

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
JOURNAL OF
ENVIRONMENTAL
SCIENCES
www.jesc.ac.cn

Spatial variability and possible sources of acetate and formate in the surface snow of East Antarctica

Gautami Samui*, Runa Antony, Kanthanathan Mahalinganathan, Meloth Thamban

National Centre for Antarctic and Ocean Research, Headland Sada, Vasco-da-Gama, Goa 403804, India

ARTICLE INFO

Article history:

Received 7 September 2016

Revised 3 February 2017

Accepted 6 February 2017

Available online xxxx

Keywords:

Monocarboxylate ions

Snowpack

Antarctica

ABSTRACT

Spatial trends of acetate (Ac^-) and formate (Fo^-) were determined in surface snow samples along a coastal-inland transect (180 km) in the ice cap region at Princess Elizabeth Land and along a coastal transect in the Amery Ice Shelf (130 km), East Antarctica. Variations in both Ac^- and Fo^- seem to be unrelated to the acidity of snow. Ionic balance determined for the snow samples indicate the availability of HNO_3 that could undergo photolysis to produce hydroxyl radical ($\cdot\text{OH}$), one of the major reactants involved in oxidation reactions with organic matter. The strong positive correlations between Ac^- and NO_3^- in snow from both regions indicate that NO_3^- mediated $\cdot\text{OH}$ -oxidation of organic compounds in snow could be an important source of Ac^- within the snowpack. On the other hand, negative correlation between Fo^- and NO_3^- might indicate that sources other than $\cdot\text{OH}$ -oxidation of organic matter may be dominant in the case of Fo^- . Higher Ac^- concentrations in the ice cap compared to the ice shelf correspond with long-range transport of biomass burning emissions to the ice cap region. Interaction of Ac^- and Fo^- with alkaline minerals could lead to their stability in the snowpack and minimize their loss from the snow surface. Resident microbial communities could also influence the budget of the carboxylic acids in snow.

© 2017 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

Carboxylic acids are one of the dominant classes of organic compounds which are ubiquitously distributed in the environment. In addition to inorganic acids such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3), organic acids also contribute to the free acidity of the environment (Galloway et al., 1982; Legrand and De Angelis, 1995). Low-molecular weight monocarboxylic acids such as acetic acid (HAc) and formic acid (HfO) are the most abundant carboxylic acids in the global troposphere (Keene and Galloway, 1988) and are present in the atmosphere mainly in the gaseous phase (Talbot et al., 1988). Formic acid and acetic acid have a variety of sources which include emissions from soil and vegetation,

fossil fuel and biomass burning, vehicular emissions and photo-chemical oxidation of organic matter (Legrand and De Angelis, 1995; Legrand et al., 2004; Paulot et al., 2011; Sanhueza et al., 1996; Souza et al., 1999; Souza and Carvalho, 2001; Talbot et al., 1988; Udisti et al., 1998). In southern latitudes, photo-oxidation of low-molecular weight alkenes by ozone (O_3), reactions of peroxy acetyl radical with peroxy radicals and oxidation of formaldehyde by hydroxyl radical ($\cdot\text{OH}$) are the major pathways that contribute to the atmospheric budgets of HfO and HAc (Legrand and De Angelis, 1995; Legrand et al., 2004).

Multiple year-round budgets of HfO and HAc in coastal Antarctica show significant inter-annual variability with higher levels of these acids in the summer. Higher summer levels of

* Corresponding author.

E-mail address: gautami@ncaor.gov.in (Gautami Samui).

HAc are mainly attributed to reactions of peroxy acetyl radical produced from propene (emitted by photo-degradation of dissolved organic matter over the Antarctic Ocean) with HO₂ and CH₃O₂ radicals (Legrand et al., 2004). On the other hand, summer levels of formic acid were attributed to have an additional and unknown source. Conversely, in winter, reactions of alkenes derived from long-range transport from temperate oceanic regions with that of O₃ is believed to account for the observed level of HFO and possibly of HAc (Legrand et al., 2004). An extended year-round study of HFO and HAc present in the lower atmosphere of coastal Antarctica, indicate that these species are abundant in the summer with significantly higher mixing ratios of HAc in the summer season of following years (Legrand et al., 2012). The higher mixing ratios were associated with the observed higher acetaldehyde concentrations indicating that ·OH-oxidation of acetaldehyde is a major precursor of HAc (Legrand et al., 2012).

A few studies have documented carboxylic acid contents of very low concentrations (few ppb) in snow/ice (Legrand and Saigne, 1988; Legrand et al., 2013; Udisti et al., 1991). The low concentrations of HAc and HFO in snow appear to result from both poor preservation and inefficient incorporation of HAc and HFO within the snow grains. Monocarboxylic acids can be lost from surface snow in days to weeks after deposition (De Angelis and Legrand, 1995). The incorporation and preservation of formate (Fo⁻) and acetate (Ac⁻) (to a lower extent) in snow increase with the increasing pH of snow (Legrand and De Angelis, 1996). Carboxylate ions may also be produced within the snowpack/firm air as demonstrated by the higher mixing ratios of HAc and HFO in the firm air as compared to the ambient air (Dibb and Arsenault, 2002). It is believed that the oxidation of carbonyls and alkenes that are produced by photo- and ·OH-oxidation of organic compounds in snow are the major sources of monocarboxylic acids within the snowpack (Dibb and Arsenault, 2002). Despite being an important source of organic acids, most studies on carboxylate ions are focused on the seasonal concentrations and variations of carboxylic acids in the atmosphere and studies in snow/ice are limited.

Carboxylic acids such as Ac⁻ and Fo⁻ along with a suite of reactive gas species that are central to the understanding of tropospheric chemistry can be released from the snow to the atmosphere (Dibb and Jaffrezo, 1997). Since, these organic acids contribute to total acidity of precipitation (Kawamura et al., 1996; Keene et al., 1983) and can potentially play an important role in the cloud condensation nuclei activity and influence the radiation budget of the earth's atmosphere (Kanakidou et al., 2005), understanding the sources and fluxes of these organic acids is important. The study of carboxylic acids in Antarctic snow can also provide useful information on the sources and transport processes of atmospheric constituents related to biogeochemical cycling (Keene and Galloway, 1988; Legrand and Saigne, 1988). In addition, carboxylic acids are one of the important components of dissolved organic matter in the snowpack (Legrand et al., 2013) and are possible carbon sources for resident microorganisms (Amato et al., 2007), potentially playing an important role in biological processes within the snowpack. Studies on organic acids in the snowpack would help better understand the sources and factors that influence their deposition in snow and their effect on the overlying atmosphere as well. To understand the sources and spatial

variability (with respect to distance from the sea and elevation) of monocarboxylic acids, 18 surface snow samples from Princess Elizabeth Land (PEL) and 13 from the Amery ice shelf, East Antarctica were analyzed for monocarboxylic acids, inorganic ions, total organic carbon (TOC), microbial cells and dust. We discuss the spatial variability of Ac⁻ and Fo⁻ and their relation with other ionic species, organic carbon, microbes and dust, with some inferences on their sources.

1. Materials and methods

1.1. Study region and sampling

Surface snow samples were collected along a coastal-inland transect (180 km) in the ice cap region at Princess Elizabeth Land and a coastal transect in the Amery Ice Shelf (130 km), East Antarctica (Fig. 1). Beginning at 10 km from coast in the ice cap, eighteen surface snow samples were collected in January 2008 at 10 km interval up to 180 km inland. Elevation of the sampling points ranged from 267 to 2210 m above mean sea level (m a.s.l.). In the Amery Ice Shelf, thirteen surface snow samples were collected along the shelf starting at 10 km from the coastline to 130 km perpendicular to the coast at every 10 km interval in January/February, 2014. In this transect, sampling was carried out at near sea level to about 62 m a.s.l. The surface snow samples (~20 cm deep) represent the early spring and summer snowfall events, based on the snow accumulation rates estimated from a series of 1 m snow cores collected along the ice shelf transect (unpublished data) and in the ice cap transect (Mahalinganathan et al., 2012).

In the ice cap transect, surface snow samples were collected using a pre-cleaned polypropylene scoop and stored in well sealed and pre-cleaned Low Density Polyethylene (LDPE) bags. Details of snow sample collection and storage are described in Antony et al. (2011). At the Amery Ice Shelf, samples for organic carbon analysis were collected in air tight, pre-cleaned and combusted (450°C, 4 hr) amber glass bottles using sterile teflon scoops. Sample collection bottles were cleaned and combusted just a few hours prior to sampling and then tightly closed until sampling in order to minimize bottle blank values. During sampling, care was taken to ensure that snow grains do not stick to the glass thread so as to prevent contamination resulting from improper closure of the glass bottle. Samples for inorganic ion analysis and microbial analysis were collected in sterile whirl-pak bags. All samples were stored and transported at -20°C in Expanded Polypropylene (EPP) boxes.

1.2. Precautions taken during sample handling and analysis

Measurement of organic carbon present at trace levels in precipitation of remote regions is influenced by contamination resulting from organic gases present in the atmosphere, sampling materials used and by photolysis on exposure to light. To avoid contamination, samples were collected and processed under stringent conditions. Containers and vials made of glass were used during preparation of standard solutions, sample processing and analysis of TOC and carboxylate ions. For TOC analysis, all glassware were soaked in 0.5%

Download English Version:

<https://daneshyari.com/en/article/5754215>

Download Persian Version:

<https://daneshyari.com/article/5754215>

[Daneshyari.com](https://daneshyari.com)