(5)     1.74
  Na       0.64
  S(6)     3.17
  -water   0.25 # kg
REACTION 1
  Calcite  0.59
  Dolomite 0.378
  Na2CO3   0.0307
  SrCO3    0.001
  1 millimoles in 300 steps
INCREMENTAL_REACTIONS False
SELECTED_OUTPUT 1
  -file     Carbonate_Outs.sel
  -high_precision true
  -reset    false
  -step     true
  -pH       true
  -pe       true
  -reaction true
  -totals   Ca  Mg  Na
  -molalities Ca+2  Mg+2  Na+
  -saturation_indices Calcite  Dolomite  Na2CO3
  -active   true
  -user_punch true
USER_PRINT
  -start
  10 PRINT "Calcium: ", MOL("Ca+2")*1000
  20 PRINT "Magnesium: ", MOL("Mg+2")*1000
```
30 PRINT "Carbonate: ", MOL("CO3^-2")*1000
40 PRINT "Sodium:    ", MOL("Na^+")*1000
50 PRINT "Strontium:    ", MOL("Sr+2")*10^6
60 PRINT "pH: ", -LA("H^+")
70 PRINT "pe: ", -LA("e^-")
80 PRINT "Reaction: ", RXN
90 PRINT "Calcite SI: ", SI("Calcite")
-end
PRINT

-alkalinity false
-echo_input false
-eh false
-equilibrium_phases false
-exchange false
-gas_phase false
-headings false
-inverse false
-kinetics false
-other false
-saturation_indices false
-solid_solutions false
-species false
-surface false
-totals false
-user_print true
-selected_output true
-status false
-warnings -1

USER_GRAPH 1

-user_print selected_output true

10 PLOT_XY RXN/1000, MOL("Ca+2")/MOL("Na^+"), color = Green, symbol_size = 6, y-axis = 1
20 PLOT_XY RXN/1000, MOL("Mg+2")/MOL("Na^+"), color = Pink, symbol_size = 6, y-axis = 1
30 PLOT_XY RXN/1000, SI("Calcite"), color = Blue, symbol_size = 6, y-axis = 2
40 PLOT_XY RXN/1000, SI("Dolomite"), color = Purple, symbol_size = 6, y-axis = 2
50 PLOT_XY RXN/1000, SI("Na2CO3"), color = orange, symbol_size = 6, y-axis = 2
Figure 29 PHREEQC code for modelling the carbonate end-member.

```c
SOLUTION 1
  temp   30
  pH     4.6
  pe     4
  redox  pe
  units  mg/kgw
  density 1
  Ca     0.28
  Cl     1.05
```

```c
- end
- active  true
USER_GRAPH 2
  - headings  Ca Mg CO3 Na
  - axis_titles "Carbonate reacted (mmol/L)" "Concentration (mmol/L)"
  - initial_solutions true
  - connect_simulations true
  - plot_concentration_vs x
  - start
  10 PLOT_XY RXN/1000, MOL("Ca+2")*1000, color = Green, symbol_size = 6, y-axis = 1
  20 PLOT_XY RXN/1000, MOL("Mg+2")*1000, color = Pink, symbol_size = 6, y-axis = 1
  30 PLOT_XY RXN/1000, MOL("CO3+2")*1000, color = Blue, symbol_size = 6, y-axis = 1
  40 PLOT_XY RXN/1000, MOL("Na+")*1000, color = Red, symbol_size = 6, y-axis = 1
  - end
  USER_GRAPH 3
  - headings  pH pe
  - axis_titles "Reaction" "pH" "pe"
  - initial_solutions true
  - connect_simulations true
  - plot_concentration_vs x
  - start
  10 PLOT_XY RXN/1000, -LA("H+"), color = Green, symbol = Diamond, symbol_size = 6, y-axis = 1
  20 PLOT_XY RXN/1000, -LA("e-"), color = Blue, symbol = Diamond, symbol_size = 6, y-axis = 2
  - end
  END
```

Figure 29 PHREEQC code for modelling the carbonate end-member.
K        0.16 charge
Mg       0.09
N(-3)    0.48
N(5)     1.74
Na       0.64
S(6)     3.17
-water    1 # kg

REACTION 1
Albite    0.282
Ca-Montmorillonite 0.289
K-feldspar 0.386
Sr2SiO4   0.000303
Talc      0.0431

10 millimoles in 300 steps

SELECTED_OUTPUT 1
-file selected_output_1.sel
-reset false
-pH true
-pe true
-reaction true
-totals Ca Mg Na Ca Mg Na
-molalities Ca+2 Mg+2 Na+
-saturation_indices Albite Anorthite Talc
-active true
-user_punch true

USER_PRINT
-start
10 PRINT "Calcium mM:  ", MOL("Ca+2")*1000
20 PRINT "Magnesium mM: ", MOL("Mg+2")*1000
30 PRINT "Carbonate mM: ", MOL("CO3-2")*1000
40 PRINT "Sodium mM:    ", MOL("Na+")*1000
50 PRINT "Strontium uM: ", MOL("Sr+2")*10^6
60 PRINT "Reaction: ", RXN
70 PRINT "Talc (SI): ", SI("Talc")
-end
PRINT
-alkalinity false
-echo_input false
-eh false
-equilibrium_phases false
-exchange false
-gas_phase false
-headings false
-inverse false
-kinetics false
-other false
-saturation_indices false
-solid_solutions false
-species false
-surface false
-totals false
-user_print true
-selected_output true
-status false
-warnings -1

USER_GRAPH 1
-headings Ca/Na Mg/Na Albite Anorthite Talc
-axis_titles "Minerals reacted (mmol/L)" "Ratios"

"Saturation Index"
-initial_solutions true
-connect_simulations true
-plot_concentration_vs x

-start
10 PLOT_XY RXN/1000, MOL("Ca+2")*1000/MOL("Na+")*1000, color = Green, symbol = Diamond, symbol_size = 6, y-axis = 1
20 PLOT_XY RXN/1000, MOL("Mg+2")*1000/MOL("Na+")*1000, color = Pink, symbol = Diamond, symbol_size = 6, y-axis = 1
30 PLOT_XY RXN/1000, SI("Albite")*1000, color = Black, symbol = Diamond, symbol_size = 6, y-axis = 2
40 PLOT_XY RXN/1000, SI("Anorthite")*1000, color = Blue, symbol = Diamond, symbol_size = 6, y-axis = 2
50 PLOT_XY RXN/1000, SI("Talc")*1000, color = Purple, symbol = Diamond, symbol_size = 6, y-axis = 2
-end
-active true

USER_GRAPH 2
-headings Ca Mg Na
-axis_titles "Carbonate reacted (mmol/L)" "Concentrations (mmol/L)"

-initial_solutions true
-connect_simulations true
-plot_concentration_vs x

-start
10 PLOT_XY RXN/1000, MOL("Ca+2")*1000, color = Orange, symbol = Diamond, symbol_size = 6, y-axis = 1
20 PLOT_XY RXN/1000, MOL("Mg+2")*1000, color = Pink, symbol = Diamond, symbol_size = 6, y-axis = 1
30 PLOT_XY RXN/1000, MOL("Na+")*1000, color = Red, symbol = Diamond, symbol_size = 6, y-axis = 1
-end
-active true

USER_GRAPH 3
Figure 30 PHREEQ-C code for modelling the silicate end-member.