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Biovolatilization of arsenic as arsines from seawater

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ABSTRACT

Marine sources of arsenic to the atmosphere are normally dismissed as minor. Here we show that arsenic can be biovolatilized from seawater, and that biovolatilzation is based on organic arsenic species present in the seawater. Even though inorganic arsenic is in great excess in seawaters, it is trimethylarsine (TMA) that is the primary biovolatilized product, with dimethylarsine (DMA) also observed if dimethylarsinic acid (DMAA) is spiked into seawaters. With respect to budgets, 0.04% of the total arsenic in the seawater was biovolatilized over a 2-week incubation period. To test the environmental significance of this finding, wet deposition was analyzed for arsenic species at coastal locations, one of which was the origin of the seawater. It was found that the oxidized product of TMA, trimethylarsine oxide (TMAO), and to a less extent DMAA, were widely present. When outputs for arsines (0.9 nmol/m^2/d) from seawater and inputs from wet deposition (0.3-0.5 nmol/m^2/d) were compared, they were of the same order of magnitude. These findings provide impetus to reexamining the global arsenic cycle as there is now a need to determine the flux of arsines from the ocean to the atmosphere.

▪ INTRODUCTION

The biogeochemical cycle of arsenic, particularly the fluxes through the atmosphere, is poorly described (1, 2). These fluxes are thought to be biovolatilization, salt spray entrainment, entrainment of soil dusts, and industrial emissions (1). The uncertainty regarding inputs of arsenic into the atmosphere is due to limited actual field measurements, using outdated analytical approaches, with limited arsenic speciation conducted (1). The observation that trimethylarsine oxide (TMAO) constitutes ~20% of arsenic in wet deposition, from weather whose back-trajectories are marine, raised the hypothesis that TMAO in the atmosphere could be of marine origin (3). TMAO is the oxidized form of trimethylarsine (TMA), the main form of arsenic biovolatilized by fungi and bacteria (4-6). However, a previous observation that TMAO was bound to marine sampled atmospheric particulates, sampled on a remote Japanese island in the S. China Sea, was attributed to evolution of arsines from (mainland Japanese) soil (7). Trace levels of monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA) and TMAO have been detected on atmospheric particulates collected on Atlantic and Pacific cruises, at similar concentrations for each ocean, circa. 10 pg/m^3, 50-500-fold lower than inorganic arsenic (8). There was not a clear pattern in MMAA, DMAA and TMAO concentrations, which contrasts with a later Argentinian terrestrial study that found TMAO at concentrations in particulates at 60 pg/m^3, with DMAA 5-fold, and MMAA 10-fold, lower (9). Soils have been widely shown to produce arsines, with TMA being the dominant species produced (5,6). This soil source hypothesis for TMAO in marine sampled particulates (7), though, ignored the fact that Japan, and other sampling locations (8,9), are surrounded by, or are beside, oceans, and that the prevailing weather trajectories originate from the oceans.

The literature on marine production of arsines is scant, though marine production of arsines is predicted to be important (2). There is only one study on marine algal isolates, showing that they could biovolatilize arsenic, though speciation of these arsines was not ascertained (4). Wet deposition studies that speciate arsenic are limited to one seaboard (3) and one continental (10) setting; with the continental low, and the seaboard one high, relatively, in TMAO. The metabolic precursors of TMA/TMAO have been found widely in seawaters, MMAA and DMAA (11, 12). TMAO can also be the product of arsenobetaine (AsB) degradation (13), a dominant arsenic species in marine biomass. Assessing arsenic speciation in seawater is difficult as the high salt content interferes with chromatography, and the chromatography is often not well resolved with key species co-eluting; such as for anion exchange chromatography where AsB, arsenite and TMAO can co-elute (3). Also, given that there are limited analytical standards in circulation for TMAO, it is not widely reported in the literature (3). In a recent study where multiple marine water certified reference materials (CRMs) were speciated by arsine generation, with those species cryo-trapped and the cryo-trap interfaced with inductively coupled plasma – mass spectrometry (ICP-MS), TMAO was quantified at ~0.2 nM concentrations (14). As well as seawater, TMAO/TMA can emanate from soils (15), and can have a volcanic/geothermal origin (16), though the contribution of soils and geothermal sources to the wider environment is relatively low (3, 15,16).

To test the hypothesis of Savage et al. (3) that TMAO in wet deposition is primarily from marine origin, natural seawaters have to be shown to produce arsines, an experiment that has not been conducted, to date. In this study, we trap arsines emanating from seawater

under both un-amended and DMAA amended conditions. The DMAA addition will show if arsines production is methylated substrate availability inhibited, and whether any DMAA is converted to TMA, to ascertain if DMMA is a precursor to biovolatilization. Furthermore, we establish organic arsenic species in wet deposition at coastal locations, rather than the inland sites used in previous wet deposition speciation studies (3, 10).

87 ▪ **MATERIALS AND METHODS**

88 **Generation of arsines from seawater**

89 Fresh seawater was obtained from Belfast Lough, Irish Sea, 54.644° N, 5.812° W (Figure 1)
90 during September 2017. The seawater was transported directly back to the laboratory (30
91 minutes from sampling site) and immediately transferred into 1 L Quickfit reaction vessels
92 fitted with a Drechsel head with a sintered glass bubbler, with the bubbler positioned below
93 the water line. Connected to the reaction chamber inlets and outlets, were silica gel
94 sampling tubes, dosed with silver nitrate according to Mestrot et al. (15). A personnel gas
95 sampling pump (Pocket Pump, SKC, Dorset, UK) was then joined to the outlet tube, with air
96 drawn into the chamber under negative pressure at a rate of 200 mls/min. Eight such
97 microcosms were set up and placed in an Memmert AtmoCONTROL incubator, set at a
98 temperature of 20°C, and lit with LED lights at an intensity of 8,000 lux. After 1-week the
99 inlet and outlet tubes were replaced, and DMAA added to four of the microcosms at a
100 dosing of 1 nM. Chemical and instrument suppliers, and analytical instruments suppliers and
101 conditions, and are given for all analysis in Table S1. This concentration of DMAA (1nM) is
102 near the upper limit of what we recorded in Irish wet deposition as outlined in this study.
103 The microcosms were then incubated for a further week, with traps removed and analyzed.

104

105 Arsenic species trapped on the silver nitrate impregnated silver gel were eluted with ~ 5ml
106 boiling water, volume accurately measured, for subsequent chromatographic quantification
107 of species (15). Arsenic species in the seawater were determined in triplicate following 10-
108 fold dilution and oxidation of any arsenite to arsenate with 0.3% final concentration of H_2O_2,
109 to move arsenite away from the co-eluting species, AsB and MMAA. For speciation, a

110 Thermo Scientific IC5000 Ion Chromatography system interfaced with a Thermo ICAP-Q ICP-
111 MS was used. Chromatography utilized a 2x250mm Thermo Scientific AS7 anion-exchange
112 column with a 2x50mm AG7 guard column and ammonium carbonate over a linear gradient
113 from 20nM to 200nM was the mobile phase. Purchased standards, suppliers detailed in
114 Table S1, of arsenobetaine, inorganic arsenic, MMAA, DMAA, and TMAO were run to
115 ascertain retention times, and for quantification of those species. Total arsenic was
116 determined in triplicate seawater samples following Millipore membrane (0.45 micron)
117 filtering on 10-fold diluted samples.
118
119 For total arsenic determination, the Thermo Scientific ICAP-Q ICP-MS was used in helium
120 collision cell mode to quantify arsenic against authentic samples with rhodium used as an
121 external standard, spiked to give a 10 µg/l concentration. For all analytical methods, blanks
122 were prepared from >18.2 MΩ.cm (at 25°C) water in the same manner as the samples and
123 included with each instrument batch. Limit of Detection (LoD) was calculated as average
124 concentration of the blank + 3 times standard deviation of a species mix dilution series.
125
126 **Arsenic speciation in wet deposition**
127 Wet deposition was collected during July and August 2015 at two sampling locations, the
128 Belfast location used for seawater collection, and an Atlantic coastal location, Caherdaniel,
129 Co. Kerry, Republic of Ireland, 51.769° N, 10.099° W. Bulk deposition was collected in 56 mm
130 mouth diameter, pre-weighed, polypropylene 30 ml sampling tubes, suspended 1.5 m off
131 the ground to avoid splash back, for 24-h and immediately frozen on collection. Volume of
132 wet deposition collected was measured gravimetrically, and then converted to a deposition
133 volume on a surface area basis. Defrosted samples were 0.45 micron filtered, H_2O_2 added

to 1%, and arsenic species quantified by IC-ICP-MS, as detailed in Savage et al. (3). The 72-h air trajectories for each location at each date was modelled by Hysplit (17) as per Savage et al. (3).

139 ▪ **RESULTS**

140 **Biovolatilization of arsenic from seawater**

141 The total arsenic present in the fresh seawater was 26.0 ± 0.6 nM. Speciation was quantified
142 using anion-exchange in a 1/10 seawater dilution. The sum of species was 18.5 nM, with 7.5
143 nM difference in total arsenic being due to arsenic species retained on column or peak
144 broadened below LoD due to salinity. Speciated compounds were inorganic arsenic at 16.5 ±
145 0.7 nM, and DMAA at 1.4 ± 0.7 nM. A peak was observed where TMAO/AsB eluted at 0.59 ±
146 1.1 nM, but was not apparent on the cation exchange chromatographic runs. TMAO has
147 severe peak broadening on the cationic column in the presence of seawater and is not
148 quantifiable. AsB is not peak broadened on the cationic column, suggesting the unidentified
149 peak is TMAO. The AsB/TMAO peak merged into the DMAA peak at lower sea water
150 dilutions (X1 and X2) and was below LoD (0.08 nM) at higher dilutions (X100). No MMAA
151 above LoD was present in any of the dilutions.

152

153 Only 3 arsenic species, TMAO, DMAA and inorganic arsenic were present on seawater
154 microcosm outlet chemo-traps; while only two were detectable on inlets, DMAA and
155 inorganic arsenic (Figure 2). The ½ Limit of Detection (LoD) for TMAO was calculated at 64
156 pM in solution extract; the trap was diluted to ~ 5ml. The inlet concentration was subtracted
157 from the outlet concentration and the data expressed on the quantity of arsines
158 biovolatilized from 1 L of seawater over one week (Figure 3). During the first week of
159 sampling, AsH_3 was produced/trapped at a rate of 2.9 pmol/L/wk, which was significant
160 based on one-way anova analysis at P= 0.05, but fluxes were negligible for week 2,
161 regardless of DMAA treatment. DMA biovolatilization was negligible for weeks 1 and 2
162 without DMAA addition, but production was 15.8 pmol/L/wk for the DMAA treatment,

163 significant at P<0.0001. TMA was produced at a rate of 3.0 pmol/L/wk for the first week
164 incubation, and increased to 8.3 pmol/L/wk in the second week without DMAA addition,
165 and 14.7 pmol/L/wk with DMAA addition, P=0.013 for the one-way anova for the 3-way
166 comparisons, with the only pairwise comparison that was significant being week 1 versus
167 week 2 with the DMA amendment (P=0.0124). The sum of (∑) arsenic species increased
168 from 5.1 to 9.0 pmol/L/wk in the absence of additional DMAA in week 2, and with DMAA
169 this figure was 32.2 pmol/L/wk, with one-way-anova being highly significant (P=0.0008). The
170 ∑ arsenic species biovolatilized was 0.01% of total seawater arsenic for week one and 0.03%
171 for week two without DMAA. The additional ∑ arsenic species biovolatilized in the week 2
172 DMAA treated minus the non-DMAA treated microcosms, expressed as a percentage of the
173 DMAA added, was 23.5%.
174
175 **Arsenic speciation in wet deposition**
176 Two sampling sites were used to study arsenic inputs in wet deposition (Figure 1). The Kerry
177 site, in the S.W. of Ireland on the Atlantic coast, is one of the most remote and unpolluted
178 regions of Europe, dominated with Atlantic originating weather trajectories delivering wet
179 deposition (Figure 1). Belfast is situated on the Irish Sea, and while still remote in a
180 European context, has a history of industrialization and is closer to Europe, but still receives
181 predominantly wet deposition from Atlantic originating trajectories (Figure 1). The Kerry
182 location had higher concentrations of TMAO and DMAA throughout, and at lower
183 depositional volumes, also higher inorganic arsenic concentrations (Figure 4 and Table 1).
184 TMAO and inorganic arsenic were routinely above the LoD (LoDs given in Table 1) at
185 deposition volumes below 5 L/m2/d, while DMAA had only one sample above LoD for
186 Belfast, but was above LoD for half the Kerry samples. DMAA was too low to observe any

clear washout, i.e. the relationship between arsenic species concentration and depositional volume, but for TMAO at both sites, and also for inorganic arsenic at the Kerry site, this was clear and steep, fitting exponential decay functions. Inorganic arsenic was more erratic, and could be high at higher depositional volumes, for Belfast, with no clear exponential decay relationship for washout.

Considering depositional inputs of the 3-arsenic species (Table 1). Inorganic arsenic inputs were 2.6-fold higher for Belfast, though not significantly so ($P>0.05$). DMAA was similar for both sites, but this is an estimate given that the Belfast sites were mainly below LoD, and ½ LoD was used in this calculation. TMAO was significantly ($P<0.0001$) higher, 1.6-fold, in Kerry compared to Belfast. Comparing these wet depositional inputs with seawater biovolatilization for TMA (Figure 3), assuming that biovolatilization is occurring to a depth of 1 M, and averaging TMA production for week 1 and 2, then 1 m^2 of seawater can produce 0.86 nmol/m^2/d. Wet depositional inputs of TMAO was at a rate of 0.31 and 0.50 nmol/m^2/d for Belfast and Kerry respectively, i.e. just lower than potential seawater TMAO production.

▪ DISCUSSION

The results presented here show that arsines, particularly, TMA, can be biovolatilized from seawaters at rates commensurate with inputs from wet deposition, suggesting very close linking between the two, and explaining observations that TMAO deposition occurs when weather trajectories are of marine origin (3). It also calls into question that TMAO observed in marine particulates are of terrestrial origin, as has previously been hypothesized (7). The fact that higher concentrations in wet deposition, and higher depositional rates of TMAO were observed in a remote S.W. Irish location, as compared to an industrialized N.E. Irish location, points to a natural origin of this TMA/TMAO for both sites, given that Belfast is also on an Irish Sea coastal location. That S.W. Irish rainwater concentrations of TMAO were higher could be due to both Kerry sitting on a larger water body, the Atlantic, and due to the fact that Belfast weather trajectories, as for Kerry, are predominantly westerly, but that they also have to travel over the Irish landmass, for most trajectory pathways. The concentrations of ∑ arsenic species recorded here relate well to previous 20th century observations for total arsenic for Bermuda, Eastern Atlantic (18) and Western Pacific locations (19), and to our own Indian Ocean measurements (3). These illustrate the ubiquity of arsenic in maritime derived wet deposition.

TMAO is rapidly washed out of the atmosphere, and thus longer weather paths over land would decrease atmospheric burdens of TMAO when precipitation is occurring. This steep washout curve, and the ubiquity of TMAO in wet deposition samples, had been shown in our previous Indian Ocean investigations (3). For the Indian Ocean (3), TMAO inputs were lower in winter as compared to summer, even though weather trajectories come from the same locations. As organic arsenic species in the water column are seasonal in the Indian

227 Ocean, with DMA being higher during summer months (13), production and availability of
228 organo-arsenic species in the water column may be key to understanding seawater
229 biovolatilization of arsenic. Atlantic algal productivity has also been linked to total arsenic
230 deposition at a west Britain location, when air trajectories were so aligned (20).
231
232 Previous studies on arsenic speciation in Atlantic waters find that DMAA concentrations of
233 0.1-0.3 nM are typical, rapidly decreasing with depth (>50 m) to below LoD. (12,21,22).
234 Higher DMAA concentrations, similar to ours at ~1 nM, were reported from the continental
235 shelf off the American east coast (12) and multiple European west coasts continental shelf
236 locations (23). This suggests that methylation of arsenic is more active in a shelf setting. In
237 deeper ocean surface-waters, the lower concentration of DMAA does not appear to be due
238 to limitation in total or inorganic arsenic, a metabolic precursor (4), as inorganic arsenic is
239 typically 10-20 nM for both open ocean and coastal shelf waters (12, 21-23). MMAA is less
240 commonly reported. It is mainly below LoD for a French coast study (23), as for our Irish Sea
241 location here. It is below LoD in other Atlantic studies (21,22), and averaging 0.13 nM in
242 another (12). It should be noted that only direct analysis of arsenic speciation was made
243 using the French study (23), while the other Atlantic studies used indirect assessment of
244 arsenic species (photo-ionization detection) (12,21,22). Using a highly sensitive and accurate
245 speciation approach, on seawater certified reference materials, Matousek et al. (14)
246 measured TMAO in coastal and off-shore waters at concentrations ranging from 0.16-0.3
247 nM, higher than MMAA (0.03-0.12nM), whereas DMAA ranged from 0.53-1.64 nM, and
248 inorganic arsenic was ~14 nM. Thus, when specifically looked for, i.e. using appropriate
249 analytical methodologies, TMAO appears to be present at lower concentrations than DMAA,
250 but higher than MMAA (14). The fact that TMAO is always higher than DMAA in wet

251 deposition, with DMAA often below LoD, yet DMAA concentrations are higher in seawaters,
252 argues for TMAO coming from a biovolatilization route rather than salt spray, as has been
253 previously postulated to be the source of arsenic in wet deposition (1). Also, MMAA and
254 TMAO appear to have similar concentrations in seawaters (14), yet MMAA is never recorded
255 in wet deposition, probably as it is below LoD, not just absent. MMAA <LoD, again, argues
256 for TMAO in wet deposition being from a biovolatilization, as opposed to a salt spray,
257 source. Low TMAO concentrations in the water column may be expected if TMAO is rapidly
258 converted to TMA and lost from the water column.
259
260 The only previous study on biovolatilization from a marine media was a micro-algal pure
261 culture study (4). Arsenate was added at 20,000 nM concentration to incubating
262 *Ostreococcus tauri* under optimal culture conditions, and 0.01% of this arsenic was
263 converted to arsines. Even though our total arsenic concentrations in seawater were a 1000
264 times lower, and that any biovolatilizing microbial community was present at natural
265 densities, we found similar conversion of dissolved seawater arsenic to arsines, 0.04% over
266 2-week incubation. While Zhang et al. (4) did not speciate trapped arsines, they did speciate
267 the incubating medium where they found 2.4% of added inorganic arsenic converted to
268 DMAA, but no MMAA was detected. TMAO and AsB were not looked for, or, at least, too
269 low to report. Given that TMAO and AsB can co-elute with other species (3), and seawater
270 interferes with TMAO detection, TMAO (if present) may not have been observed under the
271 chromatographic conditions used. In a study on freshwater photosynthetic cyanobacteria
272 where the arsenic methylating protein ArsM was isolated, it was shown to convert inorganic
273 arsenic to arsines in vitro, with 2% of arsenic in the incubating medium converted to TMA,
274 alone (24). TMAO, DMAA and MMMA were all detected in culture solution after addition of

275 inorganic arsenic, in both purified ArsM studies and where the ArsM gene was cloned into
276 *Escherichia coli*. When DMAA was added directly to our microcosms we saw a 23%
277 conversion to DMA. DMAA addition enhanced the production of TMA by 77%, showing
278 methylation and reduction of DMAA to biovolatilized TMA. As DMAA was detected in
279 seawaters at circa. the same levels as the amendment, it is likely that the exogenously
280 added DMAA was rapidly metabolized, and the natural DMAA in the seawater was within
281 cells and lysed on preparation for analysis. This is consistent with findings on algae where
282 the bulk of the arsenic in microcosms is within the cells (4,24). Another observation of our
283 study was that TMAO production from both non-amended seawater increased during the
284 second week, suggesting enhanced arsenic species turnover during week 2. The pathways
285 and regulation of arsenic methylation in natural seawaters needs further investigation. It is
286 becoming apparent that seawater contribution to the global arsenic cycle has been
287 underestimated, and marine biovolatilization as a source ignored by all but a handful of
288 studies (3,4). Matschullat (1) estimated that 27 t of arsenic in the global atmosphere was
289 derived from salt-spray. Although our measurements are limited in geography and time,
290 they are the only measurements of TMA output and TMAO input to be conducted to date.
291 There is now a need to estimate the contribution of marine produced arsines to arsenics
292 global arsenic cycle.
293
294 Wet deposition, reported here, and in Savage et al. (3), and measured seawater TMAO
295 concentrations (14), are in the same range sub-nM. It also has to be considered that wet
296 deposition direct to seawaters, or runoff from terrestrial wet deposition, will also be a
297 source of TMAO to seawaters, and there might be tight recycling of TMAO depositional
298 inputs to TMA outputs, which are then oxidized in the atmosphere to TMAO, before re-

deposition. However, demethylation of TMAO also has to be considered as a potential fate of TMAO in the water column as well (13). TMAO can also be derived from AsB degradation (13), and the role of this pathway also remains to be investigated in the context of biomethylation.

▪ ASSOCIATED CONTENT

The Supporting Information contains 1 table pertaining to analytical reagents and analytical instrument parameters.

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383 **Table 1.** Concentration and rates of deposition in wet precipitation for the Belfast and Kerry
384 sampling sites. The LoDs for arsenic species were 0.12, 0.13 and 0.288 nM for DMAA, TMAO
385 and inorganic arsenic, respectively.

		concentration (nM)			deposition (nmol/m2/d)		
	n	inorg. As	DMAA	TMAO	inorg. As	DMAA	TMAO
Belfast							
mean	32	0.64	0.05	0.15	2.32	0.19	0.31
S.E.		0.20	0.01	0.03	0.78	0.03	0.04
Kerry							
mean	8	1.14	0.26	0.58	0.89	0.20	0.50
S.E.		0.34	0.11	0.15	0.11	0.04	0.11

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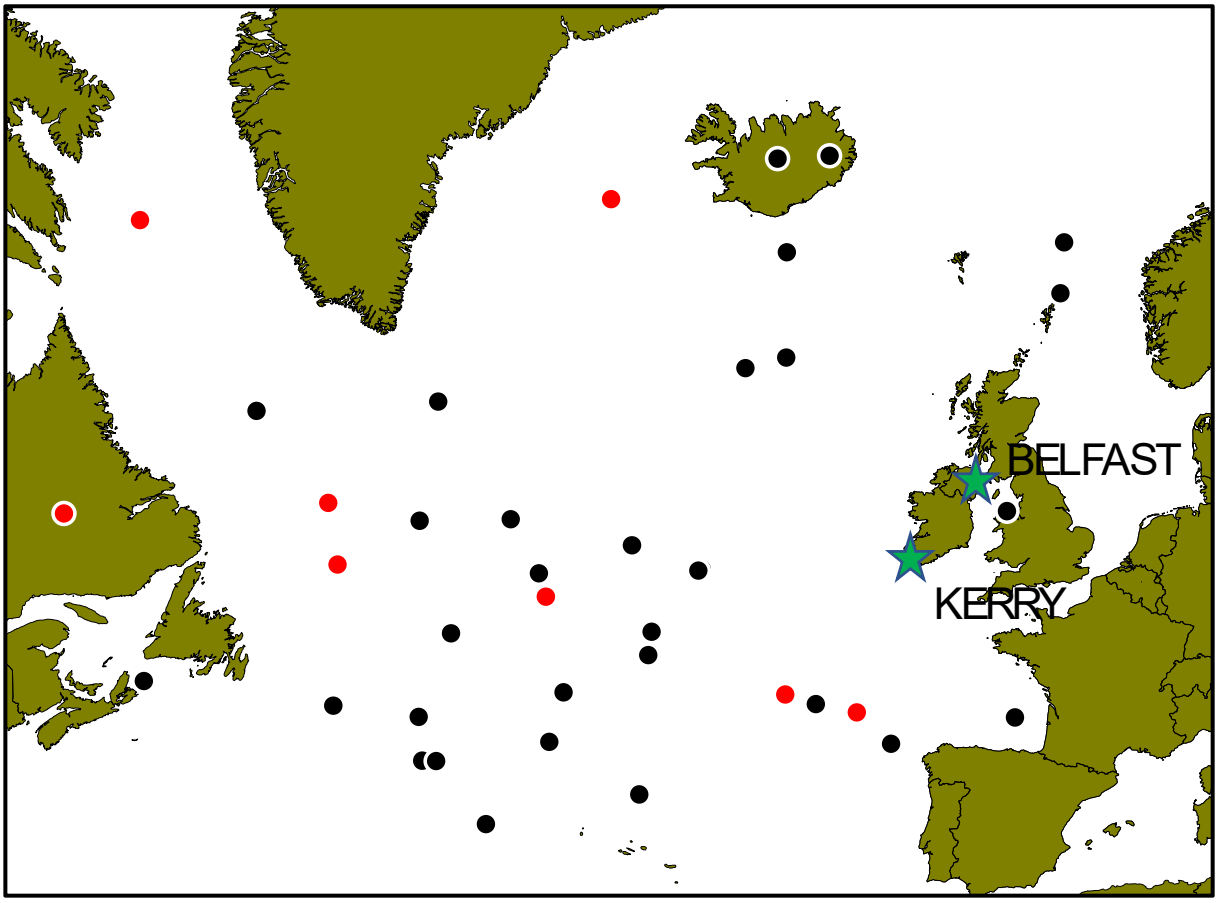
Figure 1. Geographic location of the two sampling sites, Belfast and Kerry, used in this study, along with the weather 72-h back trajectory origins modelled by HySplit. For the back trajectories, black is for Belfast, red is for Kerry. The map image was created in the Mac application MagicMaps.



402 **Figure 2.** IC-ICP-MS chromatograms for arsenic species chemo-trapped on silver nitrate from

403 incubated seawater. Chromatograms are shown in week 1 (upper) and week (2) pairs for

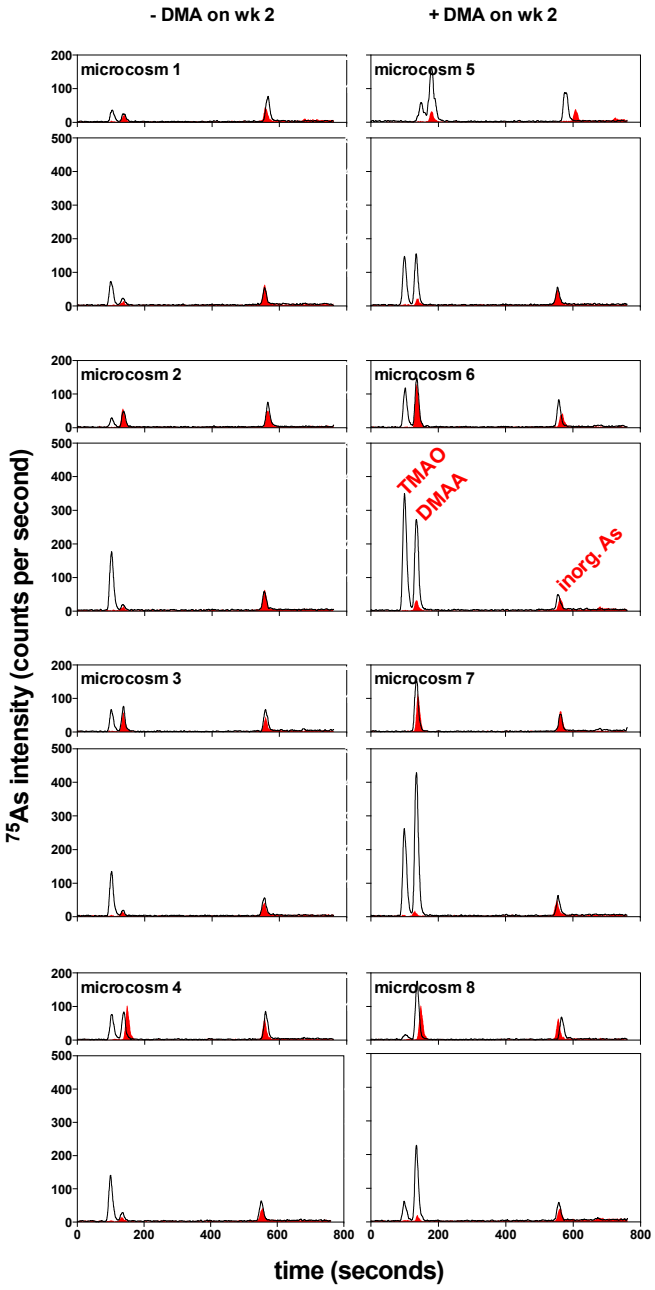
404 each microcosm. All 8 microcosms were untreated for week 1, and for week 2 half were left

405 untreated (left-hand column) and half treated with a final concentration of 1 nM DMA. The

406 red shaded chromatographic trace is for the inlet trap; the black line trace is for the outlet

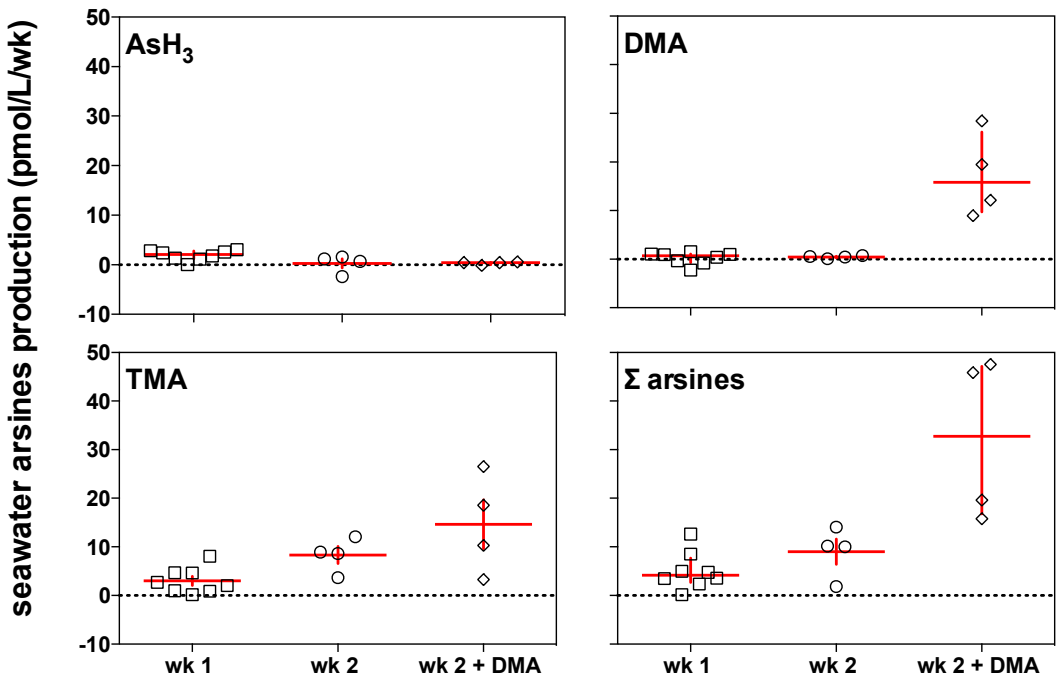
407 trap.

408



409

Figure 3. Production rate of arsines from seawater, calculated from subtracting the inlet silver nitrate traps from the outlet trap quantified chromatograms presented in Figure 2. Graphs show each individual microcosm by week and treatment. The horizontal red line is the mean, the red vertical is the standard error of the mean.



425 **Figure 4.** Concentrations of TMA, DMA and inorganic arsenic in wet deposition collected at

426 the Belfast (black asterisk and line) and Kerry (red circle and dashed line). The lines are

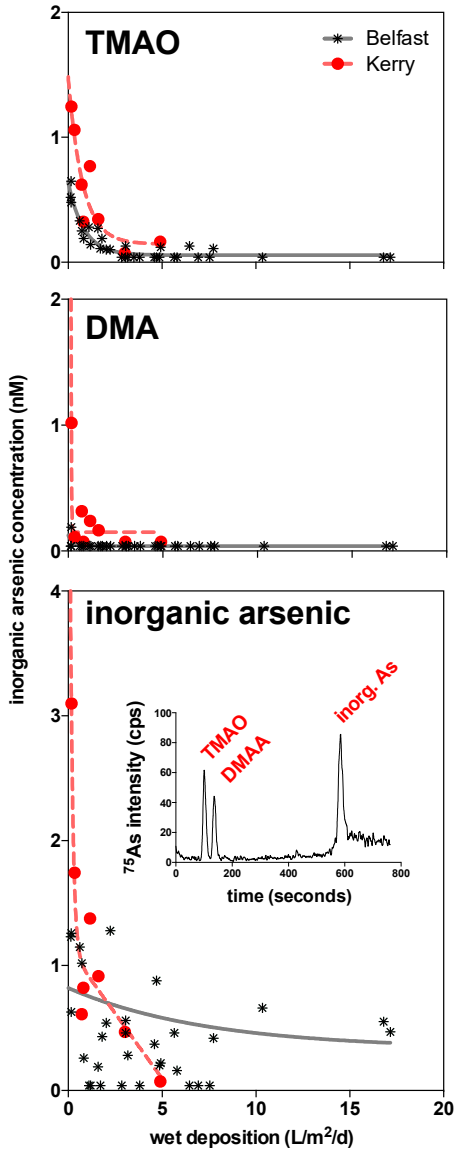
427 modeled single exponential decay functions for all data except for the inorganic arsenic at

428 the Kerry site where a double exponential decay function gave a better fit. The insert in the

429 "inorganic arsenic" panel shows a sample Kerry wet deposition chromatogram with DMAA,

430 TMAO and inorganic arsenic eluting.

431



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