Modelling arsenic hazard in groundwater in Cambodia

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Aimee Hegan & David Polya
Background (I)

- Arsenic contaminated shallow groundwaters are extensively utilized for drinking, irrigation and cooking in many parts of the world represents a major environmental hazard.
- High arsenic concentrations have also been noted in Cambodian groundwaters
  - Polya et al (2003, 2005a); Stanger (2006) Feldmann et al. (2007); Buschmann et al. (2007); Berg et al. (2007); Rowland et al. (2008); Benner et al. (2008), Kocar et al. (2008); Polizzotto et al. (2008)
- Hazardous exposure noted
  - Reiji et al. (2003), Polya et al. (2005b), Gault et al. (2008)
- Detrimental health outcomes
  - Sampson et al. (2008)
- Presented here is an objective model for the distribution of As in Cambodian groundwaters
Background (II)

• Detailed map of distribution of As in groundwaters required for robust risk assessment

• Existing maps are useful but have several shortcomings:
  – Not objective (Fredericks, 2004; Stanger, 2005; Berg et al., 2007)
  – Coarse scale (Polya et al. 2005a; Winkel et al, 2008)

• Presented here is an objective model for the distribution of As in Cambodian groundwaters
• Health Impacts of Arsenic
• Arsenic in Cambodia
  – Early Models of Distribution
  – Geostatistical Modelling
• Implications
Health Impacts of Chronic Arsenic Exposure
Some arsenicosis patients from arsenic affected districts of Bangladesh

Pigmentation
Keratosis on Palm & Sole
Ulcer on leg
Multiple Bowen's
Squamous cell carcinoma
Amputation due to Gangrene
Gangrene on leg
Mucus membrane melanosis


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Pregnancy Outcome

Pregnant women were drinking Arsenic contaminated water in Erurine village, Laksham P.S., Comilla district, Bangladesh (As.
conc. 600 – 1100 μg / L in Drinking Water.

Pregnancy Outcome per 1000 live birth (N = 26)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-term birth</td>
<td>140</td>
</tr>
<tr>
<td>Low birth wt.</td>
<td>250</td>
</tr>
<tr>
<td>Spontaneous abortion</td>
<td>200</td>
</tr>
<tr>
<td>Still birth</td>
<td>125</td>
</tr>
<tr>
<td>Neo-natal death</td>
<td>125</td>
</tr>
</tbody>
</table>

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Excess Lung Cancer Risks

Cancer risks from chronic exposure to As in drinking water

• 10 ppb = 1 in 500 die

• 50 ppb = 1 in 100 die [married to smoker]

• 500 ppb = 1 in 10 die [active smoker]

• 5000 ppb = all die

Arsenic concentrations in Antofagasta and Mejillones water by year. Arsenic contaminated water sources were used from 1958, and an arsenic removal plant was installed in 1971.

Excess Deaths Attributable to Arsenic in Region II, Chile (Males only) (after Smith et al., 2007)

Excess Deaths
Acute Myocardial Infarction
Excess Deaths Lung Cancer
Excess Deaths Bladder Cancer

Contaminated water source

Start of Time Period
1940 1960 1980 2000

Excess Deaths
0 100 200 300 400 500
Excess Deaths Attributable to Arsenic in Region II, Chile (Males only) (after Smith et al., 2007)

- Excess Deaths as a Percentage of Total Deaths
- Contaminated water source

Start of Time Period:
- 1940
- 1960
- 1980
- 2000
Arsenicosis in Bangladesh

- Small scale studies
  - prevalence 10 – 99 %
  - bias to high impact areas

- Large scale studies
  - prevalence 0.1 to 0.3 %
  - bias due to under-reporting & difficulties in diagnosis

  - prevalence 1.5 % nationwide
Health Effects in Bangladesh of Arsenic in Groundwater

- ~2,000,000 people to develop arsenicosis
- ~3,000 fatalities/year from internal cancers

Source: Yu et al. (2003) based upon present groundwater concentrations and a non-intervention policy
Arsenic Distribution in Cambodian Wellwaters
Why Cambodia?

• Increasing groundwater usage since 1990s

• Might Cambodia be an analogue for Bengal at an earlier stage of groundwater resource development?
Arsenic Distribution in Cambodia

- >> 40,000 wells installed
- > 5,000 wells tested
- > 1,000 wells test-data compiled here
  - Based upon analyses by or verified by University of Manchester

- Risk map generated on the basis of these
  - cf. Cambodian (50 ppb) and WHO (10 ppb) “MCL”s
  - Not robust in identifying all “at-risk” areas
  - Considerable heterogeneity even at local scale
Arsenic Hazard Maps - Cambodia


Environmental Mineralogy, Geochemistry and Health Thematic Issue, October 2005 (Eds. Eva Valsami-Jones, Dave Polya and Karen Hudson-Edwards)
Indicators of High Arsenic Wellwaters in Cambodia

• Holocene sedimentary aquifers
• Depths > 15 m
• Proximity to major river channels, especially Mekong and Bassac Rivers
• Downstream of Kampong Cham and especially Phnom Penh

BUT

• Criteria not wholly inclusive or exclusive
Models of Arsenic Release
Dissimilatory Fe(III) reduction

Fe(II)

Fe(III)-coated substrate

Acetate

CO₂

Cell
Anaerobic metal-reducing microbes mediate arsenic release

Comparison of Cambodian & Bengali As-rich Groundwaters

• Cambodia
  – circum-neutral
  – low Eh
  – high Fe & Mn
  – low SO$_4$, NO$_3$, Cl$^-$ & F$^-$
  – high alkalinity

• Bengal Basin
  – circum-neutral
  – low Eh
  – high Fe & Mn
  – low SO$_4$, NO$_3$, Cl$^-$ & F$^-$
  – high alkalinity

Polya (2002); Polya et al. (2003);
& this study

Smedley & Kinniburgh (2002) and
references therein
Risk of High Arsenic in Wells in Relation to Sediment Age
(after Fredericks, pers. comm. with permission)

**Moderate Risk**
- Older Sediments
  - with little or highly degraded organic matter

**High Risk**
- Holocene Sediments
  - with relatively undegraded organic matter

**Low Risk**

Tube Wells

Basement
Other Maps

Stanger (2005)

Fredericks (2004)

Berg et al. (2007)
Why geostatistics?

• Objective estimate:
  – of the As concentrations
  – of the associated uncertainty
• Auxilliary predictors with high sampling density data As can be used
• Automation
  – e.g. through R scripts
Geostatistical Modelling of Arsenic-in-groundwater

- Selection of auxiliary variables
  - Proxies for expert-determined relevant factors
  - High spatial resolution
    - Satellite derived / DEM / Slope / NDVI
    - PCA to obtain independent components
- Multiple linear regression
- Kriging of spatially distributed residuals
- Validation against validation dataset
Arsenic Database

- 9661 groundwater samples (compiled by Polya et al., 2005 and includes data from AISC)
- 7 different surveys over period 2000-2004
- Heterogeneous data quality
  - Duplicates, blank data and negative values
- Cleaned database
- Subset: 1490 samples
- Depths between 16-100 m
- As up to 830 ppb (mean = 87 ppb)
Subset groundwater database

All statistical analyses performed on logarithm transformed As data.
Groundwater database
Model and Validation datasets

1. Random selection
2. Equality of the distribution functions

Model dataset (1237 samples)

Validation dataset (253 samples)
**Multiple Linear Regression**

\[ Y_j = a_1 X_1 + a_2 X_2 + \ldots + a_n X_n + \varepsilon \]

- Spatially continuous
- Punctual
- Soil variable \( j \)
- Auxiliary data \( i \)
- Residuals \( j \)

**Kriging** (interpolation process according to spatial autocorrelations of the variable)

**Summation of the two maps**

- Regression
- Auxiliary data
- Kriging
- Residuals
- Regression-kriging
- Soil variables

Distance (m)

Semi-variance

Regression-kriging
Auxiliary variables

- Collection of auxiliary variables
  - Topographic variables- Digital Elevation Model (DEM)
    - Slope
    - Topographic Wetness Index
    - Convergence Index
    - Flow length
  - Remote sensing images (2 years)
    - Normalized Difference Vegetation Index (NDVI)
    - Principal components
  - Geology

- These auxiliary variables were transformed to 16 principal components to avoid multicollinearity.
Auxiliary variables

SRTM DEM

NDVI MODIS images

Slopes

Geology
Results: Regression model
Results: RK-model

The higher As concentrations are located in the vicinity of the Mekong river system. Positive correlation of Flow Length Index, organic-rich sediments, alluvial deposits and the Normalized Vegetation Index with increased probability of high As concentration.
Validation of RK Model

Data and regression line

- Observations
- Predictions
- Conf. on pred (95.00%)
- Conf. on mean (95.00%)
Results:
OK- model

The higher As concentrations are located in the vicinity of the Mekong river system. Positive correlation of Flow Length Index, organic-rich sediments, alluvial deposits and the Normalized Vegetation Index with increased probability of high As concentration.
RK
(Regression Kriging)

vs

OK
(Ordinary Kriging)
Uncertainty Map for RK
Conclusions (I)

- Spatial distribution of As in Cambodian groundwaters is closely connected with relief.
- Comparison of OK and RK
  - statistically similar but RK more realistic
- Communication of uncertainty
  - Uncertainty map
  - Multiple equally-likely renditions
- More samples are required to increase the accuracy of this model
  - especially in the poorly sampled areas
  - especially in parameter space (e.g. high altitude)
Rice is a major exposure route

<table>
<thead>
<tr>
<th>rice variety</th>
<th>rice distribution</th>
<th>origin (district)</th>
<th>grain</th>
<th>total arsenic</th>
<th>DMA(V)</th>
<th>As(III) + As(V)</th>
<th>species sum</th>
<th>extraction efficiency (%)</th>
<th>organic arsenic (%)</th>
<th>inorganic arsenic (%)</th>
<th>contribution to MTDI (%)</th>
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<tbody>
<tr>
<td>Chinigura</td>
<td>speciality</td>
<td>Chapai</td>
<td>medium</td>
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<td>0.01</td>
<td>0.01</td>
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<td>49 ± 19</td>
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<td>Kataribogh</td>
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<td>0.06 ± 0.00</td>
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<td>0.04</td>
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<td>77 ± 4</td>
<td>17 ± 4</td>
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<td>0.01</td>
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<td>11 ± 3</td>
<td>42 ± 1</td>
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<td>4 ± 4</td>
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<td>common</td>
<td>Sherpur</td>
<td>long</td>
<td>0.09 ± 0.00</td>
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<td>17 ± 8</td>
<td>63 ± 3</td>
<td>25</td>
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<td>long</td>
<td>0.10 ± 0.00</td>
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<td>0.07</td>
<td>0.08</td>
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<td>0.15 ± 0.00</td>
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<td>0.17 ± 0.01</td>
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<td>10 ± 8</td>
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<td>Parija</td>
<td>local</td>
<td>Bogra</td>
<td>long</td>
<td>0.20 ± 0.02</td>
<td>0.04</td>
<td>0.11</td>
<td>0.15</td>
<td>75 ± 2</td>
<td>21 ± 2</td>
<td>54 ± 1</td>
<td>46</td>
</tr>
<tr>
<td>Parija</td>
<td>local</td>
<td>Rajshahi</td>
<td>long</td>
<td>0.21 ± 0.02</td>
<td>0.05</td>
<td>0.12</td>
<td>0.17</td>
<td>83 ± 1</td>
<td>24 ± 0</td>
<td>59 ± 1</td>
<td>50</td>
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<tr>
<td>Miniket</td>
<td>common</td>
<td>Kushia</td>
<td>long</td>
<td>0.22 ± 0.01</td>
<td>0.04</td>
<td>0.19</td>
<td>0.23</td>
<td>103 ± 4</td>
<td>16 ± 0</td>
<td>86 ± 4</td>
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<td>BRRI dhan29</td>
<td>common</td>
<td>Tangail</td>
<td>long</td>
<td>0.30 ± 0.01</td>
<td>0.03</td>
<td>0.21</td>
<td>0.24</td>
<td>82 ± 2</td>
<td>11 ± 2</td>
<td>71 ± 0</td>
<td>88</td>
</tr>
</tbody>
</table>

* A contribution of inorganic arsenic to MTDI assumes a body weight of 60 kg and a consumption rate of 0.5 kg per day.

From Williams et al. (2005) *Env. Science & Technology*
• Detoxification effectiveness indicated by urine % MMAA
• Large variations between individuals & populations
• Highest in populations with long exposure history
• Lowest in women & children [i.e. most at risk]

Source: Chen et al after various sources including Hopenhayn-Rich et al., 1993, 1996; Vahter et al., 1995; Chiou et al., 1997; Del Razo et al., 1997 Concha et al., 1998
Dietary or Genetic Controls on Arsenic Uptake and Metabolism

Risk Assessment & Remediation

• Source – Transport – Receptor Models
  – Groundwater arsenic hazard
  – Exposure Routes
    • Drinking water vs food
  – Target populations
    • Age, gender, genetic disposition

• Remediation Strategies
  – *In situ* remediation (e.g. bio-, O$_2$-injection)
  – *Ex situ* remediation (e.g. filters, Fe(III) pptn.)
  – Well-switching (short-term only ??)
  – Change to treated surface water supplies
Relative Impacts of Switching: Well to Surface Waters

Disability-Adjusted Life Years (DALYs) / per capita

- DALYs due to diseases related to pathogenic microbes (NEGATIVE IMPACT)
- DALYs due to diseases related to arsenic exposure from drinking water (POSITIVE IMPACT)

NET BENEFITS FOR DEFINED MITIGATION AT As CONC. HIGHER THAN THIS THRESHOLD

Arsenic Concentration in Groundwater
Impact of Other Factors

Disability-Adjusted Life Years (DALYs) / per capita

Change in DALYs due to improvements in sanitation and treatment of pathogenic microbes (POSITIVE IMPACT)

Change in DALYs due to higher assumed value for threshold concentration for As-linked cancers (POSITIVE IMPACT)

These Other Factors Modify the Threshold between Net Negative and Postive Impacts of Defined Mitigation

Arsenic Concentration in Groundwater
From Guy Howard (2007)
Conclusions (II)

- Policy changes need to be informed by robust risk assessment
  - Objective hazard maps
  - Non-drinking water exposure routes
  - Genetic, gender & social controls
  - Future secular changes
  - Risk substitution
  - Effectiveness of remediation measures
EU ASIA-LINK
CALIBRE
NUOL (Lao PDR)
RUPP (Cambodia)
UJF, Grenoble (France)
University of Manchester (United Kingdom)
Arsenic Cycle

geo-

(CH₃)₃As

anthropo-

As

Air

rain

arsenobetaine
(CH₃)₃As⁺CH₂COO⁻

(CH₃)₂As

O

OH

methylation by algae

As (III)

As (V)

oxidation

reduction

As (0)

As (III)

As (V)

oxidation

reduction

Sediment
Policy / As / Bangladesh

- Increasing exposure to arsenic hazard in Bengal
- Policy issues remain unresolved

Implications of Models of Arsenic Release for Remediation Strategies in Cambodia
Implications of Models (I)

- Arsenic distribution is likely to be highly variable; may be lower in deeper wells.

- Well-switching to nearby wells (either deeper with lower arsenic concentrations may be an effective short-term remediation strategy for many people.)
Implications of Models (II)

- Massive groundwater abstraction (especially for irrigation purposes) may result in medium to long-term secular increases in arsenic concentrations, even at depth
  - Well-switching only effective short-term
  - Long term well water quality uncertain
- Urgently require detailed geochemical data to test conflicting models of arsenic release
Consumer Preferences

- As-bearing groundwaters often high in Fe and H₂S
- Easily noticeable:
  - Red colouration on exposure to air
  - Smell
- Tend not to be used as drinking water
- Not comprehensive screening
Well Testing

- Arsenic is not easy to detect directly
  - Tasteless
  - Colourless
  - No smell
- Well testing required