Chapter A14

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

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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

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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 furnaced 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 HCO_3^- (aq) which can neutralise added acid by the reaction:

$$HCO_3^-(aq) + H + (aq) \rightarrow H_2CO_3(aq)$$

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, HCO_3, SO_4, Sr, Ba, Cu, Pb, Zn, Li, Al, DOC (dissolved organic carbon), DIC (dissolved inorganic carbon) and (iii) laboratory determined isotopic analytes $\delta^{18}O$, δD, $\delta^{13}C$, $^{87}Sr/^{86}Sr$, ^{14}C, ^{3}T, ^{3}He, ^{4}He, ^{20}Ne and ^{22}Ne.

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 ^{74}Ge 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;

(xv) 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).

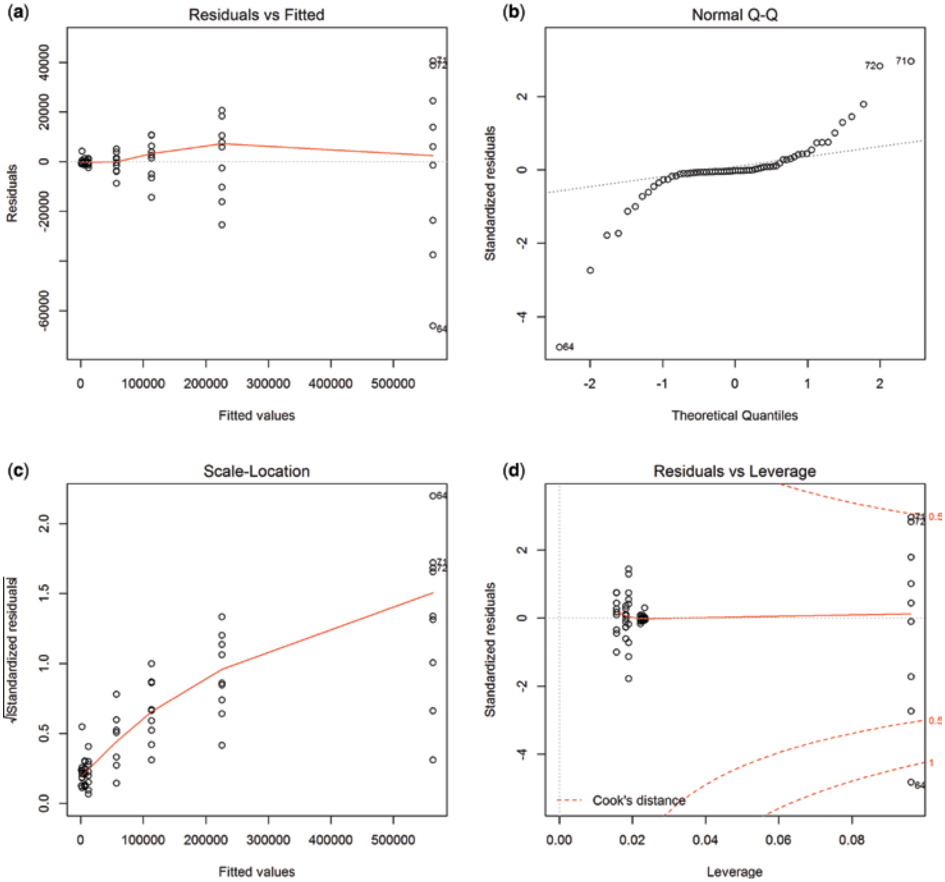

Figure A14.1 Analysis of calibration model (unweighted first order linear) for arsenic determination by ICP-MS. (a) Residuals as a function of mass spectrometry count rates at m/z = 75; (b) Standardised residuals as a function of count rate; (c) Q-Q curve for standardised residuals; (d) Standardised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

SCIENTIFIC INVESTIGATION OF HIGH ARSENIC GROUNDWATERS IN KANDAL PROVINCE, CAMBODIA

REPORT ON COMPOSITION OF WATER SAMPLED FROM BOREHOLE LRXX-XX

Borehole LRXX-XX was sampled in the year 2014 and analysed for a limited selection of chemicals. The purpose of the analysis was scientific - to better understand why high arsenic occurs in many groundwaters in Kandal province, Cambodia as well as in many other parts of the world, including parts of Bangladesh, India, Vietnam and China.

The purpose of the analysis was not to provide an assessment of water quality. However, for the information of those (e.g. landowners, tenants) with interests in the quality of groundwater in the nearby area – results for 4 chemicals, arsenic (As), manganese (Mn), nitrate (NO_3) and nitrite (NO_2) are shown below. The results are all expressed in units of µg/L (micro-gram per litre)– this is approximately equivalent to the unit of "parts per billion" or "1 part in 1,000,000,000". The results are compared to the current World Health Organization (WHO) guide values (or equivalent derivable value) for the maximum recommended concentrations of these chemicals in drinking water.

Please note: (i) Uncertainties of the reported results are typically better than 10 % or 2 µg/L, whichever is the higher; (ii) Groundwater/borehole water compositions may vary over time and from place to place; (iii) arsenic concentrations of greater than 10 µg/L (the WHO Guide value) were found in over 80 % of the borehole waters analysed in this study; (iv) The overall fitness to drink of water depends also upon the concentrations of other chemicals and particularly of pathogenic organisms – the concentrations of such organisms have not been determined in this study because it was not the purpose of this study to determine the fitness of water to drink; (v) well water or other water sources to be used for drinking should be thoroughly tested for its suitability before use.

Well Identifier: LRXX-XX ; Depth (approximate) sampled: XX m

Chemical	Result (µg/L)	WHO guide value (µg/L)
Arsenic (As)	XX	10 ^
Manganese (Mn)	XX	4,000 *
Nitrate (NO_3)	XX	50,000 ^
Nitrite (NO_2)	XX	3,000 ^

^ formal value; *derivable health-based value; not a formal WHO Guideline value

If the result for any chemical is higher than the WHO guide value then this indicates that drinking the water on a regular basis may result in unacceptably high added risks of bad long term health outcomes. For manganese these outcomes may include developmental issues in children. For nitrate and nitrite these outcomes may include "blue baby syndrome". For arsenic these bad health outcomes may include cancers, heart disease and premature death.

In order to prevent accidental drinking of borehole waters that may contain harmful concentrations of arsenic and other chemicals, boreholes drilled as part of this study have not been fitted with pumps or wellheads and are either being removed (i.e. filled in) (particularly where requested by landowners or tenants) or locked (where further useful monitoring is indicated and the landowner or tenant as appropriate is agreeable).

Further information on health risks arising from chemicals in drinking water and on water remediation and testing is provided by the WHO. Information on local groundwater and regulation may be sought from relevant national, regional and local government authorities. To comment or for further information on the chemicals found in this borehole water please email the project team at laura.richards@manchester.ac.uk, david.polya@manchester.ac.uk or chansopheaktra@gmail.com . We aim to reply within 30 days to emails received by the end of December 2018.

We thank all those who have helped us to undertake this scientific study. Key results and a summary are anticipated to be available from www.manchester.ac.uk/research/david.polya or the email addresses above by February 2017.

University of Manchester Groundwater Arsenic Team, Phnom Penh, December 2015

In the event of any discrepancies between the Khmer and English versions of this document, the original English version takes precedence.

Figure A14.2 Template of Report on Water Chemistry to Landowners/Tenants.

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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