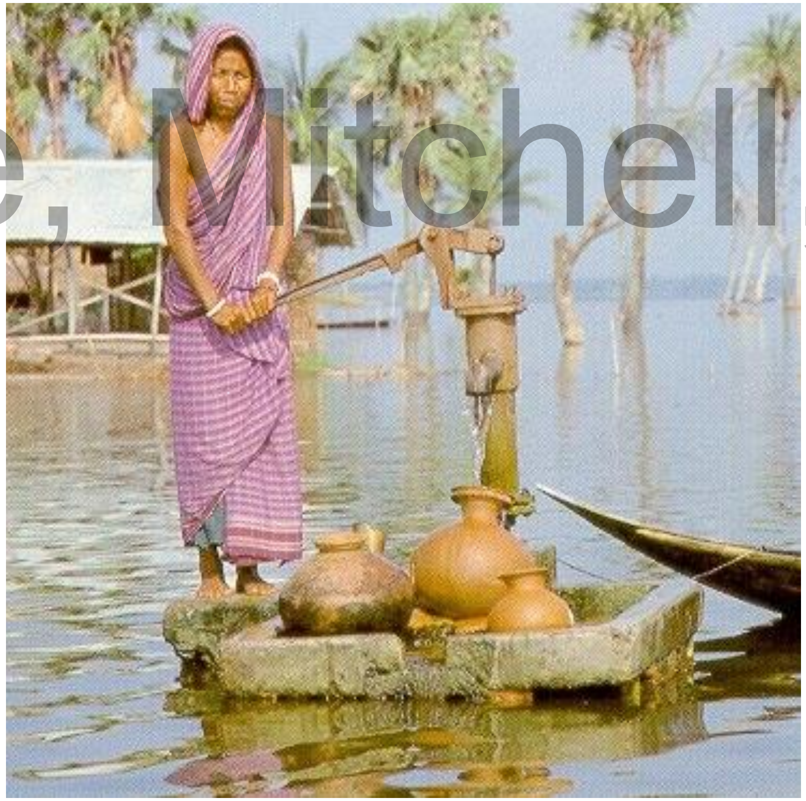
# Impact of Sea Level Rise on Arsenic Contamination in Bangladesh's Drinking Water

## Sea Level Rise from Climate Change is Expected to Increase the Release of Arsenic into Bangladesh's Drinking Well Water by Reduction and by the Salt Effect

**Seth H. Frisbie, Ph.D., Erika J. Mitchell, Ph.D., and Azizur Molla, Ph.D.**





# Impact of Sea Level Rise on Arsenic Contamination in Bangladesh’s Drinking Water

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**There are no personal financial relationships or commercial interests to disclose.**

*Seth H. Frisbie, Erika J. Mitchell, and Azizur Molla*

Frisbie, Mitchell, Molla

# The Physical Environment of Bangladesh

- **Bangladesh is located at 1 of the largest river deltas in the world.**
- **The Ganges, Brahmaputra, and Meghna rivers flow through Bangladesh and into the Bay of Bengal.**
- **The average elevation is 8 meters (25 feet) above sea level.**
- **In a typical monsoon season, about 21% of Bangladesh's land is flooded with a mixture of freshwater from its rivers and saltwater from the Bay of Bengal.**




- Dewan, A.M., M. Nishigaki, and M. Komatsu. Journal of the Faculty of Environmental Science and Technology, Okayama University. 2003.
- The United States Government. Map of Bangladesh. 1996.

# The Physical Environment of Bangladesh

- **Bangladesh, with its low-lying coastal topography, annual monsoons, and frequent cyclones, is expected to be severely impacted by flooding as sea levels continue to rise.**
- **From 1902 to 2015 the global mean sea level has risen 0.16 meters (6.3 inches).**
- **By 2050 the sea level is expected to rise another 0.16 meters to 0.25 meters (6.3 inches to 9.8 inches).**





- Dewan, A.M., M. Nishigaki, and M. Komatsu. Journal of the Faculty of Environmental Science and Technology, Okayama University. 2003.
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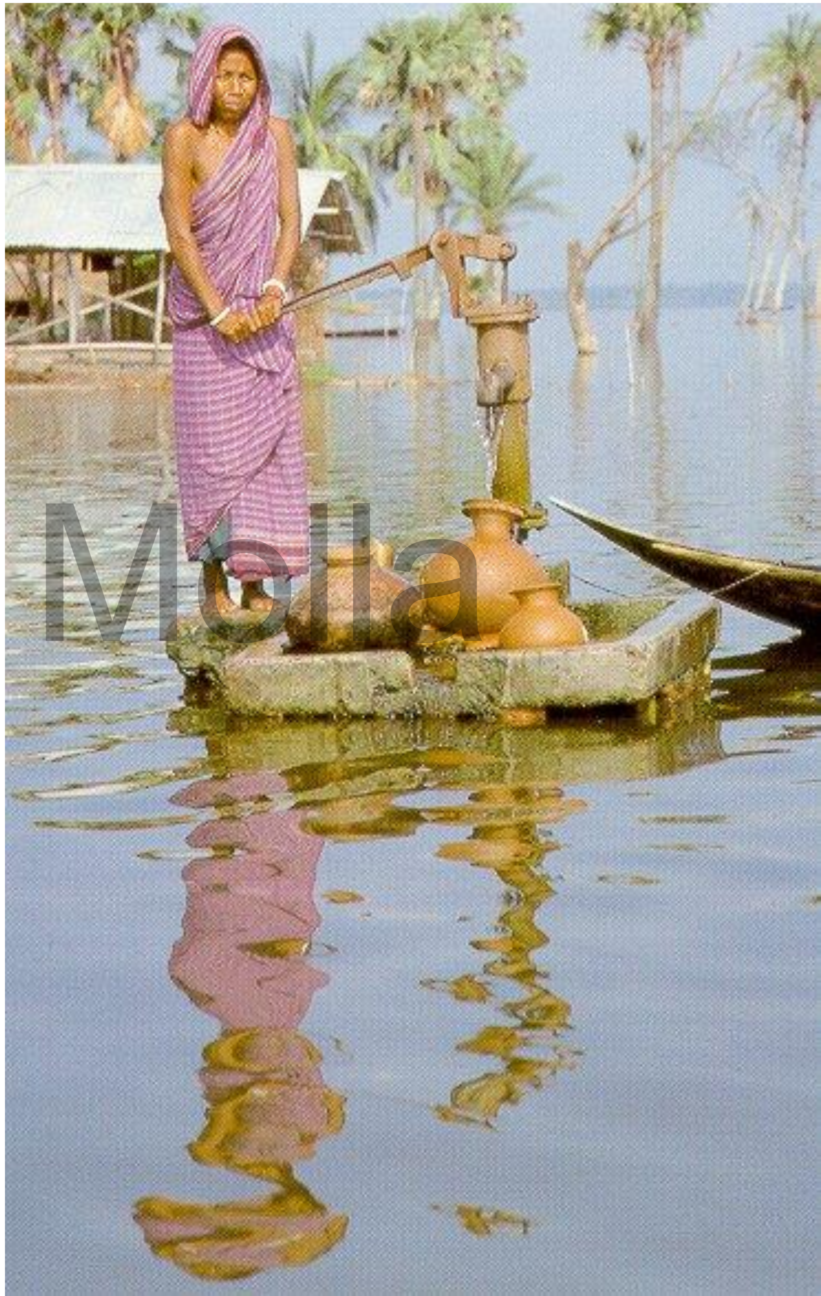
# A History of Drinking Water in Bangladesh

- **Approximately 78,000,000 Bangladeshis are drinking well water with arsenic (As) concentrations that exceed the 10 micrograms per liter (µg/L) World Health Organization (WHO) guideline.**
- **These Bangladeshis have a significant risk of death from lung, bladder, kidney, and skin cancers caused by chronic As poisoning.**






- Frisbie, S.H., D.M. Maynard, and B.A. Hoque. Metals and Genetics. 1999
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- Frisbie, S.H., and E.J. Mitchell. PLOS ONE. 2022.
- Photograph: Brace, S. Thomson Learning. 1995.

# A History of Drinking Water in Bangladesh

- **Chronic As poisoning from drinking well water has 3 common symptoms.**
- **The first common symptom is melanosis of the chest.**
- **This is a 22-year-old male from our study area in Bangladesh. He has hundreds of little spots on his chest. This is not melanoma. This is not skin cancer, but it is heading toward skin cancer.**



**Melanosis of the Chest**


- Frisbie, S.H., D.M. Maynard, and B.A. Hoque. Metals and Genetics. 1999.
- Frisbie, S.H., R. Ortega, D.M. Maynard, and B. Sarkar. Environmental Health Perspectives. 2002.

# A History of Drinking Water in Bangladesh

- **The second common symptom is keratosis of the palm (palmoplantar keratoderma).**
- **Keratin growing on the palms of the hands. This man does have cancer. There is a carcinoma on the heel of his hand. He has also lost a finger to gangrene.**



**Keratosis of the Palms**


- Frisbie, S.H., D.M. Maynard, and B.A. Hoque. Metals and Genetics. 1999.
- Frisbie, S.H., R. Ortega, D.M. Maynard, and B. Sarkar. Environmental Health Perspectives. 2002.
- Photograph: Dhaka Community Hospital, and Wilson, R. http://phys4.harvard.edu/~wilson/arsenic_project_pictures2.html. 2002.

# A History of Drinking Water in Bangladesh

- **The third common symptom is keratosis of the feet (palmoplantar keratoderma).**
- **This is a 44-year-old female with keratin growing on the bottom of her feet.**



**Keratosis of the Feet**


- Frisbie, S.H., D.M. Maynard, and B.A. Hoque. Metals and Genetics. 1999.
- Frisbie, S.H., R. Ortega, D.M. Maynard, and B. Sarkar. Environmental Health Perspectives. 2002.

# A History of Drinking Water in Bangladesh

- **In addition, you will also see Blackfoot disease (a peripheral vascular disease).**
- **This is a 12-year-old female. The veins and arteries in her legs and feet leak blood, so the circulation from her lowest extremities, her feet, back to her heart is poor. She has necrotic lesions that are subject to infection and gangrene. It is inevitable, she must have her feet amputated.**

**Blackfoot Disease**




- Frisbie, S.H., D.M. Maynard, and B.A. Hoque. Metals and Genetics. 1999.
- Frisbie, S.H., R. Ortega, D.M. Maynard, and B. Sarkar. Environmental Health Perspectives. 2002.

# A History of Drinking Water in Bangladesh

- **As sea levels continue to rise due to climate change and the annual floods and cyclones in Bangladesh increase in area and duration, chemical processes will increase the release of As into Bangladesh's drinking well water.**
- **This will increase the incidence of chronic As poisoning.**
- **These chemical processes are reduction and the salt effect.**

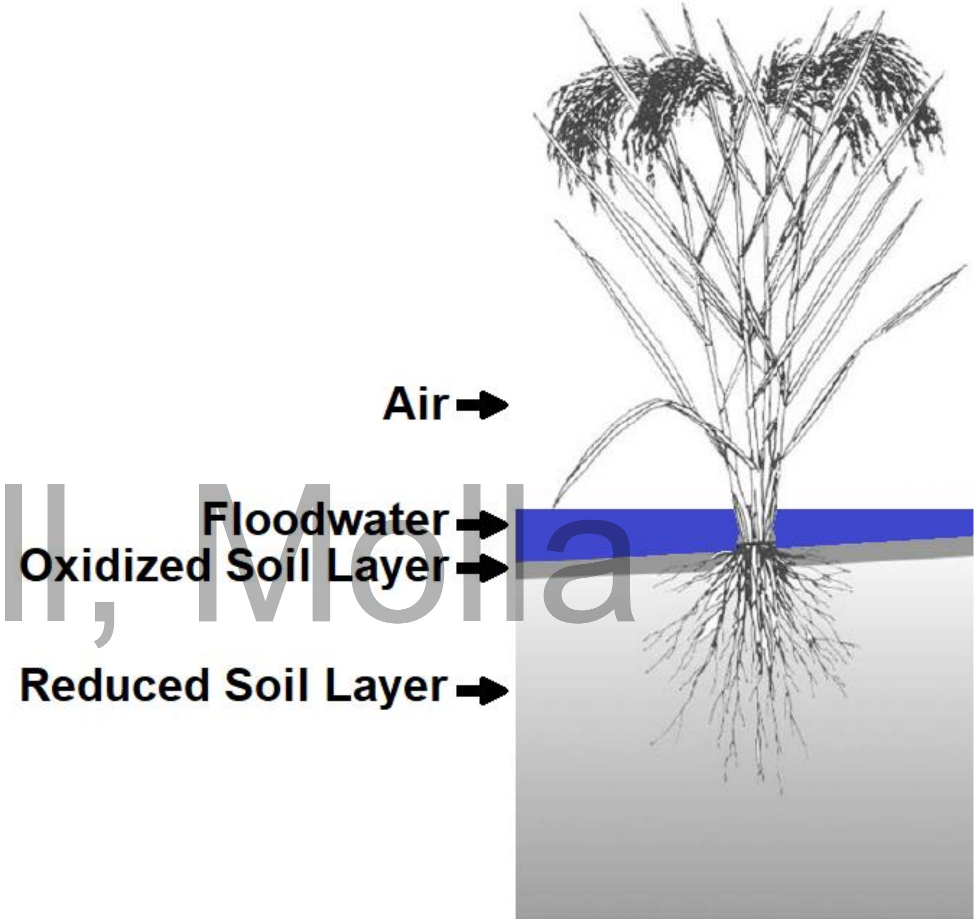
**Blackfoot Disease**



- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

# The Release of Arsenic into Drinking Well Water by Reduction

- **Seasonal flooding from the annual monsoons and cyclones, and the cultivation of rice in flooded paddies often make a reducing environment.**
- **These floodwaters are a barrier to the diffusion of oxygen ($O_{2(g)}$), a very strong oxidizing agent, from the atmosphere into the aquifer.**
- **During flooding, heterotrophic microorganisms can deplete the concentration of dissolved oxygen (DO; $O_{2(aq)}$) in groundwater; this also helps to make a reducing environment.**



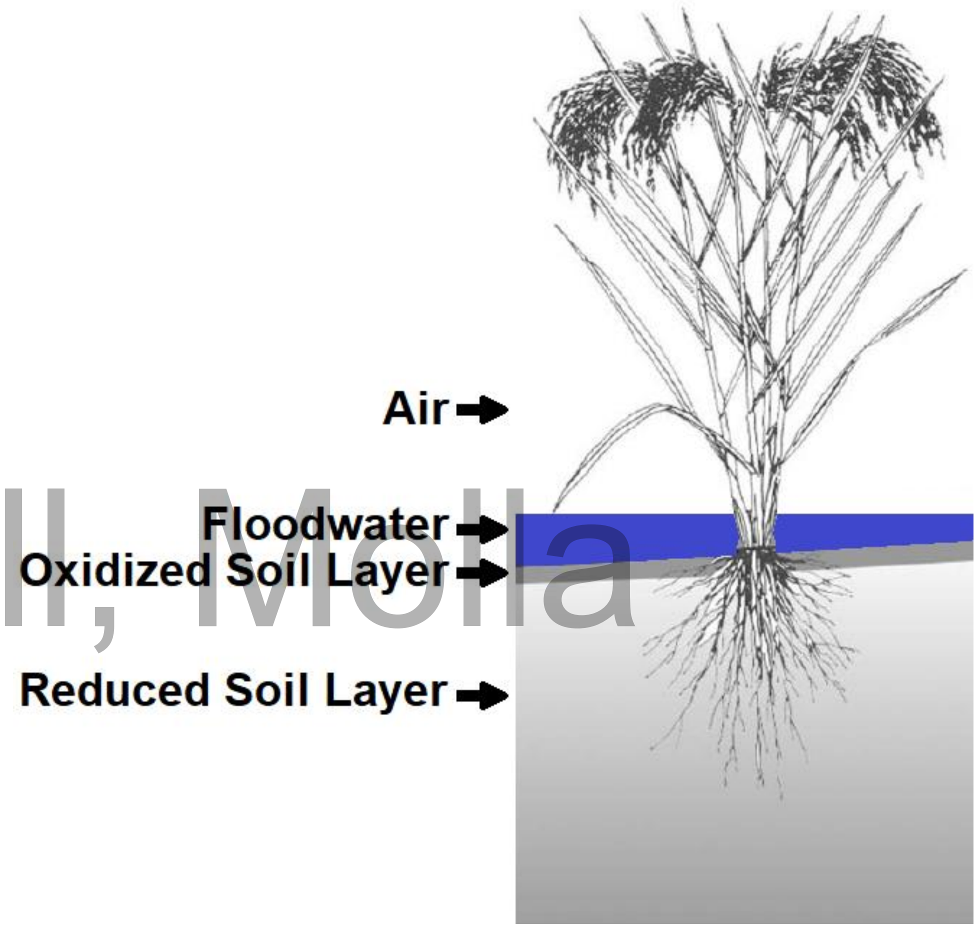



- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

# The Release of Arsenic into Drinking Well Water by Reduction

$$2H_3As(III)O_{3(aq)} + O_{2(aq)} \rightleftharpoons 2H_3As(V)O_{4(s)}$$

- **If the dissolved oxygen (DO; $O_{2(aq)}$) concentration is small, then the reduction of insoluble arsenate ($H_{3-x}As(V)O_4{}^{-x}{}_{(s)}$) to soluble arsenite ($H_{3-x}As(III)O_3{}^{-x}{}_{(aq)}$) is favored.**
- **That is, if the system is reducing; this equilibrium is shifted to the left, and the As dissolves and is added to the drinking well water.**



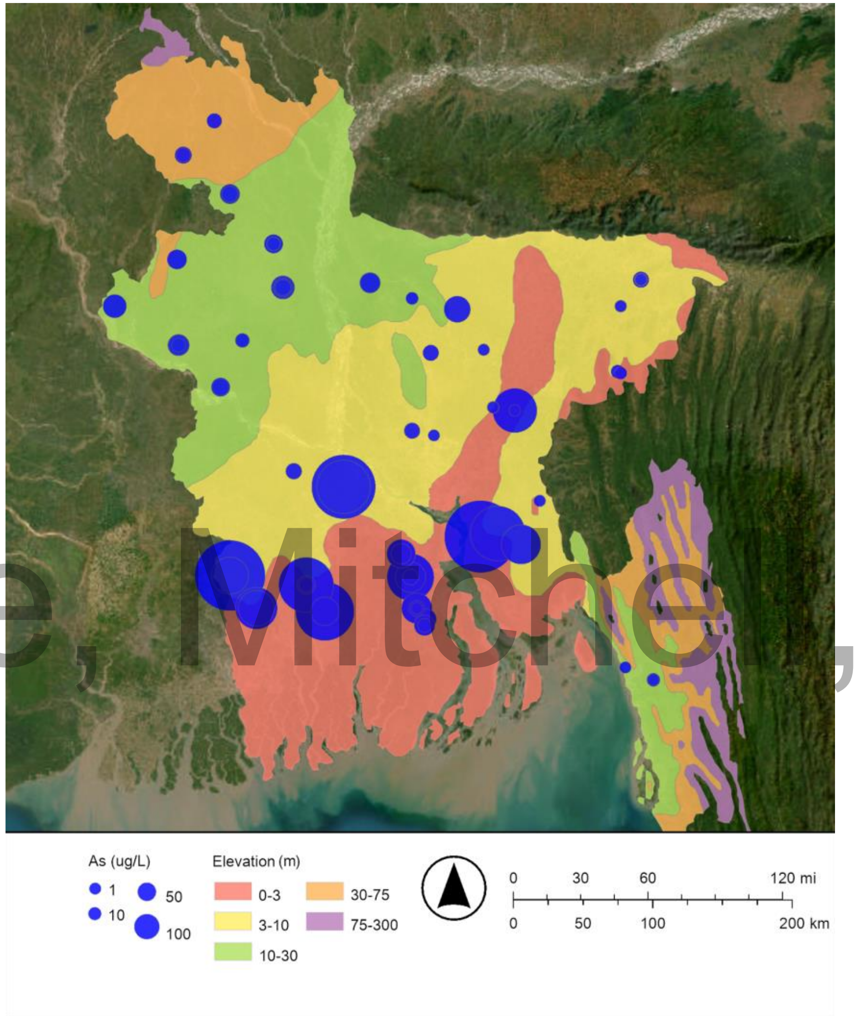



- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

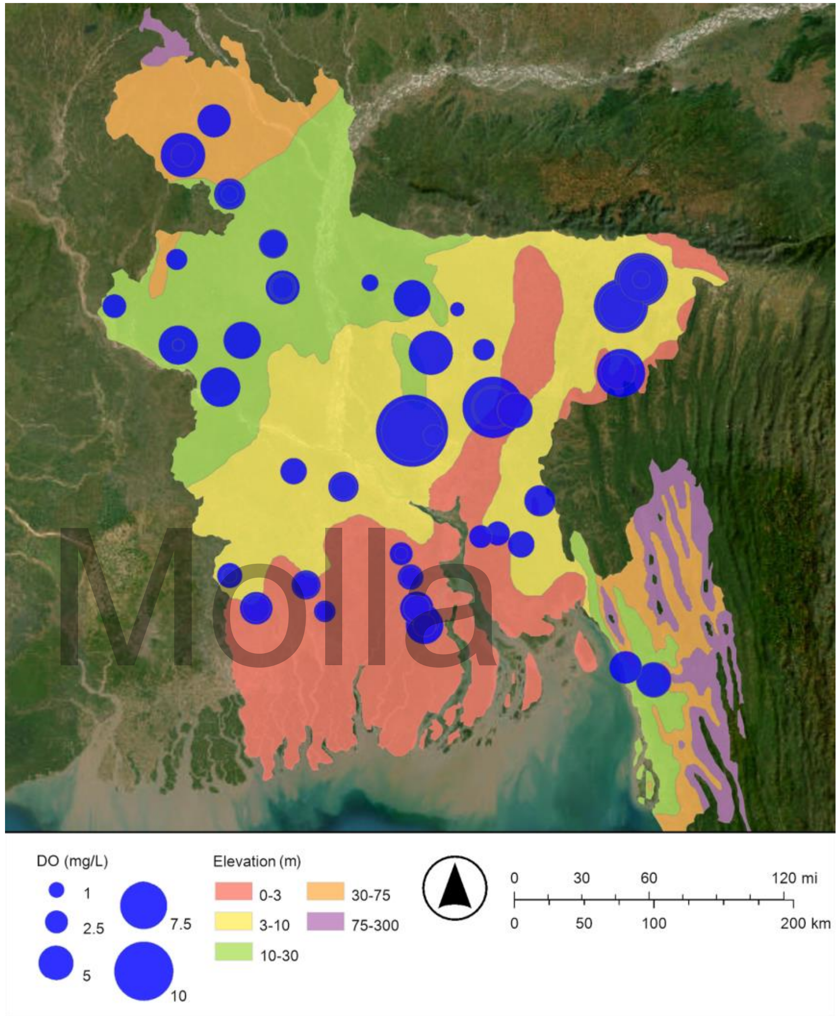
# The Release of Arsenic into Drinking Well Water by Reduction

- **Maps of the As and dissolved oxygen (DO; $O_{2(aq)}$) concentrations of Bangladesh's drinking well water suggest that when the dissolved oxygen (DO; $O_{2(aq)}$) concentration decreases, the As concentration increases.**






**Map of arsenic (As) concentration (µg/L) and elevation (m).**

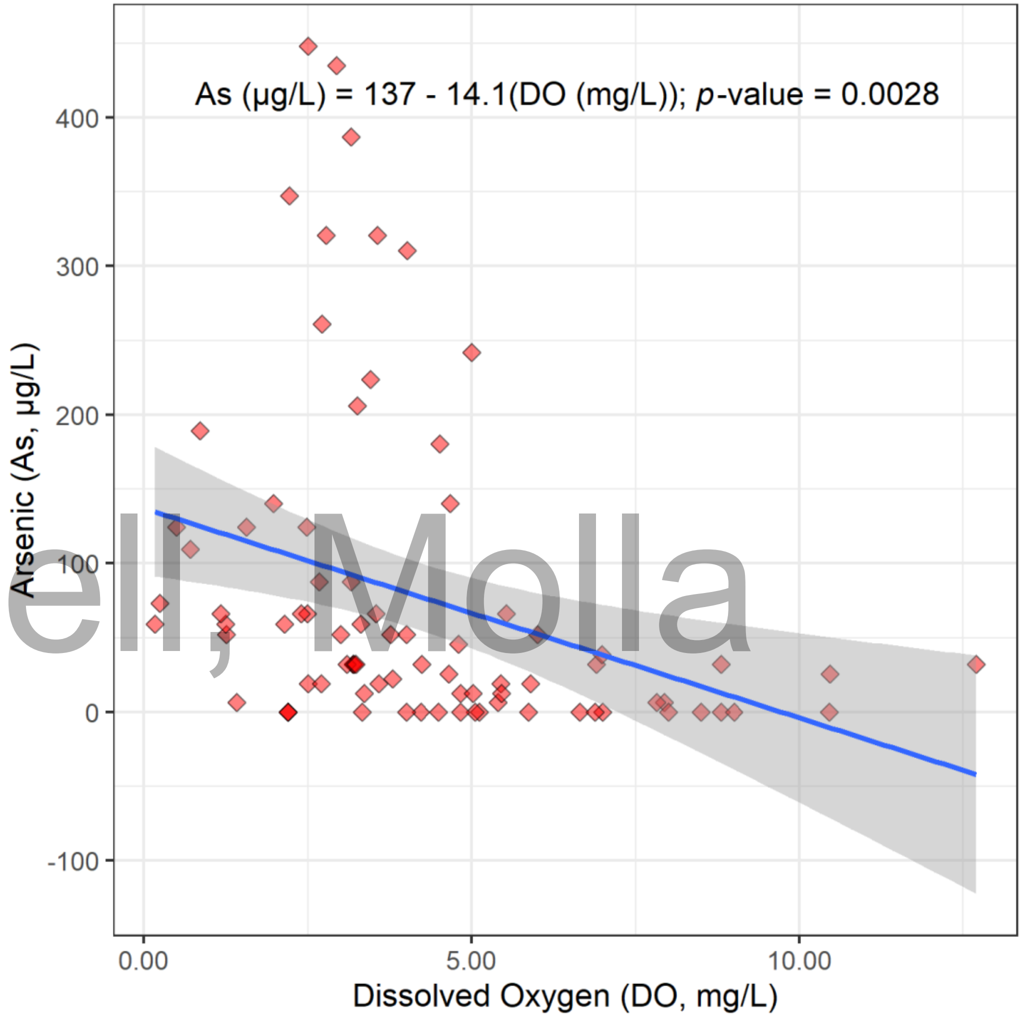



**Map of dissolved oxygen (DO; $O_{2(aq)}$) concentration (mg/L) and elevation (m).**

- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

# The Release of Arsenic into Drinking Well Water by Reduction

- **The linear regression of As concentration versus dissolved oxygen (DO; $O_{2(aq)}$) concentration gives a statistically significant negative slope (−14.1 µg/mg; *p*-value = 0.0028).**
- **This inverse relationship between As concentration and dissolved oxygen (DO; $O_{2(aq)}$) concentration suggests that in the absence of dissolved oxygen (DO; $O_{2(aq)}$), insoluble arsenate ($H_{3-x}As(V)O_4^{-x}$) from sediments is reduced to soluble arsenite ($H_{3-x}As(III)O_3^{-x}$) and released into Bangladesh's drinking well water.**




**The scatterplot, linear regression equation, 95% confidence band, and *p*-value for the concentration of arsenic (As) versus the concentration of dissolved oxygen (DO; $O_{2(aq)}$).**

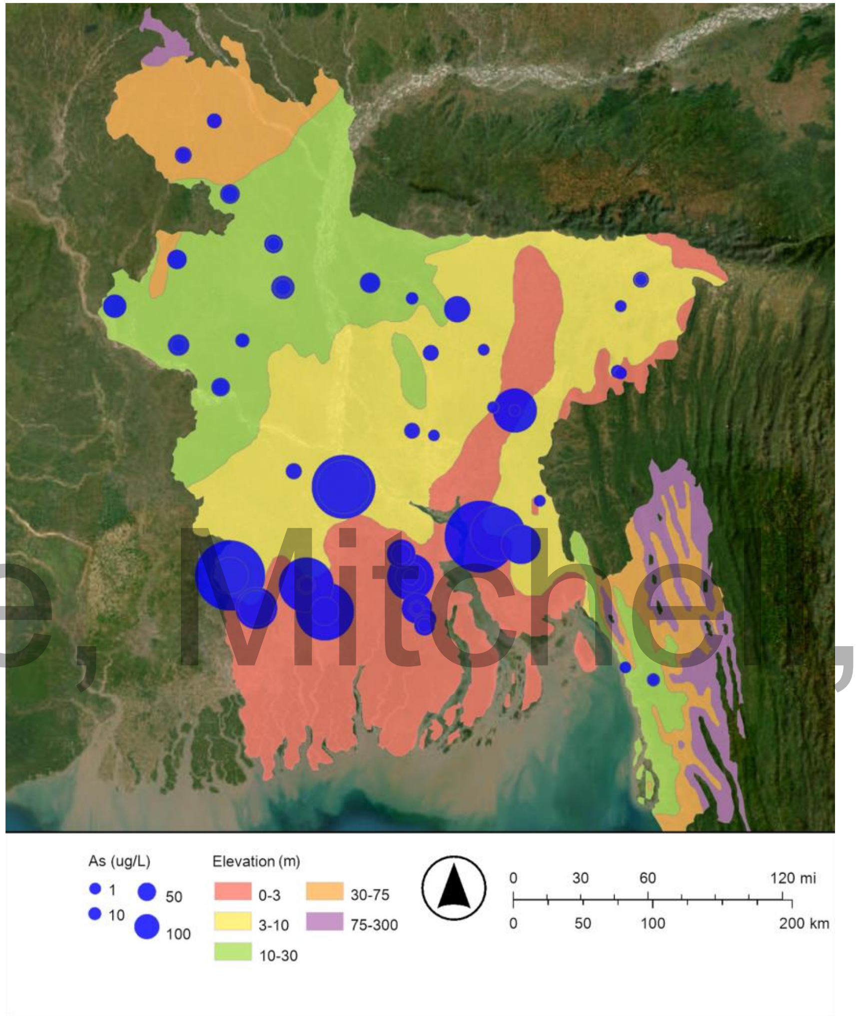


- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

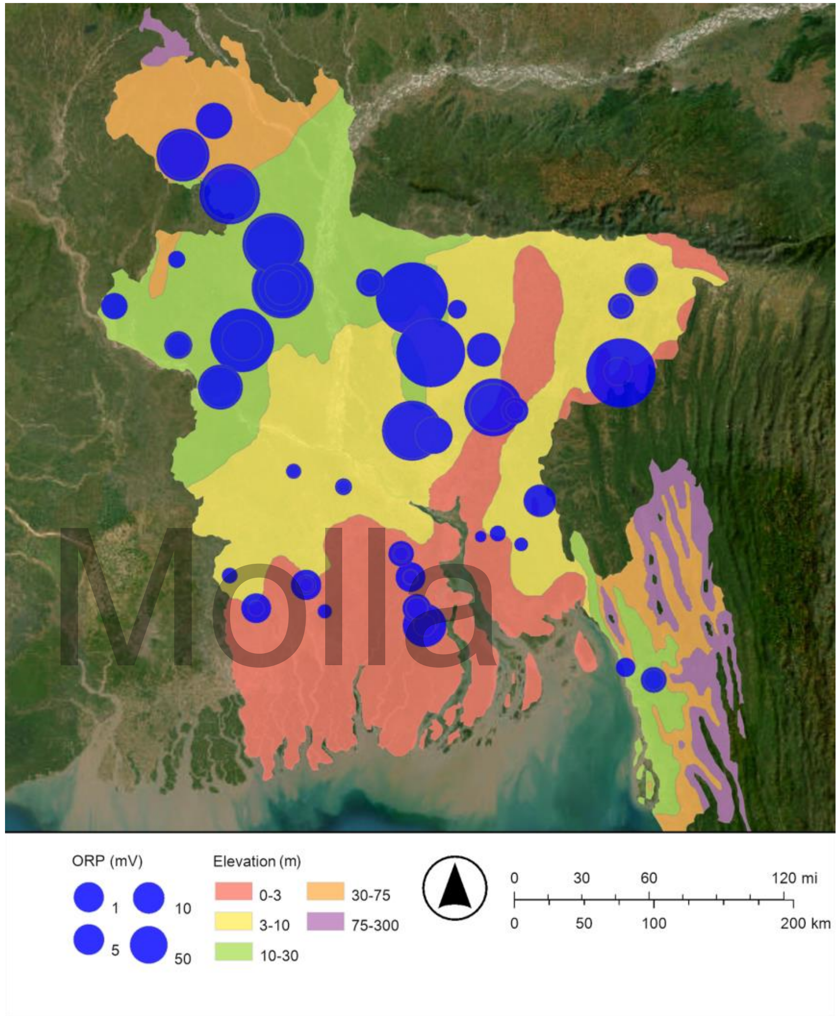
# The Release of Arsenic into Drinking Well Water by Reduction

- **Similarly, the maps of As concentration and oxidation-reduction potential (ORP) suggest that when the oxidation-reduction potential (ORP) decreases, the As concentration increases.**






**Map of arsenic (As) concentration (µg/L) and elevation (m).**



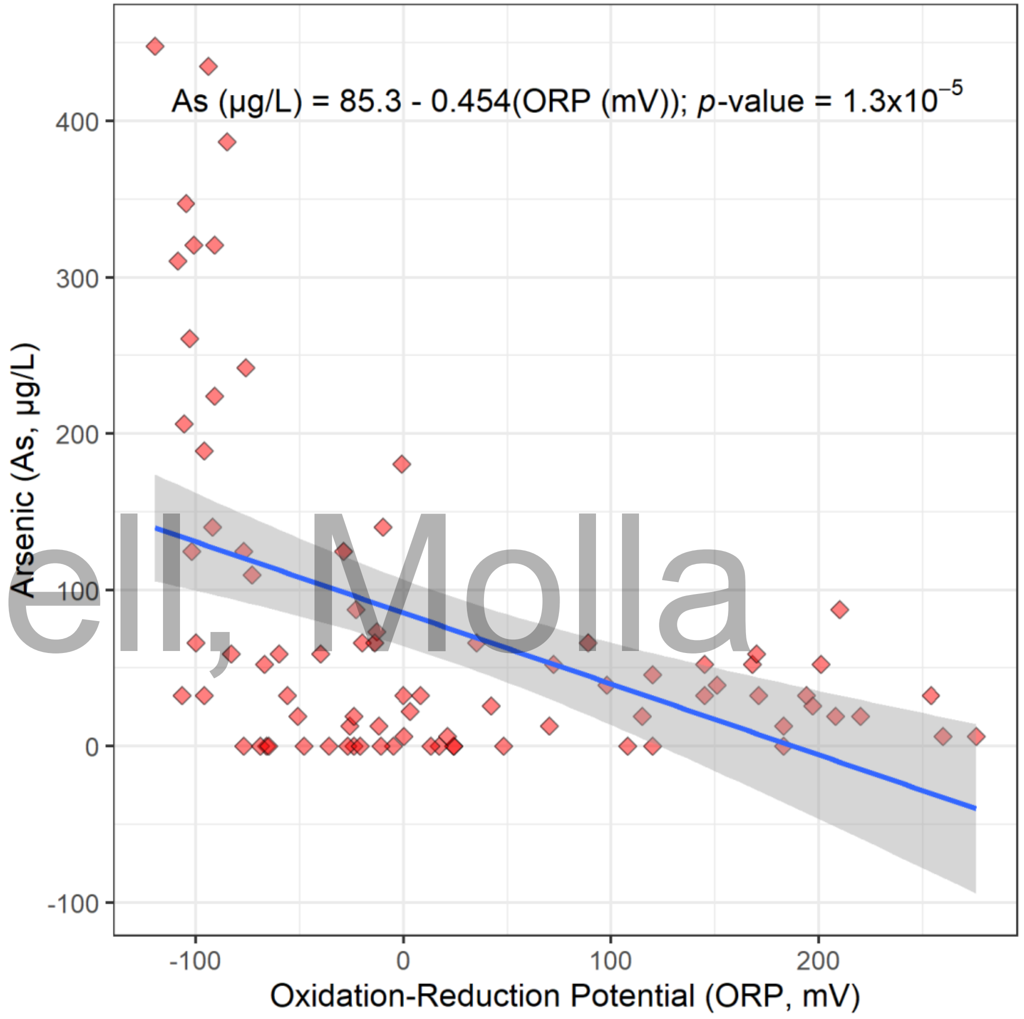

**Map of oxidation-reduction potential (ORP; mV) and elevation (m).**

- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

# The Release of Arsenic into Drinking Well Water by Reduction

- **Similarly, the linear regression of As concentration versus oxidation-reduction potential (ORP) gives a statistically significant negative slope (−0.454 µg/L mV; *p*-value = $1.3 \times 10^{-5}$).**
- **This inverse relationship between As concentration and oxidation-reduction potential (ORP) suggests that insoluble arsenate ($H_{3-x}As(V)O_4^{-x}$) from sediments in a reducing environment is reduced to soluble arsenite ($H_{3-x}As(III)O_3^{-x}$) and released into Bangladesh's drinking well water.**



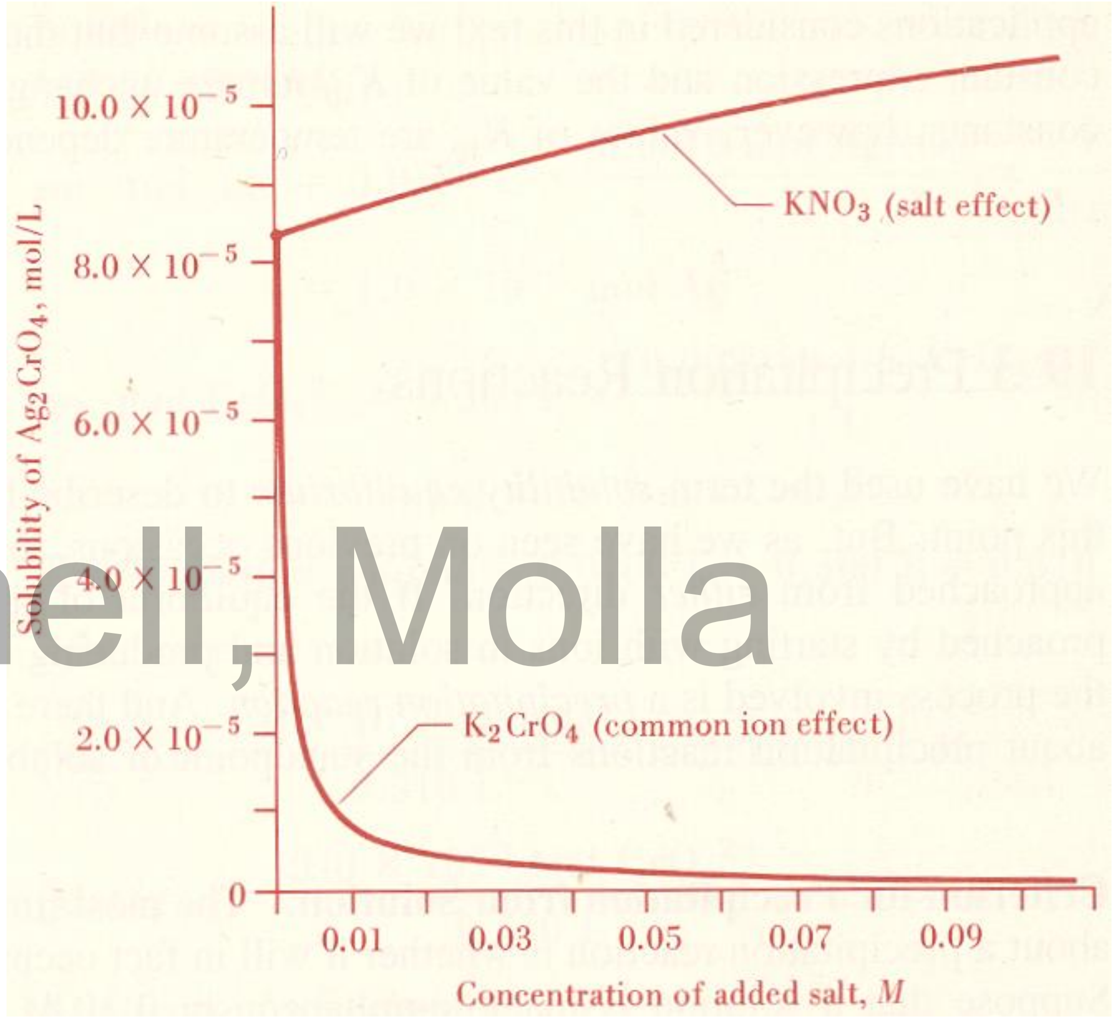



**The scatterplot, linear regression equation, 95% confidence band, and *p*-value for the concentration of arsenic (As) versus oxidation-reduction potential (ORP).**

- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

# The Release of As into Drinking Well Water by the Salt Effect

- **The salt effect, diverse ion effect, or uncommon ion effect describes the increase in the solubility of an ionic solid, such as a mineral, when it is in a solution of ions that are different than the ions in the solid.**
- **For example, the solubility of solid silver chromate ($Ag_2CrO_{4(s)}$) increases as the concentration of dissolved potassium nitrate ($K^+_{(aq)}$ + $NO_3^-{}_{(aq)}$) increases.**






Without diverse ions: $Ag_2CrO_{4(s)} \rightleftarrows 2Ag^+_{(aq)} + CrO^{2-}_{4(aq)}$

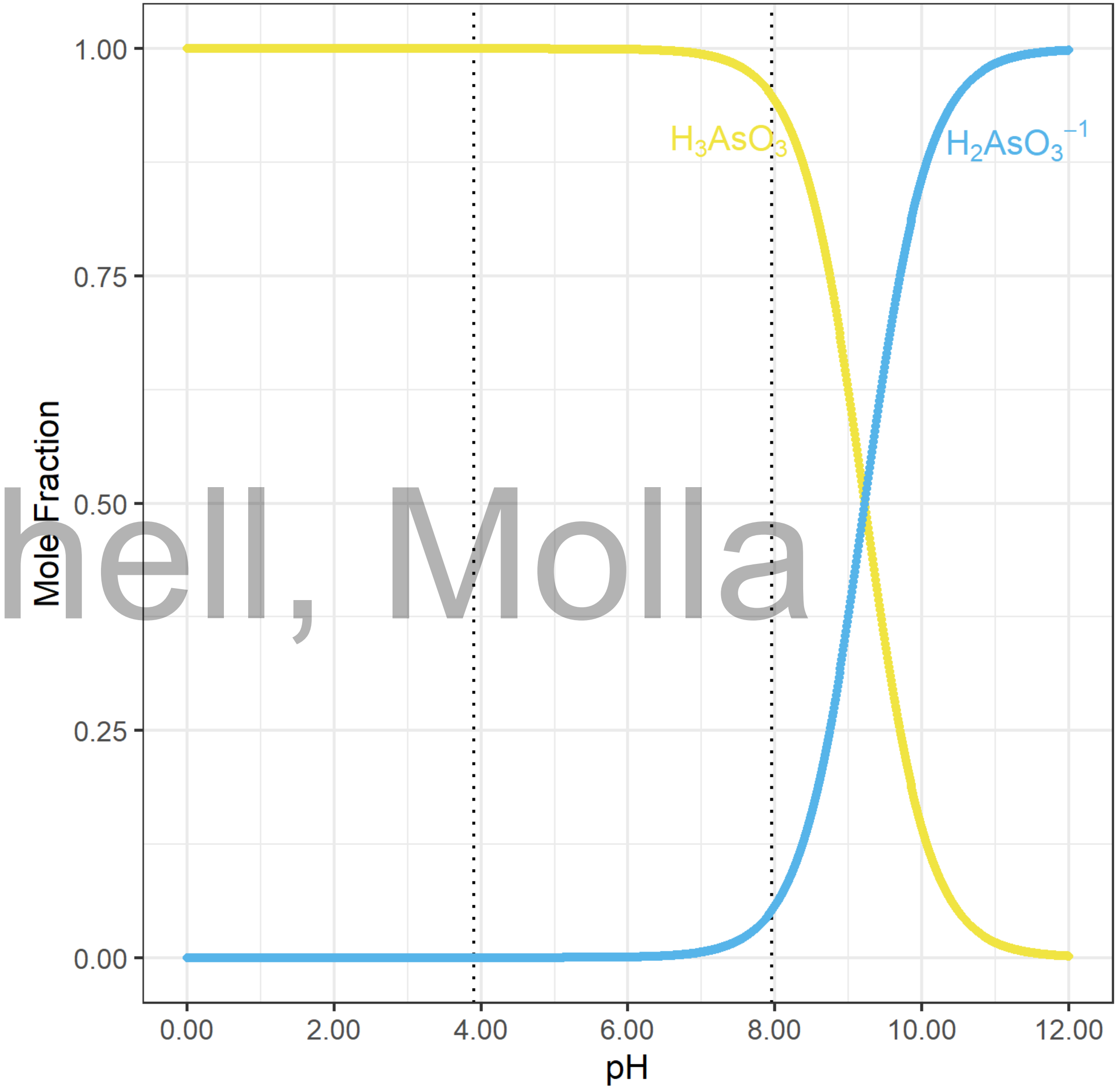
With diverse ions: $Ag_2CrO_{4(s)} + K^+_{(aq)} + NO^-_{3(aq)} \rightleftarrows 2Ag^+_{(aq)} + CrO^{2-}_{4(aq)} + K^+_{(aq)} + NO^-_{3(aq)}$

- Petrucci, R.H. General Chemistry. Principles and Modern Applications. 1982.

# The Release of As into Drinking Well Water by the Salt Effect

- The salt effect is driven by the attraction of oppositely charged particles to each other.
- Therefore, it is essential to know if a chemical is positively charged, negatively charged, or electrically neutral.
- Arsenite ($H_{3-x}As(III)O_3^{-x}$) is mostly electrically neutral, from the minimum observed pH in this study at 3.90 to the maximum observed pH of 7.96.
- Therefore, $H_3As(III)O_3$ is not involved in the salt effect.
- $H_2As(III)O_3^{-1}$ likely plays a minor role in the salt effect.





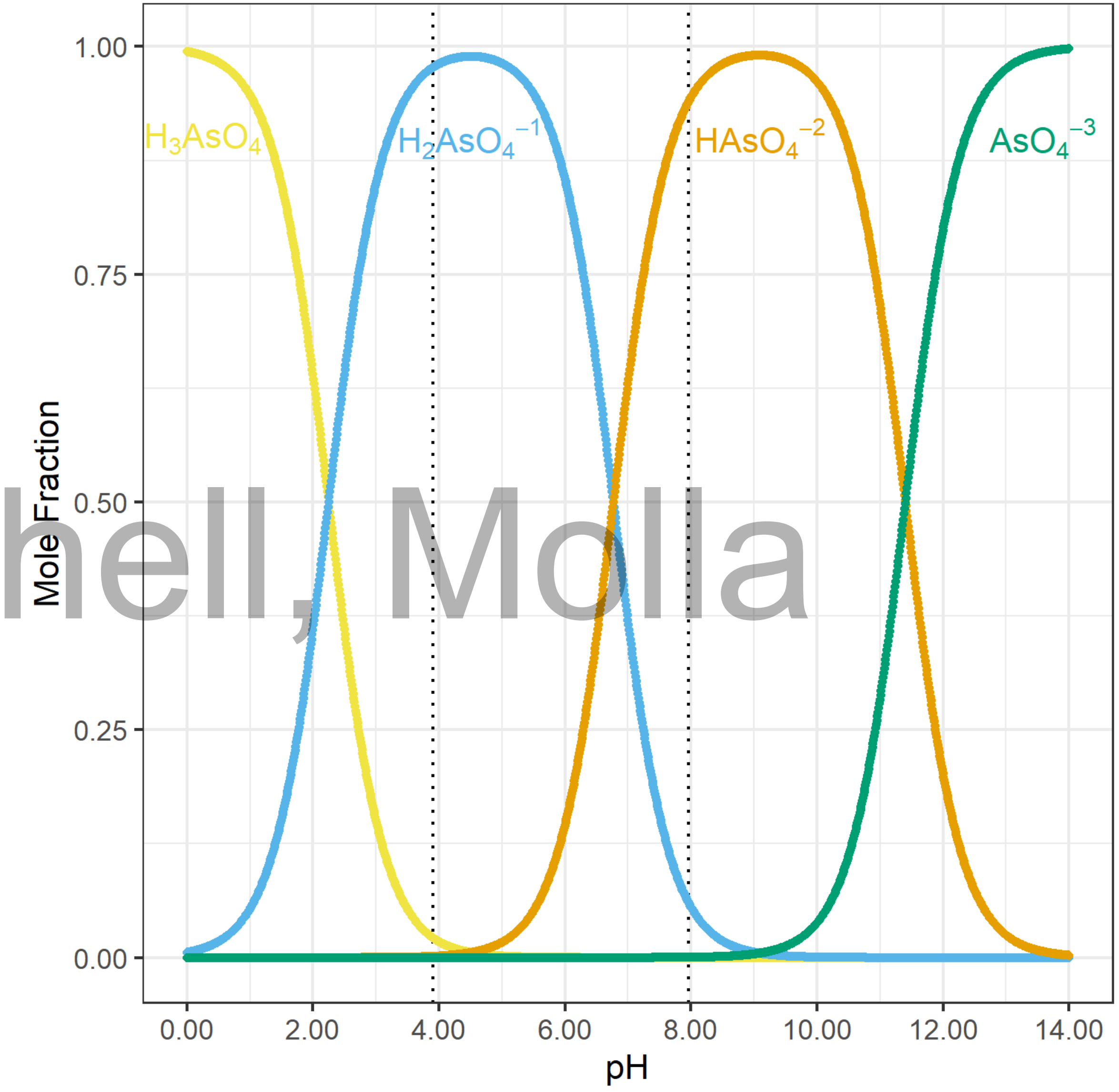

The mole fraction of arsenous acid ($H_3As(III)O_3$) species as a function of pH.

- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

# The Release of As into Drinking Well Water by the Salt Effect

- **In contrast, arsenate ($H_{3-x}As(V)O_4^{-x}$) mostly has a −1 charge, from the minimum observed pH in this study at 3.90 to pH = $pK_{a2}$ of 6.77.**
- **Arsenate ($H_{3-x}As(V)O_4^{-x}$) mostly has a −2 charge, from pH = $pK_{a2}$ at 6.77 to the maximum observed pH of 7.96.**
- **Therefore, $H_2As(V)O_4^{-1}$ and $HAs(V)O_4^{-2}$ are the dominant forms of As in the salt effect.**






**The mole fraction of arsenic acid ($H_3As(V)O_4$) species as a function of pH.**

- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

# The Release of As into Drinking Well Water by the Salt Effect

**The salt effect has 2 components:**

1. **the displacement of ions from solid surfaces by ion exchange, and**
2. **the pairing of oppositely charged ions in water.**

## 1. Ion Exchange

**Lower pH:** $[\text{Solid Surface}]^{+1}\text{H}_2\text{As(V)O}_4{}^{-1}{}_{(ex)} + \text{Cl}^{-1}{}_{(aq)} \rightleftarrows [\text{Solid Surface}]^{+1}\text{Cl}^{-1}{}_{(ex)} + \text{H}_2\text{As(V)O}_4{}^{-1}{}_{(aq)}$



**Higher pH:** $[\text{Solid Surface}]^{+2}\text{HAs(V)O}_4{}^{-2}{}_{(ex)} + 2\text{Cl}^{-1}{}_{(aq)} \rightleftarrows [\text{Solid Surface}]^{+2}(\text{Cl}^{-1})_{2(ex)} + \text{HAs(V)O}_4{}^{-2}{}_{(aq)}$

## 2. Ion Pairing

**Step 1:** $\text{CaHAs(V)O}_{4(s)} \rightleftarrows \text{Ca}^{+2}{}_{(aq)} + \text{HAs(V)O}_4{}^{-2}{}_{(aq)}$

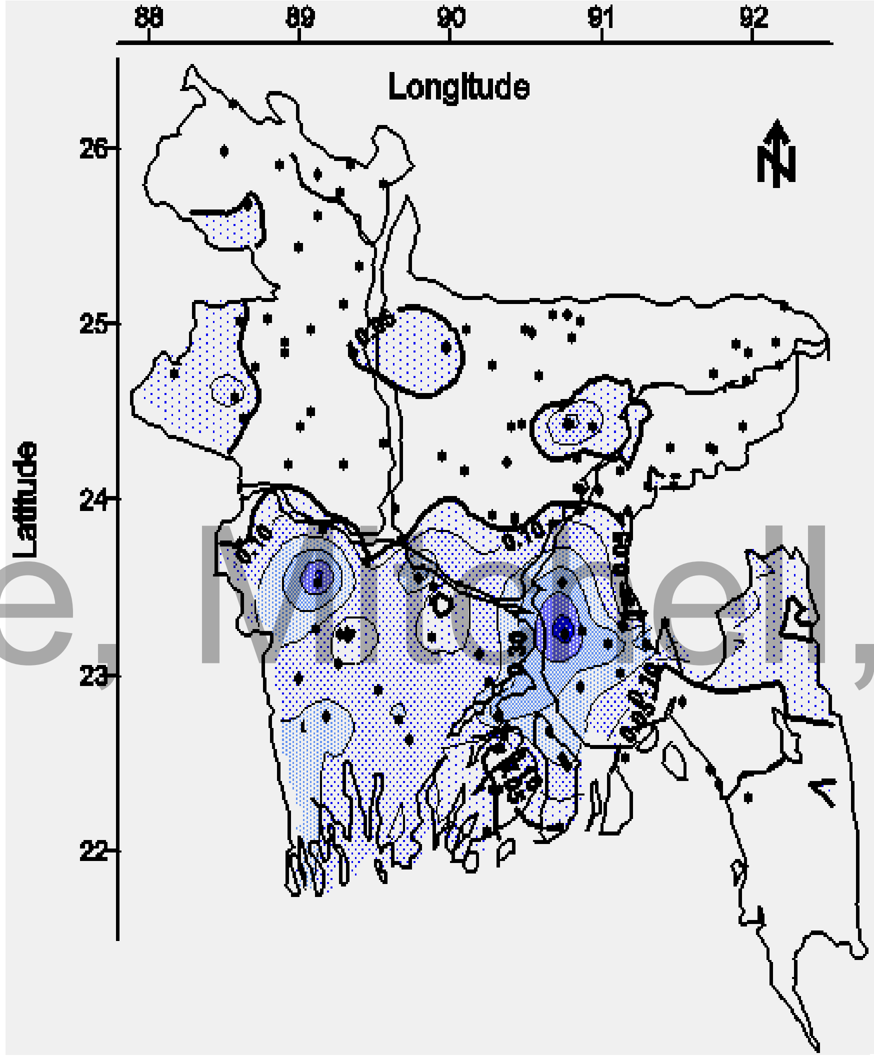
**Step 2:** $\text{Ca}^{+2}{}_{(aq)} + \text{HAs(V)O}_4{}^{-2}{}_{(aq)} + \text{Na}^{+1}{}_{(aq)} + \text{Cl}^{-1}{}_{(aq)} \rightleftarrows \text{CaCl}^{+1}{}_{(aq)} + \text{NaHAs(V)O}_4{}^{-1}{}_{(aq)}$

- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

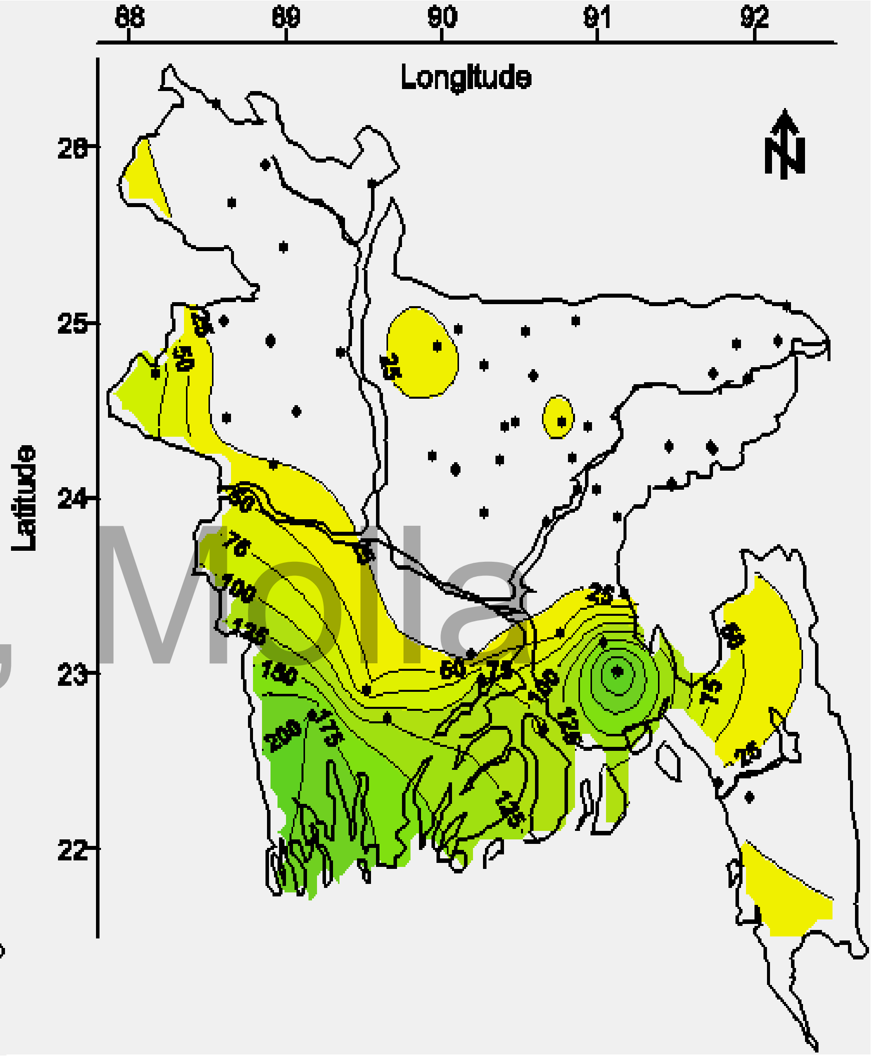
# The Release of As into Drinking Well Water by the Salt Effect

- These maps suggest this saltwater intrusion might release arsenite ($H_{3-x}As(III)O_3^{-x}$) or arsenate ($H_{3-x}As(V)O_4^{-x}$) from solids to Bangladesh's groundwater by anion exchange with chloride ($Cl^{-1}$) and ion pairing with dissolved cations.






Map of As concentration (mg/L)



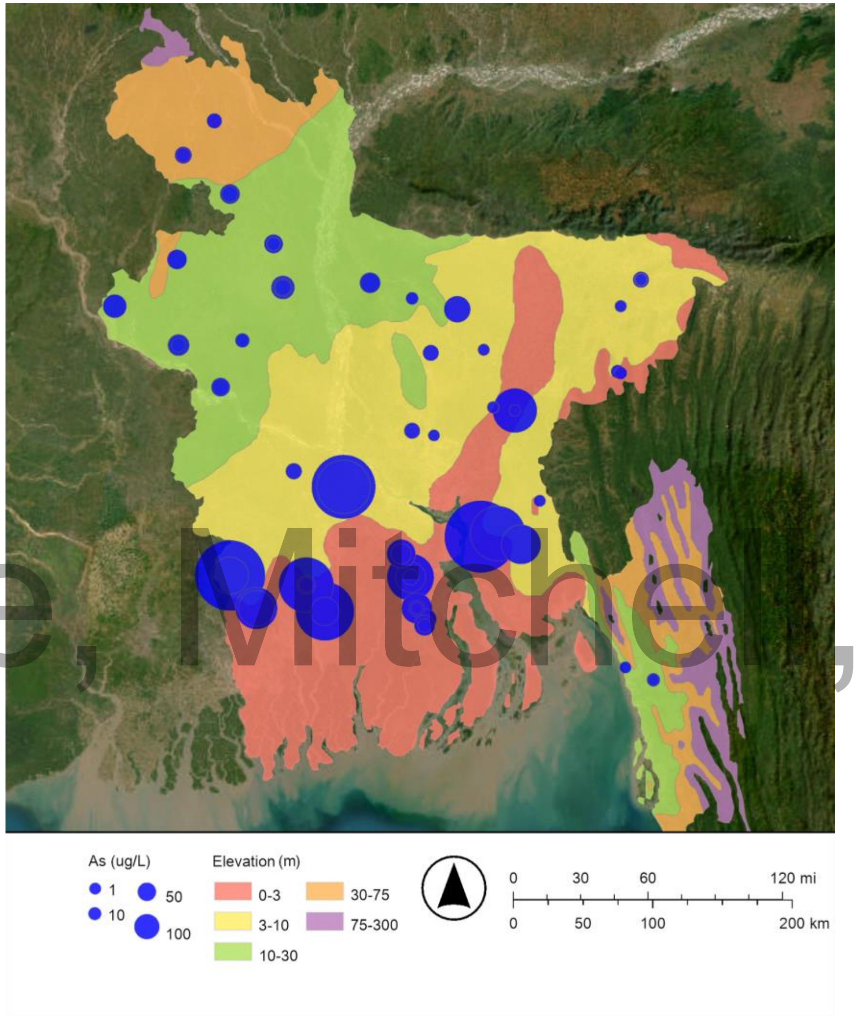

Map of $Cl^{-1}$ concentration (mg/L)

- Frisbie, S.H., D.M. Maynard, and B.A. Hoque. Metals and Genetics. 1999.
- Mitchell, E.J., S.H. Frisbie, and B. Sarkar. Metallomics. 2011.

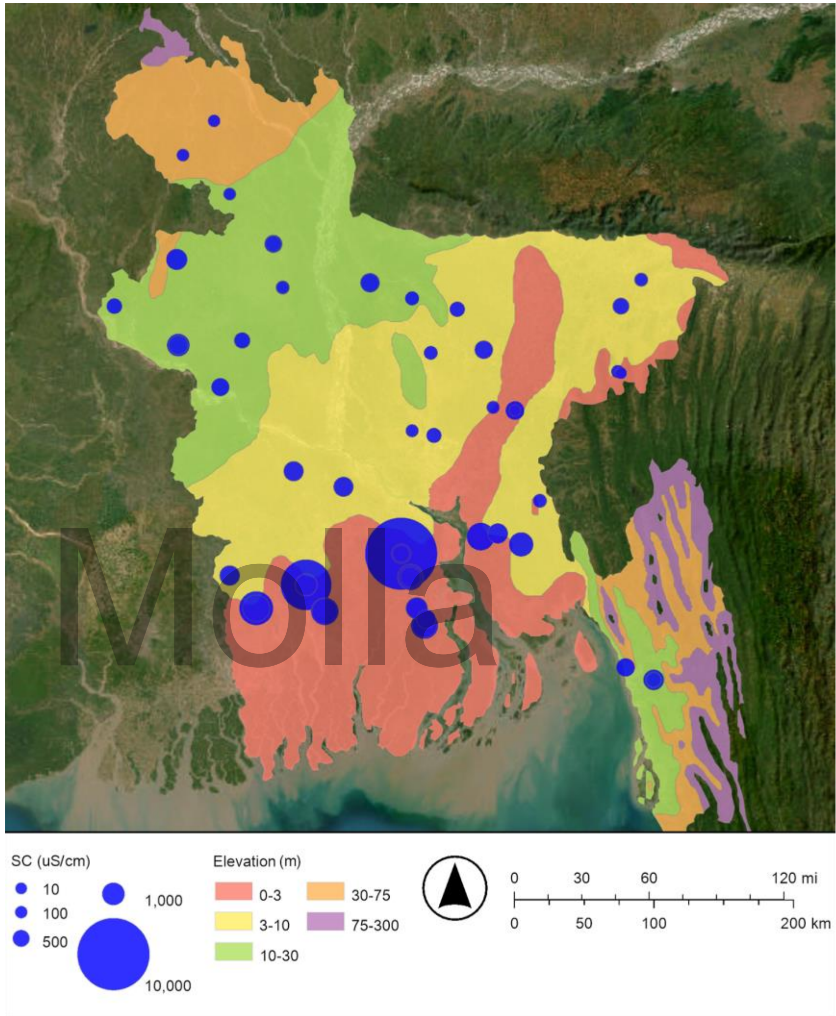
# The Release of As into Drinking Well Water by the Salt Effect

- **Maps of the As concentration and specific conductance (SC) of Bangladesh's drinking well water suggest that when the specific conductance (SC) increases, the As concentration increases.**






**Map of arsenic (As) concentration (µg/L) and elevation (m).**



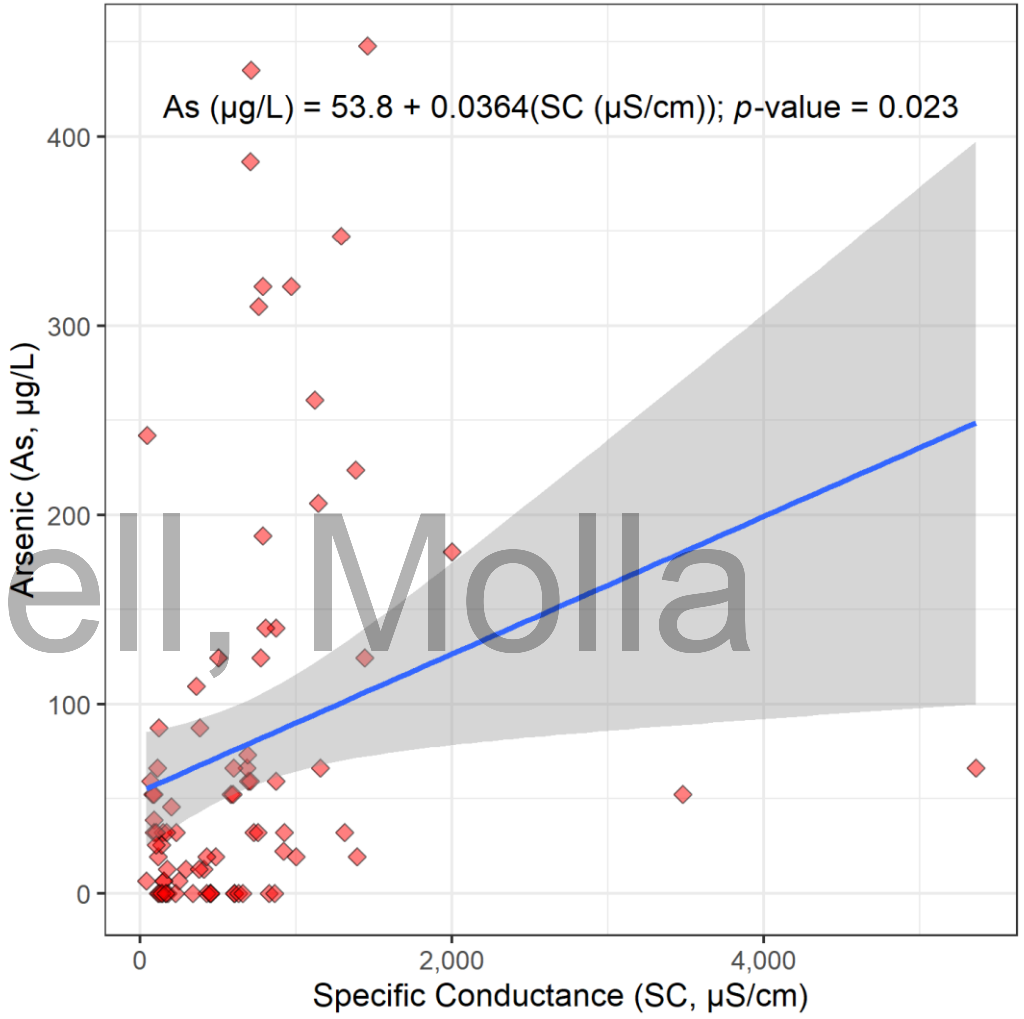

**Map of specific conductance (SC; µS/cm) and elevation (m).**

- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

# The Release of As into Drinking Well Water by the Salt Effect

- **The linear regression of As concentration versus specific conductance (SC) gives a statistically significant positive slope (0.0364 µg cm/L µS; *p*-value = 0.023).**
- **This positive relationship between As concentration and specific conductance (SC) suggests that any process that increases salinity, such as annual flooding, is expected to increase the release of arsenic oxyanions ($H_{3-x}As(V)O_4^{-x}$ and ($H_{3-x}As(III)O_3^{-x}$) from sediments into Bangladesh's drinking well water by the salt effect.**





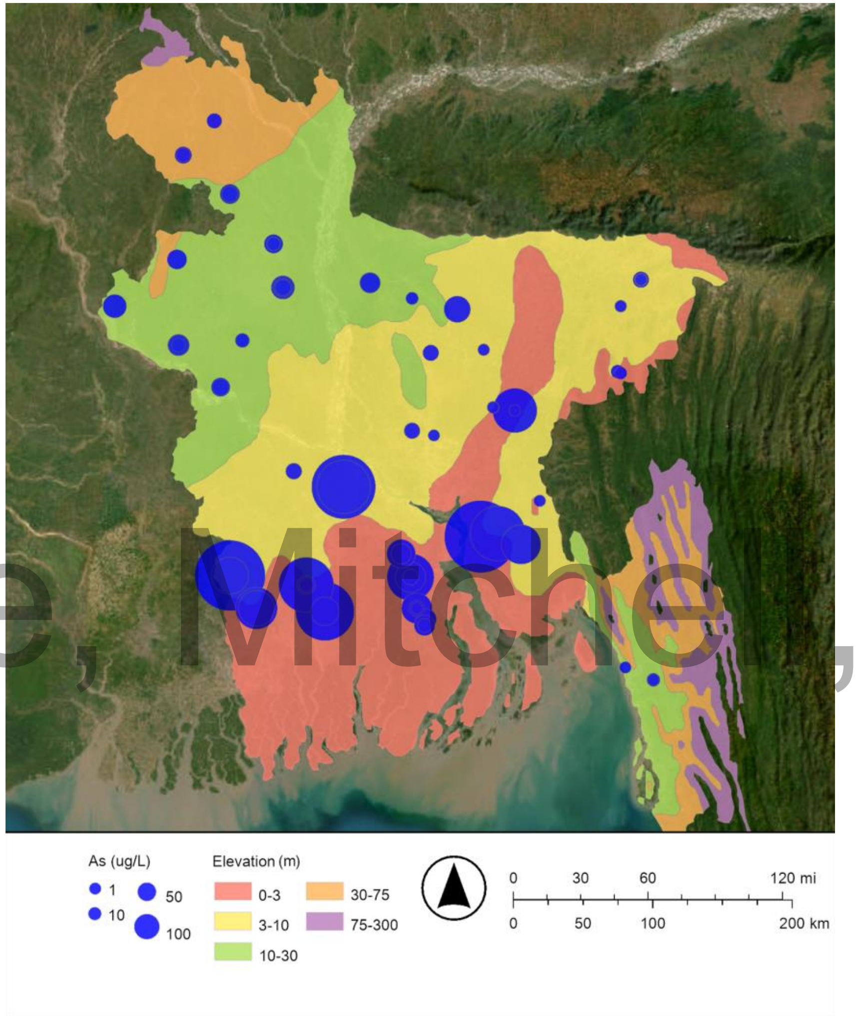

**The scatterplot, linear regression equation, 95% confidence band, and *p*-value for the concentration of arsenic (As) versus specific conductance (SC).**

- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

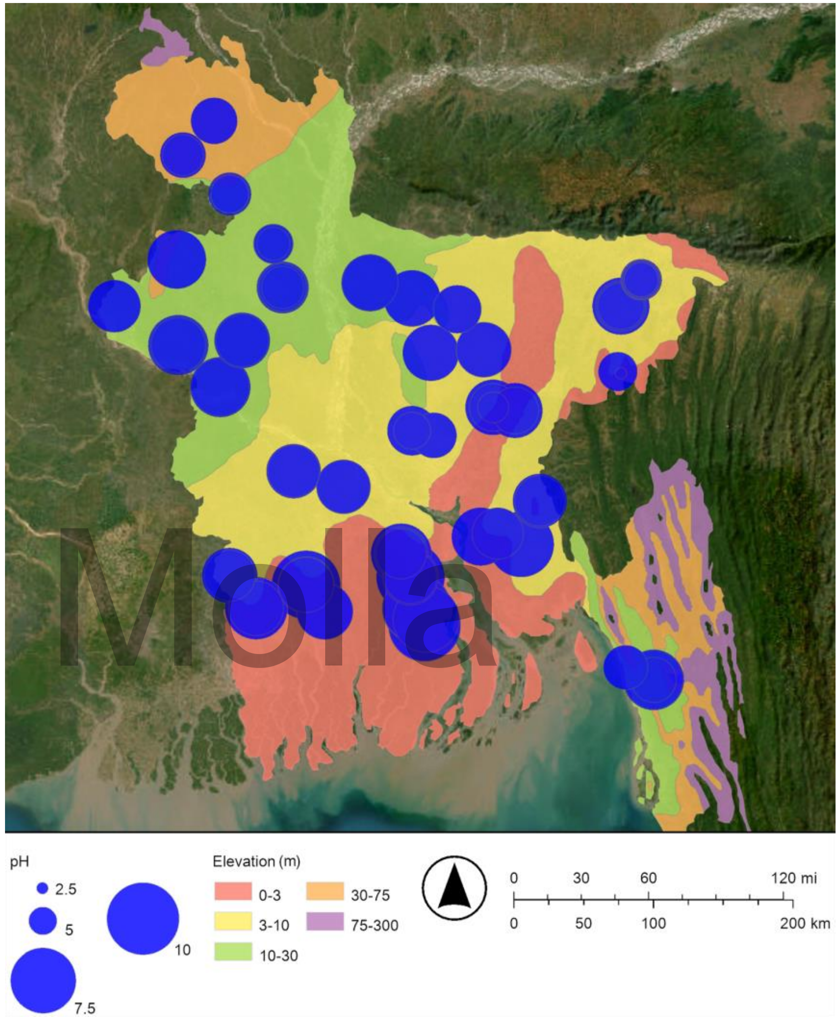
# The Release of As into Drinking Well Water by the Salt Effect

- **Similarly, the maps of As concentration and pH suggest that when the pH increases, the As concentration increases.**
- **The pH of drinking well water in this study ranged from pH 3.90 to pH 7.96. The average pH of oceanwater is pH 8.1.**






**Map of arsenic (As) concentration (µg/L) and elevation (m).**



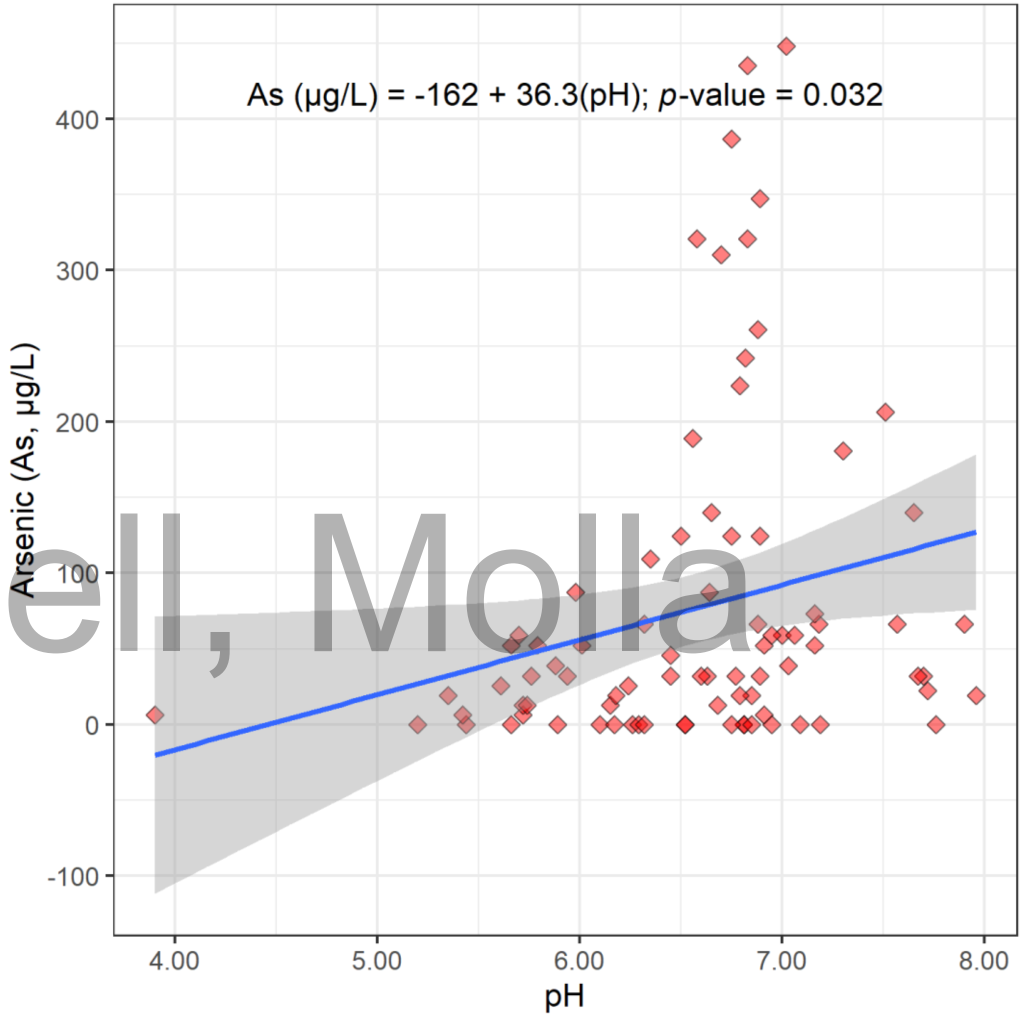

**Map of pH and elevation (m).**

- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

# The Release of As into Drinking Well Water by the Salt Effect

- **Similarly, the linear regression of As concentration versus pH gives a statistically significant positive slope (36.3 µg/L pH unit; *p*-value = 0.032).**
- **Oxyanions of arsenate ($H_{3-x}As(V)O_4^{-x}$) and possibly arsenite ($H_{3-x}As(III)O_3^{-x}$) are most likely displaced from positively charged solid surfaces in Bangladesh's aquifer by anion exchange with aqueous hydroxide ion ($OH^-_{(aq)}$) as the pH increases.**






**The scatterplot, linear regression equation, 95% confidence band, and *p*-value for the concentration of arsenic (As) versus pH.**

- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

# Conclusions

- **As sea levels continue to rise and floods and cyclones in Bangladesh increase in area and duration, the underlying aquifer can become more reducing and more saline.**
- **Our data strongly suggest that these chemical changes can increase the release of As from sediments and into Bangladesh's drinking well water.**
- **This is a significant threat to public health.**



- Frisbie, S.H., E.J. Mitchell, and A. Molla. PLOS ONE. 2023.

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