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Savage, L., Carey, M. P., Sumon, M., Islam, M. R., de Silva, P. M. C. S., Williams, P. N., & Meharg, A. A. (2017). Elevated trimethylarsine oxide (TMAO) and inorganic arsenic in northern hemisphere summer monsoonal wet deposition. *Environmental science & technology*. <https://doi.org/10.1021/acs.est.7b04356>

Published in:

Environmental science & technology

Document Version:

Peer reviewed version

Queen's University Belfast - Research Portal:

[Link to publication record in Queen's University Belfast Research Portal](#)

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Laurie Savage, Manus Patrick Carey, Mahmud Hossain, M. Rafiqul Islam, P. Mangala C.S. de Silva, Paul Nicholas Williams, and Andrew A. Meharg

Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/acs.est.7b04356 • Publication Date (Web): 04 Oct 2017

Downloaded from <http://pubs.acs.org> on October 12, 2017

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2 **northern hemisphere summer monsoonal wet deposition.**

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6 Laurie Savage¹, Manus Carey¹, Mahmud Hossain², M. Rafiqul Islam², P. Mangala C.S. de
7 Silva³, Paul N. Williams¹, Andrew A. Meharg^{1*}

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10 1. Institute for Global Food Security, Queen's University Belfast, David Keir Building,
11 Malone Road, Belfast, BT9 5BN, Northern Ireland.
12
13 2. Bangladesh Agricultural University, Mymensingh, 2202, Bangladesh.
14
15 3. Department of Zoology, Faculty of Science, University of Ruhuna, Matara, 81170, Sri
16 Lanka.
17
18 *. Corresponding author.
19
20
21
22

23 **Abstract**

24 **Arsenic speciation, their inputs, for wet deposition are not well understood. Here we**
25 **demonstrate that trimethylarsine oxide (TMAO) and inorganic arsenic are the**
26 **dominant species in monsoonal wet deposition in summer Indian subcontinent,**
27 **Bangladesh, with inorganic arsenic dominating, accounting for ~80% of total arsenic in**
28 **this medium. Lower concentrations of both species were found in monsoonal wet**
29 **deposition in the winter Indian subcontinent, Sri Lanka. The only other species present**
30 **was dimethylarsinic acid (DMAA), but this was usually below limits of detection (LoD).**
31 **We hypothesize that TMAO and inorganic arsenic in monsoonal wet deposition is**
32 **predominantly of marine origin. For TMAO, the potential source is the atmospheric**
33 **oxidation of marine derived trimethylarsine. For inorganic arsenic, our evidence**
34 **suggests entrainment of water column inorganic arsenic into atmospheric particulates.**
35 **These conclusions are based on weather trajectory analysis, and to the strong**
36 **correlations with known wet deposition marine derived elements: boron, iodine and**

37 selenium. The finding that TMAO and inorganic arsenic are widely present, and
38 elevated in monsoonal wet deposition identifies major knowledge gaps that need to be
39 addressed regarding understanding arsenic's global cycle.

40

41 **Introduction**

42 Atmospheric fluxes, with respect to the global cycling, of arsenic are poorly characterized
43 (1). Arsenic species in wet deposition have been particularly neglected, with the exception of
44 studies of Huang and Matzner (2) who systematically quantified inorganic and methylated
45 arsenic species inputs into terrestrial systems, whereas, with most wet (and dry) deposition
46 studies simply determining total arsenic inputs (3-7). Huang and Matzner found that the only
47 organic species detected in in bulk deposition for a German forest catchment was
48 trimethylarsine oxide (TMAO), but with the majority of measurements below limits of
49 detection (<LoD) (2). Monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA)
50 were below LoD for bulk deposition, but with some samples detected above LoD in
51 throughfall, which was attributed to phyllosphere microbes methylating inorganic arsenic.
52 Inorganic arsenic was measured in much higher concentrations than methylated species, by
53 10-20-fold, both in bulk deposition and in throughfall. TMAO and DMAA have been better
54 studied in atmospheric particulates where they are routinely detected (8-10). The origin of
55 these species in particulate samples is attributed to the biovolatilization of trimethylarsine
56 (TMA) and dimethylarsine (DMA) from soils (10), mediated by arsenic methylating bacteria
57 and fungi (11), with subsequent UV oxidation of these atmospherically unstable arsines to
58 their corresponding oxides, TMAO and DMAA (12). Recently, using online atmospheric
59 pressure chemical ionization, TMA, along with inorganic arsenic, was shown to be the
60 dominant gaseous arsenic species in remote Finnish ecosystems, showing a strong

61 relationship to melting of snow cover and stimulated activity of arsenic-methylating
62 microorganisms (13).
63
64 Inorganic arsenic is also not widely characterized in wet deposition, again with the most
65 detailed study conducted by Huang and Matzner (2). Studies on total arsenic deposition,
66 historically (1, 3-6), and more recently (5,7), conclude that arsenic is predominantly from
67 industrial sources. Historically, starting from when arsenic in deposition was first measured,
68 this may have been the case, but inputs of total arsenic in wet deposition have been falling
69 rapidly at long-term monitoring sites (5), attributed to less base and precious metal mining in
70 historic areas of activity and to stricter environmental regulations (14). Source appointment
71 of total arsenic in deposition is normally complex due to multiple potential inputs and to
72 shifting weather trajectories (15). However, the fact that the industrial baseline input is
73 declining (14) should make the study of natural geogenic or biogenogenic arsenic inputs into
74 the atmosphere easier to address. This study of geogenic/biogenic inputs is also aided by
75 the analytical advances that have enabled arsine effluxes from habitats to be quantified (16).
76
77 This study was to investigate wet depositional arsenic species inputs, and to identify the
78 sources of these inputs, in monsoonal settings. Sites in Bangladesh and Sri Lanka were
79 chosen because of the relatively unpolluted nature of the Indian Ocean and connected
80 landmasses, far from the major global anthropogenic sources of arsenic atmospheric pollution
81 (14,15). Also, monsoonal systems have relatively simple weather trajectories (17), which
82 enables straightforward source appointment. The findings are interpreted in light of the
83 current state-of-knowledge regarding atmospheric fluxes within arsenic's biogeochemical
84 cycle (1,3), indicating that this is limited and not well understood, and that this cycle needs to
85 be rethought due to the findings presented here.

86

87 **Materials and Methods**

88 Details of manufacturers of sampling equipment, instrument manufacturers and reagents are
89 given in Table S1. Sampling took place at Mymensingh, Bangladesh, 24°45'N, 90°24'E
90 (Figure 1) and at Matara, Sri Lanka, 5°57'N, 80°31'E (Figure 1). Bangladesh samples (n=38)
91 were collected during the summer monsoon of 2016, and Sri Lankan samples (n=17) during
92 the winter monsoon that followed. Only wet deposition samples were collected, with
93 sampling undertaken in triplicate, using pre-weighed 56 mm diameter polypropylene
94 containers, over a 24-h period, and immediate freezing until subsequent analysis. The
95 containers were on a small platform 1.5 m above the terrain surface in an open position.
96 Containers were weighed to calculate the volume of water deposited on a surface area basis.

97

98 For elemental quantification, samples were 0.45 micron filtered, before being acidified with
99 ultra-high purity (Aristar[®]) nitric acid (0.1 M), with the exception of iodine, where
100 tetramethylammonium hydroxide (0.5%) was added instead. The internal standard added
101 throughout was rhodium, spiked to give a 10 µg/l concentration. For the determination of
102 arsenic species, using a similar ion exchange- ICP-MS approach as Huang and Matzner (2),
103 samples were 0.45 micron filtered before analysis by ion-exchange - ICP-MS, using a
104 Thermo Scientific IC5000 Ion Chromatography system coupled with a Thermo ICAP-Q ICP-
105 MS. A 2x250mm Thermo Scientific AS7 anion-exchange column was used with a 2x50mm
106 AG7 guard column and ammonium carbonate over a linear gradient from 20nM to 200nM
107 was the mobile phase. Authentic standards of arsenobetaine, inorganic arsenic, MMAA,
108 DMAA, and TMAO were run to ascertain retention times. The Thermo Scientific ICAP-Q
109 ICP-MS in helium collision cell mode was used for the analysis of all elements analyzed,
110 with the exception of boron which was run in standard mode (no collision cell). To validate

111 the AS7 identification, a subset of samples was also analyzed by cation-exchange
112 chromatography and run on a 2x250mm Thermo Scientific CS12A column, with a 2x50mm
113 CG12A guard column. Pyridine mobile phase (20mM) was made up and buffered to pH 2.6
114 with formic acid for isocratic analysis and TMAO was spiked into authentic samples for both
115 columns.

116

117 For all analytical methods, blanks were prepared from $>18.2 \text{ M}\Omega\cdot\text{cm}$ (at 25°C) water in the
118 same manner as the samples and included with each instrument batch. LoD was calculated as
119 average concentration of the blank + 3 times standard deviation of a species mix dilution
120 series. For arsenic speciation and total elemental analysis a synthetic surface water CRM was
121 run. Only inorganic arsenic was present to quantify. For a subsample of unknowns, iodine
122 was spiked into samples prepared for TMAH analysis, which could then be compared to the
123 corresponding unspiked samples and a percentage recovery calculated.

124

125 To determine either the origin of rain, or the source of air that will form rain through
126 orographic lifting, 72-h backward air trajectories were calculated for each day using Hysplit
127 software and the Global Data Assimilation System (18). All statistical analysis was
128 conducted in IBM SPSS (Version 22). Normality of residuals were checked for parametric
129 analysis, and if not normal, non-parametric analysis, and reporting of medians, was
130 conducted.

131

132 **Results**

133 Representative chromatograms for monsoonal wet deposition samples for both AS7 and
134 CS12A columns are given in Figure S1, with spikes and authentic samples showing that
135 TMAO was present, along with DMAA and inorganic arsenic. MMAA and AsB were below

136 LoD. The LoDs for arsenic species were 0.117, 0.128 and 0.278 nM for DMAA, TMAO and
137 inorganic arsenic, respectively, the highest LoD of the two batches of sample runs. Half LoD,
138 was used where samples were <LoD for statistical analysis. For arsenic speciation, average
139 percentage recovery of inorganic arsenic from the CRM's was 110%, n=5 (Table S2). For the
140 full-scan analysis, the same CRM was prepared in triplicate for each batch with the individual
141 elemental average recoveries ranging from 89 to 122%, with the average iodine recovery
142 from spiked samples being 98%, n=6.

143

144 As Bangladesh was sampled through the whole of the monsoonal season, unlike Sri Lanka
145 where only a month of monsoonal wet deposition was collected, the seasonal input of arsenic
146 species into Bangladesh soils could be determined. This was 2.3 g/ha for inorganic arsenic,
147 and 0.4 g/ha for TMAO (Figure 2). DMAA was not included in subsequent correlation
148 analysis as it was primarily below LoD.

149

150 The 72-h weather trajectories for wet deposition sampling dates originated from the northern
151 Indian Ocean, the Bay of Bengal, and the Gulf of Arabia for both the summer and winter
152 monsoons (Figure 1). Median TMAO concentrations in Bangladeshi wet deposition were
153 0.30 nM compared to 0.056 nM, the $\frac{1}{2}$ LoD, for Sri Lanka (Figure 3). Median DMAA were
154 both at the LoD for Bangladesh and Sri Lanka (data not shown), while inorganic arsenic was
155 1.33 and 0.33 nM, for the Bangladesh and Sri Lanka, respectively (Figure 3). Inorganic
156 arsenic concentrations in wet deposition were ~5-fold higher than organic concentrations, for
157 both Bangladesh and Sri Lanka (Figure 3).

158

159 Relationships between other elements and TMAO (Figure 3) and inorganic arsenic (Figure
160 4), and with wet deposition volume (Figure 5) and distance from origin of 72-h weather

161 trajectories (Figure S2) were analyzed by Spearman's correlation (Table S3) for the
162 Bangladeshi and Sri Lankan data sets. Spearman's correlation showed for Bangladesh that
163 TMAO correlated well with boron ($P < 0.001$), selenium ($P < 0.001$), strontium ($P < 0.001$) and
164 chromium ($P < 0.001$), and to a lesser extent with iodine ($P = 0.035$), cobalt ($P = 0.02$), rubidium
165 ($P = 0.015$) and cadmium ($P = 0.028$). It was also negatively correlated with wet deposition
166 volume ($P = 0.031$). TMAO was poorly correlated with inorganic arsenic ($P = 0.525$), length of
167 trajectory ($P = 0.846$), and with copper ($P = 0.113$), barium ($P = 0.479$) and lead ($P = 0.299$),
168 amongst other elements. For inorganic arsenic in wet deposition there were similarities and
169 differences to TMAO (Table S3). Inorganic arsenic was, similar to TMAO, positively
170 correlated with iodine ($P = 0.001$), selenium ($P < 0.001$), and had a poor correlation with copper
171 ($P = 0.148$), and was not correlated with trajectory length ($P = 0.069$). In contrast to TMAO,
172 inorganic arsenic had a very strong negative correlation with barium ($P < 0.001$), was
173 positively correlated with lead ($P = 0.019$), and was not correlated with deposition volume
174 ($P = 0.621$), boron ($P = 0.135$) and cadmium ($P = 0.413$), amongst other elements. Correlations
175 for the Sri Lankan data (Table S3) were less significant throughout, as compared to the
176 Bangladesh data set. TMAO and inorganic arsenic, for the Sri Lankan data, were only
177 correlated with each other ($P = 0.001$), cadmium (TMAO, $P = 0.020$; inorganic arsenic,
178 $P = 0.003$) and lead ($P = 0.001$ for both TMAO and inorganic arsenic).

179

180 Considering the two datasets together, there are highly significant ($P < 0.001$) negative
181 correlations (Table S5) between wet deposition volume and rainwater concentrations of
182 boron, selenium and cadmium, with iodine, chromium, iron and lead also showing washout
183 (Figure 5). Distance to 72-h trajectory origin was only significant ($P = 0.036$) for barium. The
184 Spearman's analysis showed that there were strong correlations between elements, other than
185 arsenic species, for both Bangladesh and Sri Lanka (Table S3). This was true of elements that

186 will be primarily of marine origin such as selenium, iodine and boron, which show strong
187 inter-correlations, while transition metals tend to correlate best with themselves. The
188 elements that differ most between the two datasets, by an order of magnitude, are boron,
189 selenium, cadmium and lead (Figures 3 and 4). For boron, selenium and cadmium, this can be
190 explained at least partially by washout, with higher concentrations in Sri Lanka related to
191 lower monsoonal wet deposition (Figure 5). For lead the reason why Sri Lankan data is ~10-
192 fold lower than the Bangladeshi concentrations is not related to depositional volume.

193

194 All the sample points for Sri Lanka mapped to marine locations for their 72-h trajectory
195 origin, but some of the Bangladeshi samples trajectories mapped them back to being in
196 transects across the Indian sub-continental landmass (Figure 1). Kruskal-Wallis analysis
197 found for every parameter measured, that there was no significant difference in
198 concentrations in rain based on a Persian Gulf, continental Indian or Bay of Bengal 72-h
199 trajectory origin (analysis not shown).

200

201 To interrogate the interrelationships between the data, Principle Components Analysis (PCA)
202 was conducted, with the component factor score coefficient matrix as well all as the
203 individual sample scores (Figure 6). The Bangladesh and the Sri Lankan data followed
204 different trends, outlined by ellipses, with these ellipses being orthogonal to each other,
205 intersecting near the X-Y origin. The trends in these data suggest that there is a commonality
206 in samples that co-locate at the origin, but that these differ towards the extremes of
207 composition for the two data sets. The factor scores show that most elements pull to the right,
208 with iodine, selenium and boron closely clustered, along with iron, manganese, chromium,
209 cadmium, rubidium and strontium. Distance from origin and volume of water deposited also
210 go along with this trend, with inorganic arsenic factor loadings most closely matching these.

211 Copper, cobalt, and less strongly lead, loadings are opposite to inorganic arsenic and
212 orthogonal to most other elements. TMAO stands out by itself, diametric or orthogonal to all
213 other elements, suggesting very different regulation.

214

215 **Discussion**

216 It was found that both inorganic arsenic and TMAO were elevated in the Bangladeshi
217 summer monsoon wet deposition, as compared to Sri Lankan winter monsoon, and that
218 TMAO made up ~20% of total arsenic deposited in both environs. DMAA was a minor
219 component, with generally, levels below LoD. MMAA was not detected. TMAO
220 concentrations were 4-fold higher in Bangladeshi wet deposition as compared to previous
221 studies in a non-monsoonal continental setting, using their $\frac{1}{2}$ LoD (2), and equating to the Sri
222 Lankan data. The TMAO also seems to be differentially regulated in wet deposition between
223 the summer and winter Indian sub-continent monsoons, not correlated with inorganic arsenic
224 during the summer, but highly correlated during the winter. To explain these findings the
225 biology of TMAO production has to be considered in context of prevailing wind directions,
226 and arsenic methylation in both marine and terrestrial settings.

227

228 ***TMAO***

229 The origin of weather trajectories for both Bangladesh and Sri Lanka are both either the Bay
230 of Bengal or the Persian Gulf, with a very similar origin distribution, except that some (36 %)
231 Bangladeshi samples had 72-h weather origins that placed them as being in transit across
232 India. However, Persian Gulf, Bay of Bengal and Indian mainland origin samples did not
233 differ in any measured parameter for Bangladesh. Given that the Sri Lankan and Bangladeshi
234 samples had similar marine origins but very different TMAO concentrations and associations
235 with co-deposited elements, either the production of TMAO must differ at different times of

236 year, and/or the prevailing winds determine TMAO atmospheric loadings. As weather origins
237 of the wet deposition are marine, and with an intercontinental convergence zone (ITZ)
238 drawing air from the Indian Ocean in its northerly summer location, and from the continental
239 landmass in its southern winter location (17), it may be expected, if TMA/TMAO is of
240 terrestrial origin, that TMAO in wet deposition should be higher in the winter monsoon. This
241 is not the case and the apparent marine source of TMA/TMAO is a conundrum.

242

243 TMA/TMAO production in terrestrial habits is fairly well established (16), but in marine
244 habitats there is little evidence of it being present in environmental monitoring programmes
245 where DMAA and MMAA are routinely detected (19,20), including the Persian Gulf and in
246 the Indian Ocean just off the Sri Lankan shoreline (19). TMAO can be produced either
247 through methylation of DMAA (16,11) or through degradation of the main marine arsenical,
248 arsenobetaine (21). Previous maritime oxidized arsines monitoring, for atmospheric
249 particulates sampled on the remote islands of the Japanese archipelago in the East China Sea,
250 attributed their origin to the soils of the main Japanese islands, rather than the seas that
251 surround Japan (10). In this Japanese investigation, as for our study, TMAO was the
252 dominant organic species. They (10) argued against a marine source, but did not consider that
253 marine water as a source of TMA/TMAO, even though the Japanese land surface is very
254 small in comparison to its surrounding marine waters.

255

256 The fact that TMAO is not routinely measured in marine waters may be due to its absence, or
257 more likely to concentrations being below LoD, in marine waters, and/or due to inappropriate
258 analytical methodologies. The saline content of marine waters is challenging to most
259 chromatographic conditions. Ion chromatography can separate the methylated species in
260 waters but the TMAO LoD is much higher due to severe peak broadening under saline

261 conditions (data not shown). Most marine water studies for arsenic speciation use hydride
262 generation (19,20), sometimes followed by pre-concentration (such as cryo-trapping), and
263 these should pick up TMAO if present, as long as enough reductant is added as other moieties
264 may be preferentially reduced, and as long as chromatographic runs are long enough to pick
265 up late eluting TMA (22). When specific care was taken to speciate TMA/TMAO, where
266 analytical limitations were overcome, ~0.2 nM TMAO concentrations were detected in 3
267 seawater certified reference materials (and 2 freshwater at similar concentrations), higher
268 than MMAA (0.12 nM), 10-fold lower than DMAA (1.6 nM), and a 100-fold lower than
269 inorganic arsenic (22). No such application of this type of analytical approach to actual
270 environmental monitoring of TMAO in marine waters has been undertaken.

271

272 Even if TMAO is very low in waters, this does not preclude TMA volatilization and, indeed,
273 loss of the trimethyl arsenic species through volatilization may itself explain why TMAO
274 could be low in seawaters. No studies on marine water column arsenic biovolatilization have
275 been conducted. Marine algae have been shown to biovolatilize arsenic in culture, though the
276 volatilized forms were not speciated (11). DMAA can be observed above LoD in Bangladesh
277 wet deposition, but not in Sri Lanka; and MMA is not found at all, presumably below LoD.
278 As TMAO, it is assumed, is low in seawaters, the low DMAA and MMAA, which are
279 routinely recorded in the Indian Ocean (19), and the high TMAO, argue against entrainment
280 of seawater into atmospheric aerosols, as for boron (23), as being a major source. TMAO is
281 highly correlated with boron, whose wet deposition source is marine derived sea spray, but it
282 is also correlated with selenium and iodine that are marine biovolatilization derived in
283 terrestrial wet deposition (24,25). As sources are mixed in wet deposition, care must be taken
284 not to over interpret correlations (7,15).

285

286 Depositional rates can also be used to interpret potential inputs. The only previous TMAO,
287 and indeed DMAA and MMAA, report known to us is a continental German study, with low
288 (weekly) sampling resolution, where concentrations were generally below LoD (2). TMAO
289 deposition in that continental setting was 0.05 g/ha/y, 10-fold lower than for Bangladesh.
290 Dominant soil/sediment land-cover for Bangladesh, mangrove sediments and paddy soils,
291 have all been shown to be amongst the highest producers of arsines so far measured, with
292 TMA dominating (16). Total fluxes of arsines, including arsine, MMA, DMA and TMA,
293 dominated by TMA, from Bangladesh paddy soil and coastal mangrove sediments were
294 recorded in the field at 0.2 and 0.02 g/ha/y, respectively (16). This compares to 0.4 TMAO
295 g/ha/y for wet depositional inputs measured for Bangladesh here over the monsoon period
296 (Figure 2). While paddy ecosystem biovolatilization can contribute to TMAO inputs
297 exceeding TMA outputs, this should be roughly the same for Bangladesh and Sri Lanka for
298 wet deposition. As this is not the case, and that prevailing winds are from marine origin, it
299 suggests that wet deposition TMAO is of both of terrestrial and marine origin. The reason
300 why TMAO correlates with arsenic during the winter monsoon, but not during the summer,
301 may be due to this interplay between terrestrial and marine sources, but this remains to be
302 investigated. However, in an early study of arsenic speciation of surface waters in the
303 northern Indian Ocean, and Persian Gulf off the Indian coast, MMAA concentrations
304 decreased 6-fold, and DMAA 10-fold, during summer and winter (19). It appears that this
305 corresponds to the considerable decrease in TMAO and DMAA in our wet depositional
306 samples between the summer and winter monsoons, again pointing to a marine source for
307 these elements in wet deposition.

308

309 TMAO in Bangladesh samples was not well correlated with industrial contaminants copper
310 and lead that are normally associated with arsenic in ores (1-7), though it positively

311 correlated with cadmium. It was also not associated with inorganic arsenic which can have a
312 strong anthropogenic signal, again originating from mining and smelting activity (1-7). For
313 Sri Lankan samples, TMAO was correlated with lead and arsenic, as well as cadmium. As air
314 masses are continental for the Sri Lankan winter monsoon, the correlation with lead,
315 cadmium and arsenic may have a substantial terrestrial contribution. Lead is very high in
316 Bangladeshi wet deposition, and cadmium in Sri Lankan. The reasons for these anomalies are
317 not known. Inorganic arsenic can also be of marine origin, as outlined in the following
318 section, and it may simply be that both inorganic arsenic and TMAO are predominantly of
319 marine origin, but with different regulation: TMAO derived from biovolatilized TMA, and
320 inorganic arsenic through aerosol entrainment. TMA can be UV-photodegraded (23), with
321 TMA have a half-life of 7.2 h during the day (12). Thus, demethylation by photodegradation
322 may reduce TMAO deposition from TMA generated during daytime. This further complexity
323 in TMA/TMAO cycling may explain why the TMAO was orthogonal to all other arsenic
324 species and other elements in the PCA analysis presented here.

325

326 *Inorganic arsenic*

327 The inorganic arsenic in wet deposition may be from multiple sources such as anthropogenic,
328 volcanism and seawater entrainment into the atmosphere (1-3). The, relatively, much higher
329 concentrations of inorganic arsenic in sea waters compared to wet deposition ~10-20 nM
330 Persian Gulf/Indian Ocean waters, and 0.8 and 0.2 nM for wet deposition as reported for
331 Bangladesh and Sri Lanka, respectively, suggests that physical transport, entrainment into the
332 atmosphere from seawater as aerosols, may explain, at least partially, inorganic arsenic wet
333 deposition concentrations, given that we have remote from industrial arsenic sources
334 monitoring sites. The potential role of volatilization also needs consideration. Arsine (AsH_3),
335 which is oxidized to its oxy anions in the atmosphere (12), is normally only a minor

336 component of volatilization from soils/sediments (16). Elevated arsine concentrations are
337 found under highly reduced conditions (16), attributed to abiotic reduction. Such low oxygen
338 tensions are not typical of epipelagic waters, potentially ruling out arsine volatilization from
339 marine environments as a source. If volatilization was the dominant source of arsenic to wet
340 deposition much higher levels of TMAO and DMAA, the oxidized products of methylated
341 arsines, would be expected as compared to inorganic arsenic, as di- and tri- methylated
342 arsines are the main species volatilized (16). As this is not the case, inorganic arsenic
343 concentrations were ~5-fold higher than organic species, this again argues against
344 volatilization being the primary source of inorganic arsenic. One proviso is that arsines, or
345 their oxides, can be demethylated by UV. This has been exploited in hydride analysis where
346 separated methylated species are UV cracked to overcome kinetic interferences in hydride
347 generation (26).

348

349 Inorganic arsenic is highly negatively correlated with barium. Barium in wet deposition is
350 normally attributed to terrestrial inputs (27). Studies on Barium fluxes into the Bay of Bengal
351 show sharp clines away from deltaic zones towards the open oceans (28), again showing the
352 strong terrestrial source of this elements in our study region. The negative correlation with
353 barium for inorganic arsenic reported for Bangladesh here, is again strong evidence that, at
354 least, marine sources are a strong contributor to monsoonal wet deposition of arsenic.

355

356 *Wet deposition and arsenic's biogeochemical cycle*

357 Historically, studies have attempted to attribute total arsenic in deposition to its sources,
358 usually concluding them to be industrial (1-7). However, wet depositional inputs of arsenic
359 decreased 5-fold from 1996 to 2010 in maritime Europe (5), with the authors of this report
360 attributing this to rapidly declining anthropogenic inputs such as coal burning and metal

361 mining and processing. Studies using older deposition data (1,3,4,6) would not have been
362 able to readily identify natural sources or arsenic against this industrial background.
363 Furthermore, our study sites' weather patterns are predominantly marine, far from mining or
364 industrial centres of activity. Both the modern timing, and the locations of our study has
365 enabled us to better assess natural biogeochemical cycling of arsenic compared to previous
366 investigations. A study in Britain, with more continental influenced weather patterns, found
367 that total arsenic did have a strong marine signature when weather trajectories came from the
368 marine west rather than the continent to the east (7). Also, early studies at lower sampling
369 resolution and with measurement of total arsenic at coastal Pacific (6) and western Atlantic
370 (4) locations also found strong marine contributions to wet deposition when weather
371 trajectories were of oceanic rather than continental origin. A German study (2) that speciated
372 arsenic in bulk deposition, sampling conducted in 2004-2005, found an inorganic arsenic
373 deposition of 3.9 g/ha/y, similar to the Bangladesh location. Again, the German study is
374 historic, and with deposition being predominantly from anthropogenic sources as prevailing
375 winds cross major industrial zones.

376

377 Marine derived wet deposition of selenium (23) and iodine (24), biovolatilized by
378 phytoplankton; and iodine (24) and boron (25), entrained into the atmosphere as aerosols
379 through wind turbulence followed by evaporation, are the dominant sources of these elements
380 to soils. For example, selenium deficiencies and sufficiencies in Chinese soils map to the
381 northern limit of the monsoon (29). Total selenium concentrations in wet deposition are ~1-2
382 nM (29). Median inorganic arsenic concentrations in monsoonal Bangladesh deposition are
383 1.3 nM, *i.e.* with the range of selenium concentrations in wet deposition.

384

385 Using median As concentrations in wet deposition ranging from 0.23 to 1.75 nM for Sri
386 Lanka and Bangladesh, respectively, and a global wet deposition of $5.1 \times 10^{14} \text{ m}^3/\text{y}$ (1), this
387 equates to 9,000 – 69,000 t/y globally. While not all terrestrial landmass is monsoonal, most
388 of the Earth's surface is marine, so this calculation may be considered as an upper boundary.
389 Depositional inputs are assumed to be much lower in the southern as compared to the
390 northern hemisphere (1), both our sites being in the north, but even so, our measurements
391 suggest marine contribution to global arsenic deposition to be measured in the 10,000s per
392 annum just on a northern hemisphere contribution. As it is estimated that 26,000-82,000 t/y
393 of arsenic is deposited to the surface of the earth annually (1), marine sources are a major
394 contribution to atmospheric inputs, if our assumption is correct that arsenic in wet deposition
395 in monsoonal settings is marine derived. Matschullat (1), reviewing the available literature,
396 estimated marine inputs of arsenic into the environment to be 27 t/y, 3-orders of magnitude
397 lower than our estimates, although he cites older citations on maritime inputs that are in order
398 with ours, 30,000-78,000 t/y (29). As these reviewed studies were based on old and limited
399 analytical technologies, often with very limited actual measurements, Matschullat's argued
400 that only further work to increase the reliability of global arsenic budgeting will resolves
401 these discrepancies regarding marine contribution to global atmospheric cycling. Our
402 empirical study shows that the older estimates were more in line with reality compared to the
403 lower estimates. Furthermore, previous studies have ignored monsoonal inputs which we
404 show to be very significant in depositional inputs of arsenic due to the volume of deposition
405 associated with monsoons. Given that large tracts of the populated globe are in monsoonal
406 regions, wet deposition is a major vector for arsenic inputs into terrestrial ecosystems.
407
408 The implications of oceans being a major source of arsenic now needs to be addressed; such
409 as to how depositional inputs vary globally, temporally and what the impact of climate

410 change will have on deposition. Also, past atmospheric deposition may be a major
411 contribution to the buried sediments that constitute groundwater arsenic stores as high arsenic
412 in groundwaters are found in many delta regions with monsoonal climates (30). Intriguingly,
413 Mirlean et al. (31) had hypothesized that the major source of ancient arsenic buried in coastal
414 inter-dune swamps lacking fluvial contribution, are likely to be atmospheric in origin.

415

416 **Associated content**

417 **Supporting Information**

418 Details on the manufacturers of equipment and reagents, table of quality assurance data,
419 including LoDs and CRM recoveries, tables with Spearman's correlation coefficient matrix
420 for Bangladesh, Sri Lanka and combined sites elemental and speciation data, figures
421 containing chromatograms for speciation analysis by both anion and cation IC-ICP-MS and
422 regressions of arsenic species and trace element data for both sites with distances from 72-h
423 weather trajectories.

424

425 **Author information**

426 **Corresponding Author**

427 *Andrew A. Meharg; Email: aa.meharg@qub.ac.uk

428

429 **References**

430

- 431 1. Matschullat, J. Arsenic in the geosphere. *Sci. Total Environ.* **2000**, *249*, 297-312.
- 432 2. Huang, J. -H.; Matzner, E. Biogeochemistry of organic and inorganic arsenic species in a
433 forested catchment in Germany. *Environ. Sci. Technol.* **2007**, *41*, 1564-1569.

- 434 3. Wai, K.-M.; Wu, S.; Li, X.; Jaffe, D. A.; Perry, K. D. Global atmospheric transport and
435 source-receptor relationships for arsenic. *Environ. Sci. Technol.* **2016**, *50*, 3714-3720.
- 436 4. Cutter, G. A. Metalloids in wet deposition on Bermuda: concentrations, sources, and
437 fluxes. *J. Geophys. Res.* **1993**, *98*, 16777-16786.
- 438 5. Rowland, A. P.; Neal, C.; Reynolds, B.; Jarvie, H. P.; Sleep, D.; Lawlor, A. J.; Neal, M.;
439 The biogeochemistry of arsenic in a remote UK upland site: trends in rainfall and runoff,
440 and comparisons with urban rivers. *J. Environ. Monit.* **2011**, *13*, 1255-1263.
- 441 6. Andreae, M. O. Arsenic in rain and the atmospheric mass balance of arsenic. *J. Geophys.*
442 *Res.* **1980**, *85*, 4512-4518.
- 443 7. Blazina, T.; Läderach, A.; Jones, G. D.; Sodemann, H.; Wernli, H.; Kirchner, J. W.;
444 Winkel, H. E. Marine primary productivity as a potential indirect source of selenium and
445 other trace elements in atmospheric deposition. *Environ. Sci. Technol.* **2016**, *51*, 108-118.
- 446 8. Tziaras, T.; Pergantis, S. P.; Stephanou, E. G. Investigating the occurrence and
447 environmental significance of methylated arsenic species in atmospheric particles by
448 overcoming analytical method limitations. *Environ. Sci. Technol.* **2015**, *49*, 11640-11648.
- 449 9. Jakob, R.; Roth, A.; Haas, K.; Krupp, E. M.; Raab, A.; Smichowski, P.; Gomez, D.;
450 Feldmann, J. Atmospheric stability of arsines and the determination of their oxidative
451 products in atmospheric aerosols (PM₁₀): evidence of the widespread phenomena of
452 biovolatilization of arsenic. *J. Environ. Monit.* **2010**, *12*, 409-416.
- 453 10. Mukai, H.; Ambe, Y.; Muku, T., Takeshita, K. Seasonal variation of methylarsenic
454 compounds in airborne particulate matter. *Nature* **1986**, *324*, 239-241.
- 455 11. Zhang, S. -Y.; Sun, G. -X.; Yin, X. -X.; Rensing, C.; Zhu, Y. -G. Biomethylation and
456 volatilization of arsenic by the marine microalgae *Ostreococcus tauri*. *Chemosph.* **2013**,
457 *93*, 47-53.

- 458 12. Mestrot, A.; Merle, J. K.; Broglia, A.; Feldmann, J.; Krupp, E. M. Atmospheric stability
459 of arsine and methyl arsines. *Environ. Sci. Technol.* **2011**, *45*, 4010-4015.
- 460 13. Faust, J. A.; Junnien, H.; Ehn, M.; Chen, X.; Ruusuvuori, K.; Kieloaho, A. -J.; Bäck, J.;
461 Ojala, A.; Jokinen, T.; Worsnop, D. R.; Kulmala, M.; Petäjä, T. Real-time detection of
462 arsenic cations from ambient air in boreal forest and lake environments. *Environ. Sci.*
463 *Technol. Let.* **2015**, *3*, 42-46.
- 464 14. Chen, W. -Q.; Shi, Y. -L.; Wu, S. L.; Zhu, Y. -G. Anthropogenic cycles: a research
465 framework and features. *J. Cleaner Prod.* **2016**, *139*, 328-336.
- 466 15. O'Dowd, C.; Ceburnis, D.; Ovadnevaite, J.; Vaishya, A.; Rinaldi, M.; Facchini, M. C. Do
467 anthropogenic continental or coastal aerosol sources impact on a marine aerosol signature
468 at Mace Head? *Atmosph. Chem. Phys.* **2013**, *14*, 10687-10704.
- 469 16. Mestrot, A.; Feldmann, J.; Krupp, E. M.; Hossain, M. S.; Roman-Ross, G.; Meharg, A. A.
470 Field fluxes and speciation of arsines emanating from soils. *Environ. Sci. Technol.* **2011**,
471 *45*, 1798-1804.
- 472 17. Dimri, A. P.; Yasunari, T.; Kotila, B. S.; Mohanty, U. C.; Sikka, D. R. Indian winter
473 monsoon: present and past. *Earth Sci. Rev.* **2016**, *163*, 297-322.
- 474 18. Draxler, R. R.; Hess, G. D. An overview of the HYSPLIT_4 modeling system of
475 trajectories, dispersion, and deposition. *Aust. Meteor. Mag.* **1998**, *47*, 295-308.
- 476 19. Tanaka, S.; Santosa, S. J.; The concentration distribution and chemical form of arsenic
477 compounds in sea water. In: *Biogeochemical Processes and Ocean Flux in the Western*
478 *Pacific*. Eds Sakai, H.; Nozaki, Y. pp. 159-170, Terra Scientific Pub. Comp., Tokyo,
479 **1995**.
- 480 20. Wurl, O.; Shelley, R. U.; Landing, W. M.; Cutter, G. A. Biogeochemistry of dissolved
481 arsenic in the temperate to tropical North Atlantic Ocean. *Deep-Sea Res. II* **2015**, *116*,
482 240-250.

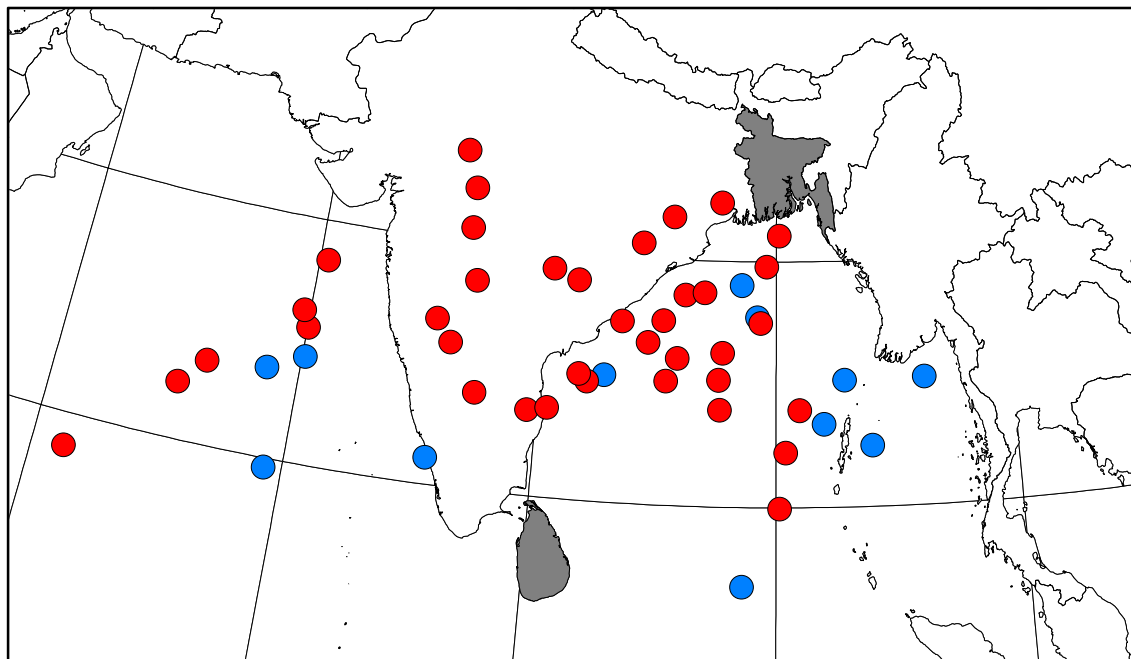
- 483 21. Hanaoka, K.; Nakamura, O.; Ohno, H.; Tagawa, S.; Kaise, T. Degradation of
484 arsenobetaine to inorganic arsenic by bacteria in seawater. *Hydrobio.* **1995**, *316*, 75-80.
- 485 22. Matoušek, T.; Currier, J. M.; Trojánková, N.; Saunders, R. J.; Ishida, M. C.; González-
486 Horta, C.; Musil, S.; Mester, Z.; Stýblo, M.; Dědina, J. Selective hydride generation-
487 cryotrapping-ICP-MS for arsenic speciation analysis at pictogram levels: analysis of river
488 and sea water reference materials and human bladder epithelial cells. *J. Anal. At.*
489 *Spectrom.* **2013**, *28*, 1456-1465.
- 490 23. Sun, G. -X.; Meharg, A. A.; Li, G.; Chen, Z.; Yang, L.; Chen, S. -C.; Zhu, Y. -G.
491 Distribution of soil selenium in China is potentially controlled by deposition and
492 volatilization? *Sci. Rep.* **2016**, doi:10.1038/srep20953.
- 493 24. Saiz-Lopez, A.; Plane, J. M. C., Baker, A. R.; Carpenter, L. J.; Glasow, R. V.; Gómez
494 Martin, J. C.; McFiggans, G.; Saunders, R. W. Atmospheric chemistry of iodine. *Chem.*
495 *Revs.* **2012**, *112*, 1773-1804.
- 496 25. Schlesinger, W. H.; Vengosh, A. Global boron cycle in the Anthropocene. *Glob.*
497 *Biogeochem. Cycl.* **2016**, DOI: 10.1002/2015GB005266.
- 498 26. Zhang, X.; Cornelis, R.; De Kimpe, J.; Mees, L. Arsenic speciation in serum of uraemic
499 patients based on liquid chromatography with hydride generation atomic absorption
500 spectroscopy and on-line UV photo-oxidation digestion. *Anal. Chim. Acta* **1996**, *319*,
501 177-185.
- 502 27. Korotkikh, E. V.; Mayewski, P. A.; Dixon, D.; Kurbatov, A. V. ; Handley, M. J.; Recent
503 increase in Ba concentrations as recorded in a South Pole ice core. *Atmos. Environ.* **2015**,
504 *89*, 683-687.
- 505 28. Moore W. S.; High fluxes of radium and barium from the mouth of the Ganges-
506 Brahmaputra River during low river discharge suggests a large groundwater source. *Earth*
507 *Plant. Sci. Let.* **1997**, *150*, 141-150.

- 508 29. Chester, D. C. *Marine geochemistry*. London, Chapman & Hall **1993**.
- 509 30. Smedley, P. L.; Kinniburgh, D. G. A review of the source, behaviour and distribution of
510 arsenic in natural waters. *Appl. Geochem.* **2002**, *17*, 517-566.
- 511 31. Mirlean, N.; Baisch, P.; Diniz, D. Arsenic in groundwater of the Paraiba do Sul delta,
512 Brazil: an atmospheric source? *Sci. Tot. Environ.* **2014**, 148-156.

513 **Legend to figures**

514

515 **Figure 1.** The origin of 72-h weather trajectories modeled using Hysplit and arsenic
516 speciation of monsoonal wet deposition for Bangladesh/summer (red) and Sri Lanka/winter
517 (blue). The map was created using the Mac App Magic Maps.
518



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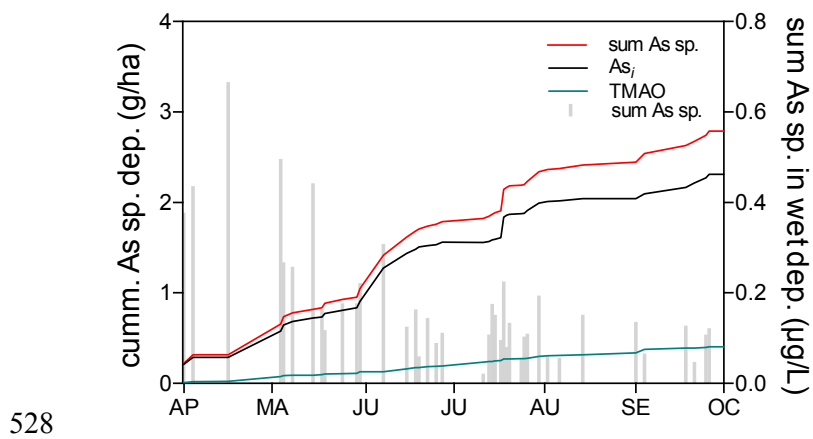
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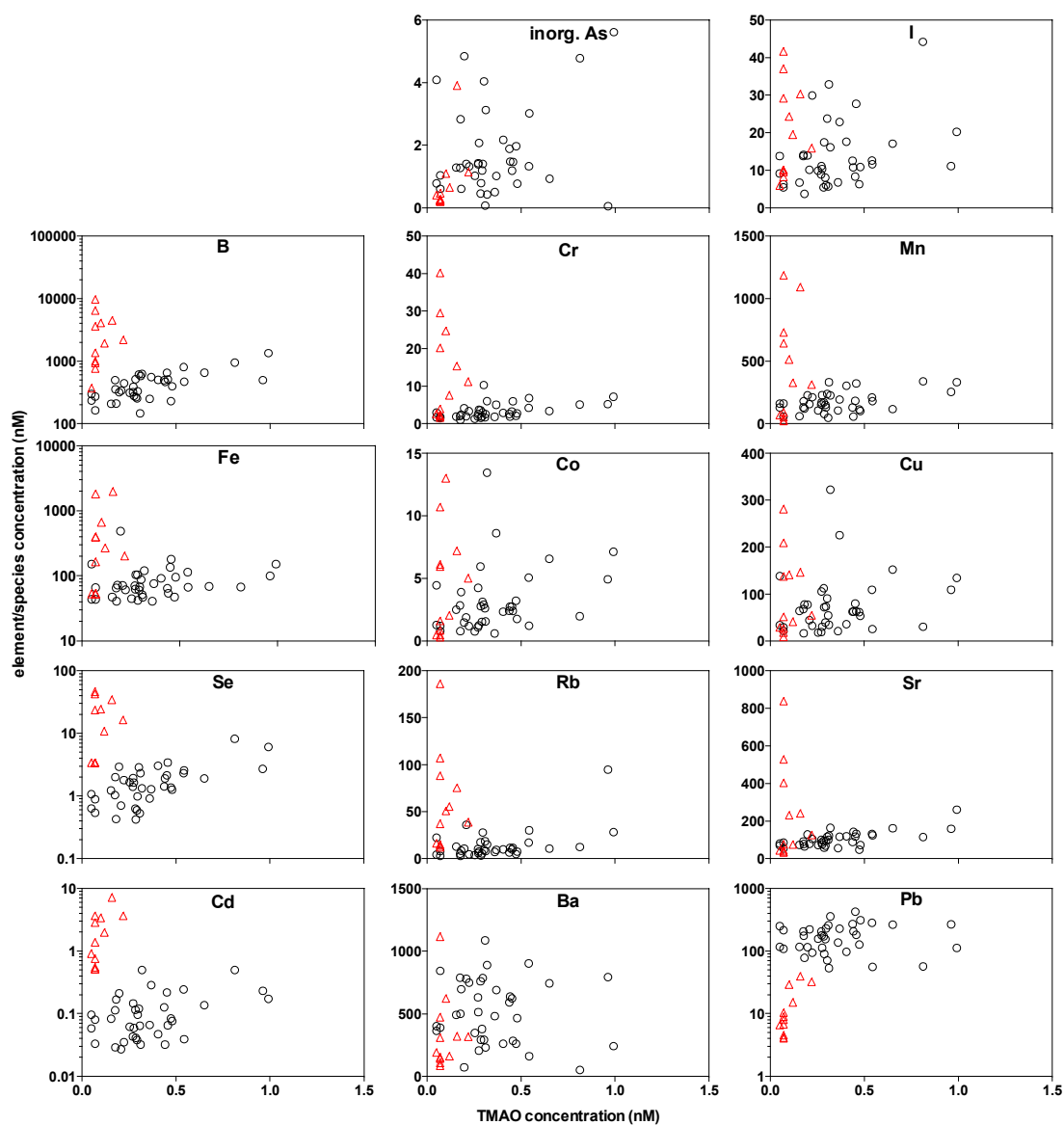
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524 **Figure 2.** The individual daily wet deposition of arsenic species for Bangladesh samples
525 collected from 01/04/2016 – 26/09/2016.
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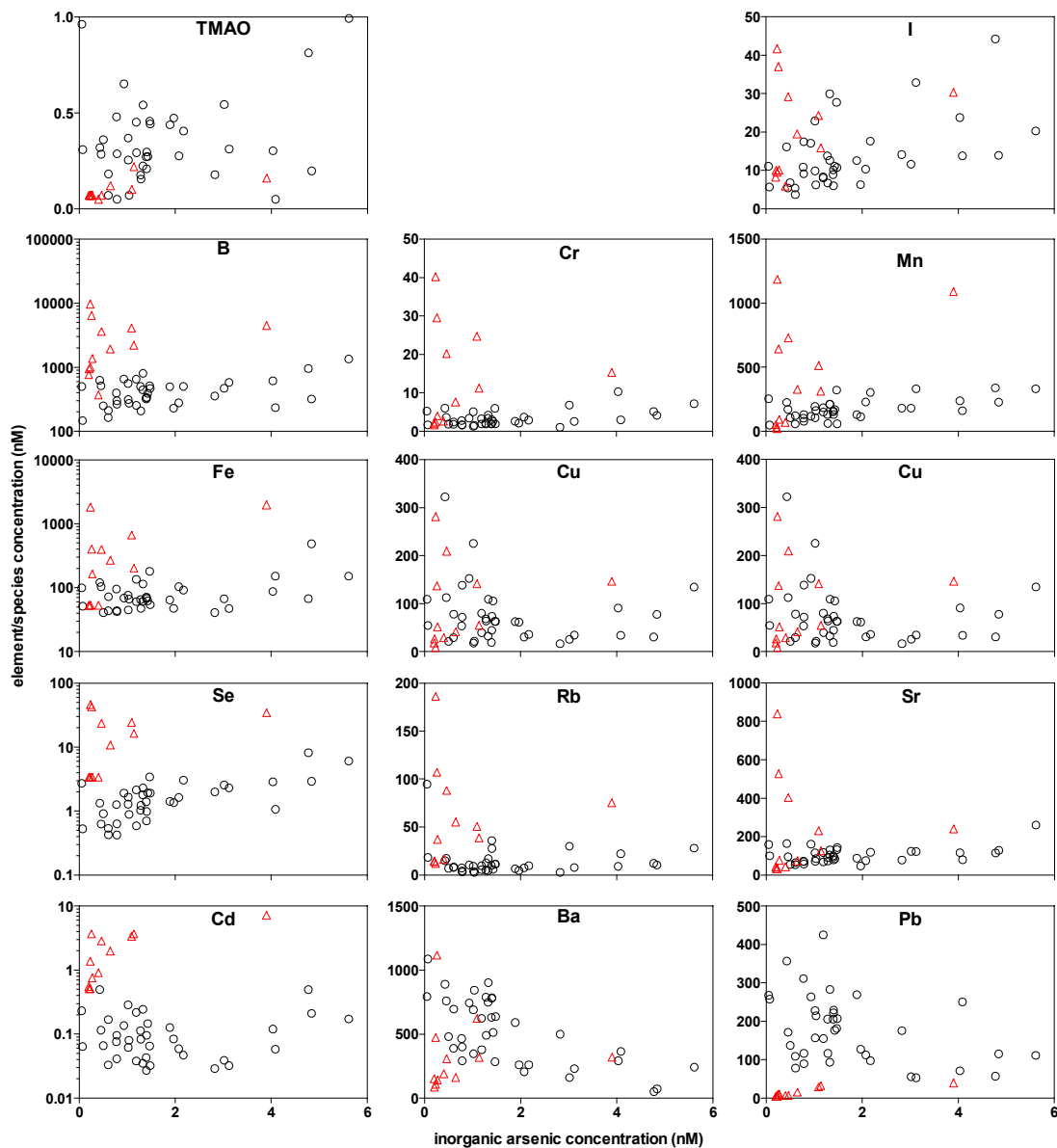


529 **Figure 3.** Relationship for both Sri Lankan (red triangles) and Bangladeshi (black circles)
530 between TMAO and other elements/species.
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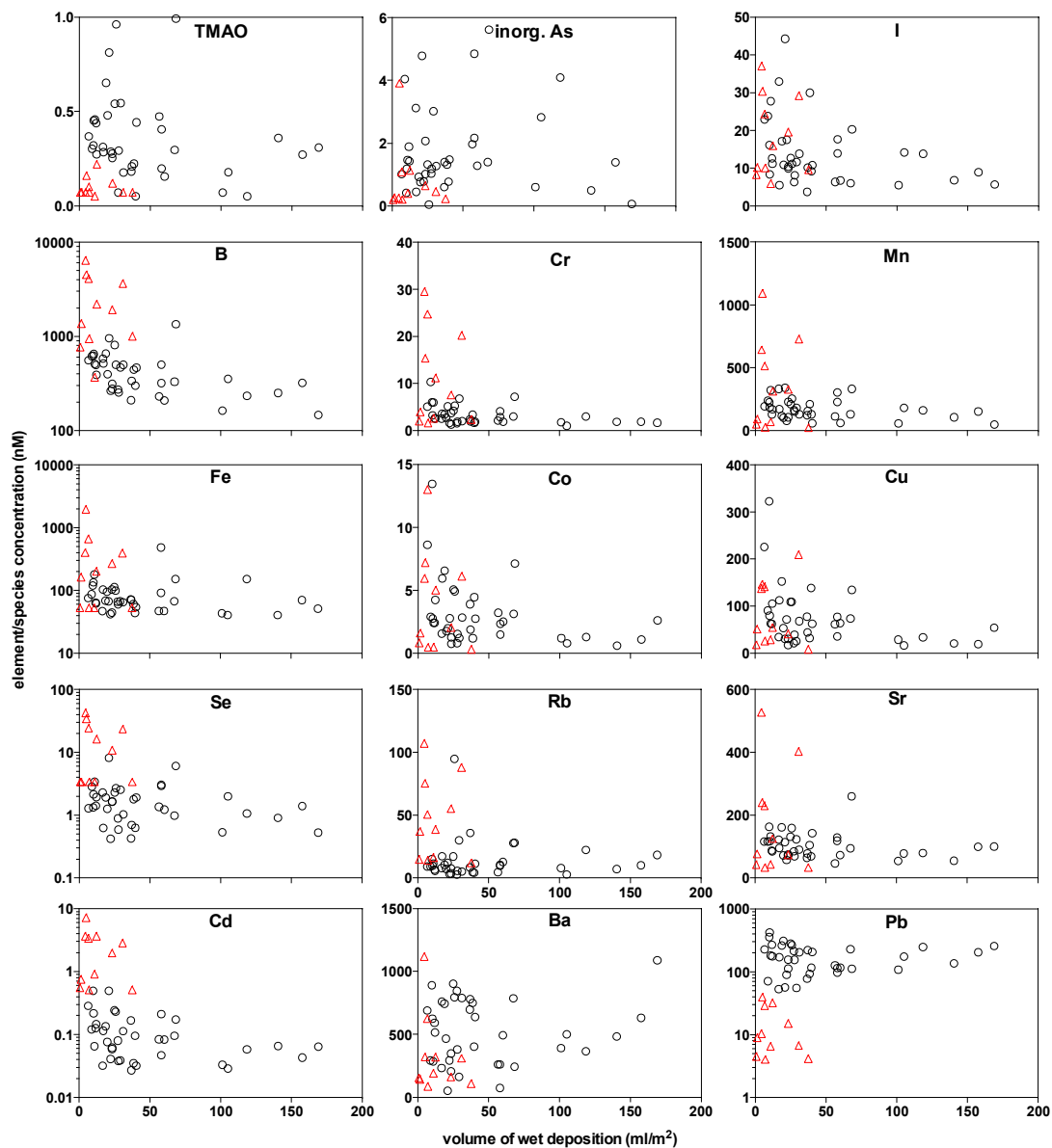
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535 **Figure 4.** Relationship for both Sri Lankan (red triangles) and Bangladeshi (black circles)
536 between inorganic arsenic and other elements/species.
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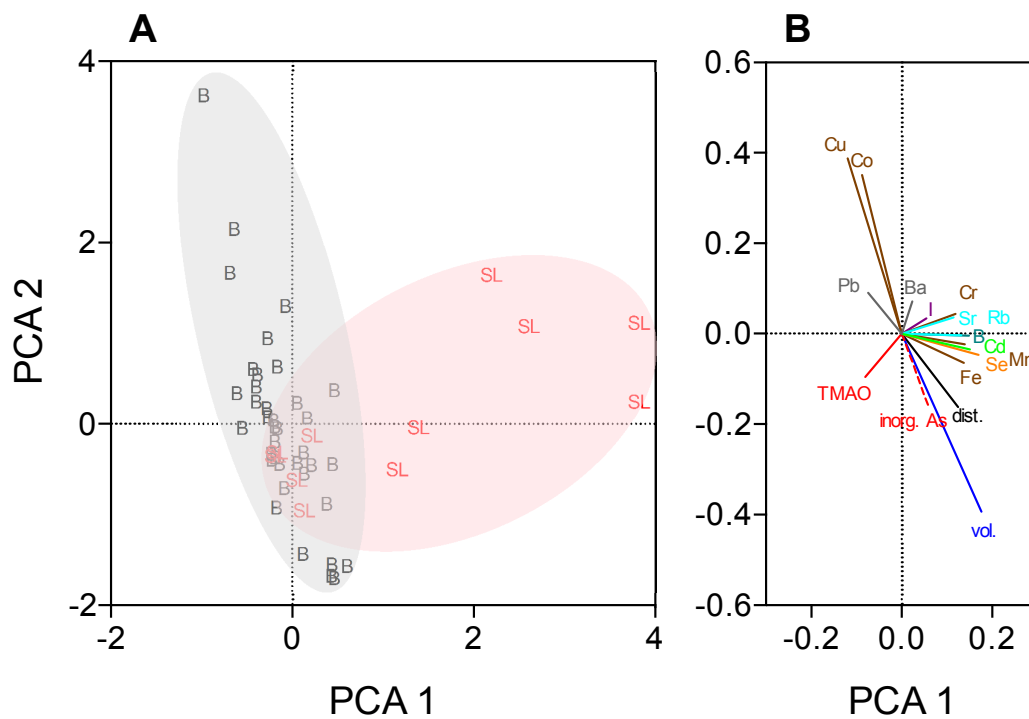
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545 **Figure 5.** Relationship for both Sri Lankan (red triangles) and Bangladeshi (black circles)
546 between deposition volume and elements/species.
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553 **Figure 6.** Principle components analysis Of Sri Lankan (red text, SL) and Bangladeshi (black
554 text, B) elemental/species data (A), along with the factor loadings (B).
555
556



557