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Response to Comments on "Large-Scale Uranium Contamination of Groundwater Resources in India"

We appreciate the feedback from Rathore[1] and are happy to address his comments and concerns. Many of his concerns can be addressed with some simple clarification and a more thorough reading of the paper.[2] When we embarked on this project, there was no routine monitoring of many trace elements in Indian groundwater, including uranium. Therefore, our paper[2] presents, for the first time, an evaluation of the large-scale prevalence of uranium in India's groundwater that we are hopeful will lead to the inclusion of uranium in the monitoring programs at both the state and federal levels.

While groundwater table decline is indeed a global phenomenon, several studies have shown that overexploitation of groundwater, particularly in northwestern India, has caused massive groundwater depletion; there is no dispute among the Indian scientists concerning the severity of groundwater depletion in many parts of the northwestern aquifers.[3−8] We agree with Rathore[1] that there are many technological solutions for uranium remediation, yet we demonstrated in our paper that in many areas where groundwater is used for drinking water there is no any technological intervention while the uranium level far exceeds the World Health Organization (WHO) provisional standard.[2] In our study, 45 of the 121 primary drinking water wells we measured in Rajasthan's alluvial aquifers exceeded the WHO provisional guidelines for uranium. Millions, particularly in rural areas where groundwater is the only drinking water source, are currently exposed to high uranium levels in their drinking water. While the Atomic Energy Regulatory Board in India may have set a standard,[9] this standard is not part of the Indian Standard Drinking Water Specification regulations, nor does it address the potential human health effects incorporated in the WHO recommendation.[10]

We believe that Rathore's[1] confusion about our discussion of the relationship between bicarbonate and uranium may come in part from a typo in the "Controls on the Occurrence of Uranium" section, in which we state that "bicarbonate complexation and oxidizing conditions are two of the most important chemical factors controlling uranium concentrations in groundwater..." We should have said "carbonate complexation". However, his claim for "inconsistency" is irrelevant because it is carbonate and not bicarbonate that is complexing with uranium, which we affirm multiple times in the paper. In the paper, we provided the background literature about the mechanism of complexation of uranium with carbonate, and we highly recommend reading this literature[11−13] to avoid confusion and misunderstanding of the uranium geochemistry in natural waters.

Rathore's[1] assertion that "there is no correlation of uranium versus bicarbonate concentration" is objectively incorrect. The table in the supporting material that he cited as evidence for the absence of correlation does not deal with the relationship between uranium and bicarbonate but instead presents the relationship between uranium and geology. Instead, Table S6 presents Spearman's rank values for the correlation between uranium and bicarbonate sorted by aquifer. The analysis shows correlation at high significance (p = 0.01) for all aquifers, except for the Gujarat Basalt and Gujarat Crystalline basement. Therefore, the statement about the lack of correlation between uranium and bicarbonate is simply incorrect. The uranium−bicarbonate correlation we showed in our paper has been also demonstrated in several previous studies.[14,15]

In the paper, we suggested that when uranium data are not available, bicarbonate concentrations could be used a rough proxy for possible uranium contents in groundwater given the correlation our study and numerous studies have shown. This is especially applicable for India where uranium is not commonly measured while bicarbonate is routinely monitored. Yet Rathore[1] missed that point and mistakenly thought we suggest that bicarbonate be measured instead of uranium. This is obviously not the case, and again, we recommend reading the paper more carefully to avoid such a misunderstanding.

Rathore[1] proposes measuring uranium in natural waters by laser-induced fluorimetry. While this method has been successfully applied for detailed studies of uranium, the method we employed through inductively coupled plasma mass spectrometry (ICP-MS) is far more common in water quality monitoring programs and covers a large spectrum of metals with low detection limits and high precision. Therefore, the argument that one analytical method is superior over the other has no basis. The detection limit performance of the ICP-MS instrument at Duke University is 0.001 ppb.

We mentioned nitrate pollution because its occurrence in water resources has been tied to uranium contamination by other studies. We did not find direct evidence of this in our study, but it was worth noting that nitrate concentrations were very high throughout our study area. We were very clear in the paper that we do not have enough information to draw specific conclusions about the relationship between nitrate and uranium. This point was, again, missed in the evaluation by Rathore.[1]

It is unfortunate that Rathore[1] doubts our fieldwork and sampling procedures. All field measurements (pH, conductivity, and temperature) were done in the field in real time using calibrated probes. Our methods section details explicitly how our samples were filtered and acidified for trace metals and major cations in the field following the U.S. Geological Survey protocol[16] for water sampling. The longest interval between sampling and data collection was ∼3 weeks. This may have some minor impact on bicarbonate measurements but no impact on uranium measurements because the samples were filtered and acidified. We also collected our samples in Nalgene HDPE screw cap bottles that remained closed until measurement, so "evaporative preconcentration" was not an issue.

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During the past decade, our lab at Duke University has measured thousands of water samples, participated in several cross-lab comparison studies, and demonstrated a high level of analytical capacity for monitoring trace metals in natural water. This level of analytical quality and accuracy was applied to the study of uranium in our paper.[2]

We understand that Rathore does not believe that uranium should be high in groundwater for many reasons, but our own independent measurements and the measurements of many other studies across India speak for themselves. Rathore's[1] claims about the "impossible high uranium in groundwater" reinforce the importance and the massage of our paper that misunderstandings and erroneous conceptual ideas about uranium in groundwater should face reality, and the paradigm of uranium occurrence and monitoring in Indian's groundwater should be changed to address this problem.

We agree that there are existing technologies to help remove uranium from drinking water or provide alternative water resources to uranium-rich groundwater, but currently these technologies are not available to many people in India. We hope that this research can raise awareness of this fact and help bring such resources to those who need it most.

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Notes
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