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Tritium Tracers of Rapid Surface Water Ingression into Arsenic-Bearing Aquifers in the Lower Mekong Basin, Cambodia

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Abstract

Arsenic (As) contamination of groundwaters in South and Southeast Asia is a major threat to public health in these areas. Understanding the source and age of the groundwaters is critically important to understanding the controls on As mobilization in these aquifers. Using tritium (^{3}H) and noble gas (He and Ne) signatures, model groundwater ages and dominant hydrological controls were identified in a transect oriented broadly parallel to inferred groundwater flowpaths in Kandal Province, Cambodia in the lower Mekong Basin. Apparent ^{3}H-^{3}He ages showed that most groundwaters are modern (< 55 years), indicating relatively fast recharge even in the absence of large-scale groundwater abstraction. The age-depth relationship indicates a strong vertical component of groundwater flow and allows for recharge rates to be estimated. Vertical and horizontal flow velocities are heterogeneous and site-specific. The conceptual framework will be used to better understand As mobilization and subsequent transport with these and similar aquifers.

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Keywords: tritium, arsenic, groundwater age, environmental pollutants, Cambodia

1. Introduction

Millions of people in South/Southeast Asia chronically consume groundwater containing dangerous concentrations of naturally-occurring As[1-4]. As release in shallow aquifers in this region is widely attributed to the

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reductive dissolution of As-bearing Fe(III) minerals[5], driven by metal reducing bacteria and bioavailable organic matter[2,5-7]. The nature of the organic matter implicated in As mobilization is generally thought to derive, in some proportion, from (i) plant-derived organic matter internal to aquifers[8,9]; (ii) external, modern surface-derived organic matter, largely from ponds, rivers and rice paddies[10-18]; and/or (iii) petroleum-derived hydrocarbons[7,19,20]. Debates surrounding the sub-surface location where As mobilization takes place and the subsequent controls on As mobility[10,14,15,17, 21-25] are intrinsically linked to the type and amount of the organic matter implicated in As release[7-10,14,15,19,20,26]. Determining the relative importance of these various inputs is essential in predicting future changes in As hazard[10,15,27]. The aim is to characterize the ^3H and noble gas (He and Ne) isotopic signature of As-affected groundwater to (i) determine groundwater age; (ii) examine dominant hydrological controls; and (iii) assess local heterogeneity, which ultimately may affect As mobilization and transport in these aquifers.

2. Methods and Materials

The field sites are located in Kien Svay, Kandal Province, Cambodia, an area heavily affected by groundwater As[11,12,14,15,19,27-30] and representative of pre-development conditions. Groundwater samples (6 - 45 m deep) were collected from flushed and developed wells[31] pre- (May – June 2014) and post-monsoon (Nov – Dec 2014). In-situ measurements of basic groundwater parameters and subsequent analysis of geochemical composition was conducted[31]. Duplicate samples for ^3H analysis were collected in 1 L argon filled amber glass bottles. Duplicate samples for He and Ne analysis were collected in flushed soft copper tubes. Analysis of ^3H, He and Ne isotopes was conducted at the "Helis – Helium Isotopes Studies Bremen" Noble Gas Laboratory (Institute of Environmental Physics, University of Bremen, Germany)[32], with apparent ^3H-^3He ages derived using previous methods[33].

3. Results and Discussion

3.1. ^3H Concentration of Groundwater and Surface Water

^3H measurements of groundwaters, river water and rain range from 0.04 to 3.6 TU (Fig. 1A). Relatively high pre-monsoon ^3H in the Mekong suggests an additional and variable upstream source for ^3H, likely from higher altitude Himalayan precipitation[34]. Concentrations of 'stable tritium' (the sum of ^3H and $^3He_{tri}$) are similar to the input function for Bangkok precipitation (Fig. 1B)[35]. The similarity in independent datasets provides verification of ^3H sampling and analysis. For all samples (except $\geq$ 30 m depth at LR09), the 'stable tritium' follows the ^3H input function for Bangkok closely, indicating that no old ^3H-free water is admixed with young groundwater at most sites.

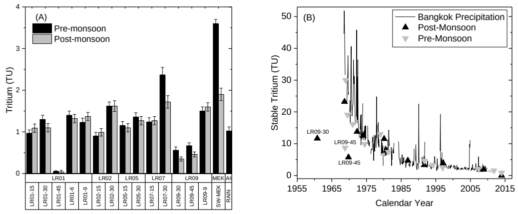

Fig. 1. (A) ^3H for pre-/post-monsoon groundwaters, Mekong River and rain. ^3H was > 0.02 TU in all groundwater samples; (B) 'Stable tritium' (the sum of ^3H and $^3He_{tri}$) values and the input function for Bangkok precipitation (WMO Code 4845500[35]) against infiltration date.

3.2. Apparent ^3H-^3He Ages of Groundwater and Surface Water

Apparent ^3H-^3He ages show distinct spatial patterns (Fig. 2A). Ages are mostly modern (e.g. < 55 years in age), with the exception of two sites (LR09-30 and LR01-45). Age increases with depth at every site, with the exception of site LR09. For the same depth there is age variation on the order of 10 – 20 years. The spatial variation of apparent ages allows for estimates of groundwater flow velocities. The overall increase in ^3H-^3He age with depth (Fig. 2B) has an overall gradient representing mean vertical flow velocity of 0.5 ± 0.1 $m.yr^{-1}$ $(t(24) = 5.62, p = 8.7 \cdot 10^{-6}$ for ages < 55 years). Depth profiles at specific sites show localized and heterogeneous vertical flow velocities. The site-specific variability gives rise to the identification of relatively rapid recharge zones.

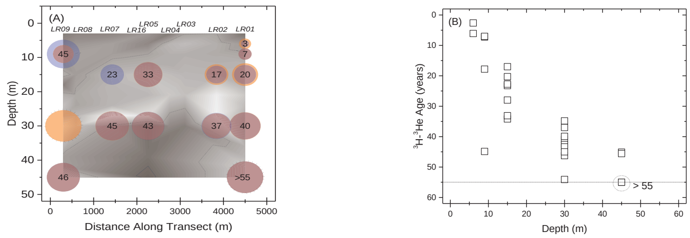

Fig. 2. (A) Apparent ^{3}H-^{3}He age (in years, 2014 basis) with increasing perpendicular distance from the Bassac River. Blue, labelled ages are pre-monsoon (orange post-monsoon). Dashed lines indicate ages > 55 years. The contour represents grain size (lighter colors are sandier); (B) Apparent ^{3}H-^{3}He age versus depth.

3.3. Implications on Arsenic Release

As concentrations are typically lower in very young waters and increase in deeper, older waters (**Fig. 3A**). This relationship allows for the calculation of an overall As loading rate of 6.3 ± 2.6 $\mu g.L^{-1}.yr^{-1}$ *(t(24) = 2.40, p = 0.0246)*. As loading is heterogeneous and site-specific, and is attributed in part to changes in lithology and the likely presence of bio-available carbon. Depth profiles allow for examination of the association of As with ^{3}H, noble gases, Eh and dissolved organic carbon (DOC) (**Fig. 3B**). In addition to the general correlation of As with depth and ^{3}H-^{3}He age, and the inverse As/Eh correlation, $^{4}He_{rad}$ increases with depth which is consistent with age.

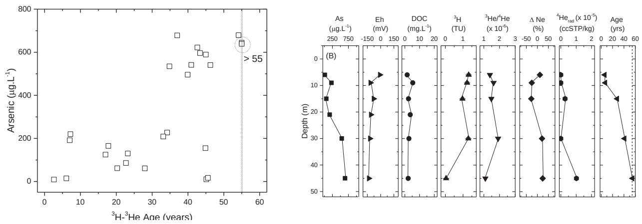

Fig. 3. (A) As versus apparent ^{3}H-^{3}He age (basis 2014). Samples in the dashed circle are > 55 years old; (B) Depth profiles for site LR01.

4. Conclusions

The ^{3}H composition of As-bearing groundwater was used to determine groundwater ages along groundwater flowpaths. Apparent ^{3}H-^{3}He ages showed that most groundwaters are modern and younger than previously considered. Consistency of 'stable tritium' with the input function for Bangkok precipitation provides independent verification of analysis. A strong depth-age relationship suggests the dominance of a vertical hydrological control. Ages can be used to estimate flow velocities and heterogeneity. Such hydrological controls provide the conceptual framework for an improved groundwater model and may affect As mobilization/transport with the aquifer.

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