Chapter A14

Groundwater sampling, arsenic analysis and risk communication: Cambodia case study

David A. Polya¹, Laura A. Richards¹, Ahmed Ali Nassir Al Bualy¹, Chansopheaktra Sovann², Daniel Magnone¹ and Paul R. Lythgoe¹

¹School of Earth and Environmental Sciences, The University of Manchester, Manchester M13 9PL, United Kingdom
²Department of Environmental Science, Royal University of Phnom Penh, Phnom Penh, Cambodia

A14.1 INTRODUCTION

As part of an on-going (2002-present) study of the controls on arsenic in shallow groundwater in Cambodia, a team from the University of Manchester working in collaboration with the Royal University of Phnom Penh, undertook a survey of arsenic and other chemical parameters in two transects through shallow aquifers in Kandal Province, Cambodia in 2013 and 2014. We report here procedures used for water sampling and preservation and chemical analysis, particularly for groundwater arsenic, as well as for the subsequent communication of arsenic-attributable health risks to those people drinking water from the same aquifers.

A14.2 DATA REQUIREMENTS & METHODS

A14.2.1 Overall aims of monitoring

The overall aim of the sampling programme was to understand better the origins of and controls on the concentrations of geogenic arsenic in shallow aquifers in circum-Himalayan aquifers, which are extensively used by hundreds of millions of people as a drinking water source. The programme targeted a region in Kandal Province in Cambodia because (i) it represents an ideal area, relatively un-impacted by massive
scale irrigation and potentially enabling a better understanding of arsenic mobilising processes to be
developed (Charlet & Polya, 2006); (ii) extensive background geographical and geological data existed for
the area (Polya et al. 2005; Polizzotto et al. 2008; Rowland et al. 2008; Benner et al. 2008; Buschmann &
Berg, 2009; Polya et al. 2010; Lawson et al. 2013; Richards et al. 2015; Lawson et al. 2016) (iii) logistical
positives, including 10 years’ experience in the area; and (iv) known groundwater arsenic concentrations
over a wide range, viz. 0.1 to 1000 µg/L (Polya et al. 2005; Rowland et al. 2008; Sovann & Polya, 2014).

A14.2.2 Representativeness
The aims of the study required the samples obtained to be collectively representative of two contrasting
transects oriented broadly parallel to the inferred predominant directions of groundwater flow. Accordingly,
for each transect, samples were obtained at roughly equally spaced intervals over the 3 km – 5 km length
of the transect and over a 6 m–45 m depth range, being typical of the overall exploited thickness of the
aquifers being studied. Thus results may be justifiably used to interpret how groundwater compositions
vary with position with respect to groundwater flow paths from recharge to discharge zones. Since the aim
of the study was not to undertake an area survey, the aggregate results may only be used in an indicative
way of the overall arsenic concentrations in the study area.

A14.2.2.1 Speciation
Previous studies have determined that groundwater arsenic speciation in this area is dominated by inorganic
arsenic and particularly As(III), with minor concentrations of methylated arsenicals. Nevertheless, further
speciation measurements (not reported here) were carried out using a cartridge-based field separation
 technique after Watts et al. (2010).

A14.2.2.2 Spatial and temporal variations
Water samples were largely taken from previously drilled and developed boreholes (Lawson et al. 2013;
Richards et al. 2015) using a flow cell apparatus to monitor sample homogeneity and after flushing
typically 2 to 3 borehole volumes depending upon the nature of the aquifer being sampled (cf. Richards
et al. 2015) to obtain a sample more representative of the aquifer at the depth of the well screening rather
than the borehole used to obtain the sample.

Since groundwater flow directions are known to be strongly seasonally dependent (Benner et al. 2008),
samples were taken in both pre-monsoon and post-monsoon seasons, with a number of samples taken at
other time intervals to better establish temporal variations in groundwater composition. The frequency of
such temporal sampling was largely determined by logistical and financial constraints.

A14.2.2.3 Contamination during sampling
Contamination of samples was minimised through (i) thoroughly washing sample vessels with nitric acid
and then deionised water and then furnace at 450°C (for glass vessels) prior to field work; (ii) sample
rinsing with the sample to be collected during field work; and (iii) flushing of several borehole volumes
through a flow cell prior to sample collection. The lack of contamination introduced from leaching of
sampling vessels or from the addition of nitric acid preservative was checked through the analysis of
procedural blanks, whilst LiCl tracers provided information on the likely extent or otherwise of drilling
fluid contamination in recently drilled boreholes (Richards et al. 2015).
A14.2.2.4 Preservation
Samples for arsenic analysis were filtered (0.45 µm cellulose and polypropylene syringe filters) and acidified with Aristar nitric acid to ensure a pH of lower than 2. The pH of the acidified samples was checked given the frequent presence of high (200–1100 mg/L) concentrations of HCO₃⁻ (aq) which can neutralise added acid by the reaction:

\[
\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3
\]

Non-acidified samples (still filtered to 0.45 µm) were also collected for analysis of anionic components. After collection, all samples were stored in an ice-box on the day of sampling and then subsequently refrigerated prior to analysis.

A14.2.3 Data & Data Quality Objectives (DQOs)
Analytes requiring determination were arsenic as well as many further geochemical parameters, measurement of which was considered likely to assist in understanding arsenic biogeochemistry.

A14.2.3.1 Field site related parameters
Sampling was informed by conceptual groundwater models (Benner et al. 2008; Polizzotto et al. 2008) and ERT (electrical resistivity tomography) investigations (Uhlemann et al. 2015). In order to model groundwater flow, piezometric levels were determined and groundwater level relative to local datum constrained using a combination of GPS and total station measurements.

A14.2.3.2 Analytes
In addition to arsenic, other analytes determined included (i) field-determined pH, Eh, dissolved oxygen, electrical conductivity (as a field proxy for total dissolved solids), and the potentially labile constituents sulphide, ammonium, nitrate, nitrite, iron, manganese, fluoride and orthophosphate; (ii) laboratory determined chemical analytes including Na, K, Mg, Ca, Si, Cl, HCO₃⁻, SO₄²⁻, Sr, Ba, Cu, Pb, Zn, Li, Al, DOC (dissolved organic carbon), DIC (dissolved inorganic carbon) and (iii) laboratory determined isotopic analytes δ¹⁸O, δD, δ¹³C, ¹⁸⁷Sr/¹⁸⁶Sr, ¹⁴C, ³⁷T, ³²He, ³⁴He, ²⁰Ne and ²²Ne.

A14.2.3.3 DQOs – required chemical measurement performance characteristics
Analytical requirements for arsenic arising from the project aims included: accuracy better than 5%; precision better than 5%; and detection limit better than 0.2 µg/L.

A14.3 ANALYTICAL METHODS & TOTAL QUALITY MANAGEMENT
A14.3.1 Analytical methods
Total arsenic was determined by ICP-MS (Agilent, 7500 cx) after shipping of preserved water samples to the Manchester Analytical Geochemistry Unit (MAGU) at the University of Manchester. Arsenic speciation was determined by a field separation method, followed by elution and subsequent determination by ICP-MS of the eluted separated fractions following the method of O’Reilly et al. (2010) and Watts et al. (2010).
A14.3.2 Analytical & data reduction protocols

A14.3.2.1 Control samples & standards
Calibration standards, with arsenic concentrations between 0 and 500 µg/L (range of anticipated sample arsenic concentrations) were used at a frequency of approximately 1 set of 8 calibration standards per 10 sample analyses. Procedural blanks were used to estimate contamination from sample processing. Blank samples were used to assess any contamination from in-laboratory handling, including dilutions where appropriate, whilst wash samples were used to determine the extent if any of any “carry over” from one sample to the next during an analytic run. Precision was estimated through triplicate analysis of samples and repeat analysis of samples at different times in an analytical session or in different analytical sessions. A mixed internal standard spike (containing 10 µg/L each of Ge, Sc, Rh and Ir) was used, although its efficacy in improving analytical accuracy and precision was ambiguous. The project requirements for geochemical modelling, including saturation index calculations, of the analysed groundwater necessitated the use of certified reference materials, notably SPS-SW1 (LGC Standards, UK), SRM1643 (National Institute of Standards and Technology, USA), TM25.2 (National Water Research Institute, Environment Canada) to ensure accuracy.

A14.3.2.2 Order of analysis – randomisation
Randomisation of presentation of samples for analysis was partially carried out although not comprehensively: any bias introduced by any systematic changes in analytical sensitivity over the course of an analytical session were monitored to ensure that this slight deviation from best practice did not materially impair analytical quality.

A14.3.2.3 Data reduction – calibration models
Calibration curves were calculated using least square methods using (i) unweighted; and (ii) inverse variance weighted first order linear models. The utility of using an internal standard was also assessed. The appropriateness of calibration curve models was assessed following the recommendations of Polya and Watts (2017).

A14.3.3 Total quality management
As a university-based laboratory undertaking a wide variety of analyses and exploratory studies and with resource constraints, our laboratory does not currently operate as a formally accredited laboratory under, for example, ISO 14001:2004. However, the laboratory follows good laboratory practice (cf. Polya & Watts, 2017) and confidence in the laboratory’s data has been obtained through longer-term involvement in inter-laboratory comparison schemes, such as run by EAWAG (Duebendorf, Switzerland) (Berg & Stengel, 2009).

A14.4 PRELIMINARY RESULTS
Measured arsenic concentrations using a simple unweighted first order linear calibration model ranged from 2 to 918 µg/L with a mean of 211 µg/L and a median of 130 µg/L. Analytical precision was strongly and systematically dependent upon concentration, varying from about ±0.3% at 500 µg/L to ±3% at 2 µg/L, the concentration dependence of analytical precision being adequately modelled by an exponential fit.

The following QA/QC check results are noted:

(i) The residuals from a first order unweighted calibration curve (see Figure A14.1, top left) show that there is no substantial correlation of the mean residuals with count rate/concentration. However the
data are clearly heteroscedastic, i.e. the magnitude of the residuals are correlated with count rate/concentration invalidating one of the assumptions of least squares fitting. This is also confirmed by the evident relationship between standardised residuals and count rate/concentration;

(ii) The Q-Q plot of standardised residuals (Figure 14A.1, top right) shows that they are for the most part normally distributed but the distribution is nevertheless “light-tailed”;

(iii) It is clear from inspection of a plot of standardised residuals vs leverage (Figure 14A.1, bottom right), there is a disproportionate leverage of the calibration curve best-fit parameters from data related to the highest concentration calibration standards;

(iv) The concentration of some of the samples exceeded that of the top calibration standards, accordingly the data for these samples are taken to be indicative only (and the samples were subsequently diluted and re-analysed);

(v) The range of analytical precisions, ±0.3% to ±3% was compliant with the analytical precision required by the project;

(vi) The detection limit determined to be around 0.5 µg/L is somewhat higher than the value ideally required by the project;

(vii) Agreement between the determined arsenic concentrations of calibration standards measured as unknown samples and the known concentrations were largely within the determined analytical precisions, with the exception of certain 0 µg/L and 1 µg/L standards – closer inspection of the data with reference to run order showed that elevated concentrations of As were measured in all 0 µg/L and 1 µg/L standards and wash samples where they immediately followed a sample with > 200 µg/L As – accordingly the removal of the impacted standards from the calibration standards was indicated and re-analysis of all the impacted samples was indicated, although in the case of the latter the estimated biases where always less than 10% and mostly less than 0.5%;

(viii) Analytical sensitivity for calibrations between 5 and 500 µg/L was determined to increase by around 20% during the course of an analytical session – this necessitates a drift correction, using for example, the 74Ge internal standard;

(ix) Arsenic spikes and standard additions (not reported here) were used to determine the magnitude of any likely matrix effects;

(x) Wash samples contained either undetectable or less than 0.7 µg/L arsenic; blank samples contained as much as 0.7 µg/L arsenic – both sets of samples indicate a level of carry-over from the previously analysed sample of as much as 0.13%;

(xi) Measured arsenic concentration in the CRMs analysed were in agreement with the certified values to within analytical precision, viz. SRM1643 (found 58 ± 6; known 60.45 ± 0.72 µg/L); TM-25.2 (found 9 ± 1; known 7.1 µg/L) and SPS-SW1 (found 11 ± 2; cf. known 10 ± 0.1 µg/L);

(xii) The total arsenic concentration method used here agreed to within 2 ± 10% of an independent method, viz. summing individual species determined by coupled ion chromatography ICP-MS, although it was noted that there were a considerable number of outliers, which are thought to relate to operator/operator training issues in field-based cartridge separation used as part of the speciation method;

(xiii) Previous inter-laboratory schemes resulted in agreement of samples analysed using the same method as reported here with agreed values to within analytical precision (cf. Berg & Stengel, 2009);

(xiv) Electrical charge balances for the samples were largely within 15% – somewhat higher than ideal and again thought to be related to operator/training issues for some field-based determinations;
Lastly, it is noted that the range of arsenic concentrations is similar to that determined by previous studies (cf. Polya et al. 2005; Polizzotto et al. 2008; Rowland et al. 2008; Sovann & Polya, 2014).

Figure A14.1 Analysis of calibration model (unweighted first order linear) for arsenic determination by ICP-MS. (a) Residuals as a function of mass spectrometry count rates at m/z = 75; (b) Standardised residuals as a function of count rate; (c) Q-Q curve for standardised residuals; (d) Standardised residuals vs leverage.

Inspection of analytical data particularly of control samples has indicated where further post-instrument analysis and further instrumental analysis is required.

A14.5 RISK COMMUNICATION

Information on groundwater compositions and possible health risks associated with chronic consumption of such groundwater for drinking was particularly sought by landowners and tenants who had given permission for work to be carried out on their land. Notwithstanding that the majority of the boreholes sampled as part of this study were not used as drinking water wells, but rather were drilled for the purposes of scientific investigation, information to landowners and tenants, who might otherwise access the groundwaters through drilling their own wells, was considered to be an important element of the communication plan for the overall
project. A template letter providing such information is shown in Figure A14.2 – it represents a balance between brevity and comprehensiveness and in particular highlights the appropriate agencies from where to seek more detailed information. The letter was provided in both English and the local language, Khmer (not shown here).

![Figure A14.2 Template of Report on Water Chemistry to Landowners/Tenants.](image-url)
A14.6 CONCLUSIONS

This case study illustrates the importance of inspection of analytical data, particularly that of control samples and standards, and the importance of consideration of the most appropriate methods for detecting and correct for, when appropriate, instrumental drift and contamination – including cross-sample contamination.

A14.7 ACKNOWLEDGEMENTS

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A14.8 REFERENCES


