

Pond-Derived Organic Carbon Driving Changes in Arsenic Hazard Found in Asian Groundwaters

Michael Lawson,^{*,†,¶} David A. Polya,[†] Adrian J. Boyce,[‡] Charlotte Bryant,[§] Debapriya Mondal,^{†,⊥} Andrew Shantz,^{||} and Christopher J. Ballantine[†]

[†]School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Oxford Road, Manchester, M13 9PL, U.K.

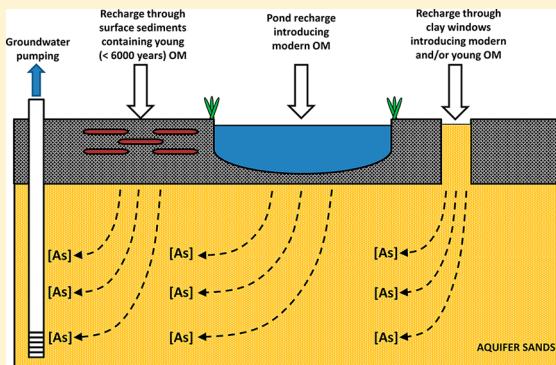
[‡]Scottish Universities Environmental Research Centre, East Kilbride, G75 0QF, U.K.

[§]NERC Radiocarbon Facility, East Kilbride, G75 0QF, U.K.

^{||}Resource Development International (Cambodia), PO Box 494, Phnom Penh, Cambodia

Supporting Information

ABSTRACT: Microbially mediated reductive processes involving the oxidation of labile organic carbon are widely considered to be critical to the release of arsenic into shallow groundwaters in South and Southeast Asia. In areas where there is significant pumping of groundwater for irrigation the involvement of surface-derived organic carbon drawn down from ponds into the underlying aquifers has been proposed but remains highly controversial. Here we present isotopic data from two sites with contrasting groundwater pumping histories that unequivocally demonstrate the ingress of surface pond-derived organic carbon into arsenic-containing groundwaters. We show that pond-derived organic carbon is transported to depths of up to 50 m even in an arsenic-contaminated aquifer in Cambodia thought to be minimally disturbed by groundwater pumping. In contrast, in the extensively exploited groundwaters of West Bengal, we show that pond-derived organic carbon is transported in shallow groundwater to greater depths, in excess of 100 m in the aquifer. Intensive pumping of groundwaters may potentially drive secular increases in the groundwater arsenic hazard in this region by increasing the contribution of bioavailable pond-derived dissolved organic carbon drawn into these aquifer systems and transporting it to greater depths than would operate under natural flow conditions.



INTRODUCTION

The daily consumption of shallow groundwater containing hazardous concentrations of geogenic arsenic by over 100 million people in South and South East Asia has long been recognized as the cause of a tragic humanitarian disaster.^{1,2} The widely accepted view is that this arsenic is released to groundwaters under anaerobic conditions following the reductive dissolution of iron oxide phases onto which arsenic is initially adsorbed.^{3,4} It has previously been shown that these reactions are microbially mediated; and that labile organic carbon is a critical, rate-limiting component of the arsenic release process.⁵ However, identification of the source of organic carbon responsible for driving arsenic release in these groundwaters remains enigmatic,⁶ and considerable controversy surrounds the various models that have been proposed.^{7–10} In particular, the suggestion by Harvey et al.⁷ that extensive groundwater pumping, and the associated drawdown of surface waters containing young labile organic matter (OM), may potentially accelerate arsenic release in these shallow reducing aquifer systems has attracted significant attention.^{11–15} Any demonstration of the link between groundwater pumping and arsenic release would surely influence future groundwater

management practices, particularly in relation to irrigation of critical food crops in the regions affected.^{16,17}

In this study, we interrogate the isotopic and chemical signature of two contrasting and well-characterized arsenic-bearing aquifers in Cambodia and West Bengal, India to identify the different sources of dissolved organic carbon that are present in these groundwaters and determine if groundwater pumping practices could influence the distribution of this known trigger in arsenic release processes.

The mean irrigation groundwater usage in the Nadia District of West Bengal, India is approximately $1 \times 10^{-8} \text{ m}^3/\text{sec}/\text{m}^2$.¹⁸ This is an order of magnitude larger than the total groundwater usage for Cambodia, which in 2002 was 750 MCM/year over 2.7 M hectares and equates to a mean groundwater irrigation rate of $8.8 \times 10^{-10} \text{ m}^3/\text{sec}/\text{m}^2$.¹⁹ With the exception of groundwater extraction rates, both systems are remarkably similar: the Cambodian and Bengali arsenic-bearing aquifer

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sediments have the same sediment source, derived from the rapid weathering of upper Himalayan rocks that are subsequently transported in rivers and deposited in the similarly low-lying alluvial floodplains of the Mekong and Ganges deltas.²⁰ The similar topography results in very small hydraulic gradients in both systems, while aquifer chemistry is dominated by calcium, magnesium, and bicarbonate in almost all of the arsenic-bearing groundwaters of this region.²¹ The Cambodian and Bengali aquifer systems also have the same extraction depth range, with tubewells screened at depths of up to 362 m in the Ganges delta,²² and to depths of up to 330 m in the Mekong delta.²³ Because of the lower pumping rates, the groundwater flow regime of the Cambodian aquifer is by comparison relatively unaffected by groundwater pumping, and therefore provides a baseline control for identifying the impact of the extensive groundwater usage that is so prevalent in the Bengal basin.^{20,24}

In the Cambodian control we show that ponds can and do act as point sources of recharge for the recent transport of young surface waters containing modern dissolved organic carbon (DOC) to depths of 50 m under natural flow conditions. In contrast, isotopic signatures of groundwaters in Bengal demonstrate that contributions of recent recharge (< 60 years) from shallow groundwaters containing relatively young DOC reach depths of greater than 100 m. This suggests that groundwater pumping practices may drive changes in the groundwater flow regime that may ultimately influence the chemistry of deeper groundwaters. Radiocarbon ages and mixing profiles of DOC in Cambodian groundwater demonstrate a requirement for surface and shallow sediment contributions to the DOC. We suggest that natural recharge through ponds and wetlands may determine groundwater arsenic concentrations on a local scale in the absence of groundwater pumping. In addition, we suggest that the presence of tritium active groundwater and relatively young DOC at depths greater than 100 m in the Bengal aquifer system, where extensive groundwater pumping remains prevalent, is indicative of changes in the natural groundwater flow regime that has resulted in the drawdown of shallow groundwater to these depths.

MATERIALS AND METHODS

Description of the Field Sites. We present data from two field areas in this study. The Cambodian study site is located in Kien Svay District, Kandal Province, Cambodia, approximately 30 km southeast of Phnom Penh and covers an area of approximately 50 km² between the Mekong and Bassac rivers. The site is characteristic of the floodplains of the lower Mekong basin, with elevated levees along the banks of the two rivers retreating to a seasonally saturated internal wetland basin that lies between the two rivers. The sedimentary deposits here typically extend to a depth of around 60 m and comprise young Holocene levee/overbank deposits of orange/gray clay containing laminations of peat and silt, which overlay fine gray sand aquifers.^{25,26} These clay deposits range in thickness from 3 to 20 m but typically are between 10 and 14 m thick. In some areas, older Pleistocene deposits of orange sands and silts underlie the Holocene sediments, and have been reported at depths as shallow as 20 m at this site.²⁷ The peat here is generally about 5 m thick and extends from a depth of approximately 6 to 11 m. The timing of this peat formation has been shown to be fairly consistent and comparable to that in the Bengal delta at 8.4–6.3 ka.^{8,27}

Given the almost negligible hydraulic gradients that derive from the flat topography of the study area, groundwater flow is driven by seasonally variable gradients developed between the Mekong and Bassac rivers and the inland wetland basins.²⁴ In the rainy season between July and November, the groundwater flow direction is from the Mekong River toward the wetlands, with this direction inverting for the remaining 8 months of the year, resulting in net groundwater flow from the wetlands to the Mekong River.²⁴

The study site in the Bengal delta is situated in the town of Chakdaha, Nadia District, West Bengal, India located 65 km north of Kolkata (Figure 1). The site covers an area of

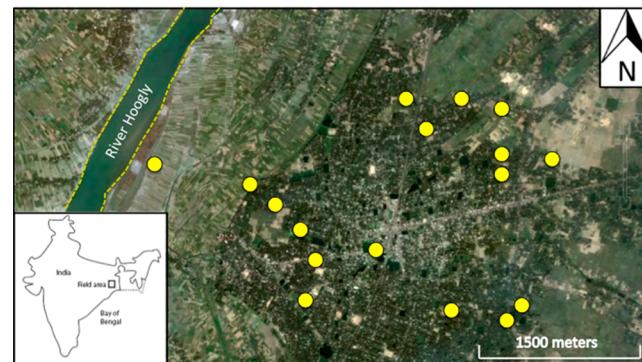


Figure 1. West Bengal field area. Groundwater-sampling locations are identified by yellow circles. The banks of the Hooghly River are delineated by dashed yellow lines.

approximately 19 km² and is bound to the west by the Hooghly River, the largest distributary of the River Ganges in West Bengal. The site is characterized by the presence of abandoned meanders and river channels, oxbow lakes, floodplains, and natural levees, with high arsenic concentrations frequently associated with abandoned floodplains, meander channel deposits, and other features indicative of river channel migration.²⁸ The sedimentary sequence at this site is comprised of organic-rich peaty silts, gray muds, and clays of the Joypur Alluvium that form a surface aquitard, which is found almost exclusively throughout the region and varies in thickness from 6 to 21 m. This aquitard is underlain by 30–40 m of gray sands from the Barasat Formation that form the shallow aquifer at this site.²² A 20-m-thick clay aquiclude then separates the shallow Holocene aquifer from the deeper Pleistocene aquifer that consists of yellow/brown gravels, sands, and muds.^{29,30}

Numerous excavated ponds are located throughout the town of Chakdaha and constitute up to 15% of the land cover. These are thought to act as sites of recharge to the groundwater during the wet season when hydraulic gradients between ponds and groundwater are favorable for downward flow.³¹ The Hooghly River shows dual behavior, acting as a source of recharge to the groundwater during the premonsoon period and as a drainage conduit for groundwater discharge in the postmonsoon period.³²

Tubewell Installation and Sediment Sampling. The installation of 5 tubewell nests (ML01–ML05), comprising 11 wells in total, was conducted at the Cambodian study site during the period of December 2008–January 2009. Tubewell nest locations were chosen to infill areas of limited spatial resolution between existing tubewells at the site. Sediment samples were obtained through rotary drilling using groundwater as the drilling fluid except within 1 m of sample collection

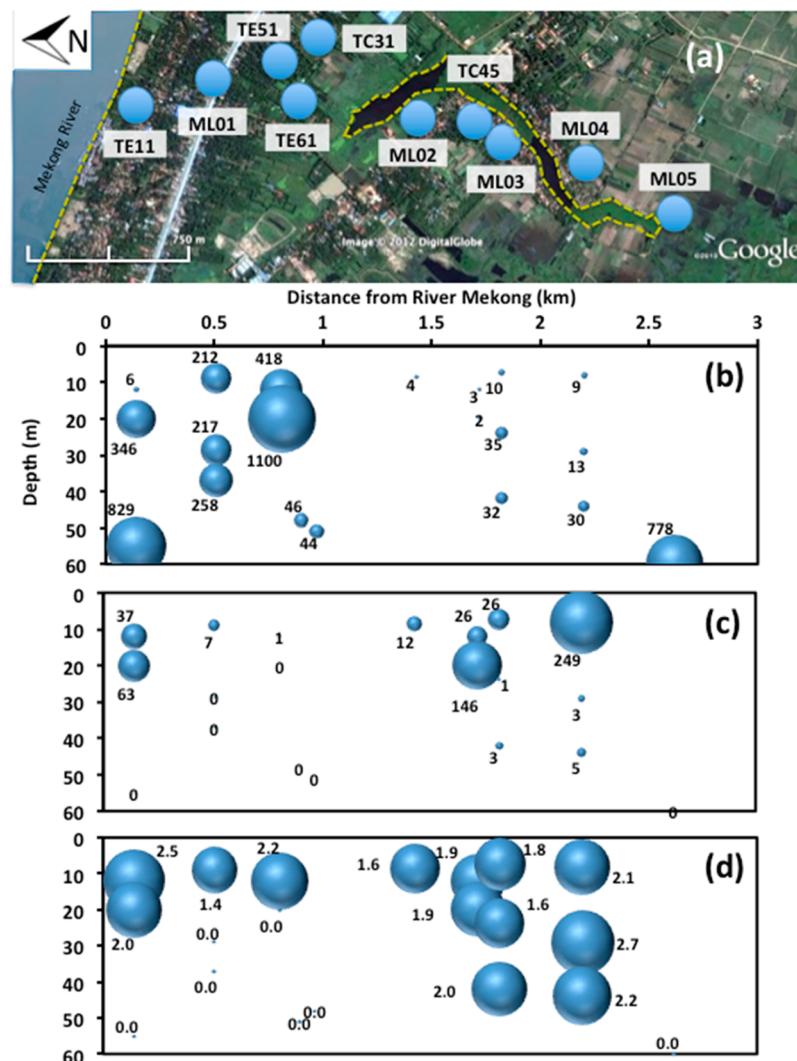


Figure 2. Cambodian field area. Well nest locations and distribution of dissolved concentrations of key redox and age indicators. (A) Location map of well nests, each of which comprise three tubewells with a depth range of 7–60 m. Predominant groundwater flow directions are perpendicular to the banks of the Mekong River marked at the northern extent of the study area. The large pond in the center of the study area is delineated by yellow dashed lines. (B) Arsenic ($\mu\text{g/L}$). (C) SO_4^{2-} (mg/L). (D) ${}^3\text{H}$ (TU). Larger bubble sizes represent higher concentrations. Arsenic concentrations are low where recent recharge delivers oxic surface waters to the aquifer system and hence is inversely correlated with SO_4^{2-} concentrations.

depths when fluid-less drilling was undertaken as described by Rowland et al.³³ and references therein. Samples were triple-bagged and stored at 4–6 °C in the dark prior to analysis.

Groundwater and Surface Water Sampling and Analysis. In Cambodia, 20 groundwater samples were collected in March–April 2009 over a 2.6-km transect perpendicular to the Mekong River and over a depth range of 7.3–60 m. A subset of tubewells lying along this transect was sampled on a monthly basis for stable isotope ($\delta^{18}\text{O}$ and δD) analysis. Additionally, surface water samples were collected from the Mekong River and the large pond situated in the center of the study area (outlined in Figure 2). In West Bengal, 22 groundwater samples were collected in April 2008 along a 5-km transect perpendicular to the River Hooghly through the village of Chakdaha over a depth range of 12.3–123.1 m.

A submersible pump (MPI, Grundfos) was used to draw water in West Bengal and in Cambodia with wells denoted ML at a discharge rate of approximately 12 L/min. In all remaining wells in Cambodia, a peristaltic pump (Geopump II, Geotech Environmental Equipment, Inc.) was used to draw water at a

discharge rate of approximately 1 L/min. Tubewells were purged for a minimum of one well volume, with measurements of temperature, pH, Eh, and electrical conductivity recorded at short intervals until the discharging waters stabilized. Groundwater samples were collected, treated, and stored depending on the intended analysis. Samples for major and trace cations, and DOC analysis were filtered through a 0.45-μm cellulose nitrate filter into 100-mL acid-washed glass schott bottles, acidified to pH <2 using trace element grade HNO_3 , and stored at 4 °C prior to shipping and analysis. Samples for anion analysis were filtered and stored as above but were not acidified. Water samples for stable isotope analysis were collected in 60-mL amber glass bottles with Polyseal caps and stored at 4 °C. Water samples for ${}^{14}\text{C}$ analysis of DIC were collected in 500-mL amber glass bottles and stored at 4 °C, while samples for ${}^{14}\text{C}$ analysis of DOC were collected in 2.5-L amber glass bottles and stored at 4 °C. Water samples for tritium analysis were collected in 1-L argon-filled amber glass bottles and stored with a 4-cm argon head. Water samples were analyzed using standard methods. Detailed descriptions of the analysis

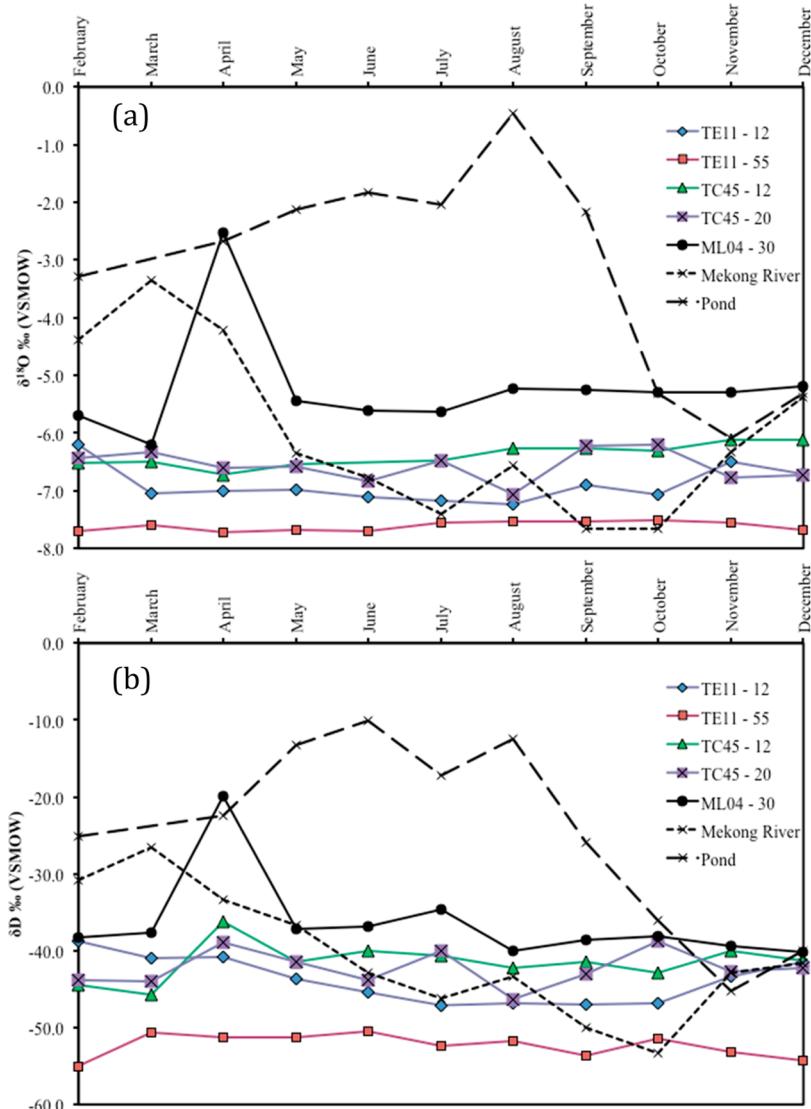


Figure 3. Comparison of seasonal variability in (a) $\delta^{18}\text{O}$ and (b) δD of tubewells and surface waters (Mekong River and pond water) at the Cambodian study site. The temporal variability in surface waters is far greater than that of the underlying groundwaters, which appear to be minimally influenced by seasonal variability in the surface water signatures. However, the groundwater signatures do appear to reflect varying degrees of contributions from overlying surface waters, with this impact particularly pronounced in tubewell ML04-30, which is located only 10 m from the large pond.

procedures can be found in the original references and the Supporting Information.

RESULTS AND DISCUSSION

Cambodia: An Insight into Pre-Groundwater Development Conditions? In the Kandal Province of Cambodia, the absence of intensive groundwater pumping provides a relatively pristine environment from which it is possible to characterize the natural hydrogeochemistry of aquifers analogous to those found in the extensively altered Bengal Basin. The hydrogeochemistry of the shallow groundwater here is clearly linked to the hydrological regime that governs groundwater flow in the aquifer system. Groundwater sulfate concentrations are almost exclusively low in the northern section of the study area within 1 km of the Mekong River (Figure 2). The two localized elevated concentrations of sulfate at well nest TE11 can be explained by river water invasion from the Mekong during June–October when river levels are rising,

as previously reported at this site through monitoring of groundwater and river levels.²⁴ Sulfate concentrations of shallow groundwater increase between 1 and 2.2 km from the Mekong River, and likely derive from the downward migration of recharge from the large pond located in the center of the study area. This trend is consistent with observations of groundwater levels for this region of the study site that suggest strong downward flow of surface pond waters to the underlying aquifer during November–May.²⁴

Dissolved arsenic concentrations are high where sulfate is essentially absent from the groundwater and low in areas that contain high concentrations of sulfate. There are several potential sources of high sulfate concentrations in the groundwaters of this region, including that derived from connate seawater trapped following the mid-Holocene transgression³⁴ or through contributions from wastewater in the recharging water source.³⁵ Given that the elevated sulfate concentrations at the Cambodian site are always associated with high concentrations of tritium (Figure 2D), which are indicative

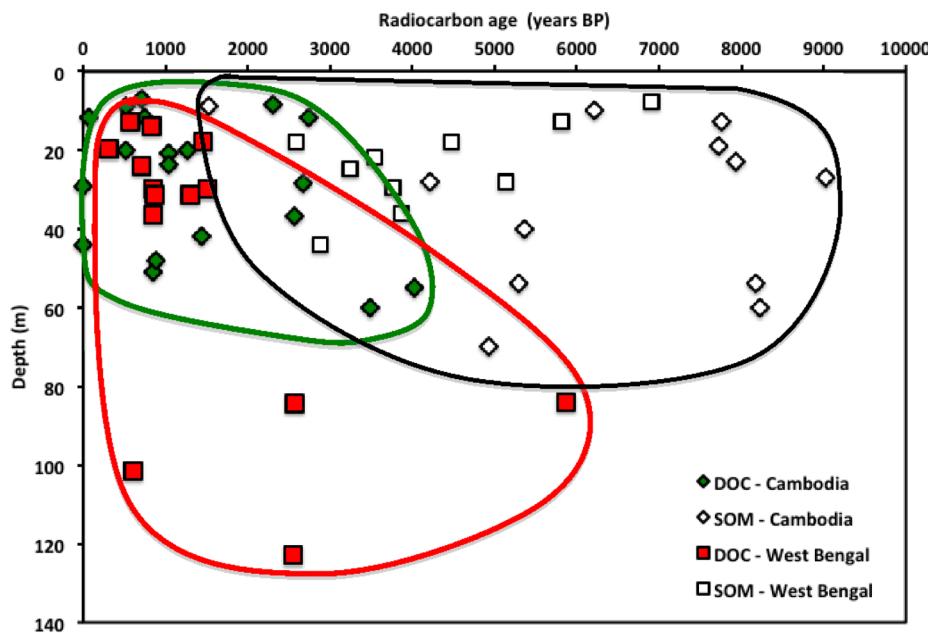


Figure 4. Comparison of radiocarbon ages of DOC and SOM in Cambodian and Bengali aquifers. Individual fields delineate Cambodian (green) and Bengali (red) DOC from the SOM of both fields (black). Bulk groundwater DOC is consistently younger than SOM over the entire depth profile at both sites and demonstrates contributions of modern DOC to the groundwater. The chemical and isotopic signature of groundwaters at both study sites shows a contribution of modern, pond-derived recharge that could transport DOC to these depths and ultimately influence the redox processes implicated in arsenic release in these aquifers.

of recent recharge, we suggest that the sulfate in these groundwaters likely derives from wastewater contributions in recharge from the nearby pond. The presence of sulfate requires that these recharging waters have not yet reached the anoxic conditions required for sulfate reduction. The release of arsenic requires reducing conditions that solubilize the Fe oxide phases onto which the arsenic is sorbed. It is therefore not a surprise that arsenic concentrations are inversely correlated to concentrations of sulfate. However, while the introduction of relatively oxic surface waters containing elevated sulfate concentrations may initially suppress arsenic pollution in regions that are proximal to the recharge source, McArthur et al.³⁵ suggest the introduction of such fluids may ultimately increase the concentration of arsenic downstream of the recharge source during the onset of reducing conditions, once all available oxygen has been consumed.

The inferred connectivity between ground and surface waters is supported by the temporal monitoring of the stable isotopic ($\delta^{18}\text{O}$ and δD) composition of surface water (Mekong River and pond) and groundwater at wells TE11, TC45, and ML04 presented in Figure 3. Both the Mekong River and the large pond show a seasonal influence in their isotopic signatures. The Mekong River develops an increasingly depleted isotopic signature (more negative) during March–October, roughly coincident with the rise in the water levels of the river. This likely reflects a Rayleigh style distillation process that correlates with the amount of precipitation that falls over the course of the rainy season.³⁶ In contrast, the pond develops an increasingly enriched isotopic signature (more positive) during November–August, which likely reflects the impact of evaporative enrichment of surface ponds. During August–November, the isotopic signature of pond water becomes increasingly depleted and evolves toward a more groundwater-like signature. Interestingly, this period coincides with strong upward groundwater flow that manifests as artesian flow in

some wells across the study site, particularly in topographic lows²⁴ and demonstrates strong evidence for groundwater–surface water connectivity.

There appears to be very little temporal variability in the isotopic composition of groundwaters at different locations and depths across the study site. However, our data show a spatial difference in the stable isotopic signature of groundwaters taken from different locations over the field site, with groundwater at a depth of 30 m at ML04 approximately 2.5‰ and 13‰ enriched in $\delta^{18}\text{O}$ and δD , respectively, compared to deep groundwater at TE11. Groundwater at depths of 12 and 55 m at site TE11 seems to be influenced by contributions of invading Mekong River water, with the isotopic signature at both depths converging with that of Mekong River water during July–October. In contrast, groundwater collected from both TC45 and ML04 have isotopic signatures that are enriched relative to TE11 that suggests a potentially different recharge source at these locations.

This enriched signature is particularly pronounced for well ML04 at a depth of 30 m for April, when the isotopic signature of the groundwater and the pond, located only 10 m away, converges to values of $-2.5\text{\textperthousand}$ and $-20\text{\textperthousand}$ for $\delta^{18}\text{O}$ and δD . It is worth noting that this sample was taken using a submersible pump at a much greater flow rate than the peristaltic pump that was used to collect all other samples for this time series analysis. While we cannot rule out the possibility that surface water was trapped within the well annulus at the time of sampling, we feel that the most likely explanation for this anomaly is that the greater flow rate induced by the use of the submersible pump may have resulted in the drawdown of water from the nearby pond along preferential flow paths to the well screen. As such we suggest that this particular sample was contaminated and the isotopic signature for this month may be unrepresentative of bulk groundwater at this location. However, all other enriched isotopic signatures for both TC45 and ML04 are

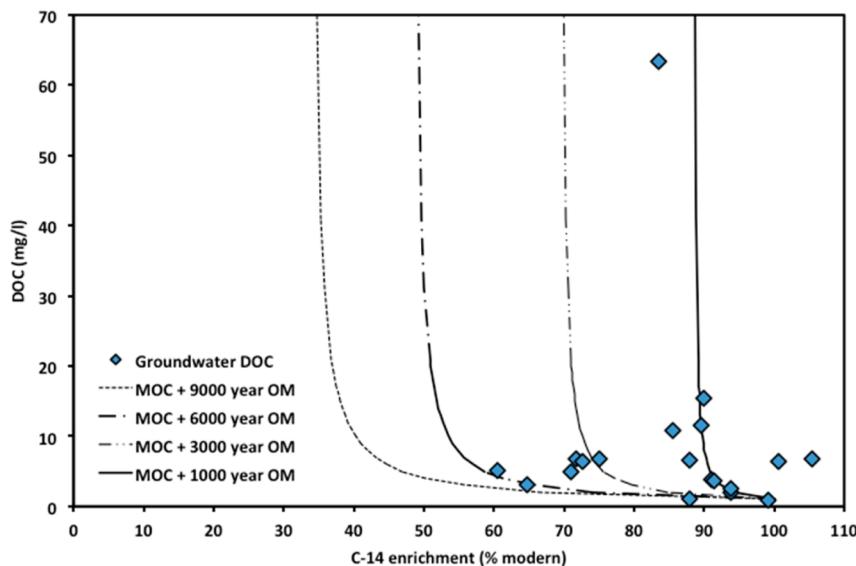


Figure 5. Radiocarbon age of DOC in Cambodian groundwaters and the modeled evolution in the age of bulk DOC through the mixing of SOM and modern DOC. Measured radiocarbon ages are compared with model ages of DOC calculated based on two-component mixing of 1 mg/L modern OM with SOM with ages of 1000, 3000, 6000, and 9000. Mixing profiles demonstrate the requirement for contributions of modern DOC and place upper limits on the age of SOM contributions of 6000 years.

consistent with contributions from an evaporated surface source of recharge that we suggest is most likely the nearby pond given that this location is beyond the possible influence of Mekong River water invasion. This observation is consistent with the hydraulic behavior of well TC45, which displays a seasonal trend that mimics that of overlying surface waters and suggests an increased influence of these water bodies at this location.²⁴ We therefore suggest that the variability in the isotopic signature of groundwaters at different depths and locations presented here preserves a signature of contributions of recharge from surface waters which decreases with increasing lateral distance between surface water bodies and the underlying groundwater.

The timescales over which recharge enters the aquifer system were assessed through the determination of the groundwater tritium content. Groundwater was shown to contain an active contribution of modern (< 60 yrs) recharge to depths of up to 12 m over the entire study area. Modeled vertical travel times through surficial clays of more than 200 years at this site² suggest a requirement for recharge through high conductivity sediments or “clay windows” in surficial clay deposits at this site. The depth to which modern recharge can be traced is greatest in wells that display an active contribution from pond water in the center of the study area. The presence of tritium active groundwater (Figure 2D) over the entire depth profile in these locations is consistent with stable isotope and sulfate profiles and suggests that pond water contributions dominate the water budget in areas that are proximal to these recharge sources.

The radiocarbon age of bulk groundwater DOC is shown relative to the bulk radiocarbon age of sedimentary organic matter (SOM) taken in and around both the Cambodian and Bengali field sites (Figure 4). Radiocarbon ages of DOC at both study sites are almost exclusively younger than SOM for equivalent depths. At the Cambodian study site, the radiocarbon ages of DOC range from modern at depths of 30 and 44 m to 4036 years BP at a depth of 55 m. In contrast, radiocarbon ages of SOM range from 1232 years at a depth of 9 m to more

than 9000 years at a depth of 27 m. Indeed, the oldest DOC measured at the Cambodian site is more than 1200 years younger than SOM at a similar depth. This difference in the radiocarbon age of DOC and SOM requires that the DOC contain either (i) modern, surface-derived OM, or (ii) contributions from younger SOM that is released from the sediment upstream and transported in the dissolved phase along a groundwater flow path. Similarly, the radiocarbon ages of DOC at the Bengali study site range from 671 years at a depth of 101.5 m to 5873 years at a depth of 84 m, while radiocarbon ages of SOM range from 2580 years at a depth of 18 m to 6916 years at 9 m. Interestingly, three groundwaters at depths in excess of 80 m contain DOC younger than the youngest radiocarbon age of SOM measured in this aquifer. As in the Cambodian system, the presence of relatively young DOC in Bengali groundwaters compared to that of SOM at equivalent depths requires that the reservoir of groundwater DOC contain contributions of younger SOM.

The difference in the ages of groundwater DOC and SOM that we present here has not previously been reported, and conflicts with a previous study by Harvey et al.⁷ that reports similar radiocarbon ages of SOM and DOC taken from equivalent depths in Bangladesh. Our observation of modern OM in groundwater at these depths is also in conflict with modeling that suggests transport times for DOC of at least 2500 years to depths of 30 m.¹⁴ This disparity between modeled and measured transport times for DOC may reflect differences in vertical groundwater velocities,¹⁴ mineralogical control on sorption,⁴² or differences in the recharge mechanisms operating at different sites. Nonetheless, our data demonstrate unequivocally that relatively young, labile surface-derived DOC can be transported into aquifers by recharge to depths of at least 50 m even in the absence of groundwater pumping at the Cambodian study site. Furthermore, the presence of young DOC at depths in excess of 80 m in Bengali groundwaters demonstrates that DOC must be transported to greater depths along flow paths that are likely to be significantly

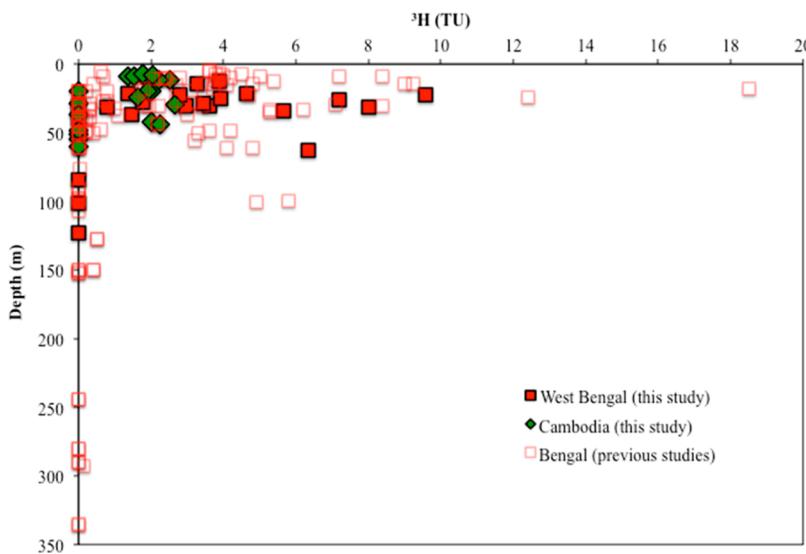


Figure 6. Comparison of the tritium content of Bengali and Cambodian groundwaters taken from this and previous studies.^{37–41} Tritium active groundwaters are found in both areas showing the rapid incursion of surface-derived waters into these aquifers. This is particularly pronounced in the heavily exploited aquifers of West Bengal where the presence of tritium active groundwaters at depths of 100 m or more requires the rapid transport of recharge to depth.

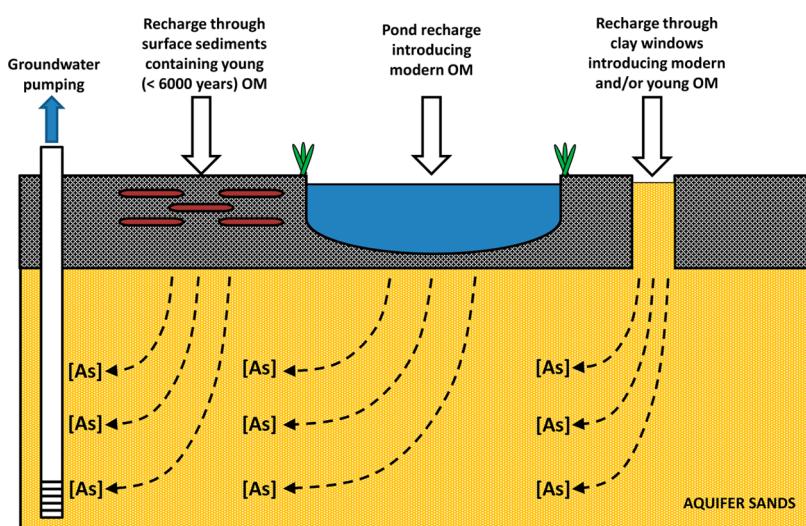


Figure 7. Conceptual model of sources and pathways for the introduction of modern and young organic matter to shallow arsenic-prone aquifers in both Bengal and Cambodia. Our data show that rapid pathways exist in the Cambodian system that transports modern DOC from surface ponds to the aquifer even in the absence of extensive groundwater pumping. In Bengal, our data suggest that groundwater pumping may decrease the travel time of young DOC to greater depths within the aquifer system. Anthropogenic activities, such as the excavation of surficial clays or extensive groundwater pumping, are likely to result in changes to the relative proportions of different organic matter sources present in groundwaters, which may ultimately influence the arsenic hazard in shallow groundwaters of this region.

impacted by the extensive groundwater pumping that prevails in this region.

While the age of SOM exceeds that of DOC at equivalent depths, the radiocarbon ages of DOC in tritium active Cambodian groundwaters, with the exception of three samples, all exceed 500 years. The observation of DOC ages older than the water in which it is transported requires contributions of DOC from older SOM. Measured groundwater DOC ages are consistent with mixing of 1 mg/L of modern DOC with SOM between 1000 and 6000 years old (Figure 5). Typical peat deposits in these alluvial floodplains have radiocarbon ages of 6000–8000 yrs at depths greater than 6 m.^{8,23} The radiocarbon ages and mixing profile presented here suggest that peat deposits contribute very little DOC to the groundwater

inventory, and that much of the subsurface sourced DOC must derive from shallow (< 5 m) sediments. This is fully consistent with a near-surface source of OM postulated to be driving arsenic release at this site.^{25,43}

Comparison with Bengali Groundwaters: An Insight into Cambodia's Future? The aquifer systems investigated in Bengal, where extensive groundwater pumping has proceeded for decades, display key differences from those in the Cambodian control system. First, almost all groundwaters up to a depth of 60 m show a significant contribution of modern recharge (Figure 6). While the tritium profile of the Cambodian groundwater system is characteristic of predevelopment conditions, the more extensive presence and deeper penetration of tritium in Bengali aquifers is consistent with groundwater

pumping practices having resulted in the recent transport of surface waters to greater depths over timescales that would not normally exist under natural conditions.

Comparison of the bulk DOC radiocarbon age of Cambodian and Bengali groundwaters (Figure 4) suggests that the relative contributions of different sources of OM are similar for shallow groundwaters at both sites. The key difference in Bengali groundwaters is the presence of relatively young DOC in deep (>100 m) groundwater, requiring recent transport of surface or shallow sediment-derived DOC to depth. While stable isotope data have provided conflicting evidence as to the source of DOC in these groundwaters,^{7,9,44} the combined tritium and radiocarbon data presented here suggest that a component of the DOC inventory must have a surface origin. We suggest this previous stable isotope data may instead reflect variance in the dominant source of recharge (pond vs clay window) to the groundwater at these sites.

Significance of Organic Matter Source and Pumping Practices for Spatial and Temporal Evolution of Groundwater Arsenic Concentrations. This comparison of Bengali and Cambodian groundwaters suggests that groundwater pumping practices may drive changes in the groundwater flow regime that can ultimately result in secular changes in the geochemical composition of these aquifers. Despite the site-specific variations in the source, processes, and timescales associated with groundwater recharge, our results are important for the provision of safe drinking water in this region. We show that dissolved organic carbon, a known trigger in the arsenic release process, clearly has both surface and sedimentary contributions to the bulk groundwater inventory. Our conceptual model of the possible origins and pathways for introducing surface-derived DOC (Figure 7) depicts two potential modes of recharge for introducing surface-derived DOC: recharge through the base of ponds or wetlands, and recharge through holes in surficial clay deposits, or "clay windows". Sedimentary-sourced organic carbon, in contrast, can be introduced to groundwater following recharge through surface sediments containing young (< 6000 years) organic matter. The spatial and temporal evolution in the groundwater arsenic hazard on a local scale may therefore be explained by the relative contribution from these two sources and the role they play in subsequent biogeochemical processes within the aquifer. One may expect that groundwaters containing a greater proportion of younger, more labile DOC are capable of supporting more extensive and increased rates of arsenic release.⁶ This is a logical extension to the recent findings of Postma et al.⁴⁵ who show that arsenic release is inversely proportional to the age of sedimentary organic carbon. Anthropogenic activities that increase the supply of surface-derived DOC to groundwaters, such as the excavation of clay or the digging of artificial ponds or intensive exploitation of aquifers through groundwater pumping, are therefore likely to have a significant impact on the groundwater arsenic risk in shallow aquifer systems.

ASSOCIATED CONTENT

Supporting Information

Supplementary methods including tubewell installation and analytical procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: michael.lawson@exxonmobil.com.

Present Addresses

[†]ExxonMobil Upstream Research Company, Houston, Texas, 77019, USA.

[‡]School of Environmental and Life Sciences, University of Salford, Salford, Lancashire M5 4WT, U.K.

Author Contributions

M.L., D.A.P., and C.J.B. designed and implemented the project. M.L., D.M., A.S., C.J.B., and D.A.P. collected samples in the field. A.J.B. provided the stable isotope analysis. C.B. provided the ¹⁴C analysis. M.L. conducted all other analyses. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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