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Bayesian modeling approach for characterizing groundwater arsenic contamination in the Mekong River basin

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HIGHLIGHTS

- The groundwater in the Mekong River basin delta contained high As_{TOT} and As(III).
- A Bayesian change-point model identified the threshold level of Eh, −100 (±15) mV.
- Below the change-point, As_{TOT} increased with increasing Eh.
- Above the change-point, As_{TOT} sharply decreased as Eh increased.
- As_{TOT} was positively related to pH over the entire range of Eh levels.

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ABSTRACT

In the Mekong River basin, groundwater from tube-wells is a major drinking water source. However, arsenic (As) contamination in groundwater resources has become a critical issue in the watershed. In this study, As species such as total As (As_{TOT}), As(III), and As(V), were monitored across the watershed to investigate their characteristics and inter-relationships with water quality parameters, including pH and redox potential (Eh). The data illustrated a dramatic change in the relationship between As_{TOT} and Eh over a specific Eh range, suggesting the importance of Eh in predicting As_{TOT}. Thus, a Bayesian change-point model was developed to predict As_{TOT} concentrations based on Eh and pH, to determine changes in the As_{TOT}–Eh relationship. The model captured the Eh change-point (∼−100 ± 15 mV), which was compatible with the data. Importantly, the inclusion of this change-point in the model resulted in improved model fit and prediction accuracy; As_{TOT} concentrations were strongly negatively related to Eh values higher than the change-point. The process underlying this relationship was subsequently posited to be the reductive dissolution of mineral oxides and As release. Overall, As_{TOT} showed a weak positive relationship with Eh at a lower range, similar to those commonly observed in the Mekong River basin delta. It is expected that these results would serve as a guide for establishing public health strategies in the Mekong River Basin.

1. Introduction

Depending on water availability and quality, drinking water resources can be obtained from various water bodies, including rivers, lakes, reservoirs, and groundwater. Although a large population resides alongside the Mekong River and its tributaries, groundwater resources remain the primary sources of drinking water, household water use, and irrigation in Southeast Asian countries. Groundwater is the preferred drinking water resource in these regions mainly due to its stable biochemical properties (Schmoll et al., 2006). However, groundwater contamination from arsenic (As) has become a critical issue in the developing world, especially in Southeast Asia. Specifically, inorganic As, the dominant form found in groundwater, is a known carcinogen, and as such poses a critical threat to public health (Bagla and Kaise, 1996; AWWA, 2001; Berg et al., 2006; Kocar and Fendorf, 2009; Sthiannopkao et al., 2010; Mondal et al., 2013).

Previous studies have reported on the status of groundwater As concentrations in Asian countries, many of which remain in

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non-compliance with 10 μg L^{-1}, the safe World Health Organization (WHO) drinking water guideline (Berg et al., 2001, 2007; Smedley and Kinniburgh, 2002; Sun et al., 2002; Polya et al., 2003, 2005; Stanger et al., 2005; Kohnhorst, 2005; Tetsuro et al., 2006; Chauhan et al., 2008; Chiew et al., 2009; Rahman et al., 2015). To this end, Sun et al. (2002) estimated that approximately 200 million people in South Asia are currently being exposed to the toxic effects of As. In the Kandal province of Cambodia, Sthiannopkao et al. (2008) found that As_{TOT} concentrations ranged from a non-detectable level to approximately 900 μg L^{-1}, and that ~54% of collected groundwater samples exceeded the safe level of 10 μg L^{-1} (Allan et al., 2002). As-contaminated regions can generally be characterized by four different hydro-geological features: (1) alluvial and mild-slope topographies, (2) fast holocene sedimentation, (3) enriched degradable organic materials, and (4) stagnant groundwater flow (Chanpiwat et al., 2011).

To address public health issues arising from groundwater As contamination, regulations and monitoring strategies should be either developed or further reinforced in Southeast Asian countries. However, intensive monitoring efforts could be a challenging task for many of these countries because groundwater As measurements typically require advanced equipment, highly experienced technicians, and incur a high maintenance cost.

Given the limited financial and human resources available, alternative modeling approaches that characterize As patterns and distributions using water quality parameters that are straightforward to measure should be developed; these can then be used to provide a scientific basis for establishing public health strategies. Previous studies developed statistical models for modeling groundwater As concentrations using water quality parameters as input variables (Purkait et al., 2008; Chang et al., 2010; Cho et al., 2011). For example, using an Artificial Neural Network (ANN) with regression models, Purkait et al. (2008) predicted the groundwater As contamination in Eastern India. Chang et al. (2010) employed an ANN model to impute missing values in As concentration datasets for an area of Taiwan. And Cho et al. (2011) compared the performance among linear and nonlinear regression models and ANNs for predicting As concentrations in Southeast Asia. Interestingly, Cho et al. (2011) found that dividing the range of the redox potential (Eh) into two groups and separately estimating the relationship of As with Eh $\geqslant 0$ and Eh < 0 substantially improved the model predictability.

Data sets spanning a wide range of As concentrations, measured in two Southeast Asian countries in 2008, 2010, and 2012, provided an opportunity to examine the patterns of groundwater As contamination and their variability. In this study, the spatial distributions of multiple As species as well as the relationships between As and water quality parameters were analyzed. We focused on the studies for exploring the inter-relationship As and water quality parameters, rather than considering of geological properties of the watershed. Building on the findings of Cho et al. (2011), we developed a Bayesian change-point (CP) model that captures the change in the relationship between As and Eh over a range of Eh levels. Here, instead of determining the change-point based on a subjective judgment, our model estimates the change-point that was the most compatible with the data.

2. Materials and methods

2.1. Study area

With the objective of exploring As contamination problems in the natural groundwater of the Lao People's Democratic Republic (Lao PDR) and Cambodia, sampling campaigns were conducted in 2008, 2010, and 2012. Because the source of the high As concentration was thought to be its release from river sediment under reducing conditions (Rawlings et al., 1998; Polizzotto et al., 2008; Sthiannopkao et al., 2008; Kocar et al., 2008), we selected the provinces located along the Mekong River as study sites (Fig. 1). Sites in the Lao PDR included Vientiane, Bolikhamxai, Savannakhet, Saravane, Champasak, and Attapeu. The provinces in Cambodia were Prey Veng and Kandal. All selected tube-wells were cement tube-wells equipped with a covered lid and hand-pumping equipment, all of which were developed and maintained by local communities and households.

2.2. Sample collection

As a result of the three sampling campaigns, a total of 112 and 80 groundwater samples were collected from the Lao PDR and Cambodia, respectively. Table S1 summarizes the samples and parameters studied in each sampling campaign. The common water quality parameters were temperature, pH, electrical conductivity, Eh, total dissolved solids (TDS), and As_{TOT} (total arsenic). However, it should be noted that the full spectrum of As species (As(III), As(V), and particulate As) and well depth information was only collected in 2012.

For groundwater collection, standing well water was first pumped out for about 10 min, and groundwater samples were then collected for As_{TOT}, soluble As, and As(III) concentration analyses. All samples were collected in clean polypropylene bottles previously soaked with concentrated nitric acid (HNO_3) and washed with groundwater water drawn from the sampling sites. For As_{TOT}, groundwater samples were directly collected with no filtration or treatment. On the other hand, filtered water samples (using a 0.45 μm pore-sized membrane filter) were collected and analyzed for dissolved As (As(III) and As(V) concentrations). Moreover, As(III) were collected using a combination of a 0.45 μm pore-sized membrane filter and As speciation cartridge. After collection, all samples were preserved using concentrated HNO_3, kept at 4 °C, and delivered to the laboratory at Gwangju Institute of Science and Technology (GIST), Korea for analysis.

At the time samples were collected As concentrations and its speciation, water temperature, pH, and Eh were measured by a Horiba D-54 meter (Horiba, Kyoto, Japan). Electrical conductivity and TDS were determined by an Orion 2-Star meter (Thermo Scientific, Waltham, MA) and a Consort C533 multi-parameter analyzer (Montreal Biotech Inc., Canada), respectively.

2.3. Sample analysis

Without pretreatment, all samples for As_{TOT}, dissolved As, and As(III) concentrations in the groundwater were determined using inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500ce, Agilent Technologies, Japan) equipped with an autosampler. The detection limits of As was 0.05 μg L^{-1}. For the solvent to be used in solution preparation, and analytical procedures, 2% (percent by volume) HNO_3 was prepared from 18.2 MΩ cm^{-1} deionized water obtained from a Millipore Milli-Q water purification system (Millipore Corp., USA). Working standard solutions were prepared in an ICP-MS range of 0 μg L^{-1}, 0.1 μg L^{-1}, 1 μg L^{-1}, 5 μg L^{-1}, 10 μg L^{-1}, 20 μg L^{-1}, 50 μg L^{-1}, and 100 μg L^{-1}. A correlation coefficient (r) of the linear regression (concentrations of working standard solutions vs. concentrations measured by ICP) of $\geqslant$0.998 was used for the standard calibration curves. Quality control and quality assurance for all instrumental analyses were conducted for each batch of 10 samples using an analytical blank sample (2% HNO_3), an external standard (a standard concentration prepared from a stock solution obtained from Agilent, USA), and a standard reference material (SRM 1640: trace metals in natural