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**JOURNAL OF THE ROYAL SOCIETY  
INTERFACE**

**Microbial metabolism directly affects trace gases in (Sub)  
Polar snowpacks**

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1 1. Title: Microbial metabolism directly affects trace gases in (Sub) Polar snowpacks

2 Running Title: Microbial metabolism in Polar snowpack

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9 Keywords: Antarctic, Arctic, firn, methyl bromide, methyl iodide

## 21 2. Abstract

22 Concentrations of trace gases trapped in ice are considered to develop uniquely from direct  
23 snow/atmosphere interactions at the time of contact. This assumption relies upon limited or  
24 no biological, chemical or physical transformations occurring during transition from snow to  
25 firn to ice; a process that can take decades to complete. Here, we present the first evidence of  
26 environmental alteration due to *in situ* microbial metabolism of trace gases (methyl halides  
27 and dimethyl sulphide) in Polar snow. We collected evidence for ongoing microbial  
28 metabolism from an Arctic and an Antarctic location during different years. Methyl iodide  
29 production in the snowpack decreased significantly after exposure to enhanced UV radiation.  
30 Our results also show large variations in the production and consumption of other methyl  
31 halides, including methyl bromide and methyl chloride, used in climate interpretations. These  
32 results suggest that this long neglected microbial activity could constitute a potential source  
33 of error in climate history interpretations, by introducing a so far unappreciated source of bias  
34 in the quantification of atmospheric-derived trace gases trapped within the Polar ice caps.

## 36 3. Introduction

37 Snow is a highly porous environment, exchanging and entrapping air from the surrounding  
38 environment. As more snow is deposited onto the surface of the snowpack, older snow layers  
39 compress eventually into ice, encasing small samples of the atmosphere existing over and  
40 within the snow at the time of deposition. This simple mechanism of glacial formation was  
41 described in the 1990's (Bender *et al*, 1997), and has been presented as a justification to use  
42 greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>) entrapped in glacial ice as a proxy for atmospheric  
43 compositions (and hence, climate conditions) back in time. This same logic has been used to  
44 justify the quantification of shorter-lived, more reactive trace gases in ice cores including

1  
2  
3 45 methyl bromide (Saltzman *et al*, 2008) and methyl chloride (Saltzman *et al*, 2009, Verhult *et*  
4  
5 46 *al*, 2013). However, these methods rest on the assumption that the snowpack is quasi-sterile  
6  
7 47 metabolically, or at least, that microbial production/consumption of these trace gases is not  
8  
9 48 significant.

10  
11  
12 49 Methyl halides, including methyl chloride, methyl bromide and methyl iodide are particularly  
13  
14 50 interesting choices due to their roles in microbial metabolism and atmospheric chemistry.

15  
16 51 Methyl chloride and methyl bromide together are responsible for approximately 25% of the  
17  
18 52 annual ozone loss (Butler, 2000). Methyl iodide affects local air quality and influences  
19  
20 53 atmospheric degradation rates for longer lived compounds such as methane through its  
21  
22 54 influence on hydroxyl radical concentrations (Tegtmeier *et al*, 2013). Methyl chloride and  
23  
24 55 methyl bromide can be formed directly through chemical interactions in soil (Keppler *et al*,  
25  
26 56 2000), but are more commonly produced through active metabolism of eukaryotic organisms  
27  
28 57 (fungi: Watling & Harper, 1998; Redeker *et al*, 2004; plants: Rhew *et al*, 2003; Redeker *et al*,  
29  
30 58 2004b; Saito & Yokouchi, 2006). To date, only prokaryotes (bacteria) have been observed to  
31  
32 59 consume methyl chloride and methyl bromide (Borodina *et al*, 2005) and they are able to  
33  
34 60 utilise these compounds as their sole energy substrate. Methyl iodide has been observed to be  
35  
36 61 produced by bacteria (Amachi *et al*, 2001), fungi (Redeker *et al*, 2004) and plants (Redeker *et*  
37  
38 62 *al*, 2004b) and is preferentially generated relative to the other methyl halides in most cases.

39  
40  
41 63 Genetic sequences and enzymatic mechanisms for bacterial consumption of methyl chloride  
42  
43 64 and methyl bromide have been identified (McAnnula *et al*, 2001), as well as a suite of  
44  
45 65 homologues for methyl halide production in plants (Nagatoshi & Nakamura, 2007). There  
46  
47 66 remains uncertainty regarding whether all primary mechanisms for monohalogenated  
48  
49 67 metabolism have been identified (Redeker *et al*, 2004b; Manley, 2002).

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52 68 Polar environments represent some of the most extreme environments on Earth, and the  
53  
54 69 assumption of an effectively biologically inactive snowpack has been considered to be well

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3 70 within reason. For example, Arctic average winter daytime temperatures range from  $-34^{\circ}$  to  
4  
5 71  $0^{\circ}$  C, and available water, nutrients and sunlight are limited throughout the year (Przybylak,  
6  
7 72 2003). Antarctic conditions can be even more extreme (Carpenter *et al*, 2000). Furthermore,  
8  
9 73 high UV levels occur commonly in Polar environments, and especially in the southern  
10  
11 74 hemisphere spring (Sept-Nov) during the maximum extent of the ozone hole (Bargagli,  
12  
13 75 2005), further limiting the ability of microbial life to maintain significant levels of activity.

14  
15  
16 76 The limitations of these extreme conditions have recently been questioned. UV radiation  
17  
18 77 appears to be significantly less harmful to sub-surface microbial communities since, while  
19  
20 78 UV is easily transmitted once it has penetrated, penetration is limited by the surface snow  
21  
22 79 which is a good scatterer (Gorton *et al*, 2003). Critically, lab-based results have shown that  
23  
24 80 the temperatures experienced by polar snowpacks, even within the most remote and extreme  
25  
26 81 locations, can support microbial metabolism (Price & Sowers, 2004).

27  
28  
29  
30 82 Microbial presence is ubiquitous in the Polar Regions, and recent research into the Polar  
31  
32 83 aerobiome points toward a dynamic Polar microbial community and the possibility of  
33  
34 84 significant input of metabolically active bacteria onto the snowpack (Pearce *et al*, 2016), even  
35  
36 85 to remote locations (Pearce *et al*, 2009; Herbold *et al*, 2014). To this end, research into the  
37  
38 86 aerobiome and Polar environments have demonstrated that microorganisms in aerial fallout  
39  
40 87 remain viable, as cultures from aerobiological samples can grow under favourable conditions  
41  
42 88 (Sattler *et al*, 2001; Harding *et al*, 2011). Furthermore, the presence of microbes in remote,  
43  
44 89 low nutrient, low water, very cold environments such as Polar glacial surfaces and their  
45  
46 90 snowpacks is well established (Larose *et al*, 2013; Hodson *et al*, 2017).

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50 91 However, the level to which microorganisms are metabolically active in the snow pack as its  
51  
52 92 water content becomes scarce and temperatures drop remains contentious, as the only  
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54 93 evidence to date remains correlative or circumstantial (Carpenter *et al*, 2000; Price & Sowers,

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2  
3 94 2004; Michaud *et al*, 2014). Research has shown that microorganisms can be incredibly  
4  
5 95 persistent, even deep within high plateau polar ice, remaining culturable even after hundreds  
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7 96 of thousands of years (See Price & Sowers, 2004 references). Lab-based evidence suggests  
8  
9 97 that microbes are at least capable of metabolic maintenance activities, even at very low  
10  
11 98 temperatures (Price & Sowers, 2004) but what potential thresholds exist that determine active  
12  
13 99 versus maintenance metabolism in polar snowpack, are unknown (Price, 2006).

16 100 It is clear that microorganisms have played a major role in the Earth's current and past  
17  
18 101 climate (Falkowski *et al*, 2008), and affect Polar biogeochemical cycles (Larose *et al*, 2013;  
19  
20 102 Hodson *et al*, 2017). Therefore, identifying whether microorganisms remain active in the  
21  
22 103 Polar snow pack, and hence which type of metabolic activity and ecological role they play, is  
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24 104 important.

28 105 Exploring Polar snowpack environments for microbial metabolism is challenging, in  
29  
30 106 particular due to the complex nature of the unconsolidated snow and a range of interfering  
31  
32 107 signals from physical, chemical and biological sources. Snowpack tends to be a high  
33  
34 108 exposure environment, with substantial wind-driven mixing of boundary layer air with sub-  
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36 109 surface snow pore space air (Massman & Frank, 2005; Redeker *et al*, 2015). Concurrently,  
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38 110 snow is readily transparent to a range of UV-Visible light, which is known to drive  
39  
40 111 substantial photochemical reactions, including methyl halide production (Swanson *et al*,  
41  
42 112 2007). The quasi-liquid layer on the surface of snow particles incorporates complex chemical  
43  
44 113 reactions and provides limited habitat for microbial life (Price, 2006) while seasonality drives  
45  
46 114 snow pack thinning and expansion (Bender *et al*, 1997), and longer timeframes lead to  
47  
48 115 compression, consolidation and removal from atmospheric influence (Bender *et al*, 1997).  
49  
50 116 Nearby and sub-snowpack soils can also influence snowpack air chemistry through  
51  
52 117 diffusion/advection from local biological sources/sinks with access to more favourable  
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54 118 environments (Swanson *et al*, 2005; Helmig *et al*, 2009).

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3 119 To explore whether it is possible to directly detect signals of ongoing metabolism from  
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5 120 microbial constituents in Polar snowpack we have developed and deployed a trace gas  
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7 121 sampling system that minimizes interfering signals from physical, chemical and alternative  
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9 122 biological sources. This sampling system uses methyl halides (and other parts-per-trillion-by-  
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11 123 volume, pptv, concentration metabolites) as chemical probes, to maximize the potential of  
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13 124 observing substantial change in metabolite concentrations over short time scales (<2 hours).  
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15 125 We tested the sampling system in optimal temperature and biological loading conditions at  
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17 126 Signy Island, Antarctica during the Antarctic Spring of 2012 and the system was re-deployed  
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19 127 in Svalbard during the Arctic Summer of 2015.

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23 128 Here, we provide the first direct *in situ* evidence of continuous microbial metabolism of  
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25 129 methyl halides in Polar snowpack. Our results show active methyl iodine production and  
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27 130 some level of methyl bromide consumption. Thus, we show how microbial activity can alter  
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29 131 the concentration of trace gases trapped within the snowpack, which could potentially  
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31 132 constitute a source of error in climate history interpretations based on firn and ice core data.  
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#### 34 133 4. Methods

##### 35 36 37 134 Study Sites

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40 135 Methyl halide and dimethyl sulphide fluxes were measured in two locations, one Arctic and  
41  
42 136 one Antarctic. The Antarctic site was located at Signy Island (60.718 S, 45.632 W) on the  
43  
44 137 Gourlay Snowfield, where measurements were taken between December 3<sup>rd</sup> and December  
45  
46 138 21<sup>st</sup>, 2012. The Arctic site was Larsbreen glacier, near the settlement of Longyearbyen,  
47  
48 139 Svalbard (78.223 N, 15.627 E), where measurements were taken between June 29<sup>th</sup> and July  
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50 140 19<sup>th</sup>, 2015 (Figure 1). Thus, the sampling dates correspond with the Antarctic Spring and the  
51  
52 141 Arctic Summer. All sampling sites presented relatively thick snowpacks (0.8 – 1.5 m) over  
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54 142 glacial ice, and they were at least 100 m from the glacier edge. Sites were selected to be far  
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3 143 enough from soils to avoid soil biological effects from trace gases diffusing through the  
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5 144 snowpack (Swanson *et al*, 2005; Helmig *et al*, 2009; Redeker *et al*, 2015).  
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7  
8 145 Environmental conditions at Signy were similar to those in Svalbard, with temperatures in  
9  
10 146 ambient air ranging from -3.0 to +15.8° C (Signy) and from +1.9 to 8.2° C (Svalbard).  
11  
12 147 Snowpack temperatures lay at the melting point at Signy and from -2.8 to 0° C on Svalbard.  
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14 148 Ambient temperatures in Signy were strongly affected by daytime sunlight, with highest  
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16 149 temperatures occurring at mid-day and coldest temperatures during the limited night.  
17  
18 150 Therefore, localised re-freezing at the surface of the snow occurred at Signy. Wind speeds  
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20 151 were between +1.5 to +8.2 m/s at Signy while Svalbard experienced winds ranging from 0.0  
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22 152 to +6.8 m/s (6.8 m/s is equivalent to ~15 miles per hour) during sampling periods.  
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### 25 153 Site preparation

26  
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28 154 We installed three paired sample chambers in Signy Island and four pairs in Svalbard. Each  
29  
30 155 pair was composed of one less-impacted, control chamber (“living snowpack”) and one  
31  
32 156 irradiated with UV light. Chamber placements of this nature will influence the local  
33  
34 157 snowpack environment through heat retention and wind blocking. Efforts were made to  
35  
36 158 reduce these impacts, particularly through limited placement periods prior to sampling. The  
37  
38 159 chambers were either placed directly into the snow (Signy), or pinned to the snowpack using  
39  
40 160 50 cm stainless steel pegs (Svalbard). The PVC chamber bases were 30 cm inner diameter  
41  
42 161 and 6 cm height. The distance between each pair of chambers was approximately 10 m  
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44 162 (Figure 2). Trace gas measurements were taken 2 to 4 days after the chamber bases were  
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46 163 installed.  
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51 164 Snow in the enhanced UV exposure chamber was irradiated using UV sterilization lamps  
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53 165 (UV Light Technology) with 2 parallel UV bulbs (17 W Phillips F17T8 bulbs UV-C), placed  
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55 166 vertically in the snowpack (UV lamp length = 61 cm), in line with the snow beneath the  
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3 167 irradiated chamber. Thus, the irradiated snowpack was directly exposed to high intensity UV-  
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5 168 C light (Figure 2). The UV lamps were placed so that there would be no direct effect on the  
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7 169 living control chamber. Although subject to surface scattering, UV transmission within  
8  
9 170 snowpack is enhanced by minimal absorption, travelling well over 1 m with high  
10  
11 171 transmission efficiencies (Wiscombe & Warren, 1980).

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14 172 Each pair of chambers was covered by an opaque 3x3 m black plastic tarp, leaving 1 m from  
15  
16 173 the chamber to the edge of the tarp, to avoid sunlight-driven photochemical reactions  
17  
18 174 (Swanson *et al*, 2007). In addition, the distance between the chambers and tarp edge reduced  
19  
20 175 the impact of wind-driven horizontal transport and mixing of atmospheric air with pore  
21  
22 176 spaces in the snowpack (Bender *et al* 1997; Redeker *et al*, 2015).

#### 23 24 25 177 Trace gas sampling

26  
27  
28 178 After  $\geq 2$  days under tarpaulin-induced blackout conditions, the section of the tarpaulin  
29  
30 179 directly over the chamber base was removed and each PVC chamber base was immediately  
31  
32 180 covered with an opaque, blacked-out polycarbonate chamber top for headspace sampling.  
33  
34 181 Trace gas samples were taken at 0 (immediately after placement), 60, and 120 min post-  
35  
36 182 chamber top placement. Trace gas sampling canisters were connected to the lid of the  
37  
38 183 polycarbonate chamber top (total chamber volume =  $\sim 28$  L) with a  $\frac{1}{4}$ " sulfinert-coated  
39  
40 184 stainless steel sampling line (Restek, Bellefonte, PA) that incorporated a 15 cm long Ascarite  
41  
42 185 trap. Gas samples were drawn via pressure differential into previously evacuated 0.5-L  
43  
44 186 electropolished stainless steel canisters (LabCommerce Inc, San Jose, CA) (Figure 2).  
45  
46 187 Chamber base, top and Ascarite traps (for carbon dioxide and partial water removal) have  
47  
48 188 previously been used for similar experiments and shown to be inert for the gases measured  
49  
50 189 here (Redeker & Cicerone, 2004; Redeker *et al*, 2007; Redeker & Kalin, 2012).

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3 190 After the first round of trace gas sampling the central sections of the blackout tarps were re-  
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5 191 installed and the irradiated chambers were exposed to high intensity UV light for one hour.  
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7 192 After UV-C light exposure the chambers were left for 30 minutes then resampled (Signy) or a  
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9 193 further 24 hours before re-sampling (Svalbard). Post-exposure time allowed reactive (Signy)  
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11 194 and both reactive and moderately reactive (Svalbard) photochemically-derived products to  
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13 195 dissipate.

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16 196 Snowpack and air temperature were measured for each trace gas flux chamber placement, as  
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18 197 was local wind speed. General weather conditions in the days before and during sampling  
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20 198 were also recorded.

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23 199 Trace gas flux analysis

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26 200 Canisters were shipped directly post-sampling to the University of York for analysis. Trace  
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28 201 gas concentrations were analysed on a HP 5972 GC/MSD fitted with a PoraPlot Q column  
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30 202 (25m, 0.32 ID, 5µm thickness; Restek, Bellefonte, PA), similar to methods used in previous  
31  
32 203 studies (Redeker & Cicerone, 2004; Redeker & Kalin, 2012). This instrument has been  
33  
34 204 equipped with low concentration halocarbon and dimethyl sulphide (DMS) gas standards and  
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36 205 calibration tests indicate detection limits of ~0.2 pptv for methyl iodide, <1.0 pptv for methyl  
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38 206 bromide, <10pptv for dimethyl sulphide and <50 pptv for methyl chloride. Method  
39  
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41 207 reproducibility is better than 8% for standard injections (Redeker & Cicerone, 2004; Redeker  
42  
43 208 & Kalin, 2012).

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45  
46 209 Fluxes from snowpack are calculated based on the difference in headspace concentration over  
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48 210 time,

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$$\text{Flux}_{\text{MeX}} = \Delta[\text{MeX}] / \Delta t$$

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3 212 where  $\Delta[\text{MeX}]$  represents the change in headspace MeX concentration over the time period  
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5 213 sampled,  $\Delta t$ . The chambers used in this study are designed to allow pressure equilibration  
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7 214 between the interior and exterior as samples are removed. Pressure equilibration is necessary  
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9 215 to avoid oversampling snowpack pore spaces (Xu *et al.*, 2006). However, as a consequence,  
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11 216 our reported fluxes slightly underestimate due to a ~3% dilution of chamber air over the  
12  
13 217 course of the experiment. Living snow samples, either pre-treatment or post-treatment were  
14  
15 218 not significantly different and were therefore combined in the comparative analyses between  
16  
17 219 irradiated treatments and non-irradiated treatments.

20  
21 220 Microbial sampling and analysis

22  
23 221 Signy

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25  
26 222 Snowpack was collected after the second set of trace gas flux samples (post-irradiation) from  
27  
28 223 within chamber footprints. At least 2 L of snow was collected, transported directly to lab  
29  
30 224 facilities located in Signy Research Station, located in Factory Cove, Borge Bay, and  
31  
32 225 analysed on site.

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34  
35 226 At the research station, we filtered 2 L of melted snow per site through a 47 mm diameter 0.2  
36  
37 227  $\mu\text{m}$  filter (Millipore, GTTP04700). DNA was recovered from the filter using a RapidWater  
38  
39 228 DNA Isolation kit (MoBio, 14810-50-NF), eluted in 100  $\mu\text{L}$  of water and stored at  $-20^{\circ}\text{C}$ .  
40  
41 229 Subsequently, 5  $\mu\text{L}$  of purified DNA was subjected to 35 rounds of PCR in a 25  $\mu\text{L}$  reaction  
42  
43 230 volume, with an annealing temperature of  $50^{\circ}\text{C}$  using GoTaq Colourless MasterMix  
44  
45 231 (Promega, M7142) and primer pairs 8f (5'-CAG ACT TTG ATY MTG GCT CAG-3') and  
46  
47 232 1492r (5'- RGY TAC CTT GTT ACG ACT T-3'), or ARCH349f (5'- GYG CAS CAG KCG  
48  
49 233 MGA AW-3') and ARCH806R (5'- GGA CTA CVS GGG TAT CTA AT-3') (Takai &  
50  
51 234 Horikoshi, 2000) at a final concentration of 10  $\mu\text{M}$ . Successful PCR reaction was confirmed  
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3 235 by electrophoresis using 1.2% Flashgel (Lonza), 4  $\mu$ L of the completed PCR reaction and 1  
4  
5 236  $\mu$ L 5x Flashgel loading dye (Lonza).  
6  
7  
8 237 Svalbard  
9  
10 238 Surface snow was collected in Twirl'em® sterile sampling bags with sterile gloves after the  
11  
12 239 second set of trace gas flux samples (post-irradiation) and from within the chamber  
13  
14 240 footprints. Samples were taken to The University Centre in Svalbard (UNIS) to be analysed  
15  
16 241 within the following 24 hours. Samples were stored in the interim at 6° C.  
17  
18  
19  
20 242 150 g of snow from each site was filtered thru a 0.2  $\mu$ m Whatman® hydrophilic  
21  
22 243 polycarbonate membrane. 10  $\mu$ l of filtrate from the first paired set of living control and  
23  
24 244 irradiated samples were inoculated on 3 different solid media: Bacto Agar, Polygalacturonate  
25  
26 245 (PGA) and Reasoner's 2A agar (R2A); and grown at room temperature (21° C) and at 6° C.  
27  
28 246 Two replicates were made for each media at each temperature. Observations were made 10  
29  
30 247 days after inoculation. 50  $\mu$ l filtrate from the remaining paired sets was placed on 0.2  $\mu$ m  
31  
32 248 Whatman® hydrophilic polycarbonate membranes with 10  $\mu$ l of 1 mM 5-cyano-2, 3-ditotyl  
33  
34 249 tetrazolium chloride (CTC- a fluorescent stain that binds to DNA of actively respiring cells)  
35  
36 250 for 10 minutes. Excess stain was removed with 500  $\mu$ l PBS and the filter was air-dried for 5  
37  
38 251 minutes before it was mounted on a glass slide. Viable, CTC-binding cells were counted (in  
39  
40 252 12 randomly selected, separate visual fields) using a Nikon ECLIPSE E200 microscope with  
41  
42 253 an E2-FM epi-fluorescence attachment. In filters where limited cells were observed, the  
43  
44 254 process was repeated with another 50  $\mu$ l of sample as described but with the addition of 10  $\mu$ l  
45  
46 255 of 1 g/ml 4'-6 diamino-2 phenylindole (DAPI) solution instead of CTC. DAPI binds to both  
47  
48 256 alive and dead cells and this step was performed as a positive control to quantify the number  
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50 257 of dead cells present.  
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55 258 5. Results  
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3 259 Trace gas fluxes from snowpack  
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5 260 All compounds studied behaved in ways consistent with biological influence, however there  
6  
7 261 were substantive differences in behaviour between sites, compounds and UV treatment  
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9 262 (Table 1; Figure 3).  
10  
11

12 263 Methyl iodide  
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14  
15 264 Methyl iodide showed consistent, significant differences in fluxes originating from enhanced  
16  
17 265 UV exposure versus living snowpack (t-test;  $p < 0.05$ ; Fig 3). At both Signy Island and at  
18  
19 266 Svalbard living snow generated methyl iodide at low rates ( $31 \pm 17$  and  $9 \pm 8$   $\text{ng m}^{-2} \text{d}^{-1}$  at Signy  
20  
21 267 and Svalbard respectively, Fig 3), despite methyl iodide's highly reactive nature (methyl  
22  
23 268 iodide has a very strong methylating capacity) (Baowei *et al*, 2006). Once irradiated, the  
24  
25 269 snowpack at both locations consumed methyl iodide ( $-290 \pm 270$  and  $-30 \pm 24$   $\text{ng m}^{-2} \text{d}^{-1}$  at  
26  
27 270 Signy and Svalbard respectively, Fig 3). Fluxes of methyl iodide were consistently,  
28  
29 271 significantly different from zero flux between snowpack and ambient air (t-test,  $p < 0.05$  for  
30  
31 272 both living controls at Signy and Svalbard, as well as snow with enhanced UV radiation at  
32  
33 273 Svalbard). There were no significant correlations between methyl iodide fluxes and snowpack  
34  
35 274 temperature, chamber temperature or local wind speeds.  
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40 275 Methyl bromide and methyl chloride  
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43 276 Methyl bromide and methyl chloride fluxes varied substantially across the sampling sites  
44  
45 277 chosen at Signy and Svalbard (Table 1). Despite this large variability in chamber-to-chamber  
46  
47 278 behaviour, methyl bromide was consistently consumed by the snowpack at both Signy and  
48  
49 279 Svalbard, for both living and irradiated conditions ( $-74 \pm 47$  and  $-19 \pm 20$   $\text{ng m}^{-2} \text{d}^{-1}$  in living  
50  
51 280 controls at Signy and Svalbard respectively, as well as  $-130 \pm 50$  and  $-6 \pm 20$   $\text{ng m}^{-2} \text{d}^{-1}$  in  
52  
53 281 irradiated chambers at Signy and Svalbard). Fluxes were significantly different from zero for  
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55 282 living controls at Signy (t-test,  $p < 0.1$ ) and Svalbard (t-test,  $p < 0.05$ ), and for enhanced UV  
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3 283 radiation snowpack at Signy (t-test,  $p < 0.05$ ) (Table 1, Fig. 3). No statistical difference in  
4  
5 284 methyl bromide behaviour was observed between irradiated and living snowpack. Similarly,  
6  
7 285 the majority of living (14 out of 21) and sterilized (5 out of 7) chamber locations at Svalbard  
8  
9 286 and Signy removed methyl chloride from chamber headspace (Table 1, Fig. 3) although  
10  
11 287 average fluxes were not significantly different from zero. While not significant, there is a  
12  
13 288 trend towards greater methyl chloride removal from irradiated chambers. There were no  
14  
15 289 significant correlations between methyl bromide and methyl chloride fluxes and snowpack  
16  
17 290 temperature, chamber temperature or local wind speeds.

#### 291 Dimethyl sulphide

292 At Signy Island dimethyl sulphide fluxes were not significantly different from zero ( $0 \pm 100$   
293 and  $70 \pm 130 \text{ ng m}^{-2} \text{ d}^{-1}$  in living controls and irradiated chambers respectively). At Svalbard  
294 however, consumption within the snowpack was observed ( $-80 \pm 150$  and  $-130 \pm 60 \text{ ng m}^{-2} \text{ d}^{-1}$   
295 in living controls and irradiated chambers respectively; t-test,  $p < 0.05$ ; Fig. 3). UV irradiated  
296 snowpack did not behave significantly differently from living snowpack during this study  
297 period. There were no significant correlations between dimethyl sulphide fluxes and  
298 snowpack temperature, chamber temperature or local wind speeds.

#### 299 Microbial analyses

300 Inoculated microbial cultures from Svalbard showed that viable cells were present in living  
301 control snowpack samples, and that a variable number of viable cells persisted in irradiated  
302 snowpack after UV exposure. These results were supported by CTC fluorescent staining,  
303 which detected the presence of viable cells within all sites after UV exposure (Table 2).  
304 Although viable cells were present after irradiation, CTC stain counts show that their number  
305 was significantly lower in irradiated sites than in living controls (ANOVA:  $F = 47.16$ ;  $d.f. =$   
306  $1.66$ ;  $p\text{-value} < 0.001$ ).

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3 307 DNA recovered from two experimental sites at Signy were examined by PCR to determine  
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5 308 whether a measurable effect could be detected in snowpack microbial communities treated  
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7 309 with UV. Results were consistent with the inoculated microbial cultures, in that they show  
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9 310 reduction (but not complete restriction) in UV exposed microbial populations. However,  
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11 311 domain-specific effects were also observed. Archaea-specific probes demonstrated significant  
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13 312 reduction, up to complete removal (2 out of 5 samples), after UV treatment, but differences  
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15 313 between treated and untreated samples were not detected when using universal bacterial 16S  
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17 314 primers (n = 5).  
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## 22 23 316 6. Discussion

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26 317 Our data represents the first unequivocal and *in situ* measurement of ongoing microbial  
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28 318 metabolism in Polar snowpack. Our observed fluxes from living snowpack are consistent  
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30 319 with microbial metabolisms previously observed in terrestrial and marine environments,  
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32 320 including methyl iodide production (Amachi *et al*, 2001), and methyl chloride and methyl  
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34 321 bromide consumption (McAnnula *et al*, 2001). Likewise, the snowpack response to  
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36 322 irradiation broadly conforms to the reduction of a microbial signal combined with an  
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38 323 enhanced chemical signal, with reduced methyl bromide consumption and little or no methyl  
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40 324 iodide production. Probable chemical uptake of methyl iodide and dimethyl sulphide is  
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42 325 observed post irradiation while methyl chloride and methyl bromide responses to irradiation  
43  
44 326 are variable.

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48 327 Based on our observed results, fluxes of trace gases from the snowpack are derived from a  
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50 328 complex mixture of physical, chemical and biological processes. Methyl iodide fluxes in  
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52 329 living, non-irradiated samples are determined primarily by biological production processes,  
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54 330 masking chemical removal rates. Fluxes of methyl bromide appear to combine chemical  
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3 331 substitution reactions with biological consumption to generate greater removal rates in  
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5 332 snowpack than either individually.  
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8 333 Our sampling methodology minimized the effects of sunlight since methyl chloride, methyl  
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10 334 bromide and methyl iodide are known to be photochemically generated in snowpack  
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12 335 (Swanson *et al*, 2007). As a consequence of this we observe, in the living snowpack, methyl  
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14 336 iodide production while methyl bromide is uniformly consumed. These processes are  
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16 337 consistent with the known metabolisms of marine and terrestrial microorganisms but are  
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18 338 inconsistent with a photochemical signal in which both methyl iodide and methyl bromide  
19  
20 339 would be expected to be produced. Furthermore, if photochemistry was the driving  
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22 340 mechanism for trace gas fluxes, we would expect to see significant increases in production of  
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24 341 all methyl halides, and especially methyl chloride, post irradiation (Swanson *et al*, 2007). In  
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26 342 the irradiated samples however methyl chloride removal rates appear to be enhanced while  
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28 343 methyl iodide is removed, in contrast to living control samples. Methyl bromide fluxes also  
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30 344 contradict a photochemically dominated process. We might expect significant enhancement  
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32 345 of methyl bromide production after UV irradiation but instead we see site-specific, variable  
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34 346 reduction in uptake, as we might expect if the bacterial population responsible for  
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36 347 consumption was both heterogeneously distributed and variably sensitive to irradiation.  
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41 348 Methyl halides are chemically removed in aqueous systems through substitution reactions  
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43 349 following the precedence of hydroxyl>chloride>bromide>iodide ions (Elliot & Rowland,  
44  
45 350 1993). In these reactions we would expect methyl iodide to be removed most rapidly since  
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47 351 available hydroxyl, chloride and bromide ions in the quasi-liquid layer substitute efficiently  
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49 352 to transform methyl iodide into methanol, methyl chloride and methyl bromide respectively.  
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51 353 These chemical reactions cannot be the determining factor for snowpack methyl iodide flux,  
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53 354 since living, non-irradiated sample fluxes were uniformly positive. The substitution reaction  
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55 355 may be an important component of the processes by which methyl iodide is removed post  
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3 356 irradiation, however the predicted reaction rates for methyl iodide substitution reactions are  
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5 357 lower than the observed snowpack removal rates.  
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8 358 Observed loss rates of methyl bromide in chambers were 12.5% over 2 hours in Signy  
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10 359 samples, and 10% over 2 hours in Svalbard. These equate to daily removal rates of >70%. If  
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12 360 we take seawater substitution reaction rates (King & Saltzman, 1997) as an extreme example  
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14 361 (temperature in snowpack is lower, and ionic concentration is higher in seawater) it is clear  
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16 362 that the observed degradation rates in snowpack are significantly higher than expected  
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18 363 through chemical reactions alone. For instance, we would expect approximately 10% of the  
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20 364 starting concentration of methyl bromide within the chamber to react over the course of a day  
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22 365 through substitution with hydroxyl and chloride ions and reactions with other available  
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24 366 organics (King & Saltzman, 1997). The room temperature, filtered/autoclaved seawater  
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26 367 chemical reaction rate measured in King and Saltzman (1997) is much smaller than the  
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28 368 observed reaction rate in Signy and Svalbard snowpack and the chemical reaction rate is  
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30 369 expected to diminish by a factor of four for each 10° C temperature drop.  
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34 370 The observed signal for methyl bromide is also greater than expected for microbial  
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36 371 consumption rates alone. Methyl bromide and methyl chloride are consumed by bacteria in  
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38 372 soils (Borodina *et al*, 2005; Redeker & Kalin, 2012). Fungal production may play a role in  
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40 373 net fluxes from terrestrial surfaces (Watling & Harper, 1998; Redeker *et al*, 2004). The  
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42 374 impact of archaea on methyl halide cycling is not yet established and they may play a role in  
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44 375 either methyl halide production or consumption within soils and snowpacks. In temperate  
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46 376 forest soils, with an estimated 0.1 billion microbial cells per cubic centimetre (Raynaud &  
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48 377 Nunan, 2014), methyl bromide is reported to be consumed at a rate of 5  $\mu\text{g m}^{-2} \text{day}^{-1}$   
49  
50 378 (Redeker & Kalin, 2012). If we assume that the density of microbial cells in snowpack is  
51  
52 379  $\sim 50,000 \text{ cc}^{-1}$  (Hell *et al*, 2013), then we would expect the microbial consumption rate for  
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54 380 methyl bromide in snowpack to be roughly equal to 2.5  $\text{ng m}^{-2} \text{day}^{-1}$ , assuming all else to be  
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3 381 equal. Observed rates of reaction within living control snowpack are roughly equivalent to  
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5 382 these estimates in Svalbard samples but exceed this estimate by an order of magnitude in  
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7 383 Signy snowpack.  
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10 384 When biological processes are impaired through irradiation the removal rate of methyl iodide  
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12 385 is significantly more rapid than that of methyl bromide, nearly 60% methyl iodide is removed  
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14 386 from the chamber headspace over 2 hours. This is equivalent to nearly complete (99.8%)  
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16 387 daily removal of methyl iodide from the surface snowpack. In non-irradiated snow pack we  
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18 388 see instead a significant enhancement of methyl iodide in the chamber headspace that cannot  
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20 389 be explained through (photo)chemical reactions. Biological explanations, however, remain  
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22 390 plausible. Cultures of marine microbes capable of producing methyl iodide do so at rates  
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24 391 between 2 and 900 fmol  $10^{10}$  cells<sup>-1</sup> day<sup>-1</sup> (Amachi *et al*, 2001). If we take the snowpack  
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26 392 beneath a square meter footprint to the depth of 0.5 meters (which equates to 500 litres of  
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28 393 snowpack) this would provide  $2.5 \times 10^{10}$  microbial cells. From this we might expect 0.7 to 25  
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30 394 ng m<sup>-2</sup> day<sup>-1</sup> of methyl iodide production, which is broadly similar to the fluxes observed in  
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32 395 Signy and Svalbard snowpack (Table 1). If irradiated samples represent chemical removal for  
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34 396 living control treatments, then microbial productivity would need to double in order to  
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36 397 generate the fluxes observed (Table 1).  
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41 398 While methyl bromide and methyl iodide fluxes were broadly consistent across both  
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43 399 sampling sites, methyl chloride and dimethyl sulphide fluxes were variable. There exist a  
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45 400 number of sources of variability within the sites selected; including snowpack and  
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47 401 methodology, site location relative to larger land masses, distance from the coast and height  
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49 402 above sea level, wind effects, annual UV intensity at ground level, as well as within-  
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51 403 community individual species' resistance to UV radiation.  
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3 404 Signy Island is a small island ( $\sim 19\text{km}^2$ ) which is part of a small island chain in the Southern  
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5 405 Ocean, itself only 90km long, and is found approximately 1000km distant from the tips of  
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7 406 both South America and the Antarctic peninsula. Svalbard ( $\sim 61,000\text{km}^2$ ) is located centrally  
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9 407 within the Greenland Sea, and is between 1000 and 1500km distant from Greenland, Iceland,  
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11 408 Norway, Sweden, Finland and Russia. Therefore, based upon location, the microbial  
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13 409 community found at Signy Island is more likely to be representative of oceanic microbes due  
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15 410 to the presence of the Antarctic circumpolar current whereas Svalbard snow and ice  
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17 411 communities are likely to have a larger terrestrial microbial component (Burrows *et al*, 2009).  
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20 412 Signy's sampling location, the Gourlay snowfield, is  $\sim 0.5\text{km}$  from the coast and 100m above  
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22 413 sea level while the sampling site at Svalbard, Larsbreen glacier, is  $\sim 7\text{km}$  from the coast and  
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24 414 600m above sea level. Hodson *et al* (2017) show how such differences in distance from the  
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26 415 coast can result in marked differences in snowpack microbial community composition and  
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28 416 resultant biogeochemical conditions. Orientation and placement of the glacier within the local  
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30 417 geological context will also play a role in modifying the snow, dust and sea salt deposition by  
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32 418 local winds. The resultant heterogeneity and variability in snowpack microorganism  
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34 419 communities is therefore a likely explanatory variable for the differences observed between  
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36 420 Signy and Svalbard, as well as the intra-site variability between replicates.  
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40 421 Local winds, as determined through local topography, bring aerosols for deposition but also  
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42 422 influence trace gas fluxes through purging the sub-surface of volatile metabolites and  
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44 423 producing quasi-advective flow in sub-surface snowpack pore spaces (Redeker *et al*, 2015).  
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46 424 We reduced the influence of wind by placing a 3m x 3m tarp over the chamber flux  
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48 425 measurement site but horizontal transport of material within the snowpack, driven by wind,  
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50 426 may have influenced our results and may be the source of some of the chamber-to-chamber  
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52 427 variability in the observed fluxes.  
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3 428 Local biology effects are also probable. Signy Island, and the Gourlay snowfield, are more  
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5 429 accessible to regionally important animal populations (seals and penguins in particular) and  
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7 430 they may have provided nutrients through faecal and urine deposits that enhance the activity  
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9 431 and modify the community of microorganisms within the snowpack (Hodson, 2006). Further  
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11 432 biological complications arise from the dispersed and spatially variable nature of the  
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13 433 biological community within the snowpacks, as observed in maritime Antarctic snow covers  
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15 434 by Fogg (1968) and Hodson *et al* (2017). Such variability, at spatial scales from centimetres  
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17 435 to kilometres, is well-known in other ecosystems. Microbial communities in terrestrial  
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19 436 ecosystems demonstrate substantial variability over all spatial scales, from centimetres to  
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21 437 kilometres (Raynaud & Nunan, 2014), leading to similar variations in microbial metabolisms  
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23 438 and metabolic outcomes that are detectable over similar spatial scales (Hartman &  
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25 439 Richardson, 2013).

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29 440 Antarctic ecosystems are exposed to greater UV radiation throughout the year, particularly  
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31 441 during the Antarctic spring during the period of maximum stratospheric ozone depletion. The  
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33 442 variable levels of resistance in archaea, algae and bacteria to irradiation, as observed in this  
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35 443 study and others (de Bakker *et al*, 2001; Jacobs *et al*, 2005), will likely lead to significant  
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37 444 variation in observed fluxes from irradiated snowpacks in Signy versus Svalbard, and  
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39 445 differences in snowpack temperature and local surface winds from chamber to chamber are  
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41 446 likely to enhance these differences (Hell *et al*, 2013; Larose *et al*, 2013).

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45 447 Using low concentration metabolites and taking precautions against wind and photochemistry  
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47 448 allows the unravelling of these small, variable biological signals from chemical and physical  
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49 449 processes with far greater sensitivity than is possible with other parameters such as CO<sub>2</sub>. We  
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51 450 calculate that, in an isolated environment, it would take ~50 to 100 years for the consumption  
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53 451 and production of methyl halides to cause a 1 ppm deviation in carbon dioxide concentration  
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55 452 within snowpack pore space. This is well below the detection limits for most analytical  
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3 453 measurements for carbon dioxide (Landwehr *et al*, 2014). This estimate, however, assumes  
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5 454 that all biologically-produced trace gases that are not consumed within the snowpack are  
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7 455 transferred into the glacial ice, and can be subsequently detected. Other potential metabolites  
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9 456 are available in ice and volatile forms within snowpack however (Price, 2000), and it is as yet  
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11 457 unclear how rapid the overall microbial metabolism in snowpack may be. These results  
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13 458 highlight the need of further studies to assess whether the gases produced by this found  
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15 459 biological activity are vertically transferred to the ice as the firn transforms into glacial ice.  
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18 460 The compounds described here have complex, often catalytic, chemistry with important  
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20 461 impacts on climate. Methyl chloride and methyl bromide trap solar energy more efficiently  
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22 462 than carbon dioxide, so biological removal and transformation of these compounds trades a  
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24 463 more effective greenhouse gas (MeX) for a less effective greenhouse gas (CO<sub>2</sub>). However,  
25  
26 464 methyl chloride and methyl bromide are both catalytically involved in ozone chemistry, so  
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28 465 reduction of these compounds in the lower atmosphere will lead to greater concentrations of  
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30 466 ozone, which itself is an effective greenhouse gas at these elevations. Production of methyl  
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32 467 iodide generates a short-lived, effective greenhouse gas which reacts rapidly to generate  
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34 468 iodide radicals which catalytically destroy ozone (more efficiently than chlorine or bromine  
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36 469 radicals), and which chemical products lead to aerosol nucleation. Both of these indirect  
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38 470 effects from methyl iodide release act to cool the planet (Table 3). Dimethyl sulphide is  
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40 471 widely recognized as the primary naturally produced organosulfur compound responsible for  
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42 472 non-sea salt sulfate aerosols, so removal of this through biological processes in snowpack  
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44 473 will act to warm the planet by reflecting less incoming sunlight.  
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49 474 Total impacts for any given compound are difficult to predict due to the often conflicting  
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51 475 nature of direct versus indirect radiative impacts (Table 3). Furthermore, a significant amount  
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53 476 of methyl halide consumption in snowpack will reduce the photochemically produced methyl  
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55 477 chloride and methyl bromide before it is mixed with overlying air, in a manner similar to the  
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3 478 reduction of methane efflux by methylotrophs in soils. Sub-snowpack soils will generate  
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5 479 significant amounts of methyl halides and these are also likely to be consumed *in situ* before  
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7 480 they can escape, especially in short-term coverage sites (winter snowpack). Snowpack in  
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9 481 direct contact with soil may act to consume methyl iodide as well (Swanson *et al*, 2005),  
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11 482 inverting the effects observed in soil-free snowpack. With these concerns noted, if we take  
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13 483 the estimated global area coverage of snow (~10% of the global surface area on average) and  
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15 484 apply our average living snowpack fluxes we find that approximately 1% of the annual  
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17 485 methyl bromide budget sink can be explained through snow-atmosphere biological processes.  
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19 486 Similarly, methyl chloride sinks are one half of 1%, and the production of methyl iodide  
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21 487 globally is enhanced to a similar degree. We propose that diminished snowpack may be, in a  
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23 488 small degree, responsible for slightly delaying the recovery of the ozone layer through a  
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25 489 reduction in methyl halide sinks.  
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29 490 Beyond climate and air quality impacts the demonstrated potential for microbes to metabolise  
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31 491 in this challenging environment has significant implications for xenobiology (expanding the  
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33 492 realms in which we might expect life to persist and reproduce), industry (through exploitation  
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35 493 of low nutrient, cold-tolerant metabolisms) and biogeochemistry (the developing fields of  
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37 494 Aerobiology and Cryosphere biology). In particular, however it requires a reconsideration of  
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39 495 the use of firm air to quantify pre-industrial levels of methyl halides (Aydin *et al*, 2004) and  
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41 496 dimethyl sulfide metabolism by-products (methane sulfonate: Saltzman *et al*, 2006; carbonyl  
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43 497 sulfide: Aydin *et al*, 2016). These measurements have not considered the impact of  
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45 498 photochemistry (Swanson *et al*, 2007) or biology (this study) on these long term storage  
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47 499 concentrations and until these impacts have been quantified and discounted the reported  
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49 500 values should be considered the net overall result of all possible biological, chemical and  
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51 501 physical effects.  
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3 503 7. Data, code and materials  
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5 504 The datasets supporting this article have been uploaded as part of the supplementary material.  
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11 506 8. Competing interests  
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13  
14 507 I/We have no competing interests.  
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19 509 9. Authors contributions  
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21  
22 510 KR participated in the design of the study, carried out components of the field work in  
23  
24 511 Svalbard, analysed trace gas samples, performed data analysis, and drafted the manuscript;  
25  
26 512 JPJC participated in the design of the study, performed all field and microbial work at Signy  
27  
28 513 Island, and aided in manuscript preparation; AA collected field samples and culturing data  
29  
30 514 from Svalbard; AH aided deployment of the field campaign in Signy and Svalbard and helped  
31  
32 515 draft the manuscript; DP participated in the design of the study, aided deployment of the field  
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34 516 campaign in Signy/Svalbard, aided in microbial culture analyses in Svalbard, participated in  
35  
36 517 data analysis and reviewed the manuscript. All authors gave final approval for publication.  
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10 528 12. References  
11  
12

13 529 Amachi, S., Kamagata, Y., Kanagawa, T., and Muramatsu, Y., 2001 “Bacteria mediate  
14  
15 530 methylation of iodine in marine and terrestrial environments” *Appl. Environ. Microbiol.* 67:  
16  
17 531 2718–2722, doi:10.1128/AEM.67.6.2718-2722.  
18

19  
20 532 Aydin, M., Saltzman, E. S., De Bruyn, W. J., Montzka, S. A., Butler, J. H., and Battle, M.,  
21  
22 533 2004 “Atmospheric variability of methyl chloride during the last 300 years from an Antarctic  
23  
24 534 ice core and firn air”, *Geophys. Res Lett.*, 31: L02109, doi:10.1029/2003GL018750  
25

26  
27 535 Aydin, M., Campbell, J. E., Fudge, T. J., Cuffey, K. M., Nicewonger, M. R., Verhulst, K. R.,  
28  
29 536 and Saltzman, E. S., 2016 “Changes in atmospheric carbonyl sulfide over the last  
30  
31 537 54,000 years inferred from measurements in Antarctic ice cores”, *J. Geophys. Res. Atmos.*,  
32  
33 538 121, 1943–1954, doi:10.1002/2015JD024235.  
34  
35

36  
37 539 Baowei, C., Guibin, J., Ruiqiang, Y., and Jiyan, L., 2006 “Methylation of tin(II) by methyl  
38  
39 540 iodide: influences of different environmental factors on the efficiency and reaction kinetics”,  
40  
41 541 *Appl Organometallic Chem.*, 20(3): 161–167. doi:10.1002/aoc.1032  
42

43  
44 542 Bargagli, Roberto, 2005: Ecological Studies 175: Antarctic Ecosystems – Environmental  
45  
46 543 Contamination, Climate Change and Human Impact, Springer-Verlag, Berlin, 395 pp  
47

48  
49 544 Bender, M., Sowers, T., and Brook, E., 1997 “Gases in ice cores”, *Proc Natl Acad Sci*, Aug  
50  
51 545 5; 94(16): 8343–8349.  
52

53  
54 546 Boden, R., Murrell, J.C., and Schäfer, H. 2011 “Dimethylsulfide is an energy source for the  
55  
56 547 heterotrophic marine bacterium *Sagittula stellata*.” *FEMS Microbiol Lett.* 322: 188-193  
57

- 1  
2  
3 548 Borodina, E., Cox, M. J., McDonald, I. R., and Murrell, J. C., 2005 “Use of DNA-stable  
4  
5 549 isotope probing and functional gene probes to investigate the diversity of methyl chloride-  
6  
7 550 utilizing bacteria in soil”, *Environmental Microbiology* 7(9): 1318–1328.  
8  
9  
10 551 Burrows, S. M., Butler, T., Jöckel, P., Tost, H., Kerkweg, A., Pöschl, U., and Lawrence, M.  
11  
12 552 G., 2009, “Bacteria in the global atmosphere – Part 2: Modeling of emissions and transport  
13  
14 553 between different ecosystems”, *Atmos. Chem. Phys.*, 9: 9281-9297, doi:10.5194/acp-9-9281-  
15  
16 554 2009  
17  
18  
19 555 Butler, J. H., 2000 “Better budgets for methyl halides?”, *Nature*, 403, 260 – 261.  
20  
21  
22 556 Carpenter, E. J., Lin, S., and Capone, D. G., 2000 “Bacterial Activity in South Pole Snow”,  
23  
24 557 *Appl Environ Microbiol.*, Oct; 66(10): 4514–4517.  
25  
26  
27 558 L.J. Carpenter and S. Reimann (Lead Authors), J.B. Burkholder, C. Clerbaux, B.D. Hall, R.  
28  
29 559 Hossaini, J.C. Laube, and S.A. Yvon-Lewis, Ozone-Depleting Substances (ODSs) and Other  
30  
31 560 Gases of Interest to the Montreal Protocol, Chapter 1 in Scientific Assessment of Ozone  
32  
33 561 Depletion: 2014, Global Ozone Research and Monitoring Project – Report No. 55, World  
34  
35 562 Meteorological Organization, Geneva, Switzerland, 2014.  
36  
37  
38 563 Chubukov, V., Gerosa, L., Kochanowski, K., and Sauer, U., 2014 “Coordination of microbial  
39  
40 564 metabolism”, *Nature Reviews Microbiology*, 12: 327–340.  
41  
42  
43 565 Ciais, P., C. Sabine, G. Bala, L. Bopp, V. Brovkin, J. Canadell, A. Chhabra, R. DeFries, J.  
44  
45 566 Galloway, M. Heimann, C. Jones, C. Le Quéré, R.B. Myneni, S. Piao and P. Thornton, 2013:  
46  
47 567 Carbon and Other Biogeochemical Cycles. In: *Climate Change 2013: The Physical Science*  
48  
49 568 Basis. Contribution of Working Group I to the Fifth Assessment Report of the  
50  
51 569 Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M.  
52  
53 570 Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)].  
54  
55 571 Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.  
56  
57  
58  
59  
60

- 1  
2  
3 572 de Bakker, N., van Beem, A., van de Staaij, J., Rozema, J., and Aerts, R., 2001 “Effects of  
4  
5 573 UV-B radiation on a charophycean alga, *Chara aspera*” *Plant Ecology*, 154: 237,  
6  
7 574 doi:10.1023/A:1012982429677  
8  
9  
10 575 Elliott, S., and F.S. Rowland, 1993 “Nucleophilic substitution rates and solubilities for  
11  
12 576 methyl halides in seawater”, *Geophys. Res. Lett.*, 20: 1043-1046. doi:10.1007/BF00694495  
13  
14  
15 577 Falkowski, P. G., Fenchel, T., and Delong, E. F., 2008 “The Microbial Engines That Drive  
16  
17 578 Earth’s Biogeochemical Cycles”, *Science*, 23 May, 320: 1034-1039. doi:  
18  
19 579 10.1126/science.1153213  
20  
21  
22 580 Fogg G. E., 1967 “Observations on the snow algae of the South Orkney Islands” *Phil. Trans.*  
23  
24 581 *Royal Soc.. London. B..* 252: 279—287.  
25  
26  
27 582 Fujimori, T., Yoneyama, Y., Taniai, G., Kurihara, M., Tamegai, H., and Hashimoto S., 2012  
28  
29 583 “Methyl halide production by cultures of marine proteobacteria *Erythrobacter* and  
30  
31 584 *Pseudomonas* and isolated bacteria from brackish water” *Limnol. Oceanogr.*, 57(1): 154–162.  
32  
33 585 doi:10.4319/lo.2012.57.1.0154  
34  
35  
36 586 Gorton, H. L. and Vogelmann, T. C., 2003, “Ultraviolet Radiation and the Snow Alga  
37  
38 587 *Chlamydomonas nivalis* (Bauer) Wille”. *Photochemistry and Photobiology*, 77: 608–615.  
39  
40 588 doi:10.1562/0031-8655(2003)0770608URATSA2.0.CO2  
41  
42  
43 589 Harding, T., Jungblut, A. D., Lovejoy, C., and Vincent, W. F., 2011 “Microbes in High  
44  
45 590 Arctic Snow and Implications for the Cold Biosphere”, *Appl Environ Microbiol.*, May  
46  
47 591 77(10): 3234–3243. doi: 10.1128/AEM.02611-10  
48  
49  
50 592 Hartman, W. H., and Richardson, C. J., 2013 “Differential Nutrient Limitation of Soil  
51  
52 593 Microbial Biomass and Metabolic Quotients (qCO<sub>2</sub>): Is There a Biological Stoichiometry of  
53  
54 594 Soil Microbes?”, *PLoS ONE*, 8(3): e57127; doi:10.1371/journal.pone.0057127.  
55  
56  
57  
58  
59  
60

- 1  
2  
3 595 Hell, K., Edwards, A., Zarsky, J., Podmirseg, S. M., Girdwood, S., Pachebat, J. A., Insam, H.,  
4  
5 596 and Sattler, B., 2013 “The dynamic bacterial communities of a melting High Arctic glacier  
6  
7 597 snowpack”, *The ISME Journal*, 7: 1814–1826; doi:10.1038/ismej.2013.51.  
8  
9  
10 598 Helmig, D., Apel, E., Blake, D., Ganzeveld, L., Lefer, B., Meinardi, S., & Swanson, A. 2009  
11  
12 599 “Release and Uptake of Volatile Inorganic and Organic Gases through the Snowpack at  
13  
14 600 Niwot Ridge, Colorado”, *Biogeochemistry*, 95(1), 167-183; doi:10.1007/s10533-009-9326-8.  
15  
16  
17 601 Herbold, C. W., Lee, C. K., Mc Donald, I. R., and Cary, C. S., 2014 “Evidence of global-  
18  
19 602 scale aeolian dispersal and endemism in isolated geothermal microbial communities of  
20  
21 603 Antarctica.” *Nat. Commun.* 5, 3875. doi: 10.1038/ncomms4875  
22  
23  
24 604 Hines, M.E., Crill, P.M., Varner, R.K., Talbot, R.W., Shorter, J.H., Kolb, C.E., and Harris,  
25  
26 605 R.C. 1998, “Rapid consumption of low concentrations of methyl bromide by soil bacteria”  
27  
28 606 *Appl Environ Microbiol* 64: 1864–1870.  
29  
30  
31 607 Hodson, A.J., 2006 “Biogeochemistry of snowmelt in an Antarctic glacial ecosystem.”,  
32  
33 608 *Water Resources Research*, 42, W11406, doi:10.1029/2005WR004311  
34  
35  
36 609 Hodson, A., Anesio, A. M., Tranter, M., Fountain, A., Osborn, M., Priscu, J., Laybourn-  
37  
38 610 Parry, J., and Sattler, B., 2008 “Glacial Ecosystems”, *Ecological Monographs*, 78(1): 41–67.  
39  
40 611 doi: 10.1890/07-0187.1  
41  
42  
43 612 Hodson, A.J., Nowak, A., Sabacka, M., Cook, J., Wharfe, E.S., Pearce, D.A., Convey, P. and  
44  
45 613 Vieira, G., 2017 “Microbial ecosystems influence the biogeochemical and optical properties  
46  
47 614 of maritime Antarctic snow.”, *JGR Biogeosciences*, 122, doi:10.1002/2016JG003694.  
48  
49  
50 615 Jacobs, J. L., Carroll, T. L., Sundin, G. W., 2005 “The role of pigmentation, ultraviolet  
51  
52 616 radiation tolerance, and leaf colonization strategies in the epiphytic survival of phyllosphere  
53  
54 617 bacteria”, *Microb Ecol.*, 49(1): 104-13. doi: 10.1007/s00248-003-1061-4  
55  
56  
57  
58  
59  
60

- 1  
2  
3 618 Keppler, F., R. Eiden, V. Niedan, J. Pracht, and Scholer, H. F., 2000, “Halocarbons produced  
4  
5 619 by natural oxidation processes during degradation of organic matter”, *Nature*, 403(6767), 298  
6  
7 620 – 301.  
8  
9  
10 621 King, D. B., and Saltzman, E. S., 1997 “Removal of methyl bromide in coastal seawater:  
11  
12 622 Chemical and biological rates”, *J. Geophys Res.*, 102(C8): 18,715-18,721. doi:  
13  
14 623 10.1029/97JC01214  
15  
16  
17 624 Larose, C., Dommergue, A., and Vogel, T. M., 2013 “The Dynamic Arctic Snow Pack: An  
18  
19 625 Unexplored Environment for Microbial Diversity and Activity”, *Biology (Basel)*, Mar 2(1):  
20  
21 626 317–330. doi: 10.3390/biology2010317.  
22  
23  
24 627 Landwehr, S., Miller, S. D., Smith, M. J., Saltzman, E. S., and Ward, B., 2014 “Analysis of  
25  
26 628 the PKT correction for direct CO<sub>2</sub> flux measurements over the ocean”, *Atmos. Chem. Phys.*,  
27  
28 629 14: 3361–3372. doi:10.5194/acp-14-3361-2014  
29  
30  
31 630 Manley, S. L., 2002, “Biochemical rationales for production of methyl halides”,  
32  
33 631 *Biogeochemistry*, 60, 163 – 180.  
34  
35  
36 632 Massman, W. J., and Frank, J. M., 2006, “Advective transport of CO<sub>2</sub> in permeable media  
37  
38 633 induced by atmospheric pressure fluctuations: 2. Observational evidence under snowpacks”,  
39  
40 634 *J. Geophys Res.*, 111: G03005, doi:10.1029/2006JG000164.  
41  
42  
43 635 McAnulla, C., McDonald, I.R., Murrell, J.C., 2001 “Methyl chloride utilising bacteria are  
44  
45 636 ubiquitous in the natural environment.” *FEMS Microbiology Letters*, 201: 151–155. doi:  
46  
47 637 <https://doi.org/10.1111/j.1574-6968.2001.tb10749.x>  
48  
49  
50 638 Michaud, L., Giudice, A. L., Mysara, M., Monsieurs, P., Raffa, C., Leys, N., Amalfitano, S.,  
51  
52 639 and Van Houdt, R., 2014 “Snow Surface Microbiome on the High Antarctic Plateau (DOME  
53  
54 640 C)”, *PLoS ONE* 9(8): e104505. doi:10.1371/journal.pone.0104505.  
55  
56  
57  
58  
59  
60

- 1  
2  
3 641 Nagatoshi, Y., and Nakamura, T., 2007, “Characterization of three halide methyltransferases  
4  
5 642 in *Arabidopsis thaliana*” *Plant Biotechnol.* 24, 503–506  
6  
7  
8 643 Pearce, D.A., Bridge, P.D., Hughes, K.A., Sattler, B., Psenner, R., and Russell, N.J., 2009  
9  
10 644 “Microorganisms in the atmosphere over Antarctica”, *FEMS Microbiol Ecol.*, Aug; 69(2):  
11  
12 645 143-57. doi: 10.1111/j.1574-6941.2009.00706.x.  
13  
14  
15 646 Pearce, D.A., Alekhina, I. A., Terauds, A., Wilmotte, A., Quesada, A., Edwards, A.,  
16  
17 647 Dommergue, A., Sattler, B., Adams, B. J., Magalhães, C., Chu, W-L., Lau, M. C. Y., Cary,  
18  
19 648 C., Smith, D. J., Wall, D. H., Eguren, G., Matcher, G., Bradley, J. A., de Vera, J-P., Elster, J,  
20  
21 649 Hughes, K. A., Cuthbertson, L., Benning, J. G., Gunde-Cimerman, N., Convey, P., Hong, S.  
22  
23 650 G., Pointing, S. B., Pellizari, V. H., and Vincent, W. F., 2016 “Aerobiology Over Antarctica  
24  
25 651 – A New Initiative for Atmospheric Ecology”, *Front. Microbiol.*, 7:16, doi:  
26  
27 652 10.3389/fmicb.2016.00016.  
28  
29  
30 653 P. B. Price, 2000 “A habitat for psychrophiles in deep Antarctic ice”, *PNAS*, 97(3): 1247-  
31  
32 654 1251. doi: 10.1073/pnas.97.3.1247  
33  
34  
35 655 P. B. Price, 2006 “Microbial life in glacial ice and implications for a cold origin of life”,  
36  
37 656 *FEMS Microbiol Ecol.*, 59: 217–231. doi: 10.1111/j.1574-6941.2006.00234.x  
38  
39  
40 657 Price, P. B. and Sowers, T., 2004 “Temperature dependence of metabolic rates for microbial  
41  
42 658 growth, maintenance, and survival”, *Proc. Natl. Acad. Sci. USA* 101, 4631–4636.  
43  
44  
45 659 Przybylak, Rajmund, 2003: *The Climate of the Arctic*, Kluwer Academic Publishers,  
46  
47 660 Norwell, MA, USA, 270 pp.  
48  
49  
50 661 Raynaud, X., and Nunan, N., 2014 “Spatial Ecology of Bacteria at the Microscale in Soil”,  
51  
52 662 *PLoS ONE*, 9(1): e87217. doi:10.1371/journal.pone.0087217.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 663 Redeker, K. R., Treseder, K. K., and Allen, M. F., 2004 “Ectomycorrhizal fungi: A new  
4  
5 664 source of atmospheric methyl halides?”, *Global Change Biology*, 10: 1009–1016, doi:  
6  
7 665 10.1111/j.1365-2486.2004.00782.x.  
8  
9  
10 666 Redeker, K. R., Manley, S. L., Walser, M., and Cicerone, R. J., 2004, “Physiological and  
11  
12 667 biochemical controls over methyl halide emissions from rice plants.” *Global Biogeochemical*  
13  
14 668 *Cycles*, 18, GB1007, doi: 10.1029/2003GB002042.  
15  
16  
17 669 Redeker, K. R. and Cicerone, R. J., 2004 “Environmental controls over methyl halide  
18  
19 670 emissions from rice paddies”, *Global Biogeochem Cycles*, 18: GB1027,  
20  
21 671 doi:10.1029/2003GB002092.  
22  
23  
24 672 Redeker, K. R., Davis, S., and Kalin, R. M., 2007 “Isotope values of atmospheric halocarbons  
25  
26 673 and hydrocarbons from Irish urban, rural, and marine locations”, *J. Geophys Res*, 112:  
27  
28 674 D16307, doi:10.1029/2006JD007784.  
29  
30  
31 675 Redeker, K. R., and Kalin, R. M., 2012 “Methyl chloride isotopic signatures from Irish forest  
32  
33 676 soils and a comparison between abiotic and biogenic methyl halide soil fluxes”, *Global*  
34  
35 677 *Change Biology* 18: 1453–1467, doi: 10.1111/j.1365-2486.2011.02600.x.  
36  
37  
38 678 Redeker, K. R., Baird, A. J., and Teh, Y. A., 2015 “Quantifying wind and pressure effects on  
39  
40 679 trace gas fluxes across the soil–atmosphere interface”, *Biogeosciences*, 12: 7423–7434.  
41  
42 680 doi:10.5194/bg-12-7423-2015  
43  
44  
45 681 Rhew R. C., Ostergaard, L., Saltzman, E. & Yanofsky, M., 2003 “Genetic control of methyl  
46  
47 682 halide production in Arabidopsis.” *Curr Biol* 13: 1809–1813.  
48  
49  
50 683 Røy, H., Kallmeyer, J., Adhikari, R. R., Pockalny, R., Jørgensen, B. B., and D’Hondt, S.,  
51  
52 684 2012 “Aerobic Microbial Respiration in 86-Million-Year-Old Deep-Sea Red Clay”, *Science*,  
53  
54 685 18 May 336: 922-925. doi: 10.1126/science.1219424  
55  
56  
57  
58  
59  
60



- 1  
2  
3 686 Saito, T., and Yokouchi, Y., 2006, “Diurnal variation in methyl halide emission rates from  
4  
5 687 tropical ferns”, *Atmos. Environ.*, 40, 2806 – 2811.  
6  
7  
8 688 Saltzman, E. S., Dioumaeva, I., and Finley, B. D., 2006, “Glacial/interglacial variations in  
9  
10 689 methanesulfonate (MSA) in the Siple Dome ice core, West Antarctica”, *Geophys. Res. Lett.*,  
11  
12 690 33, L11811, doi:10.1029/2005GL025629.  
13  
14  
15 691 Saltzman, E. S., Aydin, M., Tatum, C., and Williams, M. B., 2008 “2,000-year record of  
16  
17 692 atmospheric methyl bromide from a South Pole ice core”, *J. Geophys. Res.*, 113, D05304,  
18  
19 693 doi:10.1029/2007JD008919.  
20  
21  
22 694 Saltzman, E. S., Aydin, M., Williams, M. B., Verhulst, K. R., and Gun, B., 2009 “Methyl  
23  
24 695 chloride in a deep ice core from Siple Dome, Antarctica”, *Geophys. Res. Lett.*, 36(3), L03822,  
25  
26 696 doi:10.1029/2008GL036266  
27  
28  
29 697 Sattler, B. Puxbaum, H., and Psenner, R., 2001 “Bacterial growth in supercooled cloud  
30  
31 698 droplets”, *Geophys. Res. Lett.*, Jan 15 28(2): 239-242, doi: 10/1029/2000GL011684.  
32  
33  
34 699 Swanson, A. L., Lefer, B. L., Stroud, V., and Atlas, E., 2005 “Trace gas emissions through a  
35  
36 700 winter snowpack in the subalpine ecosystem at Niwot Ridge, Colorado”, *Geophys Res Lett.*,  
37  
38 701 32: L03805, doi:10.1029/2004GL021809.  
39  
40  
41 702 Swanson, A. L., Blake, N. J., Blake, D. R., Rowland, F. S., Dibb, J. E., Lefer, B. L., Atlas, E.,  
42  
43 703 2007 “Are methyl halides produced on all ice surfaces? Observations from snow-laden field  
44  
45 704 sites” *Atm. Env.*, 41(24): 5162-5177. DOI: 10.1016/j.atmosenv.2006.11.064.  
46  
47  
48 705 Takai, K., and Horikoshi, K., 2000 “Rapid Detection and Quantification of Members of the  
49  
50 706 Archaeal Community by Quantitative PCR Using Fluorogenic Probes”, *Appl. Environ.*  
51  
52 707 *Microbiol.* November 66(11): 5066-5072.  
53  
54  
55  
56  
57  
58  
59  
60



- 1  
2  
3 708 Tegtmeier, S., Krüger, K., Quack, B., Atlas, E., Blake, D. R., Boenisch, H., Engel, A.,  
4  
5 709 Hepach, H., Hossaini, R., Navarro, M. A., Raimund, S., Sala, S., Shi, Q., and Ziska, F., 2013,  
6  
7 710 “The contribution of oceanic methyl iodide to stratospheric iodine”, *Atmos. Chem. Phys.*, 13,  
8  
9 711 11869-11886, <https://doi.org/10.5194/acp-13-11869-2013>.  
10  
11  
12 712 Verhulst, K. R., Aydin, M. and Saltzman, E. S., 2013 “Methyl chloride variability in the  
13  
14 713 Taylor Dome ice core during the Holocene”, *J. Geophys. Res. Atmos.*, 118, 12,218–12,228,  
15  
16 714 doi:10.1002/2013JD020197  
17  
18  
19 715 Warren, S. G., and Hudson, S. R., 2003 “Bacterial Activity in South Pole Snow Is  
20  
21 716 Questionable”, *Appl Environ Microbiol.*, Oct 69(10): 6340–6341. doi:  
22  
23 717 10.1128/AEM.69.10.6340-6341.2003  
24  
25  
26 718 Watling, R., and Harper, D. B., 1998 “Chloromethane production by wood-rotting fungi and  
27  
28 719 an estimate of the global flux to the atmosphere”, *Mycol. Res.*, 102(7), 769-787, doi:  
29  
30 720 10.1017/S0953756298006157.  
31  
32  
33 721 Wiscombe, W.J. and Warren, S.G., 1980. “A model for the spectral albedo of snow”, I: Pure  
34  
35 722 snow. *J. Atm. Sci.*, 37(12), 2712-2733.  
36  
37  
38 723 Xu, L., Furtaw, M. D., Madsen, R. A., Garcia, R. L., Anderson, D. J., and McDermitt, D. K.,  
39  
40 724 2006 “On maintaining pressure equilibrium between a soil CO<sub>2</sub> flux chamber and the ambient  
41  
42 725 air”, *J. Geophys Res.*, 111: D08S10, doi:10.1029/2005JD006435.  
43  
44  
45 726  
46  
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48 727  
49  
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729 Table 1: Net fluxes of methyl halides and dimethyl sulphide from snowpack (in  $\text{ng m}^{-2} \text{day}^{-1}$   
 730  $\pm$  stderr). Samples taken from chambers before irradiation treatments and “non-irradiated”  
 731 post-irradiation treatments were combined, as they showed no statistical difference in  
 732 behaviour. Listed replicate numbers (in brackets) may not equal the maximum replicates  
 733 possible for “live” (9 in Signy, 12 in Svalbard) and irradiated (3 in Signy, 4 in Svalbard)  
 734 snowpack. When the trace gas of interest was not quantifiable (below detection limits), they  
 735 were not included in the replicate count. Negative fluxes indicate net biological or chemical  
 736 consumption within the snowpack whereas positive fluxes indicate the dominance of  
 737 production (biological) processes.

<b>Signy Island</b>					
		Methyl iodide	Methyl bromide	Methyl chloride	Dimethyl sulphide
	“Non-irradiated” control measurements	+31 $\pm$ 17 (n = 5)	-74 $\pm$ 47 (n = 7)	-380 $\pm$ 470 (n = 9)	0 $\pm$ 100 (n = 4)
	90% CI	+3 $\rightarrow$ +59	-150 $\rightarrow$ +3	-1200 $\rightarrow$ +390	-160 $\rightarrow$ +160
	UV Irradiated chambers	-290 $\pm$ 270 (n = 2)	-130 $\pm$ 50 (n = 3)	-1000 $\pm$ 1100 (n = 3)	70 $\pm$ 130 (n = 3)
	90% CI	-730 $\rightarrow$ +150	-210 $\rightarrow$ -48	-2800 $\rightarrow$ +810	-140 $\rightarrow$ +280
<b>Svalbard</b>					
		Methyl iodide	Methyl bromide	Methyl chloride	Dimethyl sulphide
	“Non-irradiated” control measurements	+9 $\pm$ 8 (n = 5)	-19 $\pm$ 20 (n = 12)	20 $\pm$ 600 (n = 12)	-80 $\pm$ 150 (n = 12)
	90% CI	-4 $\rightarrow$ +22	-52 $\rightarrow$ +14	-970 $\rightarrow$ +1000	-330 $\rightarrow$ +170
	UV Irradiated chambers	-30 $\pm$ 24 (n = 2)	-6 $\pm$ 20 (n = 4)	-280 $\pm$ 160 (n = 4)	-130 $\pm$ 30 (n = 4)
	90% CI	-69 $\rightarrow$ +9	-39 $\rightarrow$ +27	-540 $\rightarrow$ -20	-180 $\rightarrow$ -80

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742 Table 2: CTC-staining-based viable cell counts from inoculated microbial cultures. Samples  
 743 were obtained from Svalbard snowpack directly beneath paired control and irradiated  
 744 chambers. Numbers indicate viable cells per 50  $\mu\text{l}$  snowpack filtrate  $\pm$  one standard error.

	Control chamber	Irradiated chamber
1 <sup>st</sup> paired chambers	6.2 $\pm$ 0.9 (n = 12)	1.2 $\pm$ 0.4 (n = 12)
2 <sup>nd</sup> paired chambers	28.8 $\pm$ 4.6 (n = 12)	10.0 $\pm$ 1.3 (n = 12)
3 <sup>rd</sup> paired chambers	15.1 $\pm$ 1.3 (n = 8)	13.8 $\pm$ 1.2 (n = 8)

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749 Table 3: Snowpack activity, global direct and indirect effects of each trace gas measured  
 750 within this study.

	Dark processes	Net direct impact	Radiative impact of DI	Indirect effects (IE)	Radiative impact of IE (and type)
Methyl chloride	Biological and Chemical removal	MeCl → CO <sub>2</sub>	Cooling (long-wave)	-Enhanced local low atmosphere ozone concentration -Enhanced stratospheric ozone	Warming (long-wave) Warming (long wave)
Methyl bromide	Biological and Chemical removal	MeBr → CO <sub>2</sub>	Cooling (long-wave)	-Enhanced local low atmosphere ozone concentration -Enhanced stratospheric ozone	Warming (long-wave) Warming (long wave)
Methyl iodide	Biological production Chemical removal	DOC/POC → MeI	Warming (long wave)	-Reduction of local low atmosphere ozone concentration -Enhanced local aerosol concentration	Cooling (long-wave) Cooling (short-wave)
Dimethyl sulphide	Biological removal	DMS → CO <sub>2</sub>	Cooling (long-wave)	-Reduced local aerosol loading	Warming (short-wave)

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3 758 Figure 1: Site locations for Polar snowpack measurements. The Antarctic site was located at  
4 759 Signy Island (60.718 S, 45.632 W) on the Gourlay Snowfield and the Arctic site was  
5 760 Larsbreen glacier, near the settlement of Longyearbyen, Svalbard (78.223 N, 15.627 E).

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9 762 Figure 2: Snowpack trace gas-sampling methodology. Chamber installation (A); prior to  
10 763 tarpaulin cover the chamber base is visible at top, while the UV lamp is positioned vertically  
11 764 within the snow, 50cm from the chamber center. Trace gas sampling in process (B); both  
12 765 irradiated and non-irradiated chambers are visible, with tarpaulin cover outlined by wooden  
13 766 poles. Opaque chamber tops have been placed on top of the chamber bases shown in (A),  
14 767 with electropolished stainless steel canisters attached to Ascarite traps, in turn connected to  
15 768 glass-coated stainless steel lines connected to the chamber tops. The UV lamps (A) are  
16 769 oriented so that they face towards the irradiated chamber sub-surface snow while facing away  
17 770 from the non-irradiated control chamber.

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22 772 Figure 3: Comparisons of trace gas fluxes from “non-irradiated controls” (stippled, light grey  
23 773 columns) and irradiated snowpack (dark grey columns) (in  $\text{ng m}^{-2} \text{day}^{-1}$ ) and between Signy  
24 774 and Svalbard. Negative fluxes connote degradation or consumption within the snowpack  
25 775 while positive fluxes indicate production within the snowpack. Note change of scale between  
26 776 Signy and Svalbard fluxes. Error bars show  $\pm 1$  standard error.

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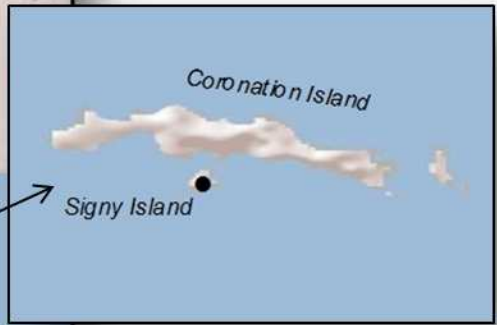
Svalbard



Spitsbergen

Larsbreen  
(Longyearbyen)

South Orkney  
• Islands



Coronation Island

Signy Island

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