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 enthuse 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.[1]'

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 ~ 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 exposure 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[3–8]. Despite its ubiquitous nature and the ever-growing number of countries affected[9] (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'[10]. Known effects of drinking water high in arsenic include skin lesions[11], bladder cancers[12], respiratory illnesses[13], developmental delays[14] and childhood morbidity[15]. For the Asian region, these effects are particularly punctuated, since nutritional limitations[16,17] and rapid development[18] 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[19] or (2) it being directly weathered deeper down, within the aquifer itself[20,21] (Figure 2). A similar debate also exists for the organic matter driving the dissolution of arsenic[22,23] 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'[24], 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[25] 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

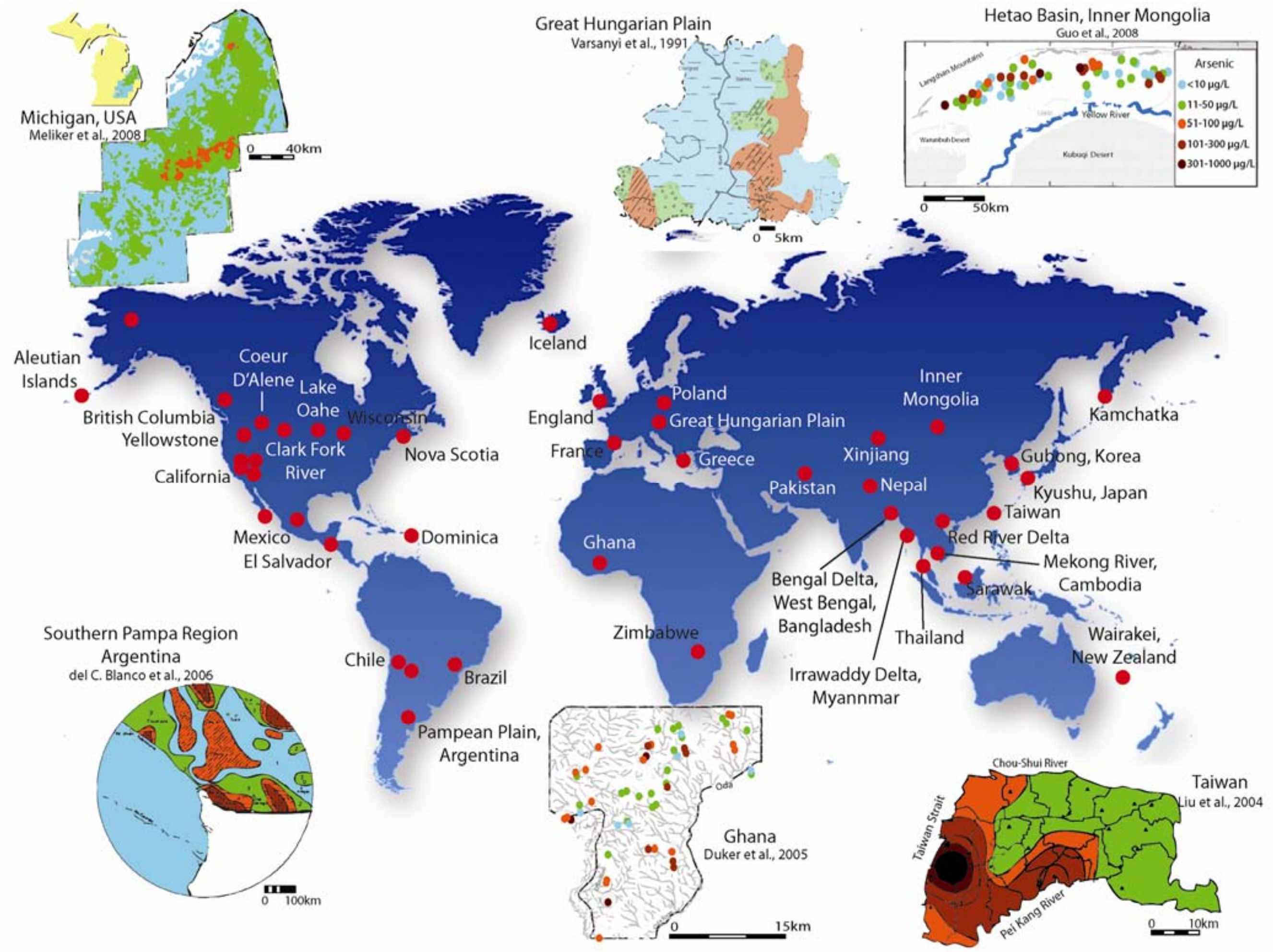

Figure 1. A world map compilation showing some of the more well-documented cases (red dots) of groundwater arsenic contamintation. Zoomed-in areas of Mongolia, Taiwan, Ghana, Hungary, Argentina and Michigan are coloured to denote how arsenic varies spatially. The colour legend for the different concentrations 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.

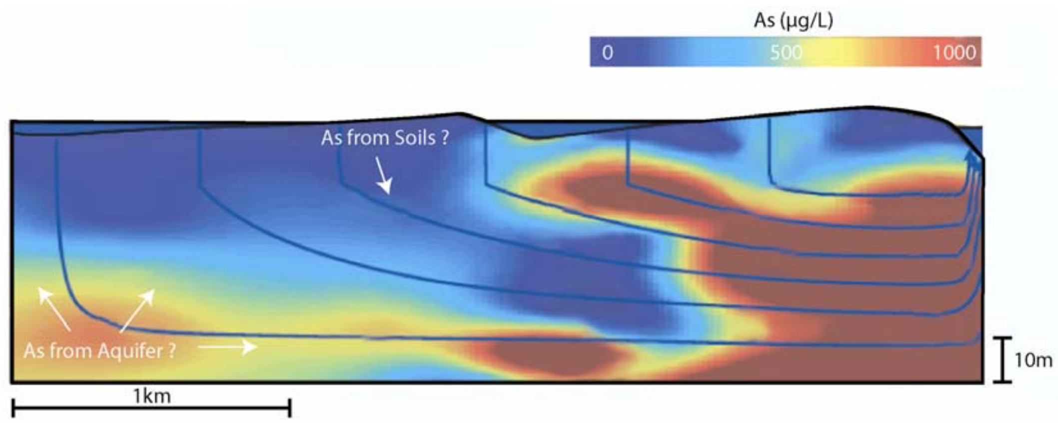

Figure 2. Alternative views of arsenic weathering (modified from Polizotto *et al.*, 2008).

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[26,27]. Our application of optically stimulated luminescence (OSL)[28] in dating aquifer deposits in Vietnam and Nepal (Figure 3) confirms this trend and its use in Bangladesh[29] (Figure 3) serves as an independent support for subsurface aquifer weathering in the critical zone (and not subareal weathering from the overlying soils).

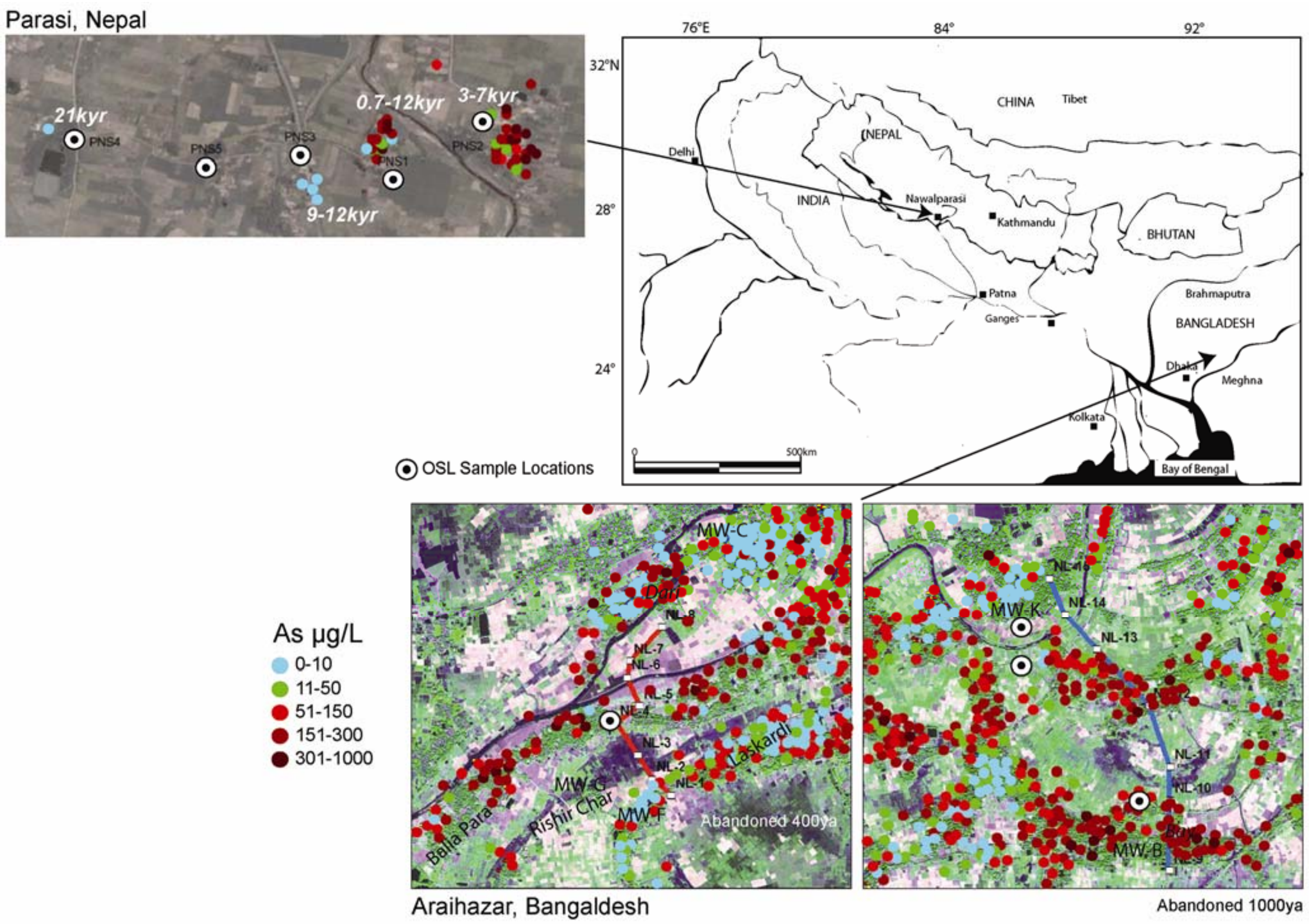

Figure 3. Study sites supporting aquifer age trends with groundwater arsenic.

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

Method	μg l^{-1} yr^{-1}
ΔPO_4^{3-}-ext As*	10–20
Stute *et al.*[33], ^{3}H/^{3}He dating	19.4
Cheng *et al.*, Time series	3–23
Larsen *et al.*, ^{3}H/^{3}He dating	14

*Using the difference in OSL age (600 yr) and the integrated labile-As sediment concentrations from two Aralhazar 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 (PO_4^{3-} extractable arsenic)[30] and dividing them by the age differential[29,31]. The optical ages provide a weathering rate of arsenic as ~10–20 µg l^{-1} yr^{-1} for Holocene aquifers in Araihazar, 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[32,33]. 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[25]. Simply put, the older aquifers tend to release less arsenic, which is why groundwater arsenic differs along our 15 m × 1 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

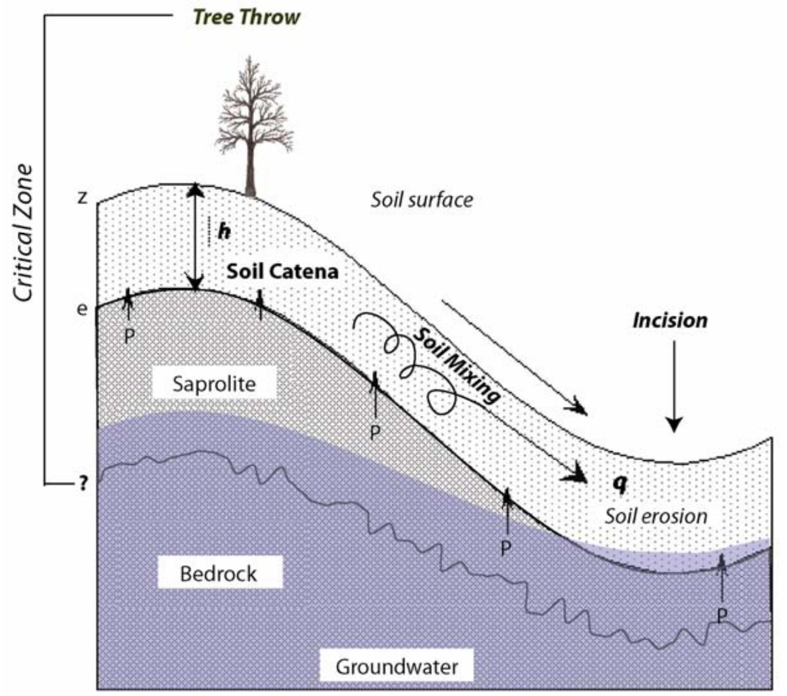

Figure 4. New concept of the critical zone, with optically stimulated luminescence delineating soil mixing.

of a soil is set below the soil–saprolite boundary[34,35]. These studies on the critical zone – along with the aquifer–arsenic work – then support the idea that a significant portion of the Earth's weathering is occurring beneath its surface soil. This is different from the current concept of how soils are formed, and raises new questions about basin-wide and regional solute fluxes. *Ipso facto*, this calls for models that better quantify weathering fluxes in subsurface flows[36]. It also calls for more insight into the processes causing differentiation within soils and how different soil horizons can develop with little to no net chemical denudation. Combined with cosmic ray-produced isotopes, new applications of OSL can provide up and down movement of soil components (i.e. mixing, Figure 4), and in arsenic-prone regions, OSL can help understand age differences between aquifers that are not always distinguishable from surface features[26]. In answering these and many other Earth surface process-type questions, we see a new role for optical dating and encourage its ongoing use in 'critical zone' studies and in guiding decisions on where to locate and how to sustainably use fluvio-deltaic shallow groundwaters. Thus, beyond the simple age of a deposit, optical ages can now shed new light on the physical (sediment/soil mixing) and chemical (chemical weathering) dynamics essential to our critical zone processes.

Conclusion

Here, we re-introduce ideas about Earth's critical zone and how Asia's shallow groundwater arsenic problem constitutes a critical zone process. Currently, models of soil formation do not include chemical differentiation and groundwater formation. This leaves much of the weathering that occurs below the topsoil surface unaccounted for and under-appreciated. To join aquifer weathering, such as arsenic release, within the context of critical zone processes, we link our OSL aquifer age results with seminal weathering ideas by White and Brantley[25], by suggesting that 'younger' aquifer deposits weather faster than older deposits. Altogether, our aquifer and soil work is supporting newer ideas about subsurface subsoil weathering, indicating that a good deal of weathering is occurring below the zone of soils. Ultimately, our goal here is to advance the need for better inclusion of shallow groundwater processes within current critical zone studies. We thus conclude that weathering within the critical zone can be measured by using a new application of OSL, where integrated geochemical differences divided by the OSL age differential yield elemental weathering rates from a depositional material (assuming similar starting materials).

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Climate change and its impacts on Indian birds: monsoon phenology and monitoring heronry birds

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Field ornithology has provided important data about the impacts of climate change on biodiversity. Long-term nesting record-keeping traditions in Europe have played a crucial role in advances in our understanding of these phenomena. In the context of Asia, the seasonal monsoonal rains are the primary drivers of bird nesting and some studies have sought to establish a relationship between monsoon regimes and reproduction cycles of birds across India by elucidating the manner in which the rains trigger the food cycles of birds. An important group of birds which can further enhance our understanding of the underlying causal relationships between the monsoon and bird reproduction is heronry birds. These birds depend upon wetlands for food resources and long-term heronry monitoring programmes can be useful for conservation.

Birds are excellent indicators of their environment[1] and their study can give information about the impacts of climate change on biodiversity[2]. Some decades ago, when climate change fears first surfaced, wader researchers had already embarked upon elaborate model-building exercises to predict impacts of habitat loss on coastal bird populations (e.g. see ref. 3). The reasoning was that as sea levels rise, coastal zones across many parts of the world will be submerged, resulting in reduced foraging area for migratory waders which use these habitats as staging or overwintering sites. But, besides modelling exercises, recent empirical studies utilizing large databases have provided evidence about phenological changes in nesting and migration dates of migratory birds due to climate change[4–6]. It is noteworthy that the long-term record-keeping traditions in many parts of the world have been crucial in our understanding of these phenomena[7].

In the context of Asia, the seasonal rains (monsoon), arising due to the differential heating of the oceans and the subcontinental land mass during the summer, have a major impact on biodiversity and economy. Moisture is a crucial resource for all life processes and the monsoon brings it, albeit only in certain months of the year, by way of precipitation. Arising from the Indian Ocean in May–June, moisture-laden winds move towards the subcontinental land mass. Known as the summer or 'southwest' monsoon, it brings rain across large parts of northern and NE India and also along the western coast, but after September these winds reverse their direction and flow outwards to the sea. Known as the winter or 'withdrawal' or 'northeast' monsoon, it then brings rain across several parts, though not uniformly, of South India. Though the broad impacts of monsoon on the reproductive cycles of Indian birds have long been known[8], recent studies seeking to establish a relationship between monsoon regimes and nesting cycles of passerines across India have elucidated the manner in which the rains trigger the food cycles of birds[9]. However, the influence of the monsoon can also be along non-trophic lines. For instance, nest placement in some passerines is strongly influenced by the monsoon winds[10].

Climate change will severely impact the Indian monsoon in terms of both creating more extremes and El Niño events and also impacting phenology[11,12]. Besides influencing biodiversity in general, this is bound to have an impact on birds, primarily by influencing their food cycles and indirectly their nesting times,