Formate and acetate as recorded in a mid-latitude glacier in west China

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Abstract Formate and acetate are ubiquitous in the troposphere. Their occurrence is closely related to processes in the biosphere and contributes to an understanding of carbon biogeochemical cycles. A 43-year record of formate and acetate in an ice core from Glacier 1 (43°06 N. 86°49 E) at Urumqi river head, Tianshan, west China was investigated. Fluctuating between 22.7 ng \cdot g⁻¹ and 2830.7 ng \cdot g⁻¹, acetate concentration averages 373.2 \pm 376.1 ng \cdot g⁻¹ (mean \pm 1s, N = 541) and is the highest anion in the record. Next to acetate, the concentration for formate varies between 2.1 ng \cdot g⁻¹ and 795.5 ng \cdot g⁻¹ and averages 61.1 ± 89.0 ng \cdot g⁻¹ (N = 541). The formate to acetate ratio averages 0.22 ± 0.25 (N = 541), indicating that the chief source is from fossil fuel combustion, coal burning in particular. The two species co-varied in the past four decades and exhibited periods of high concentration from the early 1960s to the middle of 1970s and from the early 1980s to the middle of 1990s, separated by a time of the lower concentration between 1975-1980. These variations may reflect the local/regional anthropogenic pollution to the atmosphere as well as the economic development of northwestern China.

Keywords: carboxylic acid, coal combustion, atmospheric pollution, cryosphere, alpine glacier, Tianshan.

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Formic (HCOOH) and acetic (CH₃COOH) acids are the chief carboxylic compounds in the troposphere^[1]. Although weak acids, they contribute significantly to the free acidity, ionic balance of precipitation and the chemical reactions in the atmosphere, especially in the remote areas^[2–4]. General sources for formate and acetate have been identified in the past 3 decades although a satisfactory source attribution is lacking to explain atmospheric observations^[5]. Possible sources include emission^[6,7], burning^{[7} – biomass vegetation anthropogenic pollution by fossil fuel combustion and wood and garbage burning^[7,10,11]. as well as

photochemical reactions of unsaturated hydrocarbons^[12–15]. In the tropics, soil and formicine ants also contribute^[16,17]. Because their sources are closely related to the biosphere, the study of the carboxylic acids in the environment helps our understanding of carbon biogeochemical cycles.

Polar ice sheets and alpine glaciers provide information in a unique way on the past variations of carboxylic compounds in response to climatic and environmental changes. Their potential was first identified in 1987 when Saigne and his colleagues reported their analysis of formate and acetate in ice core of Dome C, Antarctica^[18]. The decades afterwards saw multiple research on the carboxylic acids in ice and snow of both Antarctica^[19,20] and Greenland^[21 – 25]. Few studies, however, were undertaken on ice cores of mid and low latitude mountain glaciers.

In this work, we investigate formate and acetate record in an ice core from Glacier 1, a mid-latitude glacier in western China, and its relationship with anthropogenic pollution to the regional atmosphere.

1 Environmental settings and the ice core

Located at 43°06 N, 86°49 E in the central Eurasian continent, Glacier 1 is a valley glacier at Urumqi River head, Xinjiang Uygur Autonomous Region, China^{126]}. It is surrounded by vast areas of desert and Gobi (Fig. 1). In contrast to the mountainous topography, the Tarim and Junggar basins are located to the south and north, respectively. Around the edges of the two basins are scattered a few cities and towns with industrial facilities. Urumqi, the capital city of Xinjiang Uygur Autonomous Region, is situated approximately 105 km far away to the northeast. 50 km down the Urumqi River valley lies the town Houxia, at which a steel works and a cement plant have been in existence since 1958.

High above the Tianshan, the prevailing westerly jet brings water vapor from Atlantic Ocean: this forms the main contribution to precipitation in the area, which mainly occurs from May to September^[27], while below 1500 m altitude, cyclonic and anticyclonic circulation systems develop^[28]. Moreover, the composite geographic environment of high mountains and desert basins also provides source areas for the valley wind that prevails from March to September^[29].

The ice core studied here is 14.08 m long and was retrieved in October 1998 at 4040 m a.s.l. in the superimposed ice zone of the east branch of the glacier, close to the monitored point H'_2 at 4042 m a.s.l. (Fig. 2). It is composed of clear dense ice with scarce bubbles, which formed in the superimposed ice zone, and opaque bubbly ice with spherical bubbles of 1—2 mm in diameter, which formed in the percolation zone, as well as a few dust layers. In the upper part of the ice core, a nearly-vertical crack cut through from 138 to 386 cm, and this has affected the ice within 2 to 3 cm of the fracture plane by

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Fig. 1. Geographic environment around Tianshan.

inducing the surface melt water^[30]. The core was crossdated by δ^{18} O, β activity, and variations of pyruvate and ECM. It covers a period of 43 years from 1955 to 1998 with an uncertainty about one year. For more details of the dating, see ref. [31].



Fig. 2. Glacier 1 and the drilling site which is located near the monitored point H'_2 at the east branch of the glacier.

2 Analytic procedures

Samples were selected every 2 cm from the central part of the ice core. In the fractured section (FS), however, they were selected to avoid the fracture as much as possible. Around the depth of 260 cm where the fracture

cuts through the center of the core, samples were selected on both sides. In order to avoid the outer one-centimeter of the core that is susceptible to the drilling contamination^[22], however, the sampling was compromised by including part of the ice influenced by the crack. The samples were kept frozen in glass vials with airtight covers until analysis.

The selected samples were exposed to the air, albeit very briefly. In order to evaluate possible contamination from this exposure, blank analysis was carried out. Newly-made ultra-pure water (18.2 M Ω cm⁻¹) was frozen quickly into cylindrical ice in glass containers. The artificial ice was then sectioned and analyzed exactly in the way the samples were processed. Two species were detected in the blanks, which are CH₃COO⁻ and Cl⁻. The blank value for CH₃COO⁻ is 31.7 ± 23.7 ng \cdot g⁻¹ (mean ± 1 σ , *N* = 12, the same for the following statistics).

Formate and acetate were determined by Ion Chromatography (DX-300) with AS4A separator using a gradient method. In order to separate light carboxylates that are very close in retention time, a very weak solution of tetraborate (2%) was employed in the first stage of the gradient elution. Calibrated with AccuIonTM Reference IC-FORM-1X-1 (for formate) and IC-ACET-1X-1 (for acetate) of Aldrich Chemical Company, the relative standard deviation for the two species is 2.0% and 4.5%, respectively. For more details of the analysis, see ref. [31].

3 Results and discussions

Acetate is the most abundant chemical species recorded in the ice core, even allowing for the inorganic species. Fluctuating between 22.7 and 2830.7 ng \cdot g⁻¹, it

averages $373.2 \pm 376.1 \text{ ng} \cdot \text{g}^{-1}$ (N = 541, not allowing for the concentration in the FS, the same with the following statistics). The high concentration is corroborated by the analysis of snow pack in the same glacier where acetate is observed to be a few hundreds ng \cdot g^{-1 [32]}. Variation of acetate in the ice core reveals reaches an initial peak from the early 1960s to the middle of 1970s followed by another period of high abundance from the early 1980s to the middle of 1990s (Fig. 3). This trend is further testified by the data that were averaged in five-year intervals (Table 1). The occurrence of the crack in the ice core corresponds approximately to the period 1986-1993. The influence from the crack, which enhanced the concentration^[30], however, exists only around 1989 ± 2 years (shaded depth in Fig. 3). Therefore, the period from 1985-1989, which includes the time interval saw the highest acetate in 632.1 ng \cdot g⁻¹. In the adjacent part corresponding to 1980-1984 that is free from the influence, however, acetate still has a high concentration (365.8 ng \cdot g⁻¹), indicating the onset of the other high period of the species. Between the two high periods is 1975—1979 that has relative low acetate in 280.8 ng \cdot g⁻¹, close to the concentration in 1955-1959.

Formate varies between 2.1 ng \cdot g⁻¹ and 795.5 ng \cdot g⁻¹ and averages 61.1 ± 89.0 ng \cdot g⁻¹ in the record (N = 541). These values are in agreement with those observed in snow packs of the glacier, where formate is between a



Fig. 3. Record of acetate and formate in the ice core of Glacier 1. The width of the shaded square indicates the core section that was affected with the two species by the crack.

Table 1 Average value for acetate and formate in the five-year interval from 1955 to 1998^{a)}

	$CH_3COO^-/ng \cdot g^{-1}$	HCOO ^{-/} ng \cdot g ⁻¹
1995—1998	317.3(261.3)	73.8(40.6)
1990—1994	301.3(240.9)	188.1(58.6)
1985—1989	632.1(525.8)	331.7(184.4)
1980—1984	365.8(298.6)	62.4(90.0)
1975—1979	280.8(230.8)	46.0(50.1)
1970—1974	496.4(420.5)	111.8(65.2)
1965—1969	423.5(289.6)	79.0(86.0)
1960—1964	382.4(249.8)	38.2(39.2)
1955—1959	225.1(120.1)	20.0(9.9)

a) Numbers in parentheses designate the standard deviation (1σ) .

hundred to a thousand $ng \cdot g^{-1}$ [32]. In the FS, formate is much more affected by cracking effect^[30] and thus exhibits a larger peak around 260 cm (shaded depth in Fig. 3). Despite this, however, formate is consistent with acetate in the variation in the past four decades. From the early 1960s to the middle of 1970s and the early 1980s through to the middle of 1990s are also two high periods punctuated by the low interval of 1975-1979 (Fig. 3 and Table 1). The covariation of formate with acetate can be further illustrated in the logarithmic curve of the two species (Fig. 4). Not only the general trends are in agreement with each other, but also the most peaks and valleys of one species can find their counterparts in the other though not necessarily proportional in the extent. The covariation of the record suggests that formate and acetate in the area have been controlled by the same processes or sharing the same sources in the past four decades.



Fig. 4. Comparison of formate and acetate record in logarithmic curves. Note that formate is much more enhanced by the cracking effect and thus is higher around 1990. The width of the shaded square indicates the core section that was affected with the two species by the crack.

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The ratio of formate to acetate has been considered as an indicator of the sources for the two species. The relative importance of anthropogenic emission to natural emission was thought to determine the ratio in the atmosphere^[33]. Based on analysis of various sources, Talbot and his colleagues^[7] found that air masses that were influenced chiefly by anthropogenic emissions had ratios lower than 1, while those influenced mainly by natural sources, vegetation emissions in particular, had the ratios larger than one except pollen, which has the ratio very close to automobile exhaust. Formate to acetate ratios in the record of Glacier 1 range between 0.0 and 2.5. If not taking into account those enhanced values in the FS, the ratios average 0.22 ± 0.26 (N = 539) with only a few high peaks exceeding unity. The lower-than-unity ratio suggests an anthropogenic source. This is consistent with the fact that the Chinese Tianshan is surrounded by vast areas of desert and Gobi. Therefore the direct emission from vegetation could not have been a major source to the organic species, nor could forest fires. Furthermore, since Tianshan is situated in the mid latitudes, soil and ant emissions could not be a major source either. Compared with the source experiment^[7], the mean ratio of formate to acetate in Glacier 1 is close to emissions of vehicular combustion and biomass burning (Fig. 5). Considering the limited cities and industrial towns as well as the low level of human population in the surrounding area, automobile combustion and wood burning for daily life should not be the major provenance. Fossil fuels, coal in particular, have been widely used in the area as the energy supply for electricity generation, home heating and cooking. The fossil fuel combustion is the principal form of biomass burning; therefore, it might be the principal source for the organic species.



Fig. 5. Formate to acetate ratios of various sources. The cross designates the mean ratio in Glacier 1 record. Other ratios together with their error bars are digitalized from Fig. 10 in ref. [7]. Ratios that lie in the shaded area indicate sources relating to anthropogenic sources.

The retention time for formate and acetate in the atmosphere was considered to be several hours to several days^[34] or several weeks^[7,14,35]. They can be transported 200 km away from the sources before deposition or decomposition^[1,34]. Accordingly, atmospheric pollution from cities and industrial towns within the vicinity must have been responsible for the organic compounds in the area. Urumqi is a hundred kilometers from Glacier 1. Atmospheric pollutants from the city can be transported to the glacier by the prevailing cyclonic or anticyclonic circulation^[28]. Additionally, Houxia, though a small town, should not be underestimated in contributing the organic species to the glacier. Clouds from the factories drift in the valley and can readily reach up to Glacier 1 by the prevailing valley wind.

Coal consumption, to some extent, reflects economic development. Formate and acetate in the ice core are mainly from pollution of local and/or regional coal combustion. The record of the species in Glacier 1, therefore, may reflect economic development of the region as well as, because of the widespread and synchronous socialist constructions of China, of the whole country. China began its industrialization at the end of the 1950s and the beginning of 1960s. Many of the coal consuming factories were built in the period. The practice lasted until the late 1970s when economic development slowed. Corresponding to the movement, the formate and records exhibit their first concentration acetate enhancement during 1960-1974 and then the decrease in about the next five years. From the beginning of the 1980s, China experienced a new period of rapid development, during which time the glacier recorded the second increase of the organic compounds. The record has not, however, kept rising during the last ten years, and this probably reflects improvement of the atmospheric environment due to pollution treatment and prevention in the regional industrial activities.

4 Conclusion

Located in the mid latitude, Glacier 1 at Urumqi river head, Tianshan, China, is surrounded by areas with not only limited vegetation but also limited industrial cities. Therefore, it provides a simplified background for studying biogechemical cycles of the carboxylic compounds. Formate and acetate, the chief constituents of the organic compounds, average 61.1 ± 89.0 and $373.2 \pm$ 376.1 ng \cdot g⁻¹, respectively. The two species co-varied in the past 43 years and mainly came from fossil fuel combustion. Their records, therefore, may reflect regional anthropogenic pollution to the atmosphere as well as, to some extent, the regional economic development of northwest China.

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