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## Amorphous silica transport in the Ganges basin: Implications for Si delivery to the oceans

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### Abstract

Rivers transport  $\sim 6 \times 10^{12}$  mol yr<sup>-1</sup> of dissolved Si (DSi) from the continents to the oceans. They also carry amorphous silica (ASi), solid phases likely to dissolve in seawater. Unfortunately, the magnitude of this flux is poorly constrained at a global scale. We present 92 new ASi values from suspended particulate matter (SPM) from the Ganges basin. Bulk SPM is  $\sim 1.2\%$  ASi, and mean ASi concentrations are  $\sim 65$   $\mu\text{M}$ , of comparable magnitude to DSi concentrations. Our results also indicate a) ASi is not evenly distributed in the water column of large rivers, b) the ASi is not a wholly biogenic Si endmember and c) the ASi flux is, to a first order, a function of the SPM load. Our results suggest that the ASi particulate load is much greater than previously believed, rivaling that of the DSi load with important implications for the global Si cycle and oceanic Si isotopic budget.

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### 1. Introduction

The global biogeochemical Si cycle is characterised by sub-cycles on the continents and in the ocean<sup>1</sup> that are mainly linked by rivers. The majority ( $\sim 75\%$ ) of oceanic Si is derived from the continents, and of this almost 90% arrives via rivers<sup>2</sup>. Rivers carry Si as both dissolved Si (DSi;  $\text{H}_2\text{SiO}_4$ ) and as particulate Si in the suspended particulate matter (SPM) load. The ultimate source of all DSi is the chemical weathering of mineral silicates, although most Si will experience biological cycling before entering the fluvial system<sup>3,4</sup>. The amount of particulate

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Si dwarfs the DSi<sup>5</sup> by approximately a factor of 50, but is typically assumed to be inert at biological timescales and thus irrelevant to the Si cycle. However, this particulate Si may contain an amorphous Si (ASi) fraction that is liable to dissolve rapidly in seawater<sup>6</sup>. This ASi is significant since it implies a) more Si is released during weathering and b) more DSi is delivered to the oceans. In 1997 Conley<sup>7</sup> estimated the riverine flux of biogenic silica (i.e. diatoms, phytoliths, etc.) to be  $1.1 \times 10^{12}$  mol yr<sup>-1</sup>, but with substantial uncertainties. Almost 20 years later, river ASi is still not routinely determined, though exceptions exist<sup>8</sup>. Here, we present ASi data from analyses on samples collected in the Ganges Plain, including the first ASi samples collected over the whole water column.

## 2. Methods

Water samples were collected from 51 sites within the Ganges basin in a three-week post-monsoon period in October 2013 (Figure 1). Samples were collected in 5l containers and filtered within a few hours through 147 mm diameter, 0.45  $\mu$ m polycarbonate filters (Millipore Durapore PVDF) in a Teflon-coated pressure filtration system. Where possible, samples were collected from the channel centre via local boat, at the surface, the deepest point (i.e. a quasi-bedload sample) and at a mid-depth using a Van-Dorn style horizontal water sampler. Filtered water samples were retained for analysis of major cations and anions, trace elements, and water ( $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ) carbon ( $\delta^{13}\text{C}$  of DIC) and silicon ( $\delta^{30}\text{Si}$  of DSi) isotopes, the results of which will be presented elsewhere. The sediment was disaggregated from freeze-dried filters and weighed. ASi content of the sediment was determined following an established protocol<sup>9,10</sup>. Briefly, freeze-dried material was dissolved in a weak base (1% [0.094M] Na<sub>2</sub>CO<sub>3</sub>) while shaking at 85°C for 5 hours at a solid:solution ratio of 0.75 g/l. A 0.5ml aliquot was taken after 3, 4 and 5 hours, and neutralized and diluted with 0.021M HCl. A subset of the surface water samples had a second set of aliquots taken at 22, 23 and 24 hrs. The DSi concentrations of all aliquots were determined colourimetrically<sup>11</sup> on a SmartChem 200 discrete chemical analyser. This protocol was originally designed to quantify biogenic Si (BSi) in marine sediments<sup>12</sup> and makes the assumption that all amorphous Si dissolves completely and rapidly within the two hours of extraction; any remaining increase in Si released with time is attributed to a background dissolution rate of mineral silicates. The intercept of a least-squares regression of Si released against time provides an estimate of ASi

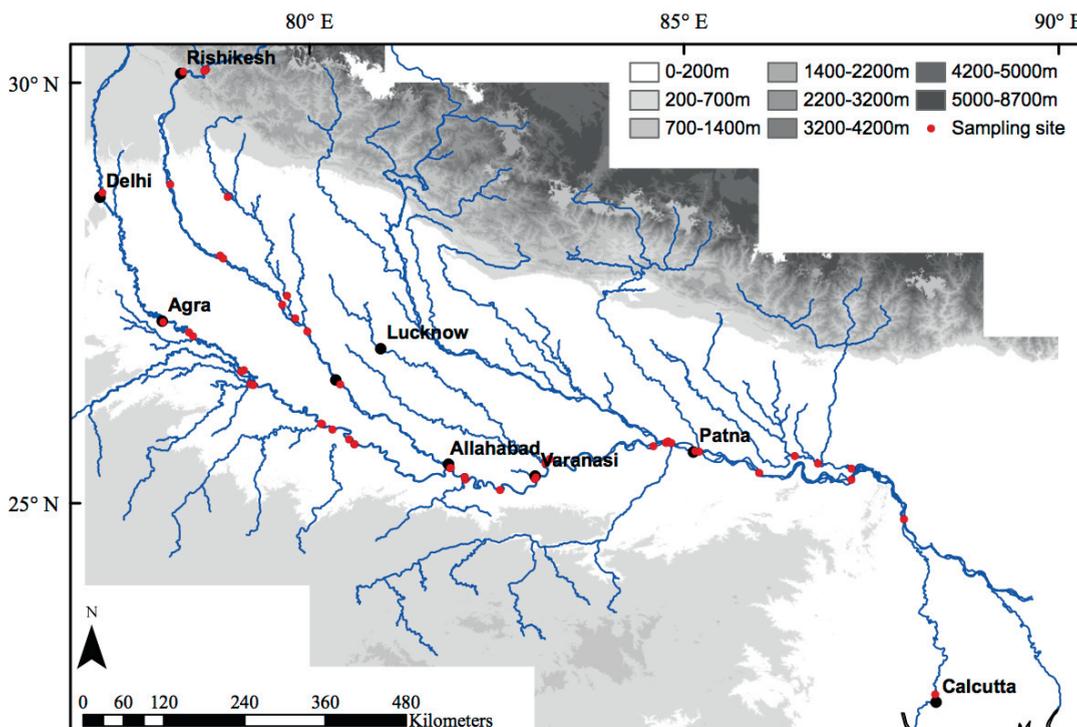


Figure 1: Location of sampling sites in the Ganges Alluvial Plain, northern India

content<sup>9,10,12</sup>. A secondary parameter is calculable: the (operationally defined) dissolution rate of the background mineral fraction ( $\text{wt}\% \text{SiO}_2 \text{hr}^{-1}$ ), i.e. the gradient of the regression.

### 3. Results

The Ganges and its tributaries carry large and variable amounts of sediment. SPM concentrations ranged across two orders of magnitude, from  $49 \text{ mg l}^{-1}$  to  $>11 \text{ g l}^{-1}$  (small stagnant streams and the bedload of large mountain channels, respectively). As a fraction of the SPM, ASi was relatively invariant between 0 and 3 wt% (mean $\pm$ 1sd =  $1.20\pm 0.78$ ). ASi concentrations in the Ganges basin range from below detection to  $>300\mu\text{M}$  (mean =  $68 \mu\text{M}$ ) and increase with increasing SPM concentration, with the highest ASi values derived from bedload samples (Fig. 2a). With decreasing SPM concentrations, ASi became a larger component of the SPM, such that surface samples tended to have a greater proportion of SPM as ASi (Fig. 2b). Greater Si release rates between 3-5 hours are also observed at lower SPM concentrations (Fig. 2c). For the subset of samples of that were extracted for a 24 hour period, the dissolution rates slowed to mean  $0.12 \text{ wt}\% \text{SiO}_2 \text{hr}^{-1}$  (equal to a primary silicate mineral; ref 13) and the y-axis intercept based on the second aliquot set correspondingly increased (mean = 3.10% of SPM or  $210 \mu\text{M}$ ).

### 4. Discussion

There is an inverse relationship between the particulate load and the ASi content. Sites with lower SPM tend to have a larger ASi component and a more quickly dissolving mineral component. The relative variation observed in SPM concentrations is greater, so it acts as a first order control on total ASi concentrations in the Ganges basin. The weak base, e.g.  $1\% \text{Na}_2\text{CO}_3$ , is thought to extract poorly- to non-crystalline Si phases formed a) as secondary weathering products or b) during pedogenic processes. Samples with high solid loads may reflect high physical denudation rates in systems with low chemical weathering intensities and thin, poorly developed soils, conditions unfavourable for ASi formation. Conley<sup>7</sup> microscopically identified Si extracted with this protocol as biogenic silica and derived a mean concentration in global rivers of  $28\mu\text{M}$ . The data presented here, and other new and unpublished data suggest this may be an underestimate. In the intervening years, based on the Al content of dissolving phases, we have learnt that this fraction may also be of non-biogenic origin<sup>14</sup>. These data suggest the majority of ASi transported by rivers is associated with the coarse, detrital sediments largely unsampled before.

There are still methodological issues to resolve; the  $1\% \text{Na}_2\text{CO}_3$  protocol appears to extract more ASi than protocols that correct for Si associated with Al (e.g. ref 15). Any definition of ASi is ultimately operationally defined by the extraction conditions. A more useful approach for future research may be to investigate the fraction truly liable to release Si in estuaries or the coastal zone. If the mean Ganges value (i.e. 1.2% of sediment) can be used to represent the ASi fraction, then using the global sediment flux of  $18000 \text{ Mt yr}^{-1}$  (ref 16) suggests  $3.6 \times 10^{12} \text{ mol yr}^{-1}$  of ASi is delivered to the coastal zone, considerably larger than the estimate of Conley<sup>7</sup> and  $>50\%$  of the riverine DSi flux<sup>2</sup>. The importance of this flux will also depend on the dissolution and burial efficiencies of ASi in the coastal zone, but recent work suggests that riverborne particulate matter may have a much greater effect on some

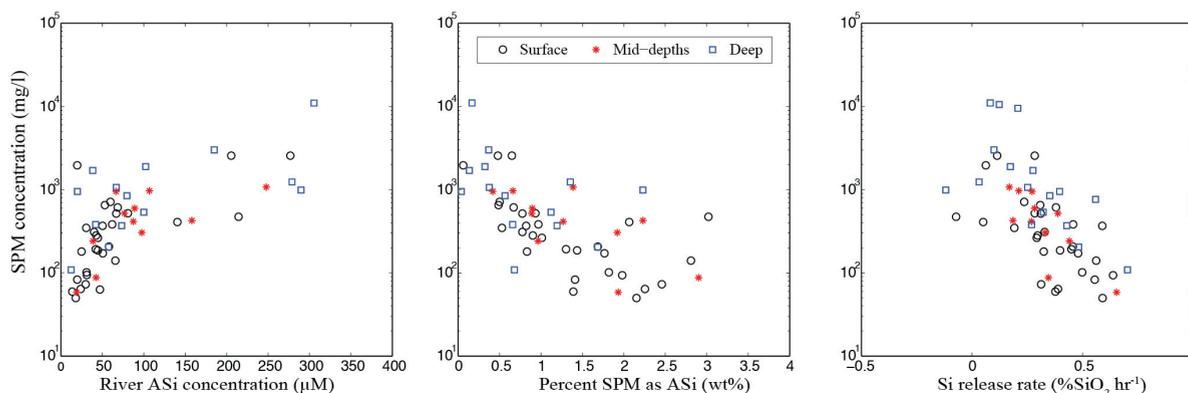


Figure 2: Variation in ASi parameters with SPM concentrations (log scale).

ocean elemental and isotope budgets than previously thought<sup>17</sup>; it is likely true for the Si cycle. River DSi has a typical Si isotope composition (expressed as  $\delta^{30}\text{Si}$  relative to NBS28) of  $\sim 1$  to 2‰, higher than the minerals the DSi derives from ( $-0.3\text{‰}$ ), due to fractionation during clay formation and biological uptake. This requires the mean riverine SPM load has low  $\delta^{30}\text{Si}$  ( $<0.3\text{‰}$ ), to balance the continental Si isotope budget, consistent with  $\delta^{30}\text{Si}$  determinations on secondary silicates and terrestrial biogenic Si. Dissolution of riverine ASi in the coastal zone will therefore affect not only the elemental Si budget in the global ocean, but also the isotopic mass-balance by introducing an unaccounted for source of  $^{30}\text{Si}$  depleted DSi to the ocean. Hypotheses have been advanced<sup>18,19</sup> for mechanisms to change whole-ocean  $\delta^{30}\text{Si}$  on timescales short enough to impact palaeoclimatic interpretation of Si isotope archives. We suggest variations in the delivery of ASi to the ocean may be a further mechanism.

## 5. Conclusions

Total ASi concentrations measured in waters of the Ganges basin are substantially higher than those measured elsewhere. Other particulate-rich systems should be examined for the contribution of ASi to the total available Si load. If we extrapolate these results globally, the ASi particulate load may be as large as the DSi load with important implications for the global Si cycle and oceanic Si isotopic budgets.

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