

## Chemical-weathering rates of aquifers and the mixing of soils: the role of optical dating in quantifying near-surface processes on earth and their timescales

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*In arsenic-prone regions, an important question is the provenance of arsenic in shallow groundwaters (< 30 m). Some studies suggest that arsenic is sourced from the overlying local soils of an aquifer, whereas others surmise it to be due to weathering of the underlying aquifer matrix. Most work on chemical weathering suggests that 'younger/fresher' material 'weathers' faster than 'older/indurated' material. New optical dates suggest that the depositional-age of the sediments comprising an aquifer is an important parameter in arsenic groundwater chemistry. Here, we re-introduce the concept of the critical zone, explain how Asia's shallow groundwater arsenic is a process occurring within the critical zone and show a new application of optical dating methods to help determine critical zone chemical weathering rates, such as the release of arsenic into Asia's groundwaters.*

### Introduction – what is the critical zone?

Here we discuss the seminal importance of the critical zone to elucidate the source and concentration of arsenic in groundwaters, so as to enthruse more research in this emerging scientific field. Conventionally, the critical zone is defined as:

'... the heterogeneous, near surface environment in which complex interactions involving rock, soil, water, air, and living organisms regulate the natural habitat and determine the availability of life-sustaining resources.'<sup>1</sup>

As defined by the Natural Resources Council, there is a portion of the Earth's surface where a complex set of interactions that are critical for life occur. Remarkably, these zones occur within a thickness that is  $\sim 10^{-5}$ % of the Earth's radius. From the air-soil interface down to the lowest point of bedrock weathering (which as yet remains poorly identified), this 'critical zone' is the region from which soils and the shallowest of groundwaters are being sourced. For humans, this zone serves as a natural filter against the water-borne diseases that plague surface waters and it is also where life-sustaining crops are grown. Despite all the sustenance yielded by this tiny zone, its resources can also be life threatening. Abnormally higher or lower concentration of any element can be detrimental to the life supported by it. These include deficiencies and/or toxicities related to essential elements like Fe, Cu, Zn, Co, Mg, Cr and Se (ref. 2) and expo-

sure to elements like arsenic, which has no known beneficial dose (for healthy individuals).

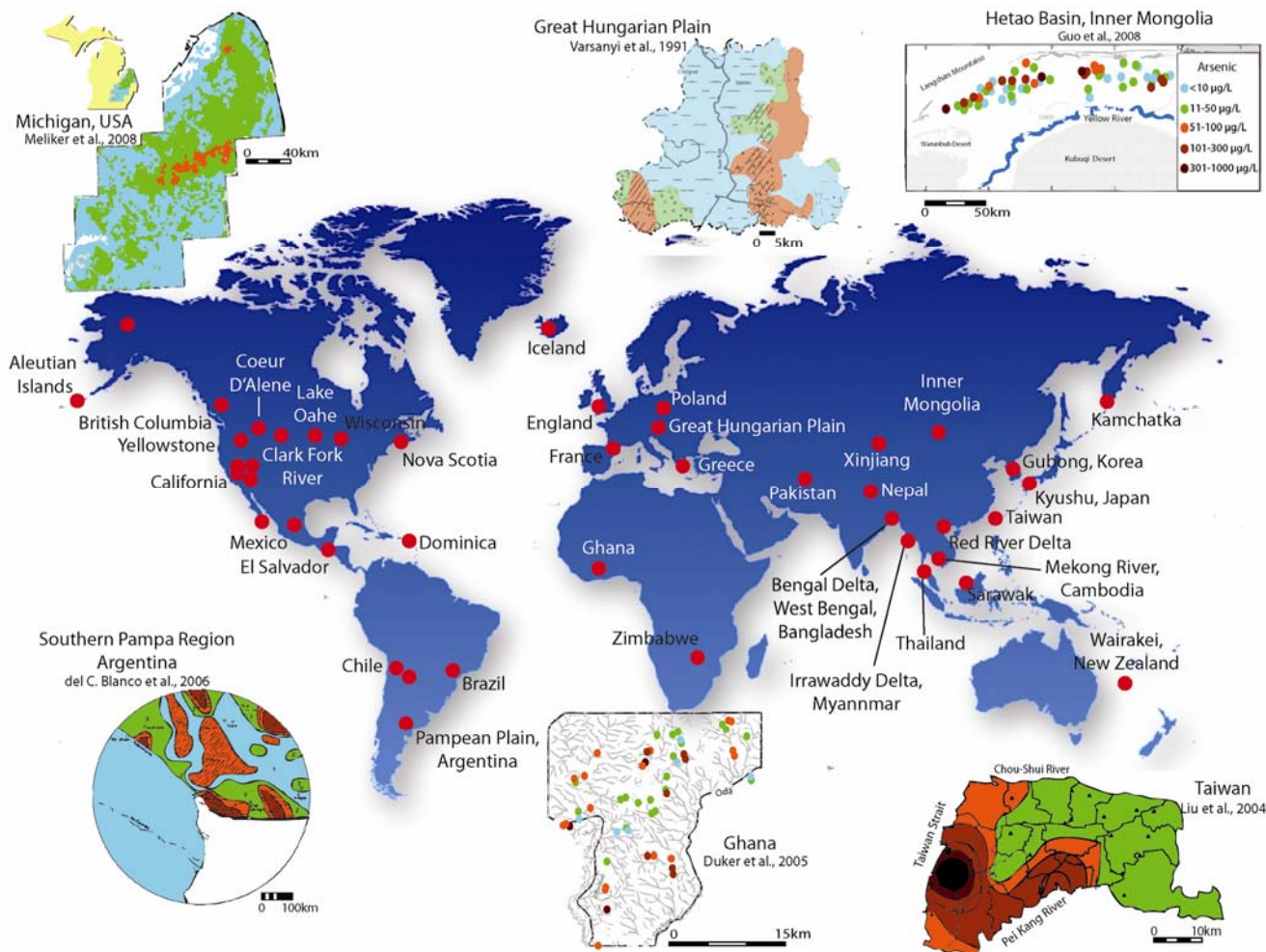
Focusing on arsenic, we see that nowhere is its toxicity more evident than in the Asian and South East Asian aquifer systems, where it is estimated that over 60 million people are at risk from arsenic-laden groundwater<sup>3-8</sup>. Despite its ubiquitous nature and the ever-growing number of countries affected<sup>9</sup> (Figure 1), continued uncertainty about the processes, causes and consequences still exists. Arsenic has been dubbed one of the world's 'worst calamities on record'<sup>10</sup>. Known effects of drinking water high in arsenic include skin lesions<sup>11</sup>, bladder cancers<sup>12</sup>, respiratory illnesses<sup>13</sup>, developmental delays<sup>14</sup> and childhood morbidity<sup>15</sup>. For the Asian region, these effects are particularly punctuated, since nutritional limitations<sup>16,17</sup> and rapid development<sup>18</sup> can make it even more necessary to have good quality water.

Although most researchers agree that arsenic is being naturally weathered into the groundwater, we do not know exactly where the arsenic is derived from. Suggestions include: (1) it being sourced from the overlying soils of an aquifer<sup>19</sup> or (2) it being directly weathered deeper down, within the aquifer itself<sup>20,21</sup> (Figure 2). A similar debate also exists for the organic matter driving the dissolution of arsenic<sup>22,23</sup> leaving many questions about the location of critical processes that deliver arsenic into groundwater. Is it in the top few centimetres of the overlying soils of an aquifer or a few metres deeper down, in the shallow aquifer below? And, perhaps more importantly,

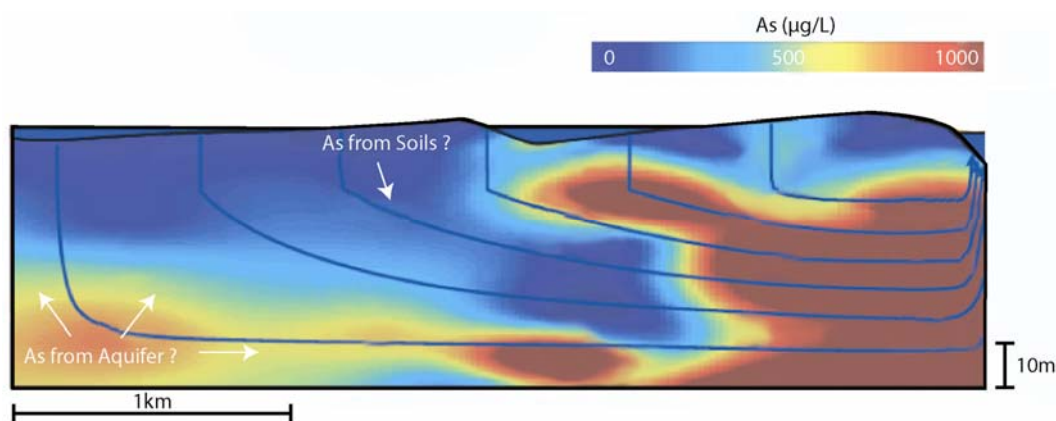
does arsenic come from 'the critical zone'?

### Why shallow groundwater arsenic is the result of a 'critical zone' process?

Since the critical zone encompasses the 'outer extent of vegetation down to the lower limits of the groundwater'<sup>24</sup>, the processes responsible for the natural release of groundwater arsenic – whether it is from the soils, or the shallow aquifer below – can and should be classified as a process occurring within the critical zone. In some of their initial work on weathering, which eventually branched into surface weathering and the current refinement of the critical zone, White and Brantley<sup>25</sup> observed differences in weathering rates between 'new' and 'old' versions of the same material. With other parameters being the same, they found that fresh 'newer' granite weathers faster than 'older', already exposed granite. Applying this analogy to the groundwater arsenic in Asia, one could argue that some of the shallow groundwater heterogeneity could be due to the aquifers being located in sediments of different ages. For the type of heterogeneity between individual tube wells, this would mean differences in aquifer ages between sediments that are located only a few metres away from each other. In the dynamic fluvio-deltaic systems of Asia – which have undergone extensive sediment-building, reworking and river avulsions/migrations since the last interglacial – juxtaposition of different-aged deposits can account for exactly the



**Figure 1.** A world map compilation showing some of the more well-documented cases (red dots) of groundwater arsenic contamination. Zoomed-in areas of Mongolia, Taiwan, Ghana, Hungary, Argentina and Michigan are coloured to denote how arsenic varies spatially. The colour legend for the different concentrations is in the upper right corner in the map showing Inner Mongolia's groundwater arsenic distribution. The world map is overlain with worldwide arsenic sites from the IBRD 33757 April 2005 map.



**Figure 2.** Alternative views of arsenic weathering (modified from Polizotto et al., 2008).

observed type of arsenic heterogeneity. Indeed, numerous studies now show that much of the local shallow groundwater arsenic heterogeneity is due to unconformable variations between Holocene

and Pleistocene deposits at the local scale<sup>26,27</sup>. Our application of optically stimulated luminescence (OSL)<sup>28</sup> in dating aquifer deposits in Vietnam and Nepal (Figure 3) confirms this trend and

its use in Bangladesh<sup>29</sup> (Figure 3) serves as an independent support for subsurface aquifer weathering in the critical zone (and not subareal weathering from the overlying soils).

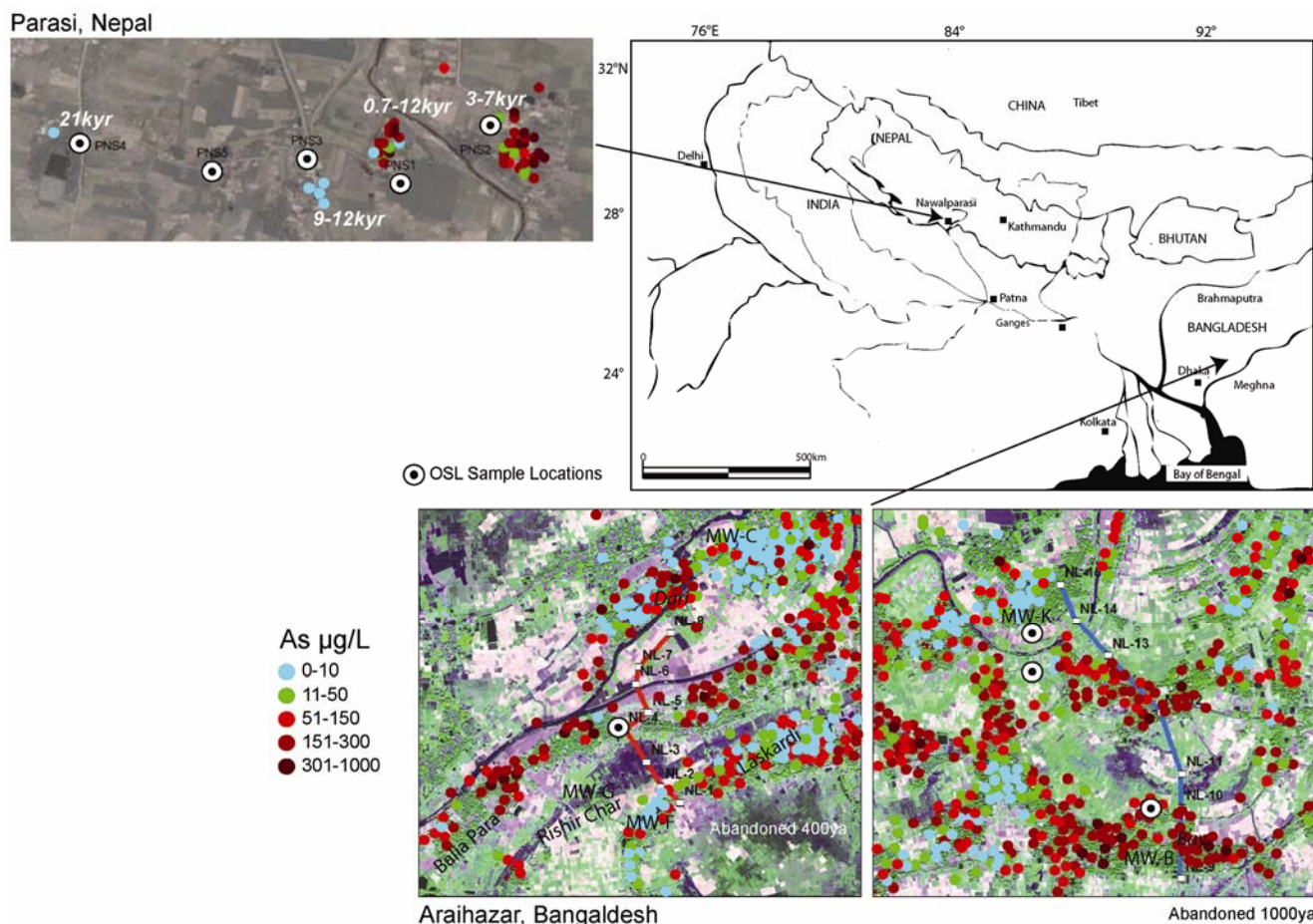


Figure 3. Study sites supporting aquifer age trends with groundwater arsenic.

Table 1. OSL, He/H and time-series agreement for rates of aquifer-arsenic weathering

Method	$\mu\text{g l}^{-1} \text{yr}^{-1}$
$\Delta\text{PO}_4^{3-}\text{-ext As}^*$	10–20
Stute <i>et al.</i> <sup>33</sup> , $^3\text{H}/^3\text{He}$ dating	19.4
Cheng <i>et al.</i> , Time series	3–23
Larsen <i>et al.</i> , $^3\text{H}/^3\text{He}$ dating	14

\*Using the difference in OSL age (600 yr) and the integrated labile-As sediment concentrations from two Araihaazar transects.

### Using OSL to determine arsenic (and potentially other) critical zone weathering

Using optical dating, a weathering rate can be calculated from aquifers of different ages by measuring the integrated differences in their labile-sediment arsenic ( $\text{PO}_4^{3-}$  extractable arsenic)<sup>30</sup> and dividing them by the age differential<sup>29,31</sup>. The optical ages provide a weathering rate of

arsenic as  $\sim 10\text{--}20 \mu\text{g l}^{-1} \text{yr}^{-1}$  for Holocene aquifers in Araihaazar, Bangladesh, which accords remarkably well with other estimates on weathering rates (Table 1). This is a new application of optical dating, not previously used, which we present here, and suggest the use of optical dating as an alternative technique for determining elemental weathering rates in sedimentary systems (i.e. versus more synoptic time-series and/or helium-tritium age-dating studies).

For the arsenic problem, these weathering rates indicate that groundwater arsenic heterogeneities within the Holocene units can occur simply by differential weathering and flushing: aquifers comprising coarser sand facies with more transmissive units (i.e. bedload from a former river channel) can flush more and accumulate less groundwater arsenic than finer portions of the aquifer – like mud-capped point bar, flood and/or relict levees – which flush less and accumulate more groundwater arsenic<sup>32,33</sup>. Furthermore, lack of arsenic in the groundwaters

of older Pleistocene units indicates that arsenic release is a function of time (i.e.  $C(t) = C_0 e^{-kt}$ , where  $C$  is concentration,  $k$  is a rate constant and  $t$  is time), analogous to the weathering work of White and Brantley<sup>25</sup>. Simply put, the older aquifers tend to release less arsenic, which is why groundwater arsenic differs along our  $15 \text{ m} \times 1 \text{ km}$  transect in Parasi, Nepal (Figure 3; 21 versus 3–7 kyr aquifer deposits).

### New support for subsurface, subsoil chemical weathering

Combining this idea of aquifer weathering with the recent weathering work by Yoo and Mudd (pers. commun.), a new concept that emerges is that the chemical loss from sediments (i.e. chemical denudation and mass loss from chemical weathering) may be occurring deeper down, beneath the Earth’s soil. In the Sierra Nevada, mass loss (with respect to zirconium) shows that bulk geochemistry



## COMMENTARY

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ACKNOWLEDGEMENTS. We thank S. K. Tandon an anonymous reviewer and *Current Science* editors for suggestions which helped improve the quality of this manuscript. We also thank Kyungsoo Yoo and Simon Mudd for their interests in using OSL and helping to advance its utility within the fields of surface and soil sciences.

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