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Abiotic pathways for the formation of ozone-depleting and other trace gases in the polythermal glacier on Galindez Island, Maritime Antarctica

Abstract. The study aims to analyze trace gases in the composition of the polythermal glacier on Galindez Island in Maritime Antarctica (65°14′ S, 64°16′ W) and possible pathways for their abiotic formation in the snowpack and the superimposed or old cold ice. Polythermal glaciers are the most sensitive indicators of climate change. They are ideal for studying chemical post-depositional processes that alter the trace gas composition of the ice core air and the mechanisms involved under the current climate warming. This study is the first attempt to assess the concentration range of a large number of trace gases (except the previously studied O_2, N_2, Ar, and CO_2) in polythermal and temperate glaciers, which are widespread in Greenland, Svalbard, Canadian Arctic, Alaska, Alps, Andes, Tibet, Altai, and Maritime Antarctica. The ice porosity varies from 0.6% to (unique to superimposed ice) 7%. Qualitative analysis by GC-MS was done for more than 200 organic and inorganic trace gases. A quantitative analysis of 27 compounds was performed along the vertical profile of the glacier, including CO_2 and N_2O, freons, chlorine-based solvents that are prohibited by the Montreal Protocol, F-, Cl-, Br- and I-containing halocarbons, COS, CS_2, CH_3SCH_3, CH_3SSCH_3, and propene. Statistical data (mean, minimal, and maximum values) for ten horizontal levels of the glacier were calculated for their mixing ratios compared to background air. Most halocarbons, sulfur-containing compounds, and propene are characterized by high enrichment factors. This suggests that the species can be formed in the snowpack and firn of the glacier or its deep bubbling superimposed and old cold ice. Possible pathways of the gases formation include direct and indirect photochemical reactions of the triplet state dissolved organic matter (DOM) in snowpack without or in the presence of X^- ions (X = Cl, Br, I), dark redox reactions of Fe^{3+}, Mn^{4+}, Cu^{2+}, O_3, H_2O_2 or radicals HO_x (HO_x = HO·, HO_2·) with DOM in the presence of X^-, reactions of HO_X with DOM (with the participation of HO_x, H_2O_2 or O_3), free radical reactions with alkenes, alkynes, and alkyl radicals, and miscellaneous reactions of methylmethionine and/or S-containing peptides.

Keywords: firn, halocarbons, hydrocarbons, S-containing peptides, snowpack, superimposed ice

1 Introduction

Firn and ice hold air entrapped in the past. Analysis of this air enabled to study the change of main greenhouse gases, such as CO_2 (Petit et al., 1999; Lüthi et al., 2008), CH_4 (Brook et al., 1996), and N_2O (Sowers et al., 2003) during industrial and pre-industrial periods. However, the cores were recovered from cold sites that experience little or no melting, i.e., in the central regions of the large ice sheets of Antarctica and Greenland. Thus, it is necessary to consider the atmospheric chemistry data available from those glaciers where summer melting is significant. Fortunately, the ice core records are also available from polythermal glaciers (Arctic (Koerner & Fisher, 1990), the Andes, Africa (Mt. Kilimanjaro), and Central Asia (Thompson, 2000)) that experience moderate melt.

Fowler and Larson (1978) were the first who proposed the term polythermal glacier, which consists of both temperate ice (i.e., ice at the melting point) and old cold ice (i.e., ice below the melting point). They are the most available indicators of climate change and chemical post-depositional processes that alter the trace gas composition of the ice core air and the mechanisms involved under the current climate warming. However, the original composition of firn air and ice core bubbles of glacier can be changed by meltwater.

The meltwater in polythermal glaciers can percolate through the firn layers and the solution of the chemicals can be enriched in the firn layers if the temperatures are low for refreezing or at the impermeable ice layers. Such a process may even increase with the number of freeze-thaw cycles (Davis, 1991). Studying these glaciers would significantly extend the areas of the world accessible for climate and atmospheric chemistry research.

The atmosphere above West Antarctica is warming at 0.14 °C decade^{-1}, and over the Western Antarctic Peninsula (WAP) at 0.4 °C decade^{-1}; the trend is stronger than anywhere else in the world (Vaughan et al., 2003; Turner et al., 2005; Vaughan, 2006; Steig et al., 2009). One of the strongest trends was detected at the Ukrainian Antarctic Akademik Vernadsky station (formerly the UK British Antarctic Survey station Faraday): 0.56 °C decade^{-1} (1951—2000), especially during winter seasons in the 1990s. Since then, the trend seems to have plateaued or decreased (Turner et al., 2005; Chapman & Walsh, 2007). Of the 244 marine glacier fronts on the Antarctic Peninsula, 87% are retreating (Cook et al., 2005). The mass balance of the AP is negative, with a loss of ~38.1 Gt yr^{-1}, mostly in the central and northern regions (~ −28.6 Gt yr^{-1}) (Chen et al., 2009). The AP has greater similarity to subpolar glacial systems (e.g., coastal Greenland, Svalbard, Patagonia, and Alaska) known to be more sensitive to atmospheric warming than to the cold ice sheets over the rest of the continent.

The Argentine Islands are located between 65°12′ S and 65°16′ S and 64°11′ W and 64°21′ W ~8 km from the Graham Land's coast. From observations at the islands during 1934—1937, Fleming (1940) believed that the ablation of ice caps far exceeded accumulation and that the ice caps were ephemeral features and would quickly disappear. Glaciological studies were carried out by Roe from 1958 to 1960 (Thomas, 1963) on Galindez Island (65°14′ S, 64°16′ W); he found the formation of superimposed ice to be important in maintaining the ice caps, even during a warm summer. Thomas (1963) conducted more in-depth glaciological observations from 1960 to 1962. He showed that over a few years, the budget state of the island was one of equilibrium with minor oscillations in surface level. Sadler (1968) showed that ablation removed 66% of the gross accumulation and that 22% of this resulted from calving at the ice cliffs. Thomas (1963) and Sadler (1968) suggest a relict nature for the ice cap because the very low elevation should not support the ice cover present. From the observations, the ice cap lies exclusively below the saturation line, and the facies present are soaked, superimposed ice, and ablation. As the initial volume of the glacier (2002) was 2 038 367 m^3 and the volume in 2019 was 1 750 317 m^3, the total loss of the initial volume (2002—2019) was 14% (Cisak et al., 2008; Tretyak et al., 2016; Karušs et al., 2019). According to Karušs et al. (2019), the maximum ice thickness of the glacier is 35 m. The glacier is thus related to typical polythermal glaciers, which are depleted under the action of present-day climate change in the AP region.

When glacier ice is formed by cold-snow compaction, 3 to 10% of air volumes are incorporated as bubbles into the ice, and high polar glaciers might give information about atmospheric composition when the ice was formed (Coachman et al., 1956). This condition is changed, however, if melting occurs. The components dissolve in proportions different from those present in the atmosphere. While O_2 composes 20.9% of the air, it becomes 34.9% when air dissolves in ice-cold water. Likewise, Ar and CO_2, which are 0.9% and 0.03% in air, respectively, become 1.9% and 1.8% of the air dissolved in water (Scholander et al., 1961). Therefore, if air-equilibrated melt water seeps through the snow and freezes, the dissolved gases separate and enrich any entrapped air with CO_2, Ar, and O_2. In polythermal glaciers, the composition of trapped gases may be altered due to the different solubilities of the gases in meltwater. The gases in glaciers subjected to partial melting were preferentially depleted in order of their solubilities: $CO_2 > Ar > O_2 > N_2$. Alder et al. (1969) presented two quantitative models (*bulk process* and *Rayleigh process*) consistent with the N_2, Ar, and O_2 variations they observed. Thus, depending on the temperature in the glacier, one can expect either an enrichment of trace gases in the firn air or air bubbles in the ice as the temperature decreases and water freezes, or a significant decrease in their concentration due to their dissolution and leaching from the glacier with melt water.

The firn air and ice cores have been used to examine the atmospheric variability of less abundant trace gases such as CH_3Cl, CH_3Br, CH_3I and COS (Butler et al., 1999; Sturges et al., 2001a, b; Montzka et al., 2004; Trudinger et al., 2004; Saito et al., 2007; Williams et al., 2007; Saltzman et al., 2008; Aydin et al., 2008). The measurements of trace gases in air trapped in polar firn from Greenland and Antarctica show natural sources of chlorofluorocarbons, halons, persistent chlorocarbon solvents, and SF_6 in the atmosphere to be minimal or non-existent (Butler et al., 1999). CH_3Br concentrations at the top of the firn air profiles at the two Antarctic sites are 20% higher than at the bottom. More disturbing, however, are the samples from seasonally warm and coastally influenced Greenland site (Tunu): the CH_3Br concentration reaches mixing ratios of nearly 50 pptv at the firn-ice transition. This enrichment at depth is not an artifact of analysis, storage or sample collection. Concentrations of CH_2Br_2 and CH_3I also increased at depth, although the anomalies were smaller than for CH_3Br, and the abiotic chemical transformation cannot be ruled out. Sturges et al. (2001a) measured brominated, bromochlorinated, and iodinated methanes in air extracted from deep firn at three polar locations (two Antarctic and one Arctic) and showed that the Arctic firn also contained extremely high levels of CH_3Br and numerous other organic gases, evidently produced *in situ*. Carpenter et al. (2005) performed observations of CH_2I_2, CH_2IBr, and CH_2ICl in Arctic air and snowpack, as well as other volatile organohalogens (VOXs), including $CHBr_3$. The VOXs in snowpack were present at the highest levels yet reported in the air. Swanson et al. (2002) showed significantly enhanced concentrations of several trace gases in the snowpack (firn) pore air relative to the atmosphere at Summit, Greenland. The alkenes, VOXs, and alkyl nitrates are typically 2–10 times higher in concentration within the snow air than in the ambient air above the snow.

Swanson et al. (2007) compared two high-latitude locations (Summit, Greenland, and the South Pole) and two mid-latitude ones (northern Michigan and Niwot Ridge, the USA). At each site, CH_3I and C_2H_5I were more enriched within the interstitial air near the snow surface than in the boundary layer air. Except for the Niwot Ridge, CH_3Br was released from surface snow to the atmosphere. The methyl halide mixing ratios in firn air were significantly greater at the Summit than at the South Pole, with the Summit showing a strong diurnal cycle in the production of VOXs that was well correlated with actinic radiation and firn temperature. Jacobi et al. (2004) performed measurements of trace gases in air filtered through the pore spaces of the surface snowpack at Summit, Greenland. The firn air concentrations of NO, NO_2, HONO, HCHO, HCOOH, and CH_3COOH (but not HNO_3 and H_2O_2) were enhanced compared to the atmospheric boundary layer above the snow. The differences were highest during the day hours and lowest during nighttime. Kos et al. (2014) measured halogenated, aromatic, and oxygenated volatile organic compounds (VOCs) in snowpack in Alert, Canada. Maximum concentrations in snow were 39 μg L^{-1} (styrene). Snow profiles showed an enrichment of most VOCs close to the surface. Maximum VOC concentrations were up to 1.3 μg L^{-1} (acetophenone). Bromoform in frost flowers averaged 0.19 μg L^{-1}, indicating the potential to contribute to bromine generation. Abrahamsson et al. (2018) measured bromocarbons in sea ice, snow, and air during the Antarctic winter. They found an unexpected new source of organic bromine in the atmosphere during periods of no sunlight. The Antarctic winter sea ice provides ten times more bromocarbons to the atmosphere than the Southern Ocean waters and much more than summer sea ice. In the ice core record from the remote sub-Antarctic Island Bouvet (3 °E, 54 °S), it was quantified the presence of many organic compounds and chemicals more commonly measured in ice cores (King et al., 2019). Chloride, bromide, nitrate, sulfate, potassium, calcium, magnesium, ammonium, methanesulfonic acid (MSA), oxalate, formate, acetate, oleic acid, D-malic acid, pimelic acid, meso-erythritol, and β-nocaryophyllonic acid were all detected in significant concentrations in the core.

The above observations of trace inorganic and organic volatile compounds, in higher than usual amounts in the bottom layers of ice cores, firn air, and in snowpack in polar regions with moderately warm conditions, can be evidence of formation of the species as a result of the abiotic or biotic transformations of their precursors in such media. These compounds can then be concentrated in deeper layers of the glaciers during their transport with infiltration water and the repetition of freeze-thaw cycles in the glaciers in moderately warm regions of coastal Antarctica (Bazylevska & Bogillo, 2003; Bogillo et al., 2003). An increase in the intensity of iceberg calving from outlet and shelf glaciers of coastal Antarctica and an increase in the rate of glacier ablation with an increase in temperature in these regions can enhance the emission of these substances into the atmospheric boundary layer and coastal surface waters.

This paper presents the results of analyzing trace gases in the composition of the polythermal glacier on Galindez Island in Maritime Antarctica. It considers possible pathways for their abiotic formation in the snowpack and the superimposed or old cold ice. Preliminary results of the study for the trace gases in the upper and bottom layers of the glacier only were reported in (Bogillo et al., 2003). However, the applied approach for estimating atmospheric mixing ratios for the gases with Xe, possessing relatively high solubility in water, as a measure of relative air amount in the ice sample, was more appropriate for high polar glaciers than for the superimposed ice in polythermal glaciers. Also, our choice of a standard gas such as CO_2 could have been unfortunate. This gas is the final product of numerous abiotic and biotic organic matter decomposition processes of in oxic conditions. Therefore, its concentration in ice samples can exceed the atmospheric concentration due to its dissolution and refreezing of meltwater and the dissolved organic matter (DOM) fate following the photochemical and dark redox reactions in the snow and ice (Jaworowski, 1994).

2 Materials and methods

Ice was sampled in February—March 1998 on the ice cliff of the main glacier (Galindez Island, Argentine Islands, West Maritime Antarctica) 40 m above sea level. The procedure included the sampling of ice blocks for 9 levels of sloping glacier from levelling holes (horizontal ice tunnels) at 1 to 2 m from the vertical outer wall of the glacier, using a chain saw to cut out large blocks of solid ice (40 × 40 × 30 cm). The sample from the top of the glacier was taken using a chain saw to cut out the ice block from the vertical borehole (2 m) on the plateau of the upper part of the glacier at ~2 m from the outer wall. The surface of all walls of the selected samples was thoroughly cleaned with a metal scraper (up to 3 cm); they were packed in plastic containers, sealed, and kept in a freezer at the Akademik Vernadsky station. Their transportation to Odesa and further along the route Odesa — Kyiv — Frankfurt on Main — Katlenburg — Lindau was carried out, respectively, by the RV *Ernest Krenkel* and cars at T < −10 °C.

The extraction and cryogenic concentration of trace gases in the ice samples and their analysis by gas chromatography-mass spectrometry were carried out under the direction of Dr. Reinhardt Borchers in his laboratory in the former Max-Planck Institute for Aeronomy, Katlenburg-Lindau, Germany (Max-Planck Institute for Solar System Research after June 2002). Ice samples were stored in sealed containers (high-density polyethylene) in a Liebherr freezer at −25 °C. Before analysis, ice blocks were cleaned by cutting ice layers 4—5 cm thick from all walls with a special steel saw. Up to approximately 2.5 liters of crushed ice sample was taken for analysis. The analyzed part of the sample was placed in a cylindrical glass vessel with a capacity of more than 3 liters, equipped with a steel lid with pipes and valves. The lid was sealed with steel clips and an intermediate O-shaped silicone rubber gasket.

In the initial experiments, a wet extraction procedure (repeated melting of ice samples from −20 °C to 5 °C and their subsequent freezing under vacuum) was used for an ice sample from the upper layer of the glacier. This procedure continued for almost 10 hours. Volatile compounds released from the walls of the sample during the warming cycles were collected using a vacuum pump. The control of volatile impurities adsorbed on the outer walls of the ice sample was carried out by gas chromatography with a mass spectrometric detector (GC-MS: Varian 3300/Saturn 4D).

Due to the possible emission of some gases (COS, hydrocarbons, organosilicon compounds, etc.) from the ring used for sealing under the lid of the glass vessel, in further experiments, this vessel was replaced by a steel one. The connection of the vessel with a steel top cover was carried out without silicone rubber. This improved the quality of further GC-MS analysis. The procedure of repeated melting and freezing of ice samples described above was replaced by continuous melting of samples from −25 °C to 0 °C for six or more hours.

During the melting process, analysis of desorbing gases was periodically performed. This change in the procedure was due to the high adsorption and dissolution of the trace gases in thin water films from the air falling on the outer walls of ice samples during their preparation and operations in the laboratory. The level of freons produced after 1931 (CFC-11, CFC-12, and HCFC-22) in the air released during the melting of samples was used as an indicator of their contamination from modern air. Full gas extraction by helium and analysis were performed only after establishing a constant minimum signal of these compounds in the mass spectra. The average amount of air extracted from ice samples ranged from 10 to 30 cm^3 per kilogram of solid sample.

Before the analysis, the carrier gas (ultrapure He) passed through the sample vessel and a short trap filled with a water vapor absorber (dry magnesium perchlorate) at a constant flow rate. After this trap, the gas containing extractable gases from the ice fell into a steel concentration loop (0.7 ml) filled with glass beads and immersed in a Dewar vessel filled with liquid nitrogen at −196 °C. After the most volatile gases (helium, etc.) were pumped out, this loop was heated to 80 °C in a desorber filled with boiling water, and its contents were transferred by the carrier gas to the next small empty focusing loop placed in a Dewar vessel at −196 °C. The sample was injected into the gas chromatograph by rapidly heating this loop in the next desorber.

Chromatographic separation was done on a capillary column filled with OV-101 silicone stationary phase (60 m × 0.32 mm, film thickness 1 μm) using the following temperature program: initial temperature −60 °C, rate of its increase from 10 °C min^{-1} to 150 °C. MS analysis of individual peaks in the chromatogram was performed in the scanning range of 48—200 amu. They were identified by the most characteristic ion of the fragment for compounds and based on the ratio between the number of scan cycles (directly proportional to the retention time of the gas, τ_R) and the gas's boiling point at a given temperature program.

Calibration for CH_3I, C_2H_5I, CS_2, CH_3SCH_3, CH_3SSCH_3, and COS was performed by threefold dilutions of standard compounds (Aldrich) in artificial air prepared in the laboratory. For quantitative analysis of other compounds, the intensities of their characteristic peaks in the mass spectra were compared with those known for these compounds in a calibrated air standard (Max Planck Institute for Chemistry, Mainz, Germany, 1997) under the same chromatographic conditions.

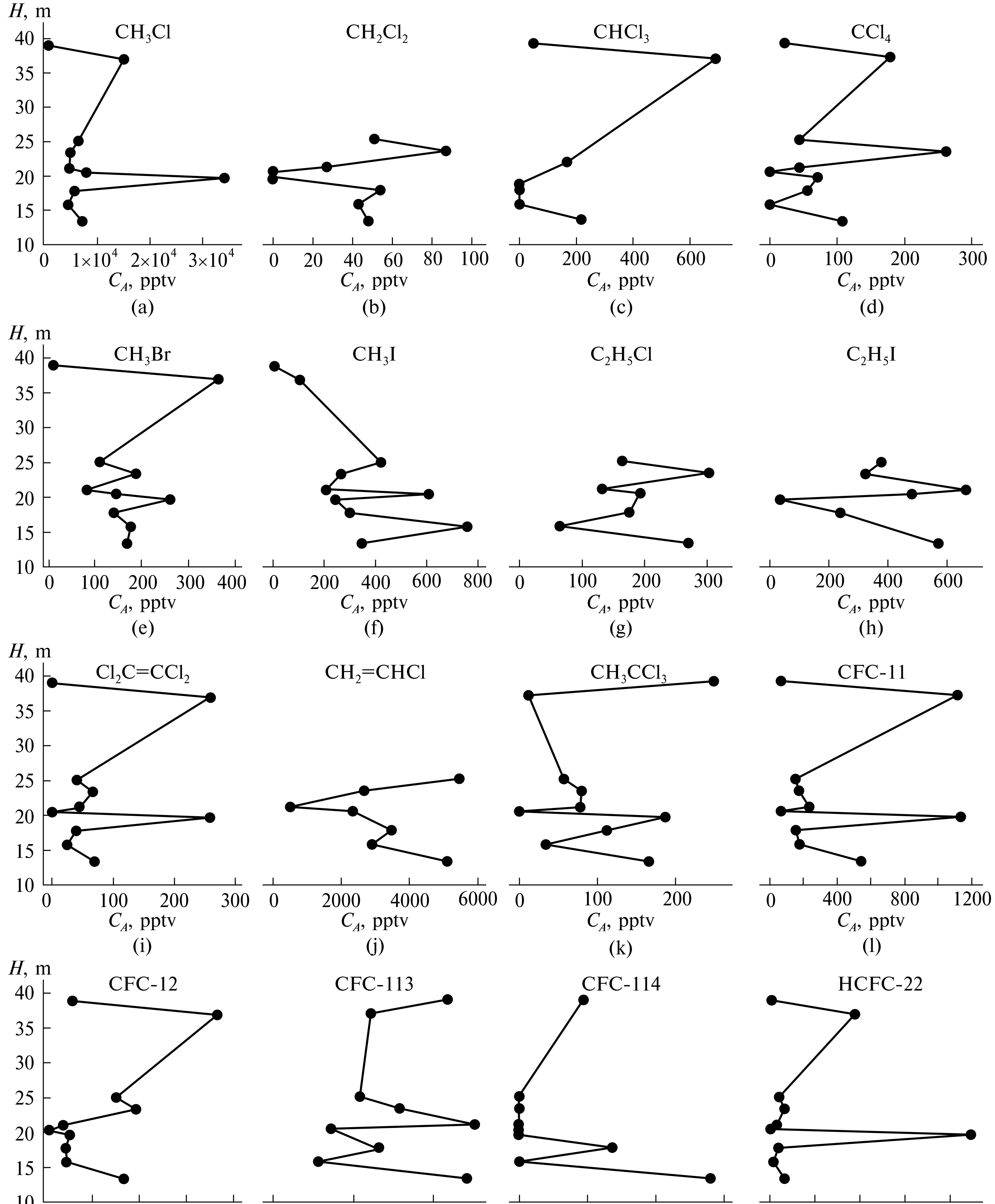
In subsequent calculations of atmospheric mixing ratios of the gases with respect to air, xenon (^{136}Xe isotope in the mass spectra) was used as a standard. It was assumed that the current atmospheric mixing ratio for this gas (7.1 ppbv) in the coastal Antarctic atmosphere has not changed over the past 4 000 years, and its concentration in ice samples is proportional to the total air concentration from the samples studied. Therefore, to calculate the enrichment factor for the gases in ice samples, we used data on the relative concentration of xenon, atmospheric mixing ratios of gases in calibration mixtures, and the peak intensities in the mass spectra of gases in ice samples. Xe, CO_2, and CF_4 analysis in air from ice samples was performed on a gas chromatograph with a GC ParaPlot capillary column and a Baltzers quadrupole MS detector. The following temperature program was used: the initial temperature was −20 °C, the heating rate was 15 °C min^{-1}, and the final temperature was 155 °C. N_2O analysis was performed by GC with a helium discharge detector under isothermal conditions at 30 °C on a GC ParaPlot Q column. The relative error in determining the atmospheric mixing ratios using these methods was 15–20%.

Ice cores from boreholes at the top of the glacier were obtained in February 2019 with a thermal core drill. Measurements of electrical conductivity and *pH* values of melt from the ice samples of the cores (the core overall length was 400 cm, and the length of each ice sample was 10 cm) were performed with conductometers EZDO (KUSAM-MECO, India), SX-650 (UK) and pH-meter Hanna pH 211 (UK). The density of the ice samples was determined using the volumetric and gravimetric methods.

3 Results

More than 200 VOCs have been identified in the upper layers of the glacier, including saturated and unsaturated hydrocarbons, alcohols, phenols, aldehydes, ketones, carboxylic acids, ethers and esters, heterocyclic compounds, F-, Cl-, Br-, I-, S- and Se-containing acyclic, aromatic, and heterocyclic compounds. Most compounds have known natural sources (emission by land and ocean vegetation, from the lithosphere) or are formed in reactions with reactive radicals, H_2O_2 and O_3 in the troposphere (Seinfeld & Pandis, 1997).

In the subsequent analysis of ice samples taken from different levels of the glacier, the compounds present in Table 1 and Figure 1, as well as N_2O, CH_3SCH_3, CH_3SSCH_3, CF_4, CH_2Br_2, $CHBr_3$, and $CH_2{=}CHI$, were quantified. Besides the gases, many other compounds were identified in the ice sample from the upper part of the glacier, such as VOXs ($ClC\equiv CH$, $BrC\equiv CH$, $CH_3CH_2CH_2Cl$, $CH_3CH{=}CHCl$, CH_3CH_2Br, $ClC\equiv CCl$, $ClCH_2CH{=}CH_2$, $CH_3CHClCH_3$, CH_2ClBr, $ClCH{=}CH\text{-}CH_2CH_3$, $CH_3C(CH_3){=}CHCl$, $CH_3CH{=}CHCl$, $ClCH_2CH{=}CHCH_3$, $ClCH_2CH_2Cl$, $CH_3CCl{=}CHCH_3$, $CH_3CH_2CH_2CH_2Cl$, 2-Cl-C_4H_3O, 3-Cl-C_4H_3O, $CHCl_2Br$, $Cl_2C{=}CHCl$, $CH_3CH_2CH_2CH_2Br$, CH_2ClI, $ClCH_2CH(Cl)CH_2CH_3$, Br-C_4H_3O, CCl_3Br, $CHBr_2Cl$, $BrClC{=}CHCH_3$, Cl-C_4H_3S, C_6H_5Cl, $C_6H_{13}Cl$, $Cl_2C{=}CClCH{=}CH_2$, C_6H_5Br, Cl-$C_6H_4CH_3$, 1,4-$Cl_2C_6H_4$, 1,2-$Cl_2C_6H_4$, $CH_3C({=}O)Cl$, $CH_3C({=}O)Br$) as well as S- and Se-containing compounds (COSe, C_4H_4S, 3-$CH_3C_4H_3S$, 2-$CH_3C_4H_3S$, 2-$C_2H_5C_4H_3S$, 2,3$(CH_3)_2C_4H_2S$, 3,4-$(CH_3)_2C_4H_2S$, 2-$C_3H_7C_4H_3S$, 2-C_2H_5-5-$CH_3C_4H_2S$). Also, we identified C_1-C_4 saturated carboxylic monoacids; 11 alcohols, phenols, ethers, and esters; 24 heterocyclic compounds, including substituted furans and thiophenes;



H, m
CH_3Cl
CH_2Cl_2
$CHCl_3$
CCl_4
0
1×10^4
2×10^4
3×10^4
0 20 40 60 80 100
0 200 400 600
0 100 200 300
C_A, pptv
(a)
(b)
(c)
(d)
CH_3Br
CH_3I
C_2H_5Cl
C_2H_5I
0 100 200 300 400
0 200 400 600 800
0 100 200 300
0 200 400 600
(e)
(f)
(g)
(h)
$Cl_2C{=}CCl_2$
$CH_2{=}CHCl$
CH_3CCl_3
CFC-11
0 100 200 300
0 2000 4000 6000
0 100 200
0 400 800 1200
(i)
(j)
(k)
(l)
CFC-12
CFC-113
CFC-114
HCFC-22
0 500 1000 1500 2000
0 50 100
0 5 10 15
0 1000 2000
(m)
(n)
(o)
(p)
10 15 20 25 30 35 40

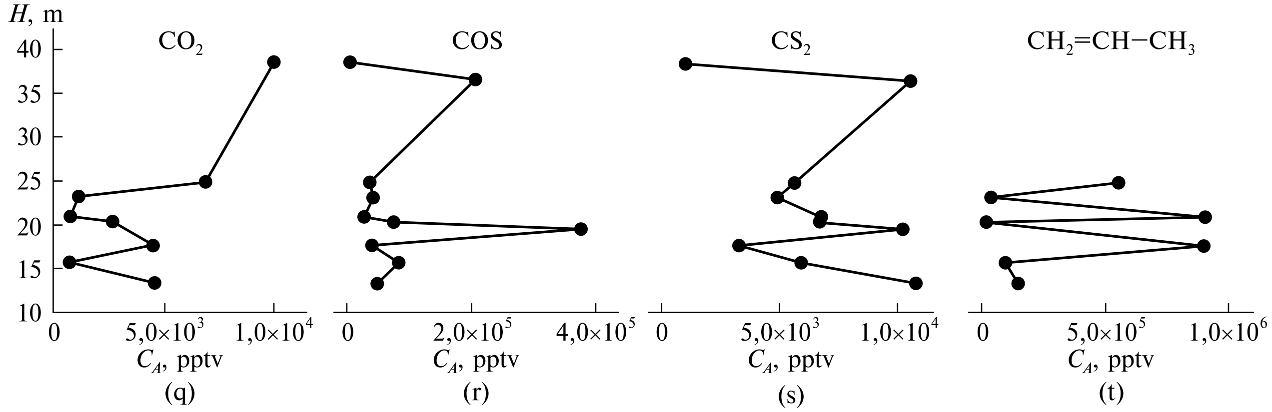


Figure 1. Atmospheric mixing ratios of trace gases in ice samples taken along the vertical profile of the glacier on the Galindez Island: CH_3Cl (a), CH_2Cl_2 (b), $CHCl_3$ (c), CCl_4 (d), CH_3Br (e), CH_3I (f), C_2H_5Cl (g), C_2H_5I (h), $Cl_2C=CCl_2$ (i), $CH_2=CHCl$ (j), CH_3CCl_3 (k), CFC-11 (l), CFC-12 (m), CFC-113 (n), CFC-114 (o), HCFC-22 (p), CO_2 (q), COS (r), CS_2 (s), $CH_2=CH-CH_3$ (t)

18 aromatic hydrocarbons; 3 substituted ethynes, and 35 acyclic and cyclic alkenes.

The atmospheric mixing ratio of CF_4 found in a sample from the bottom part of the glacier, which is 50% lower than its current content in the atmosphere, is close to that obtained from pre-industrial firn air and ice cores, ~34.05 ± 0.33 pptv (Trudinger et al., 2016). It confirms the natural origin of CF_4. In addition, a three-fold enrichment was found in ice samples from the bottom of the glacier for a greenhouse gas such as nitrous oxide (N_2O), which has both natural and anthropogenic sources. A quantitative analysis of air from an ice sample taken from the upper part of the glacier showed the presence of other VOXs: $CH_2=CHI$, CH_2Br_2, and $CHBr_3$.

Measured profiles of atmospheric mixing ratios for 20 trace gases in the ice samples along the height of the glacier are shown in Figure 1 (a)–(t).

One of the probable reasons for the enrichment of trace gases in the ice of a polythermal glacier after deposition on the snow surface may be their dissolution in meltwater during summer, percolation in dissolved form into pores of deeper layers of snow and firn in the upper part of the glacier, the formation of a hard impermeable ice crust over these layers during the cold seasons, the repetition of such freeze-thaw cycles, and mixing of dissolved gases with a part of the gases that were in a gaseous and adsorbed state in the pores. During the firn-ice transition, these pores close, and the air bubbles formed in the ice already contain these gases in concentrations that can far exceed their levels in the atmosphere.

As follows from (Butler et al., 1999), the freon CFC12 is of fully technogenic origin. It has not been detected in the air of polar firn older than 100 years and does not decompose in the troposphere, seawater, soils, or bottom sediments. Thus, CFC12 was selected as a standard in our subsequent calculations. The enrichment factor (*EF*) for each gas is calculated as the C_A/C_A^o ratio, where C_A is the apparent mixing ratio of the gas in the air space of an ice sample, and C_A^o is the mixing ratio of the gas in modern boundary atmospheric layer or air in the upper firn. The C_A^o values for the gases were taken from (Berresheim, 1987; Rudolph et al., 1989; Reifenhäuser & Heumann, 1992; Langenfelds et al., 1996; Berresheim et al., 1998; Lewis et al., 2001; Sturges et al., 2001a; Fischer et al., 2002; WMO, 2002; Sturrock et al., 2002; Kepler et al., 2002; Low et al., 2003; Trudinger et al., 2004; Read et al., 2008; Bonsang et al., 2008; Atkinson et al., 2012; Sander & Bottenheim, 2012; Lennartz et al., 2020).

Table 1 shows C_A^o values for the trace gases and statistical data for apparent C_A values, the ratios of enrichment factors (*EF*) for the gas (X) to *EF* for CFC12 (EF_X/EF_{CFC12}), and those normalized to the water/air partition coefficients for gases at 0 °C (K_{WA}) for X and CFC12 ($EF_{X/Kwa}/EF_{CFC12/Kwa}$) in ice samples from layers of the glacier. The dimensionless K_{WA} values were obtained using Henry's law constants for the gases in water (in Pa m^3 mol^{-1}) and their water/air partition enthalpies (in kJ mol^{-1}) for the gases from (Sander, 2015).

As evident from Table 1, most VOXs, S-containing gases, CO_2, and propene demonstrate high median EF_X/EF_{CFC12} ratios (except for CFC (11, 113, 114), HCFC22, CCl_4, CH_2Cl_2, and $C_2H_3Cl_3$). This can be interpreted as evidence of the possible formation of the gases in the snowpack, firn, and/or ice of the glacier or, again, for the effect of the gases' high solubility in the cold water of the glacier on the apparent mixing ratios in ice samples (C_A). Exact estimation of the solubility effect is impossible without knowledge of the distribution of liquid water in the polythermal glacier. To consider the effect of gas solubility, we used an empirical ratio as $EF_{X/Kwa}/EF_{CFC12/Kwa}$. From Table 1, these ratios for most gases are substantially lower than the previous EF_X/EF_{CFC12} ratios. This demonstrates the necessity of accounting for the contribution of the gas solubility to the apparent atmospheric mixing ratio of a gas in an ice sample. High enrichment factors in comparison with their content in background air over Antarctic Peninsula are also found for such trace gases as CH_3SCH_3 (12 000), CH_3SSCH_3 (>15 000), CH_2Br_2 (25), $CHBr_3$

Table 1. C_A^o values for the trace gases and statistical data for apparent C_A values, the ratios of enrichment factors for the gas (X) to *EF* for CFC12 (EF_X/EF_{CFC12}), and those normalized to the water/air partition coefficients at 0 °C (K_{WA}) for X and CFC12 ($EF_{X/Kwa}/EF_{CFC12/Kwa}$) in ice samples

Trace gas	C_A^0, pptv	C_A, pptv			EF_X/EF_{CFC12}			$EF_{X/Kwa}/E_{FCFC12/Kwa}$		
		Min	Max	Median	Min	Max	Median	Min	Max	Median
CH_3Cl	538	725	34148	6053	2.60	147	14.8	0,06	3.44	0.35
C_2H_5Cl	1.60	64	303	176	73	1200	113	3.12	51.2	4.80
C_2H_3Cl	25	528	5459	2914	53	941	156	4.48	80	13.26
CH_3Br	8.00	12	364	158	3.00	183	21	0.06	3.5	0.39
CH_3I	2.00	7.00	758	283	7.00	3040	197	0.10	42	2.74
C_2H_5I	0.20	35	664	378	350	24050	1903	5.38	370	29.24
CO_2 (ppmv)	370	635	10000	3529	1.56	70	11	0.19	8.5	1.30
COS	325	2862	376311	44761	17.6	2316	197	2.55	335	28.56
CS_2	10	1016	10377	6324	203	6733	769	8.53	283	32.28
HCFC22	120	6.20	2231	102	0.40	37	1,00	0,03	3,22	0,09
CFC12	540	37	1824	276	1.00	1.00	1.00	1.00	1.00	1.00
CFC11	260	68	1135	177	0.39	8.8	1.45	0.10	2.36	0.39
CFC113	82	28	126	66	0.21	4.00	1.00	0.02	0.29	0.07
CFC114	17	0.00	14	0	0.00	1.00	0.00	0.00	3.93	0.00
$C_2H_3Cl_3$	80	0.00	249	79	0.00	6.20	1.20	0.00	0.28	0.05
CH_2Cl_2	9.0	0.00	87	46	0.00	15.0	4.73	0.00	0.10	0.04
$CHCl_3$	6.0	0.00	692	49	0.00	91	15.60	0.00	0.76	0.13
CCl_4	98	0.00	262	50	0.00	1.50	0.63	0.00	0.10	0.05
C_2Cl_4	1.50	0.00	258	42	0.00	344	35.34	0.00	11.70	1.20
C_3H_6	46	13860	905405	144867	416	49207	5052	168	19858	2039

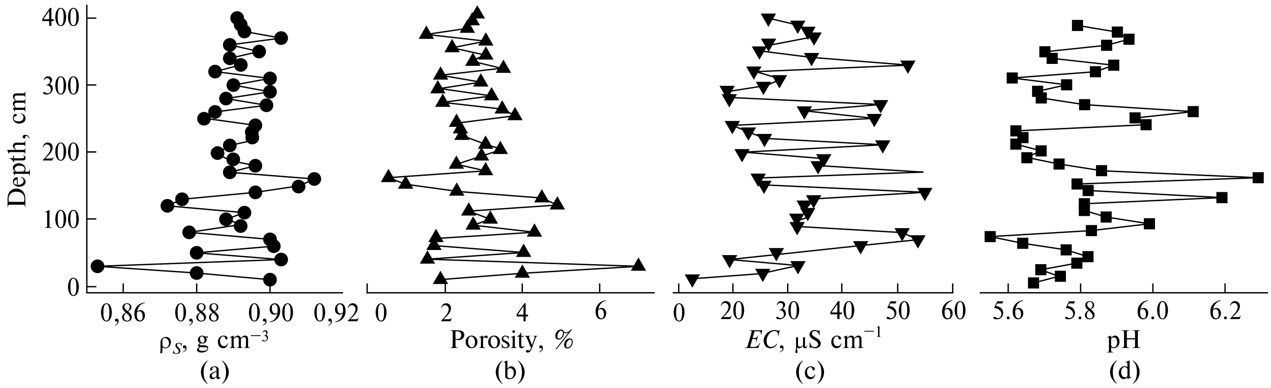


Figure 2. The density (a), porosity (b), electrical conductivity (melt) (c), and *pH* value (melt) (d) of the ice samples taken along the ice core drilled in the top of the glacier on Galindez Island

(360), and CH_2=CHI (600) in the upper part of the glacier.

Figure 2 (a)–(d) shows profiles of density (ρ_S), porosity (*P*), electrical conductivity (*EC*, melt), and *pH* value (melt) of the ice samples taken along the ice core drilled at the top of the glacier. The porosity of the samples (*P*) was calculated as $P = (1 - \rho_S/\rho_0) \times 100\%$, where ρ_0 is the density of clear ice (0.917 g cm^{-3}). The ionic concentrations (proportional to EC values) vary with depth, implying that percolating water does not destroy primary seasonal and storm variations in soluble aerosols in the snow and ice. The ice core consists of alternating layers of superimposed ice and normal glacier ice containing air bubbles. The density of the layers varies between 0.85–0.91 g cm^{-3}.

In contrast to cold glaciers, where density increases gradually down to 50 m, in the polythermal glacier, the density reaches 0.8 g cm^{-3} at 0.5–3 m. Surface melting on the glacier affects the fractionation of trace gases between ice, liquid water, particulate phase, and air, resulting in spatial redistribution of gases.

Statistics for the parameters (ρ_S, *P, EC*, and *pH*) along the ice core profile (400 cm deep) at the top of the glacier are presented in Table 2. Between total dissolved substances (*TDS*, mg L^{-1}) and electrical conductivity (*EC*, in µS cm^{-1}), there exists a simple relation: $TDS = 0.64 \times EC$. On the other side, NaCl in the sea spray aerosols contributes the main part of the total dissolved substances in snowpack in this coastal region (up to 80%) (DeFelice, 1998; Jammoul et al., 2009; de Leeuw et al., 2011; Nowak et al., 2018). A crude relation between *EC* value (µS cm^{-1}) and NaCl concentration (80% of *TDS*, mg L^{-1}) in the melt of coastal snow is $TDS(\text{NaCl}) = 0.55 \times EC$.

Table 2. Statistics for parameters along ice core profile (400 cm deep) on the glacier (Galindez Island, Maritime Antarctica)

Parameter	Unit	Min	Max	Mean	s. d.	Median
Density	g cm^{-3}	0.853	0.912	0.891	0.011	0.892
Porosity	%	0.550	6.980	2.827	1.147	2.730
Porosity	Volume fraction	0.0055	0.0698	0.0283	0.0115	0.0273
Conductivity	µS cm^{-1}	12.6	55.0	32.57	11.10	31.70
TDS(NaCl)	mg L^{-1}	6.3	27.5	16.29	5.55	15.85
TDS(NaCl)	mmole L^{-1}	0.108	0.471	0.279	0.095	0.271
pH	–	5.55	6.29	5.80	0.16	5.79

All total ionic concentrations and *pH* values vary with depth, implying that the percolating water does not destroy primary seasonal variations in impurities and storm events in the ice core. If meltwater had a significant effect on conductivity and *pH* values along the glacier's vertical profile, we would obtain smooth curves of conductivity and *pH* increasing or decreasing with ice core depth. In addition, an increase in the amount of meltwater in the glacier is usually observed in the spring-summer season, which affects the electrical conductivity of the ice (probably reducing it, which may indicate a change in season).

The density of the samples ranges from 0.85 to 0.91 g cm^{-3}, which is characteristic of infiltration ice bands and lenses, superimposed or refrozen infiltration, and dynamically metamorphized ice.

The porosity of ice samples varies in a narrow range (0.6–7.0%; mean $P = 2.8\%$); this is below the mean ice porosity in polar glaciers ($P \sim 10\%$). Because the ice sample consists of three phases: bulk ice with relative volume θ_I, liquid water with θ_W, and gaseous air with θ_A, their sum is $\theta_I + \theta_W + \theta_A = 1$. Then, the ice sample's relative total porosity is $P \approx \theta_W + \theta_A$. Marchenko et al. (2021) calculated the volumetric water content of firn as 1.0–2.5 vol.% above the depth of 5 m and <0.5 vol.% below the accumulation zone of Lomonosovfonna, Svalbard. Pettersson et al. (2004) obtained a mean water content of 0.8% of Storglaciären, northern Sweden. Then, possible gas phase reactions of VOXs precursors, and especially liquid-phase reactions, can occur in very confined spaces of air bubbles in the superimposed ice samples from polythermal glaciers. The possible impacts of such bubbles' geometry on the rate and direction of chemical reactions are discussed below.

4 Discussion

4.1 Abiotic pathways of the trace gases' formation in the environmental compartments

Photochemical pathways

The sea surface microlayer (SML) concentrates many chemical compounds, such as amino acids, proteins, fatty acids, lipids, sugars, phenols, and humic substances, compared to the sub-surface water (Liss & Duce, 1997). Sea spray aerosols (SSA) contain a large fraction of the organic compounds in the SML (Clark & Zika, 2000). They are also clearly enriched in dissolved organic matter (DOM) with chromophoric dissolved organic matter (CDOM), containing carbonyls and aromatics with multiple double bonds, enabling them to absorb light (McNeill & Canonica, 2016). Such compounds will act as photosensitizers for other dissolved compounds, which are photochemically inactive (by absorbing irradiation and transferring this energy) (Canonica et al., 1995). Such photosensitized processes can bring about the production and emission of VOCs from the air-sea interface (Ciuraru et al., 2015; Fu et al., 2015; Brüggemann et al., 2017; Mungall et al., 2017; Kaur & Anastasio, 2018).

Halide anions (Cl$^-$, Br$^-$, and I$^-$) are present in seawater (Carpenter & Nightingale, 2015), in the SML, and marine aerosols. The aqueous phase oxidation of halides can occur by electron transfer from the halide anion to the excited state of photosensitizer (e.g., aromatic ketones) (Jammoul et al., 2009; Tinel et al., 2014).

As it follows from (Grannas et al., 2007), radiation scattering leads to the high albedo of snow in the visible and UV regions, and enhances the absorption probability and photochemical rates for photosensitizers and other absorbers in the snowpack. The e-folding depth of the radiation in the UV-B to visible part of the spectrum in snowpack is in the range from 5–25 cm, however more largger values around 50 cm are observed in temperate snowpacks with large grains formed by melt-freeze cycles (Domine et al., 2008).

The formation of reactive halogen atoms may lead to the formation of VOXs that may partially degas in the air aloft. Under simulated solar irradiation, different VOXs were detected when a proxy of DOM, i.e., 4-benzoyl benzoic acid, was excited into its triplet state (Roveretto et al., 2019). These photochemical reactions occur at the air/sea interface and can potentially supply VOXs to the atmosphere. Such transformations are also possible at a glacier's air/snow interface during sunny days (Domine et al., 2008; Grannas et al., 2007). Liu et al. (2020a) established the photochemical production of CH_3Br from syringic acid (SA) as a model compound for DOM. Two pathways have been proposed for CH_3Br formation from SA in the Br^--enriched water under sunlight irradiation: via attack of Br^- on the protonated SA in the excited state and via the recombination of $CH_3\cdot$ radical and $Br\cdot$ when Fe(III) was present. Also, Liu et al. (2020b) investigated how CH_3Cl is produced from the humic acid (HA) in sunlit saline water and how it is affected by the concentration of HA, Cl^-, Fe(III), and *pH.* CH_3Cl was generated upon irradiation, and its amount increased with increasing irradiation time and light intensity. Mendez-Díaz et al. (2014) established the formation of organobromine and organoiodine during solar irradiation of DOM in artificial and natural seawaters. Increasing I^- concentrations promoted increases of up to 460% in organoiodine content at the expense of organobromine formation under the same conditions.

The TiO_2 nanoparticles (NPs) can photocatalytically halogenate DOM to form a large number of organobromine (OBCs) and organoiodine compounds (OICs) (Hao et al., 2018). Various OBCs and OICs were detected in freshwater and seawater under sunlight irradiation, even in the presence of 1 mg L^{-1} NPs, indicating the photocatalytic roles NPs played in DOM halogenation. The OBCs in freshwater were found to be formed mainly via substitution or addition and accompanied by other reactions such as photo-oxidation. In contrast, the OBCs in seawater and OICs were formed primarily via substitution.

The oceans are a net source of light nonmethane hydrocarbons (NMHCs) to the atmosphere, being likely relatively more important in the Southern Hemisphere, where land and industrial sources are less abundant. According to (Ratte et al., 1998), alkenes are not directly produced by marine organisms but are formed by the photochemical degradation of DOC. The likely source of propene, found in high concentrations in ice samples from the upper and lower parts of the glacier, is the photochemical decomposition of DOC produced from macro- and/or microalgae during their growth or death and transferred on the glacier surface as well as emitted by primary sea aerosols enriched by sea microfilm DOC. It is described by a type II Norrish photoreaction scheme (α-cleavage of carbonyls in aqueous solution) (Ratte et al., 1998):

$$R(C{=}O)CH_2CH_2CH_3 + \lambda\nu \rightarrow$$
$$\rightarrow RC{=}O\cdot + \cdot CH_2CH_2CH_3$$
$$RC{=}O\cdot + \cdot CH_2CH_2CH_3 \rightarrow$$
$$\rightarrow R(C{=}O)H + CH_2{=}CHCH_3$$

It can be assumed that a DOC transported from the ocean surface in stormy weather towards the surface of a coastal glacier will behave similarly to the oceanic SML. Propene can dissolve in quasi-liquid layer on the ice particles surface, in percolating water, etc. Its formation in the photochemical reactions in snowpack is well-confirmed (Swanson et al., 2002). Therefore, propene can also be formed directly during the photolysis of the oceanic DOC deposited on the surface of the upper part of the glacier.

The main natural source of COS in the atmosphere above the oceans is the photolysis of DOM in the SML, which is described by (Flöck & Andreae, 1996):

$$R(C{=}O)R' + \lambda\nu \rightarrow [RC{=}O\cdot + \cdot R']$$
$$[RC{=}O\cdot + \cdot R'] + R''SH \rightarrow$$
$$\rightarrow R''S\cdot + RC{=}O\cdot + \cdot R'H$$
$$R''S\cdot + RC{=}O\cdot \rightarrow RC{=}O\text{-}SR''$$
$$RC{=}O\text{-}SR'' + \lambda\nu \rightarrow R\text{-}R'' + COS$$

The most probable pathway for the formation of CS_2 can also be the photolysis of DOM in the ocean's surface layer (Xie et al., 1998). Such components of DOM in the surface layer of seawater as cysteine and cystine can serve as precursors of

CS_2, and OH radicals are important intermediates of this process:

$$HSCH_2CH(NH_2)C(=O)OH \xrightarrow{h\nu, O_2}$$
$$\xrightarrow{h\nu, O_2} HSCH_2CHO + NH_3 + CO_2$$
$$HSCH_2CHO \xrightarrow{OH} HCS + CO_2$$
$$2HCS \rightarrow CS_2 + CH_2:$$

Thus, CS_2, like COS and propene, is formed in the ocean along a similar path of photolysis of DOM of biogenic origin in the surface water layer. By analogy with the formation of propene found by Swanson et al. (2002) during the photolysis of DOM on the snow surface, we can assume the same source for the formation of CS_2 and COS in the glacier snowpack.

Since the pathway of most considered trace gases can be the photochemical decomposition of DOM of biogenic origin in the snowpack and subsequent free-radical transformations of the intermediates, it is necessary to consider such a source for the chlorohydrocarbons.

The results of numerical simulation (Herrmann et al., 2003) indicate that the main contribution to the formation of Cl atoms in the marine boundary layer (MBL) includes such liquid-phase processes as: $ClOH^- + H^+ \rightarrow Cl + H_2O$, $SO_4^- + Cl^- \rightarrow Cl + SO_4^{2-}$ and $NO_3 + Cl^- \rightarrow NO_3^- + Cl$, as well as the gas-phase reactions: $HCl + OH \rightarrow Cl + H_2O$, $HOCl + \lambda\nu \rightarrow Cl + OH$, $Cl_2 + \lambda\nu \rightarrow 2Cl$ and $BrCl + \lambda\nu \rightarrow Cl + Br$. The interaction of the Cl atoms formed in these transformations with DOM in the snowpack can lead to the formation of CH_3Cl, C_2H_5Cl, and $CH_2{=}CHCl$ due to addition and substitution radical reactions. An argument in favor of the assumption about the predominant formation of CH_3Cl as a result of radical reactions initiated by the photolysis of DOM can be the observed relationship between its amount in ice samples and that of COS formed in this way: $[CH_3Cl] = (0.080 \pm 0.006) \times [COS]$; $r = 0.973$.

The volume mixing ratio of CH_3Br in ice samples from the glacier, as well as in the firn air from the Arctic (Butler et al., 1999; Sturges et al., 2001a), significantly exceeds its ratio in the present atmosphere, and its enrichment factor in these samples varies from 10 to 45. From a comparison of changes in the ratios of CH_3Br and other trace gases in ice samples, positive trends were found: $[CH_3Br] = 120 \pm 30 + (0.005 \pm 0.003) \times [CH_3Cl]$; $r = 0.617$, $[CH_3Br] = 110 \pm 30 + (0.09 \pm 0.06) \times [CH_3I]$; $r = 0.493$ and $[CH_3Br] = 120 \pm 30 + (0.0006 \pm 0.0002) \times [COS]$; $r = 0.745$.

These trends may indicate a common source of formation of these compounds in the ice samples. We can assume the free-radical pathway for the formation of CH_3Br, initiated by solar irradiation of a DOM containing carbonyl groups and/or methyl thiol groups (Swanson et al., 2002):

$$R'(C{=}O)CH_3 + \lambda\nu \rightarrow R'C{=}O\cdot + CH_3\cdot$$
$$OH\cdot\ (RO\cdot,\ ROO\cdot) + Br^- \rightarrow$$
$$\rightarrow OH^-\ (RO^-,\ ROO^-) + Br\cdot$$
$$CH_3\cdot + Br\cdot \rightarrow CH_3Br$$
$$CH_3SCHO + OH\cdot \rightarrow CH_3S(OH)CHO\cdot$$
$$CH_3S(OH)CHO\cdot + Br\cdot \rightarrow$$
$$\rightarrow COS + CH_3Br + H_2O$$

Thus, the role of solar irradiation is reduced to the photochemical dissociation of α-carbonyls (the Norrish reaction of type II) and the photochemical formation of Br· atoms and OH· radicals. The common source of CH_3I and C_2H_5I in samples from different layers of the glacier is indicated by the obtained trend of an enhancement in the mixing ratio of C_2H_5I with an increase of that for CH_3I: $[C_2H_5I] = (0.8 \pm 0.6) \times [CH_3I]$; $r = 0.600$.

The observed higher enrichments of iodinated hydrocarbons compared to bromine derivatives can be explained by significant enrichment of the atmosphere of coastal Antarctica with inorganic iodine compounds in soluble form and associated with solid particles (Vogt, 1999) and a higher reactivity of ions and radicals containing I, compared with similar species including Br in photolysis processes (Swanson et al., 2002) as well as in the redox reactions (Keppler et al., 2000; 2003).

Pathways with the participation of hypohalogenous acids/molecular halogens

Martino et al. (2009) observed the formation of CH_2I_2, $CHClI_2$, and CHI_3 when seawater was exposed to ambient ozone levels. They are produced from the reaction of marine DOM with hypoiodous acid (HOI)/molecular iodine (I_2), formed at the sea surface in the reaction of ozone with dissolved iodide. A possible mechanism for the release of gaseous iodine compounds from the ocean is the production of molecular iodine and hypoiodous acid in the surface seawater by the reaction of ambient ozone with iodide:

$$O_3 + I^- + H_2O \rightarrow HOI + O_2 + OH^-$$
$$HOI + I^- + H^+ \rightarrow I_2 + H_2O$$

A common source for the formation of the C1/C2-chlorohydrocarbons can be the reaction of H_2O_2 and Cl^- ions with organic compounds containing a C−H group activated by a carbonyl group (Walter & Ballschmiter, 1992):

$$H_2O_2 + Cl^- \rightarrow H_2O + OCl^-$$
$$OCl^- + H^+ \rightarrow HOCl \rightarrow HO^- + (Cl^+)$$
$$R'(CO)RH + (Cl^+) \rightarrow RCl + R'(CO)H^+$$
$$(R = CH_3,\ C_2H_5,\ CH_2{=}CH)$$

It is unlikely that the photolysis of DOM and its redox reaction with Fe^{3+} ions were the sources of high concentrations of CH_2Br_2 and $CHBr_3$ in ice samples since these processes result in the formation of only monohalogenated bromine- and iodoalkanes (Keppler et al., 2000; 2003). Although the mechanism of formation of polyhaloalkanes is still poorly understood, it is assumed that they are formed as a result of the reactions of electrophilic halogen compounds, such as hypohalogenous acids (HOX, X = Cl, Br, I) (Urhahn & Ballschmiter, 1998). Subsequent halogenation of the methyl group activated by the neighboring carbonyl group leads to the formation of trihalo- or dihalomethanes (haloform reaction):

$$R{-}C({=}O) + Br^{(\delta+)} + H_2O_2 \rightarrow$$
$$\rightarrow R\text{-}COOH + CHBr_3$$

A similar reaction (halogen-sulfonic rearrangement) is possible with the participation of methyl sulfones:

$$R\text{-}S(O_2)CH_3 + Br^{(\delta+)} \rightarrow R\text{-}S(O_2)CBr_3$$
$$R{-}S(O_2)CBr_3 + OH^- \rightarrow$$
$$\rightarrow RS({=}O)OOH + CHBr_3$$

Redox pathways

In soils and sediments, halide ions can be alkylated during the oxidation of DOM by an electron acceptor such as Fe(III) (Keppler et al., 2000). When the available halide ion is Cl^-, the reaction products are CH_3Cl, C_2H_5Cl, C_3H_7Cl and C_4H_9Cl. The corresponding alkyl bromides or alkyl iodides are produced when Br^- or I^- are present.

Until now, vinyl chloride ($CH_2{=}CHCl$) was believed to be exclusively man-made or resulting from the degradation of other anthropogenic substances, such as $ClCH_2{=}CCl_2$ and $Cl_2C{=}CCl_2$. We identified this compound with a high *EF* value in the ice samples from the upper and bottom layers of the glacier. Keppler et al. (2002) investigated soil air and ambient air from a rural area in Northern Germany for VOXs. Vinyl chloride in the soil air was significantly more concentrated than in ambient air, which is evidence of its natural formation in the soil. This compound is highly reactive; it can be formed during the oxidative degradation of DOM in the soil, for example, when humic substances react with chloride ions and an oxidant (Fe(III) or OH· radicals.

It is shown that the highly reactive chloroethyne ($ClC{\equiv}CH$) is also a product of natural processes in soil (Keppler et al., 2006). We also identified this compound in the ice sample from the upper layer of the glacier. Keppler et al. (2006) used redox-sensitive catechol as a discrete organic model compound to show the formation of chloroethyne when Fe(III) and H_2O_2 were added to the system. Different organic-rich soils and humic acid were investigated for releasing volatile organoiodides (Keppler et al., 2003). The CH_3I, C_2H_5I, 1-C_3H_7I, 2-C_3H_7I, 1-C_4H_9I, and 2-C_4H_9I were identified, and their release rates were determined.

The abiotic reaction mechanism was induced by the oxidation of organic matter by Fe(III).

Synthetic manganese oxide (birnessite, MnO_2) can also catalyze the formation of CH_3I in the presence of natural organic matter (NOM) and I^-. CH_3I formation was only observed at acidic *pH* (4–5) where I^- is oxidized to iodine and NOM is adsorbed on MnO_2 (Allard et al., 2010; Allard & Gallard, 2013). The Lewis-acid property of MnO_2 leads to a polarization of the iodine molecule and catalyzes the reaction with NOM. Jiao et al. (2022) investigated the effect of Cu(II) on CH_3Br and CH_3Cl production from soil, seawater, and model organic compounds. $CuSO_4$ enhances CH_3Br and CH_3Cl production from soil and seawater; hydrogen peroxide (H_2O_2) or solar radiation may further amplify it.

Du et al. (2022) reported that reactive iodine (RI) and OICs are produced from I^- oxidation in the presence of Fe(III) and NOM in frozen solution. In contrast, their production is insignificant in aqueous solution. Thawing the frozen solution induces production of OICs. They detected 352 OICs in the freeze-thaw cycled reactions of Fe(III)/I^-/humic acid solution, which is five times as many as OICs in aqueous reactions. Using model organic compounds (e.g., phenol, aniline, *o*-cresol, and guaiacol) induces higher OIC yields (10.4–18.6%) in the freeze-thaw Fe(III)/I^- system than those in aqueous (1.1–2.1%) or frozen (2.7–7.6%) solutions. The formation of RI is enhanced in the frozen solution but its further reaction with NOM is hindered. Thus, the freeze-thaw cycle of RI being formed in the frozen media and being consumed by reaction with NOM in the subsequently thawed solution produces OICs more efficiently than the continuous reaction in the frozen solution.

Besides the above process in frozen solution, Jeong et al. (2012) investigated the dissolution of iron oxide particles trapped in ice as a new pathway of iron supply. The dissolution of iron oxides in ice is mainly enhanced by the "freeze concentration effect", which concentrates iron oxide particles, organic ligands, and protons in the liquid-like ice grain boundary region and accelerates the dissolution of iron oxides. The ice-enhanced dissolution effect gradually decreased when the freezing temperature went from −10 °C to −196 °C, implying a critical role of the liquid-like ice grain boundary region. The reaction between iron oxides and I^- was markedly accelerated to produce bioavailable iron (Fe(II)aq) and tri-iodide (I_3^-: evaporable in the form of I_2) in frozen solution (both with and without light irradiation). At the same time, it is negligible in the aqueous phase (Kim et al., 2019).

A possible way for the formation of CH_3X (X = = Cl, Br and I) in snow and firn which makes it possible to explain the accumulation of CH_3Br in deep ice and firn layers established in (Butler et al., 1999; Sturges et al., 2001a), i.e., its formation in the absence of solar irradiation, is the oxidation of DOM by Fe^{3+} ions, similarly to the reaction occurring in soil (Keppler et al., 2000; 2003):

$$PhOCH_3 + Fe^{3+} \rightarrow PhOCH_3^{+\cdot} + Fe^{2+}$$
$$PhOCH_3^{+\cdot} + Br^- \rightarrow CH_3Br + Ph{=}O$$

Miscellaneous pathways

Mulder et al. (2015) present data about terrestrial sources for atmospheric VOXs and volatile organosulfur compounds (VOSCs) in hypersaline salt lakes. They checked whether methionine or methylmethionine could be a precursor for CH_3Cl and CH_3SCH_3 (DMS) formation in salt-lake environments. Next to CH3Cl, hypersaline soil samples incubated in headspace vials emitted an array of VOSCs, including DMS and CH_3SSCH_3. An abiotic mechanism for their formation is possible, given the fast response of emission to heating freeze-dried samples at 40 °C.

DMS is a product of base-catalyzed hydrolysis of dimethylsulfonium propionate ($(CH_3)_2S^+CH_2CH_2COO^-$, DMSP), which is synthesized by various marine phytoplankton species, in particular, ice microalgae (van Rijssel & Gieskes, 2002). This process is described as follows:

$$(CH_3)_2S^+CH_2CH_2COO^- + OH^- \rightarrow$$
$$\rightarrow (CH_3)_2S + CH_2{=}CH\text{-}CHO$$

In addition to DMSP, other natural precursors of VOSCs include methionine, cysteine, glutathionine, dimethyl sulfoxide, dimethylsulfoniopentanoate, dimethylsulfonioacetate, methionine sulfoxide, methionine sulfone, S-methylcysteine and mercaptopropionate.

$$2\text{R-O-CH}_3 + \text{H}_2\text{S} \rightarrow 2\text{R-OH} + \text{CH}_3\text{SCH}_3$$

$$[\text{C}_6\text{H}_2\text{OH(OCH}_3)_2\text{COO}^-] + \text{HS}^- + \text{H}_2\text{O} \rightarrow$$
$$\rightarrow [\text{C}_6\text{H}_2(\text{OH})_2(\text{OCH}_3)\text{COO}^-] + \text{CH}_3\text{SH} + \text{OH}^- \rightarrow$$
$$\rightarrow 3\text{CH}_3\text{COO}^- + \text{CH}_3\text{SCH}_3 + \text{HCO}_3^- + 2\text{H}^+$$

The formation of dimethyl disulfide is possible as a result of the following transformations:

$$(\text{CH}_3)_2\text{S}^+\text{CH}_2\text{CH}_2\text{COO}^- \rightarrow$$
$$\rightarrow \text{CH}_3\text{SCH}_2\text{CH}_2\text{COO}^- + \text{CH}_3\text{OH}$$
$$\text{CH}_3\text{SCH}_2\text{CH}_2\text{COO}^- \xrightarrow{2H^+} \text{CH}_3\text{SH} +$$
$$+ \text{CH}_3\text{CH}_2\text{COOH}$$
$$(\text{CH}_3)_2\text{S} \xrightarrow{H^+, OH^-} \text{CH}_3\text{SH} + \text{CH}_3\text{OH}$$
$$2\ \text{CH}_3\text{SH} \xrightarrow{OH^-} \text{CH}_3\text{SSCH}_3 + \text{H}_2\text{O}$$
$$\text{CH}_3\text{SH} + \text{CH}_3\text{SH} + \text{O}_2 \rightarrow \text{CH}_3\text{SSCH}_3 + \text{H}_2\text{O}$$
$$\text{CH}_3\text{SH} + \text{Fe(III)} \rightarrow \text{CH}_3\text{S}\cdot + \text{Fe(II)} + \text{H}^+$$
$$\text{CH}_3\text{S}\cdot + \text{CH}_3\text{S}\cdot \rightarrow \text{CH}_3\text{SSCH}_3$$

Precursors for abiotic pathways of trace gases' formation in the Antarctic snow and ice environment

If we assume that the trace gases are formed as a result of natural abiotic processes in the snowpack of the glacier, then, based on the above results, we can assume the following pathways for their formation:

(a) Direct and indirect photochemical reactions of triplet state dissolved organic matter (^{3}DOM*) without (C_3H_6, COS, CS_2), or in the presence of X^- ions (X = Cl, Br, I): RX (R = CH_3, C_2H_5, CH_2=CH).

(b) Redox reactions of Fe^{3+}, Mn^{4+}, Cu^{2+}, O_3, H_2O_2 or HO· and HO_2· radicals (assisted by Fe^{2+} and TiO_2) with the DOM in the presence of X^- ions: RX. Those include cleavage of alkoxy- and alkylgroups, benzene rings of DOM, and, possibly, CH_3SCH_3 and CH_3SSCH_3 release.

(c) Reactions of HOX (X = Cl, Br, and I) with DOM (with the participation of HO·, HO_2·, H_2O_2 or O_3): CH_2Br_2, $CHBr_3$.

(d) Free-radical reactions of Cl·, ClO·, Br·, BrO·, I· and IO· with alkenes, alkynes and alkyl radicals.

(e) Decomposition of methylmethionine or S-containing peptides: CH_3SCH_3 and CH_3SSCH_3.

These reactions can be greatly accelerated if they occur in quasi-liquid layers of aqueous solution on the grain surface of ice in the confined space of microcavities and trenches of snow and firn. This may be due to the well-known "concentration freezing effect", the change in the freezing potential, the variation in *pH* values, and the "cage effect" of cryochemistry (Grant & Alburn, 1967; Cobb & Gross, 1969; Park et al., 2010; Watanabe et al., 2014). Such transformations can be even more accelerated by the repetition of freeze-thaw cycles, characteristic of temperate or polythermal glaciers.

Thus, for the aforementioned reactions to occur in a snowpack, firn, and ice, the presence of the following precursors is necessary: DOM, ions (Fe^{3+}, Mn^{4+}, Cu^{2+}, Ti^{4+}, Cl^-, Br^-, I^-), and H_2O_2. The concentrations of metals in ice samples from the glacier on Galindez Island (determined by ICP AES) were 0.012–0.020 mg L^{-1} (Mn), 0.010–0.090 mg L^{-1} (Fe) and 0.007 mg L^{-1} (Cu). The maximum concentrations of the metals in the snowpack on neighboring islands (Adelaide, Alexander, and Anchorage) are 0.00095 mg L^{-1} (Mn), 0.00075 mg L^{-1} (Cu), 0,0012 mg L^{-1} (Ti) and in the snowmelt: 0.013 mg L^{-1} (Fe), 0.023 mg L^{-1} (Mn), 0.0081 mg L^{-1} (Cu) and 0.0062 mg L^{-1} (Ti) (Nowak et al., 2018). The estimated atmospheric iron flux on the snow surface in East Antarctica varies from 0.03 to 0.11 mg m^{-2} yr^{-1} (Edwards & Sedwick, 2001).

The concentration of DOM in ice samples from the glacier on Galindez Island was not determined. However, its maximum concentration in the snowpack on neighboring islands (Adelaide, Alexander, and Anchorage) is 1.26 mg L^{-1} and 4.45 mg L^{-1} in the snowmelt (Nowak et al., 2018). The DOC concentration in the fresh snow on neighboring Anvers Island was 9.7 mgC L^{-1} (DeFelice, 1998). The higher concentrations of the organic compounds (propene, CH_3Cl, C_2H_5Cl, CH_3Br, CH_3I, and C_2H_5I) in the glacier of Maritime Antarctica in comparison with their content in snowpack of Central Greenland (Swanson et al., 2002; 2007) may be due to the higher content of DOC in the Antarctic snow, which is an order of magnitude higher than in the snow of Central Greenland (0.1 mg C L^{-1}) (Swanson et al., 2002), and higher temperature and snowmelt index in Maritime Antarctica compared to Central Greenland.

The Cl^- and Br^- concentrations in the fresh snow on Anvers Island are 4.54 and 0.025 mg L^{-1}, respectively (DeFelice, 1998). Heumann et al. (1987) measured a maximum iodine concentration of 1800 ng L^{-1} in snow samples near the coastal Neumayer station in February 1985. They found I/Cl ratios in snow samples 10–190 times higher than in seawater. The MAX-DOAS measurements of IO, together with total iodine measurements from snow pits at Neumayer Station, Antarctica, suggest that the snowpack represents a strong source of iodine radicals in the boundary layer of coastal Antarctica (Frieß et al., 2001). The total bromine, iodine, and sodium concentrations were examined in a series of 2 m snow cores collected during a traverse from Talos Dome to the GV7 site (Maffezzoli et al., 2017). Iodine shows average concentrations of 0.04 ppbm with little variability. The average iodine concentration in an ice core collected at Dome C (East Antarctica), covering the period of 1800–2012, for the period of 1800–1974 remains constant at 0.060 ng g^{-1}, decreasing by almost half to an average concentration of 0.032 ng g^{-1} from 1975 to 2011 (Spolaor et al., 2021).

The results from (van Ommen & Morgan, 1996) show mean H_2O_2 concentrations of approximately 37 pptv over the past 4 kyr and a tendency for concentrations to decrease with age. The H_2O_2 concentration in the surface snow ranges from 300 to 1200 ppbv, whereas that in firn ranges from 2.1 ppbv (1000 yr) to 1.0 ppbv (2400 yr). The H_2O_2 content varies in the Palmer ice core (1621–2011 C.E., one of the oldest Antarctic Peninsula cores) from 20 to 80 ppbv (Emanuelsson et al., 2022).

5 Conclusions

The currently observed intense increase in ambient temperature in the coastal Antarctic Peninsula leads to an increase in the ablation rate of outlet and shelf glaciers due to their melting and an increase in the volume of calved icebergs. Since these glaciers contain many trace gases and other impurities that are formed in bio- and/or abiotic reactions on their surface, they can be sources of secondary emission of sulfur- and halogen-containing species, and the current global warming should amplify the role of this local source.

Until now, CH_3Cl was considered the most significant natural-origin chloroalkane in the stratosphere, contributing up to 13% of organic chlorine (Khalil, 1999). Since the mixing ratios of C_2H_5Cl and $CH_2{=}CHCl$, also formed from natural sources, are an order of magnitude lower than CH_3Cl, these gases are responsible for more than 1% of organic chlorine in the stratosphere. In addition to them, several naturally occurring bromoalkanes (CH_3Br, CH_2Br_2, and $CHBr_3$) were also found in the ice samples. Bromine atoms are 50–60 times more efficient ozone depletion catalysts than chlorine atoms. From 20 to 25% of ozone layer depletion over Antarctica during the austral spring, about a third of the winter depletion of the ozone layer in the northern middle and high latitudes, and almost 100% of the destruction of surface ozone in the Arctic with the onset of the polar day are explained by the occurrence of the corresponding reactions involving bromine atoms (Singh & Fabian, 1999). The most significant sources of organic bromine in the stratosphere and troposphere are CH_3Br (50%), CH_2Br_2 (15%), and $CHBr_3$ (15%) identified in the glacier. It follows from the above estimates that the Cl- and Br-hydrocarbons from natural sources can be responsible for 40% of the destruction of the ozone layer over Antarctica during the austral spring, and temporal variations in their atmospheric content must be taken into account when interpreting stratospheric ozone trends.

CH_3I, C_2H_5I, and $CH_2{=}CHI$ found in high mixing ratios in the ice samples can also significantly contribute to the destruction of surface ozone, especially in the oceanic MBL (Vogt, 1999). The IO· radical formed in these reactions is the precursor of effective cloud condensation nuclei over the oceans, and its level in the ocean boundary layer largely determines the content of clouds over the oceans and, thus, the temperature of MBL (O'Dowd et al., 2002).

Let us consider the effect of climate warming in the coastal Antarctic Peninsula on the emission of trace gases from polythermal glaciers. It can be assumed that an increase in temperature and UV-B radiation (arising from the depletion of the stratospheric ozone layer) in this region leads to the following changes in the environment:

1. An increase in the rate of photochemical, thermal, and biochemical processes of the gases' formation in snowpack, firn, and ice.
2. Increasing evaporation of the gases from the snowpack.
3. An enhancement in the liquid water content in the snowpack and increase of the water-soluble gases amount in meltwater.
4. A rise in the ablation rate of glaciers in the Antarctic Peninsula and the islands, leading to the washing out of gases with meltwater into the oceanic coastal zone and atmosphere.
5. An increase in the number of icebergs calved from the coastal shelf and outlet glaciers and melted releases the gases into the atmosphere and ocean.

The current warming of West Maritime Antarctica leads to a redistribution of chemicals in snowpack and ice between their soluble and adsorbed forms towards solutions and the gas phase. Due to the large volume of icebergs formed from the temperate degrading glaciers of the coast of Antarctica and the melting of these glaciers in recent years, coastal waters will be enriched with haloalkanes and sulfur-containing gases of natural and anthropogenic origin. Although the fluxes of the gases into the environment from the considered sources (glaciers + icebergs) do not exceed a few percent of their global fluxes (Bogillo et al., 2003), nevertheless, they can have a significant local effect on the chemical composition of the troposphere, stratosphere, and, forming I- and S-containing tropospheric and stratospheric aerosols, on the radiation balance of the atmosphere over the Southern Ocean.

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Conflict of Interest. The authors declare that they have no conflict of interest.

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Абіотичні шляхи утворення озоноруйнуючих та інших слідових газів у політермальному льодовику на острові Галіндез, морська Антарктика

Реферат. Метою дослідження є аналіз слідових газів у складі політермального льодовика на острові Галіндез у морській Антарктиці (65°14′ пд.ш., 64°16′ зах.д.) та можливих шляхів їх абіотичного утворення в сніговому покрові та в накладеному або старому холодному льоді. Політермальні льодовики є найбільш чутливими індикаторами зміни клімату та ідеальними регіонами для вивчення хімічного складу атмосфери, снігу, фірну та льоду під впливом поточного потепління клімату. Це дослідження є першою спробою оцінити діапазон концентрації великої кількості слідових газів (крім раніше досліджених O_2, N_2, Ar і CO_2) у політермальних і помірних льодовиках, які поширені в Гренландії, Шпіцбергені, Канадській Арктиці, Алясці, Альпах, Андах, Тибеті, Алтаї і в морській Антарктиці. Пористість льоду коливається від 0.6% до (характерних для накладеного льоду) 7%. Якісний аналіз за допомогою GC-MS було проведено для більше ніж 200 органічних і неорганічних слідових газів у складі цього льодовика. Було проведено кількісний аналіз 27 сполук уздовж вертикального профілю льодовика, включаючи CO_2 і N_2O, фреони, хлорвмісні розчинники, які заборонені Монреальським протоколом, F-, Cl-, Br- та I-вмісні галогеновуглеводні, COS, CS_2, CH_3SCH_3, CH_3SSCH_3 і пропілен. Більшість галогеновуглеводнів, сірковмісних сполук і пропілен характеризуються високими коефіцієнтами збагачення. Це свідчить про можливість їх утворення в сніговому покрові та фірні льодовика або в його глибокому льоді. Можливі шляхи утворення газів включають прямі та непрямі фотохімічні реакції триплетного стану розчиненої органічної речовини (РОР) без або в присутності йонів X (X = Cl, Br, I), окисно-відновні реакції Fe^{3+}, Mn^{4+}, Cu^{2+}, O_3, H_2O_2 або радикалів HO_x з РОР у присутності X^-, реакції HOX з РОР (за участю HO_x, H_2O_2 або O_3), вільнорадикальні реакції з алкенами, алкінами та алкільними радикалами, а також різноманітні реакції метилметіоніну та/або S-вмісних пептидів.

Ключові слова: S-вмісні пептиди, вуглеводні, галогеновуглеводні, накладений лід, сніговий покров, фірн