

Stable bromine isotopic composition of atmospheric CH₃Br

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(Manuscript received 4 April 2013; in final form 20 August 2013)

ABSTRACT

Tropospheric methyl bromide (CH₃Br) is the largest source of bromine to the stratosphere and plays an important role in ozone depletion. Here, the first stable bromine isotope composition ($\delta^{81}\text{Br}$) of atmospheric CH₃Br is presented. The $\delta^{81}\text{Br}$ of higher concentration Stockholm samples and free air subarctic Abisko samples suggest a source/background value of $-0.04 \pm 0.28\text{‰}$ ranging up to $+1.75 \pm 0.12\text{‰}$. The Stockholm $\delta^{81}\text{Br}$ versus concentration relationship corresponds to an apparent isotope enrichment factor of $-4.7 \pm 3.7\text{‰}$, representing the combined reaction sink. This study demonstrates the scientific potential of atmospheric $\delta^{81}\text{Br}$ measurements, which in the future may be combined with other isotope systems in a top-down inverse approach to further understand key source and sink processes of methyl bromide.

Keywords: tropospheric methyl bromide, 81Br/79Br, bromine isotopes, halogens, Stordalen, Arctic, ICPMS

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1. Introduction

Methyl bromide (CH₃Br) is the main source of bromine to the stratosphere. There, Br can catalyse ozone loss. CH₃Br has an average tropospheric mixing ratio of about 8 ppt (parts per trillion) and an atmospheric lifetime of 0.8 years (Montzka et al., 2011). The Montreal Protocol has led to cuts in the anthropogenic production of methyl bromide and thus to a decrease of the atmospheric Br load (Montzka et al., 2003). However, CH₃Br is also produced by a broad range of natural sources, such as macroalgae (Laturnus, 2001), salt marshes (Rhew et al., 2000), rice paddies (Redeker et al., 2000) and peatlands (White et al., 2005), amongst others. Ocean uptake and decomposition by atmospheric OH radicals are currently believed to

greatly outweigh known sources. Thus, the atmospheric CH₃Br budget remains unbalanced, as either the magnitude of sinks is overestimated or sources are underestimated or have not yet been identified (Yvon-Lewis et al., 2009).

Stable isotope systematics may add further constraints to the global budget of CH₃Br. Stable carbon isotope ($\delta^{13}\text{C}$) analysis of CH₃Br has been reported for atmospheric free air (Bill et al., 2004), emissions from salt marshes (Bill et al., 2002) and industrially produced CH₃Br (McCauley et al., 1999). Atmospheric $\delta^{13}\text{C}$ signatures ($-43 \pm 2\text{‰}$ VPDB, Vienna Pee-Dee Belemnite) are indistinguishable from salt marsh emissions ($-43.1 \pm 1.5\text{‰}$ VPDB) and anthropogenic CH₃Br (-43‰ to -66.4‰ VPDB) at present limit the source-diagnostic value of $\delta^{13}\text{C}$ -CH₃Br used in isolation. Hence, for methyl bromide, further insights to the source and sink dynamics may require the use of the additional isotope systems of stable hydrogen and/or bromine.

We have recently developed a novel cryosampling method for collecting large volumes of CH₃Br from the

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atmosphere (Thornton et al., in press) and a sensitive analytical method for stable bromine isotopes in CH_3Br (Horst et al., 2011). Here, we report on the first exploratory application of $\delta^{81}\text{Br}$ to ambient CH_3Br in temperate-boreal suburban Stockholm, Sweden and a well-studied subarctic wetland/permafrost site near Abisko, Sweden.

2. Methodology

2.1. Sampling sites

Two studies were accomplished in 2011. The first sampling site was in Stordalen Mire, located in the Stordalen Nature Reserve 10 km east of Abisko in subarctic northern Sweden (68.354°N, 19.048°E, 359 m above sea level). Stordalen Mire is a 25 ha peat *palsa* plateau system with raised hummocks, uplifted by permafrost interspersed with wet fens (Callaghan et al., 2010). The area is surrounded by birch forest and bordered by lakes to the northwest and southeast. The annual mean temperature is 0.7°C and annual precipitation is about 300 mm. Due to decadal scale temperature increases, the permafrost underlying the peatland is currently thawing, which may have a major influence on the future release of CH_3Br and other gases (Christensen et al., 2004), although a recent study suggests that Stordalen is a net sink of CH_3Br based on field chamber measurements (Hardacre et al., 2009). Generally, air at this site, north of the Arctic Circle, can be expected to have less recent anthropogenic influences than air in Stockholm.

The second sampling site, Stockholm University, is located about 4 km north of central Stockholm in a semi-forested park-like area. The Stockholm area has numerous lakes and borders on the Baltic Sea; local air masses frequently come from mainland Europe. Our measurement site was located on a balcony on the fifth floor of the Geosciences building (59.366°N, 18.058°E), about 10 m above ground level (35 m above sea level).

2.2. Field sampling

We used a cryogenic collection system previously described by Thornton et al. (in press), capable of isolating CH_3Br from several cubic metres of air to yield the amounts necessary for Br isotope analysis (~ 20 ng Br/measurement) without causing any isotope fractionation. Samples of 2.7–4.8 m³ were taken from the free air as well as from soil air (only Stordalen Mire). Briefly, a KNF 145 diaphragm vacuum pump (KNF Neuberger GmbH, Freiburg, Germany) was used to pull air through a 1-L liquid-nitrogen-cooled cryotrap at a flow rate of 15 L/min. The air stream was dried using a Drierite® trap. After sampling, the cryotrap was heated to 50°C and the concentrated CH_3Br sample transferred to a 2.58-L stainless steel canister (OPSIS AB,

Furulund, Sweden) equipped with a bellows valve (Nupro Company, Willoughby, OH). During transfer to the canister, CO_2 was removed by using a 100-mL Carbosorb®-trap.

For the Abisko free air samples from Stordalen Mire, a stainless steel tube was used to sample air 3.5 m above ground. We collected air only under turbulent boundary layer (BL) conditions to minimise the potential influence of local soil exchange. The four atmospheric samples collected on 2–3 August 2011 are thus referred to as ‘Abisko free air’ samples. Additionally, we collected five samples of air from the ground at Stordalen on 3–5 August 2011. A polypropylene probe (5 cm i.d., perforated with 3 mm holes over the lowermost 15 cm length) was introduced into dry and uplifted soil areas (*palsa*) with the perforations starting at a depth of 15–20 cm. Frozen soil and high soil water content hampered deeper sampling. A 16 m² polyethylene sheet was used to cover the ground around the probe, with its edges ballasted to minimise intrusion of atmospheric air. The cylindrical volume of soil under the tarp (assuming the shortest distance from the probe to the edge) was more than 3.8 m³ for the observed unfrozen soil depth of at least 30 cm. Pore volumes can be up to 90% in peatland systems (e.g. Letts et al., 2000), hence the atmospheric influence on sampled air was considered to be small. The soil air was then pumped from the probe into the cryosampling system in the same manner as the atmospheric samples. These are referred to as ‘dry’ soil air samples. For two more samples, we covered moss-dominated damp areas (*sphagnum*) with the polyethylene sheet and collected from the air under it. The probe was again placed in the middle of the sheet but not pushed into the soil. In that way, we sampled air that was in contact with the soil surface and the plants only to test if there would be any isotopic shift in comparison to the atmospheric samples. These are referred to as ‘damp’ soil air samples.

Six samples of 4.8 m³ were collected on the Stockholm University campus between 29 September and 19 October 2011 (Table 1). They were sampled and stored in the same manner as the Abisko free air samples. We refer to these as ‘Stockholm free air’ samples.

2.3. Clean up and quantification

Although the cryosampler removes O_2 , N_2 , Ar and the majority of CO_2 , the remaining interfering components of the atmospheric matrix had to be removed before Br isotope analysis could be carried out. This was performed by using preparative gas chromatography on a packed column (Thornton et al., in press). Briefly, the sample gas was transferred from the canisters to a liquid-nitrogen-cooled pre-concentration trap and from there released onto the packed column by rapid heating. After separation the CH_3Br peak was heart-cut and transferred to a liquid-nitrogen-cooled stainless steel loop. Five percent of

Table 1. Results from concentration and isotope measurements

Sample ID	Field campaign	Sample date	$\delta^{81}\text{Br}$ [SMOB] (‰)	RSD ² (‰)	N	Mixing ratio ppt	SD ppt	Sample type	Sample volume (m ³)	BT region	BL height (m)
1	Abisko	2 August 2011	−0.01	0.12	2	10.4	2.3	Free air	4.5	1	583
2	Abisko	2 August 2011	−0.14	0.43	1	9.3	2.1	Free air	2.7	1	118
3	Abisko	3 August 2011	−0.04	0.43	1	14.1	3.2	Free air	3.4	1	497
4	Abisko	3 August 2011	0.48	0.43	1	5.4	1.2	Free air	3.6	1	185
5	Abisko	3 August 2011	−0.25	0.43	1	5.0	1.1	Dry soil	3.0	—	—
6	Abisko	4 August 2011	0.88	0.43	1	6.6	1.5	Dry soil	3.0	—	—
7	Abisko	4 August 2011	0.15	0.43	1	1.7	0.4	Dry soil	4.6	—	—
8 ¹	Abisko	5 August 2011	0.04	0.43	1	10.4	2.3	Damp soil	3.8	—	—
9	Abisko	5 August 2011	1.42	0.43	1	8.2	1.8	Damp soil	3.6	—	—
10	Stockholm	29 September 2011	−0.08	0.43	3	15.8	1.6	Free air	4.8	4	450
11	Stockholm	3 October 2011	1.17	0.43	1	12.6	1.4	Free air	4.8	2	527
12	Stockholm	4 October 2011	0.81	0.43	1	14.5	1.5	Free air	4.8	2	1476
13	Stockholm	5 October 2011	1.75	0.13	2	12.6	1.3	Free air	4.8	2	1016
14	Stockholm	18 October 2011	0.47	0.27	2	12.9	1.6	Free air	5.0	5	960
15	Stockholm	19 October 2011	−0.47	0.43	1	18.3	1.8	Free air	4.8	3	872

¹This sample was compromised by free air because of leakage around the sampler intake and is not included in statistical calculations.

²The standard deviations for isotope values based on one measurement were set to 0.43‰ (in italic), which was the largest value, found throughout this campaign for triple injections.

the sample was redirected over a custom-made split to the mass spectrometer for peak detection. After transfer, the loop was sealed with end caps and stored in a freezer at −20°C until further analysis.

The collected samples were quantified, before purification for isotope analyses, by injecting a 1-mL aliquot from the sample canisters on the gas chromatography (GC) system equipped with a DB-1 column and an on-column cryofocussing device (SMART CRYO, Weatherford Laboratories, Houston, TX). After heating the trap, the compounds were released onto the column and analysed with quadrupole mass spectrometry using m/z 94 for quantification. The GC was operated at isothermal conditions (80°C, 3 psi). For the Stockholm samples, the propagated error estimate (Table 1) comprised the analytical uncertainty (1σ) for four single analyses per sample being usually smaller than 5%. The cryosampling caused an additional uncertainty of 10%, which was calculated from four individual replicates. The Abisko samples were quantified only during the purification procedure and the analytical uncertainty was determined from two individual analyses (1σ between 5 and 10%).

For Br isotope determination, the collected amounts of CH_3Br would usually allow each sample to be analysed only once on the GC/MCICPMS system (Gas chromatography/multicollector inductively coupled plasma mass spectrometry), although some samples were large enough for multiple injections. Samples were extracted from the storage loops using a 10-mL gas-tight syringe (Hamilton, Reno, NV) and septa fitted at both ends of the loop. The injected samples were separated on a DB-624 column (Agilent, Santa Clara, CA) and introduced to the plasma.

Two detectors (Ax0 and H1) were aligned for the simultaneous detection of masses 79 and 81. The results were recorded into an Excel[®] sheet. This method yields a precision of <0.1‰ for Br amounts of 40 ng and <0.7‰ for 5 ng of Br. The Br-isotope method is described in detail in Horst et al. (2011).

2.4. Bromine isotope analysis

Isotope analysis was performed using gas-chromatography inductively coupled plasma multicollector mass spectrometry (GC/MCICPMS) as detailed by Horst et al. (2011). The Br isotope ratio ($R = {}^{81}\text{Br}/{}^{79}\text{Br}$) between the sample and a standard reference material is reported as follows:

$$\delta^{81}\text{Br} [\text{‰}] = (R_{\text{sample}}/R_{\text{reference}} - 1)$$

Bromine isotope data are conventionally referenced against standard mean ocean bromide (SMOB). Our internal laboratory standard is a commercially available CH_3Br purchased from Sigma Aldrich Sweden AB (Stockholm, Sweden; Catalog No. 65950), with a $\delta^{81}\text{Br}$ of $+0.12 \pm 0.02\text{‰}$ ($n=3$). Referencing versus SMOB was carried out as a commercial service by the Environmental Isotope Laboratory at the University of Waterloo (Canada) using continuous-flow isotope-ratio mass spectrometry (CF-irMS; Shouakar-Stash et al., 2005).

2.5. Back-trajectories

Five-day back-trajectories (BTs) were calculated using the NOAA HYSPLIT_4 model (Draxler and Hess, 1997;

Draxler, 1999) to identify the travel paths of the air masses 5 d before sampling and to calculate BL heights. Five single trajectories were calculated for every sample in time steps of 1 hour bracketing the whole sampling time of 4 hours. The starting height was set to 50 m for Abisko free air samples and to 100 m for the Stockholm samples.

3. Results and discussion

A total of 15 air samples were collected in this first study of the bromine isotope composition of ambient CH_3Br . In Abisko, the four free air samples taken at the beginning of August had an isotopic range of -0.14‰ to $+0.48\text{‰}$. The three dry soil air samples showed $\delta^{81}\text{Br}$ values of -0.25‰ to $+0.88\text{‰}$ while the two damp-soil air samples had isotopic values of $+0.04$ and $+1.42\text{‰}$. The six September–October atmospheric samples taken in Stockholm yielded $\delta^{81}\text{Br}$ that ranged from -0.47‰ to $+1.75\text{‰}$ SMOB (see Table 1). Generally, the $\delta^{81}\text{Br}$ of the Stockholm free air samples spanned over a wider range than the Abisko free air samples. The concentration for Stockholm was on average $14.4 \text{ ppt} \pm 2.1 \text{ ppt}$. The average concentration for Abisko samples was $9.8 \text{ ppt} \pm 3.1 \text{ ppt}$. The mixing ratios from damp-soil sites were

indistinguishable from free air samples ($9.3 \text{ ppt} \pm 1.1 \text{ ppt}$) while the dry soil samples showed lower mixing ratios of $4.5 \text{ ppt} \pm 2 \text{ ppt}$. This cryosampling procedure is optimised for the high-volume sampling and elaborate subsequent handling necessary for isotope analysis. Such high-volume sampling leads to relatively larger uncertainties in the CH_3Br quantification; the concentration measurements were primarily to provide a check for proper operation of the cryosampling system. However, they also give a rough idea of relative ambient CH_3Br concentrations.

3.1. Meteorological setting

BTs were assessed to investigate the near-term origin of the air masses reaching the sampling points (detailed in Figs. S1.1–S1.10, SI). Given an atmospheric lifetime for CH_3Br of about 0.8 years, BTs are likely only informative if they had passed recently over a major source region and if the air masses at that point were in contact with the BL as indicated with dotted ellipses in Fig. 1. Three samples (11–13), described by BT 2 in Fig. 1, have a similar origin. Air masses travelled from Greenland over the Atlantic Ocean to Stockholm touching the north of the British Isles.

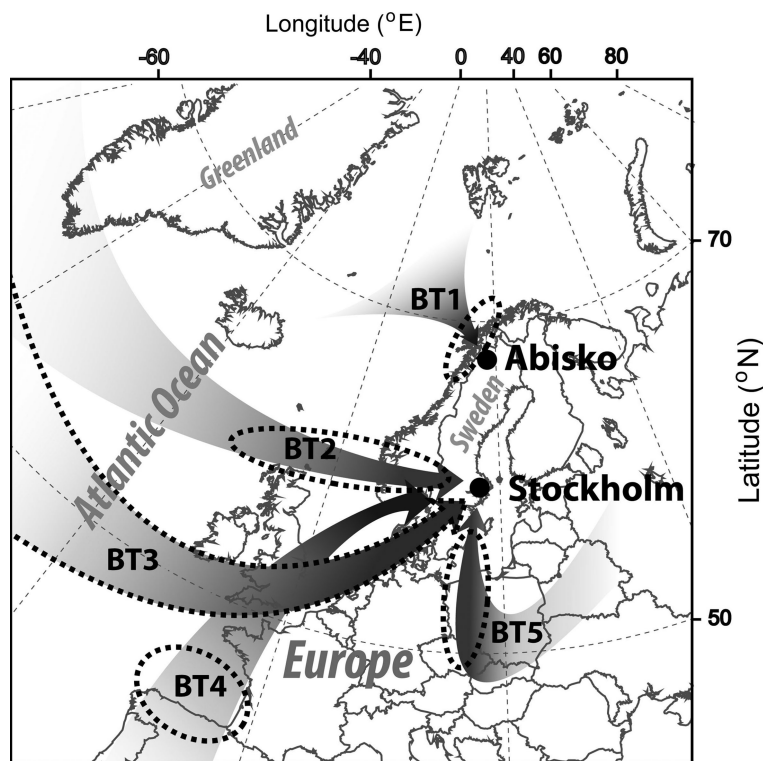


Fig. 1. Back trajectories (BTs) of sampled air, as determined by HYSPLIT4 model. The arrows are describing the path of the air mass BTs and the dotted ellipses are indicating the area where it was last in contact with the ground (i.e. in the boundary layer). The BT 3 contact region is described by the entire arrow (dotted margins).

Despite the same travel path, the residence time in the BL varied from 30 hours prior to arrival for sample 11 to 120 hours for sample 13. The recent air masses of sample 10 (BT 4) had their origin in the northwestern Iberian coastal region and were transported rapidly from there in the free atmosphere towards the north. Sample 14 air masses (BT 5) indicate a south to north travel path from Central Europe and contact with the mixed layer during the last 40 hours before arrival. Sample 15 (BT 3) was along the 5-d travel time in contact with the BL. It took a track over southern British Isles/northern Europe. This may have provided some opportunity for recent influence by anthropogenic sources to its CH_3Br load. However, given the long lifetime of CH_3Br (0.8 years) only large nearby sources could have altered the isotopic composition and mixing ratios. For the Abisko free air samples (BT 1), all of the BTs were similar. They travelled slowly over the Norwegian–Greenland Sea and crossed the Norwegian mountains during the preceding 5 d, staying generally within the BL below 500 m altitude.

3.2. Free air concentrations of methyl bromide

The free air mixing ratios for both sampling sites show higher values compared to the long-term middle/high-latitude background concentrations from the AGAGE station Mace Head, Ireland (7.3–7.6 ppt for August–October) located more than 2000 km away. Air masses sampled in Stockholm may have been affected by CH_3Br enrichment from recent sources. The Abisko free air samples were statistically indistinguishable from the average background values (p -value 0.4), suggesting that this subarctic site only received minor amounts from local CH_3Br sources.

In Abisko, additionally to free air samples, soil air samples were taken for dry (three samples) and damp (two samples) soil areas. One of the damp samples (No. 8) is not considered in the subsequent statistical evaluation because a leak around the probe caused sampling of large amounts of pure free air (> 50%), which did not undergo soil/plant exchange as intended. The soil air samples (dry+damp) showed a lower mean concentration of 5.4 ppt in comparison to mean free air mixing ratios (9.8 ppt) at the 90% confidence interval (Student's t -test, p -value 0.09) (Fig. 2 and Table 1). The lower soil air concentrations suggested a net soil uptake of CH_3Br , which might be due to biological processes and/or oxidation (e.g. Harper et al., 2000). This agrees with the findings of Hardacre et al. (2009) who investigated methyl halide exchange on the Stordalen Mire and observed these sites to be an overall weak CH_3Br sink ($-25 \text{ ng m}^{-2} \text{ h}^{-1}$) for all types of investigated soil (dry, damp and wet).

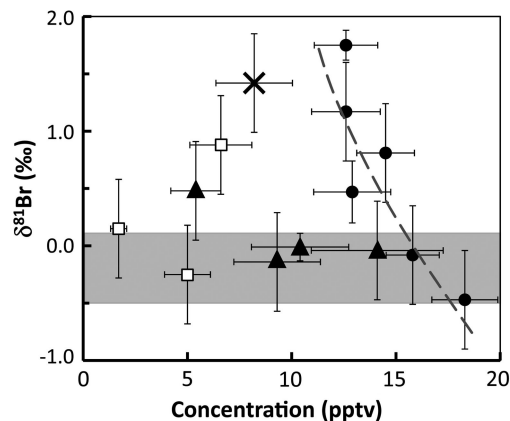


Fig. 2. Methyl bromide isotope composition as a function of concentration for Stockholm free air (filled circles), Abisko free air (open squares), Abisko dry soil air (filled triangles) and Abisko damp-soil air (cross). A logarithmic regression line (dashed, grey) shows the enrichment in $\delta^{81}\text{Br}$ as the CH_3Br concentration decreased in the Stockholm free air. The grey-shaded area indicates the lowest values found throughout both field campaigns and indicates a range of suggested background composition.

3.3. Free air bromine isotope composition

Several features indicative of CH_3Br sources and sinks were apparent in the $\delta^{81}\text{Br}$ - CH_3Br signals observed for both the subarctic soil and the free air at both sites. First, we note that the isotopically least-enriched (i.e. lowest $\delta^{81}\text{Br}$) values in each soil and free air system were in the range of -0.5 to $+0.1\text{‰}$ (Table 1 and Fig. 2), representing a putative $\delta^{81}\text{Br}$ source range. For instance, the mean of the Abisko free air samples and the two least isotopically enriched (or least degraded; see the following text) Stockholm free air samples yielded a $\delta^{81}\text{Br}$ value of $-0.04 \pm 0.24\text{‰}$. This field-data low range end-member value for $\delta^{81}\text{Br}$ were quite similar to $+0.12 \pm 0.05\text{‰}$ constrained for three commercially available CH_3Br (Horst et al., 2011) although, again, mixing with other sources and decomposition might have changed the initial $\delta^{81}\text{Br}$.

The Stockholm free air samples showed an inverse relationship between mixing ratios and $\delta^{81}\text{Br}$ values (correlation coefficient -0.86). This trend of enrichment in $\delta^{81}\text{Br}$ with decreasing concentrations may be consistent with a significant influence on the overall fate of atmospheric CH_3Br from sink processes that induce a kinetic isotope effect (KIE; corresponding to the isotope enrichment factor $\varepsilon = [1 - \text{KIE}] \times 1000\text{‰}$), for example the combined effects of atmospheric as well as biological processes (e.g. microbiological transhalogenation/degradation in soils) (Harper et al., 2000). While sinks in soils and the ocean are likely to be important (e.g. Yvon-Lewis et al., 2009), the rate-limiting step in those processes is the net partitioning between air – soil air and air–seawater; such

phase partitioning is unlikely to induce a substantial KIE (Huang et al., 1999). Laboratory experiments have demonstrated vapour-phase reactions of CH_3Cl with Cl and OH radicals inducing a strong KIE for stable carbon isotopes in the remaining methyl halide substrate pool (Gola et al., 2005). We derived an apparent isotope enrichment factor (ϵ_{app}) for the Stockholm free air $\delta^{81}\text{Br}$ - CH_3Br dataset (i.e. linear regression of the natural logarithm of the $\delta^{81}\text{Br} + 1000$ vs. the concentration expressed as the logarithm of the remaining fraction from the highest measured mixing ratio of the Stockholm campaign; see Fig. S2, SI) of $\epsilon_{\text{app}} = -4.7 \pm 3.7\text{‰}$ (95% confidence interval). This ϵ_{app} thus includes effects presumably by all removal reactions in the atmosphere, acting to enrich the $\delta^{81}\text{Br}$ of the decreasing CH_3Br pool. Removal due to partitioning into soil and the ocean decreases the mixing ratio presumably with a much smaller, if any, effect on the $\delta^{81}\text{Br}$ of the remaining atmospheric CH_3Br .

The reasons for ϵ_{app} value for $\delta^{81}\text{Br}$ - CH_3Br of $\sim -5\text{‰}$ being substantially lower than the previously noted ϵ for $\delta^{13}\text{C}$ - CH_3Cl of $-59 \pm 3.7\text{‰}$ (Gola et al., 2005), is likely to reflect dilution of the CH_3Br concentration by non-fractionating sink processes, the mass dependency (smaller shifts for heavier atoms) and the characteristics of the primary tropospheric isotope fractionating atmospheric sink (e.g. the reaction with the hydroxyl radical). A calculated indicative primary ϵ_{Br} for the abstraction of the bromine atom ($-0.25\text{‰} < \epsilon < 0\text{‰}$; see Supplementary Information 1 calculations) showed that the observed ϵ_{app} was likely too large to be consistent with just a mass-dependent isotope fractionation associated with the hydroxyl radical sink. The atmospheric hydroxyl radical reaction occurs at one of the hydrogen atoms, and would be expected to induce a secondary, if any, KIE for the bromine group in the CH_3Br molecule. Such secondary effects are generally smaller than the primary effects (Wolfsberg, 1960), although specific data for the present case are not available in the literature. Hence, the observed ϵ_{app} is more likely to reflect some unidentified reaction with a larger isotope effect. Photolysis with concomitant mass-independent isotope fractionation (Gao and Marcus, 2001; Laube et al., 2010) has the potential to cause unexpectedly large isotope effects but is not a major loss process in the troposphere. Large effects for chlorine isotopes have also been found for natural deposits of perchlorate, with measured $\delta^{37}\text{Cl}$ values in the range -15‰ to -10‰ (Bohlke et al., 2005). However, that KIE may result from the perchlorate source/formation rather than from sink processes.

Isotopic data may also be assessed with a two-component mixing model, where $\delta^{81}\text{Br}$ values are plotted versus the reciprocal concentrations (also known as a Keeling plot). The linear regression ($\delta^{81}\text{Br} = 70.1 \pm 19.8 \cdot 1/\text{conc.}$

-4.3 ± 1.4 , $R^2 = 0.76$; Fig. S3, SI) can be extrapolated and viewed as a mixing line between two end members: (i) a combined source signature ($\text{conc.} = \infty$); and (ii) background CH_3Br (8 ppt). For our observations, the corresponding extrapolated $\delta^{81}\text{Br}$ values would be: (i) $-4\text{‰} \pm 4\text{‰}$ (95% confidence interval) for the source; and (ii) $+4\text{‰} \pm 3\text{‰}$ for the background. Known anthropogenic source signatures ($+0.12\text{‰} \pm 0.05\text{‰}$) are in the higher estimated $\delta^{81}\text{Br}$ range and the Abisko free air samples, which might reflect background air because of their low concentration, were in the high end of these crude and extrapolated $\delta^{81}\text{Br}$ estimates of background values. The aforementioned degradation/sink effects may have had an impact on the slope of the mixing line (increasing the slope) and caused an under-/overestimation of source/ background $\delta^{81}\text{Br}$ values. This mixing plot can only provide a very vague view on conceivable combined source and sink signatures until further studies confirm or invalidate this estimate. Taken together, the Stockholm free air data indicate that the combination of sink processes induces an isotope effect in atmospheric CH_3Br and in combination with mixing effects cause distinct $\delta^{81}\text{Br}$ signatures.

The Abisko free air samples, which collected air with similar northern North Atlantic BTs, showed a relatively narrow $\delta^{81}\text{Br}$ range (0.62‰) and concentrations comparable to longer term background values at for example Mace Head. The mean $\delta^{81}\text{Br}$ was $+0.07 \pm 0.24\text{‰}$, which was nearly the same as for industrially-produced CH_3Br ($+0.12\text{‰}$) and close to the presumably least-degraded source signature for the Stockholm campaign. Thus, there was no statistically significant degradation or mixing trend (i.e. correlation) amongst these four delta values.

For the Abisko soil air samples, the Br isotopic signatures showed a wider spread ($+1.77\text{‰}$) than the free air sample values (Fig. 2). The soil air samples also tended on average to be more enriched ($+0.55\text{‰}$ SMOB), although this was not statistically significant (Student's t -test, p -value 0.28). This tendency in the isotopic composition may be the sum of all microbial/enzymatic degradation as well as production mechanisms. However, the data presented here only give a very first preliminary view on a conceivable bulk isotope effect due to processes in the soil. Isotope fractionation of the actual processes will be the subject of future studies. Taken together and consistent with the study by Hardacre et al. (2009), particularly the concentration trend suggests that there is a net uptake of CH_3Br by these subarctic soils.

4. Conclusions

This study contributes a baseline view of bromine isotopes in atmospheric methyl bromide. The results demonstrate $\delta^{81}\text{Br}$ isotope signatures from different atmospheric source

regions spanning a $\delta^{81}\text{Br}$ range from -0.47‰ to $+1.75\text{‰}$ SMOB. The $\delta^{81}\text{Br}$ versus concentration relationship indicates a mixing trend and isotope-fractionating processes acting as a sink of atmospheric CH_3Br . The field-based estimate of the apparent isotope enrichment factor suggests that there are additional sink processes inducing a higher ϵ than the hydroxyl radical reaction and uptake in soil and/or oceanic water. The coupled $\delta^{81}\text{Br}$ -concentration measurements in subarctic soil systems and free air support the conclusion of an earlier study that these wetlands act as a weak net sink for CH_3Br .

5. Acknowledgments

This research was funded as part of the HVOCSIA (Halogenated Volatile Organic Compound-Specific Isotope Analysis) project by the Swedish Research Council (VR grant 311-2007-8381). Örjan Gustafsson acknowledges financial support as an Academy Research Fellow from the Swedish Royal Academy of Sciences through a grant from the Knut and Alice Wallenberg Foundation. Brett Thornton acknowledges funding from the Bolin Centre for Climate Research. The authors thank Julia Steinbach for field assistance in collecting the Stordalen samples.

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