

SIR,

Recent 180 year oxalate ($C_2O_4^{2-}$) records recovered from the Mount Everest ice core: some environmental implications

Carboxylic acids (e.g. formate, acetate, glycolate and oxalate) are common constituents of global precipitation (Galloway and others, 1982) and are major contributors to the acidity of precipitation in the remote atmosphere at low and mid-latitudes (Keene and Galloway, 1986). Despite their potentially important roles in tropospheric chemistry, few investigations of snow carboxylic acids have been conducted in remote areas, particularly in Asia. There is only one report of organic acids in snow from the Guliya ice cap in the northwestern Qinghai–Tibetan Plateau, which covers the period 1977–91 (Sun and others, 1998), and a few from polar regions (Legrand and others, 1992; Legrand and Angelis, 1995). To get a first understanding of atmospheric organic-acids variations and their environmental significance, we present the ice-core record of oxalate ($C_2O_4^{2-}$) from Far East Rongbuk (FER) Glacier, Mount Everest.

During the Sino-U.S. Cooperative Glaciological Expedition to Mount Everest in May 1997, a 41 m core, covering the period AD 1814–1997, was collected from a site at 6500 m a.s.l. on FER Glacier on the northern slope of Mount Everest. Detailed methods of ice-core sampling and chemical analysis are described by Kang and others (2000) and Qin and others (2000). The ice core was dated by Qin and others (2000), and ice-core sampling was similar to the method of Legrand and De Angelis (1995), in order to reduce contamination for trace carboxylic acid determination.

Variations of the 10 year mean of $C_2O_4^{2-}$, Ca^{2+} and NH_4^+ concentrations and $\delta^{18}O$ values during the past 180 years from the FER ice core are shown in Figure 1. The mean $C_2O_4^{2-}$ concentration is 13.7 ng g^{-1} for the last 180 years (Table 1). During the 19th century, $C_2O_4^{2-}$ concentrations were $0.0\text{--}45.5 \text{ ng g}^{-1}$ with a mean value of 7.9 ng g^{-1} . In the 20th century, $C_2O_4^{2-}$ concentrations were $0.0\text{--}332.5 \text{ ng g}^{-1}$, with a mean value of 18.6 ng g^{-1} , and the highest values occurred during the 1960s. Considering 10 year averages, $C_2O_4^{2-}$ concentrations were lowest from the 1840s to the 1870s and have increased since the beginning of the 20th century, reaching their highest values in the 1960s. The highest $C_2O_4^{2-}$ mean concentration, which occurred from the 1950s to the 1980s with a mean value of 24.8 ng g^{-1} , is three times higher than that of the 19th century. From error bars (± 1 std dev.) (Fig. 1) and standard deviations (Table 1), the fluctuations of $C_2O_4^{2-}$ are small in the 19th century, suggesting that the variations of $C_2O_4^{2-}$ may be seasonal fluctuations around the background level. During the 20th century, however, especially during the 1950s–80s, many peaks of $C_2O_4^{2-}$ concentration occur and the fluctuations are dramatic, indicating that short episodes with high $C_2O_4^{2-}$ concentrations account for elevated mean values in the 20th century.

In order to investigate the environmental implications of $C_2O_4^{2-}$ variations, the sources of $C_2O_4^{2-}$ should be considered. Carboxylic acids come from vegetation emissions and biomass burning (Andreae and others, 1988; Talbot and others, 1988; Legrand and others, 1992), the oxidation of various alkenes (Jacob, 1986) and anthropogenic emissions (Talbot and others, 1988; Legrand and others, 1995).

The apparently increasing tendency of $C_2O_4^{2-}$ concentrations during the 20th century is not consistent with that of Ca^{2+} , which is representative of atmospheric dust (Kang and others, 2000) in the Himalaya (Fig. 1), suggesting that the source of $C_2O_4^{2-}$ has very little relation to atmospheric dust. NH_4^+ comes mainly from biogenic sources in the Himalaya (Mayewski and others, 1983; Davidson and others, 1986), and the general trend of variations is not obvious (Fig. 1), suggesting that the distinct increase of $C_2O_4^{2-}$ concentrations is not mainly related to biogenic sources and hence may be caused by other sources. Ice-core $\delta^{18}O$ (as a temperature proxy) has increased since the beginning of the 20th century, and the general tendency broadly follows that for the $C_2O_4^{2-}$ variations (Fig. 1). However, the increase of $C_2O_4^{2-}$ in the 20th century is more dramatic than that of $\delta^{18}O$. The temperature increase may influence the $C_2O_4^{2-}$ concentration (e.g. the strength of the emissions by vegetation or the oxidation of various alkenes) but is not the dominant factor for higher $C_2O_4^{2-}$ concentrations in the 20th century, particularly during the 1950s–80s.

Oxalate has been mass-produced by industry since the 1940s (e.g. in Germany) (Hong, 1997). Thus we assumed that $C_2O_4^{2-}$ concentrations in the 19th century are not influenced by industrial emissions and may represent the background values, while higher $C_2O_4^{2-}$ concentrations, especially those peaks due to short episodes during the 1950s–80s, may be caused by industrial emissions. As industrial chemicals, oxalate and its derivatives are used

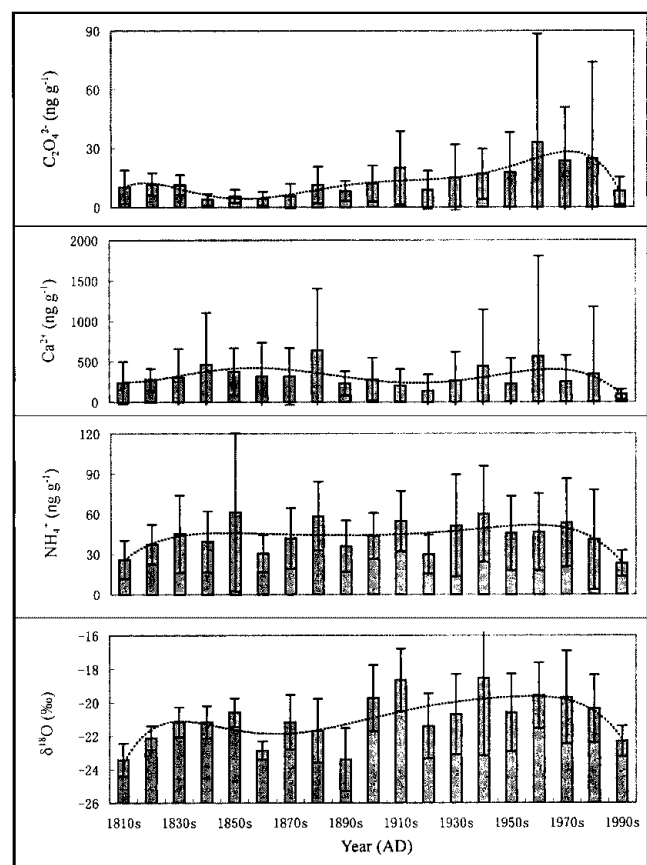


Fig. 1. Variations of 10 year mean of $C_2O_4^{2-}$, Ca^{2+} and NH_4^+ concentrations and $\delta^{18}O$ values and their tendencies from FER ice core. Dashed lines represent the multinomial of the power of six. Error bars represent ± 1 std dev.

Table 1. Ten-year mean of $C_2O_4^{2-}$ concentrations ($ng\ g^{-1}$) from FER ice core

Years	Max.	Min.	Mean	Std dev.
1810s	28.0	0.0	10.3	8.5
1820s	20.9	0.0	11.8	5.7
1830s	22.2	0.0	11.4	5.1
1840s	11.2	0.0	3.9	3.0
1850s	16.7	0.0	5.6	3.4
1860s	20.2	0.0	4.3	3.6
1870s	30.0	0.0	5.8	6.2
1880s	45.5	0.8	11.5	9.3
1890s	27.5	1.5	8.4	5.0
1810s–90s	45.5	0.0	7.9	6.4
1900s	45.0	0.0	12.1	9.2
1910s	82.5	1.4	20.1	18.6
1920s	46.4	0.0	8.8	9.7
1930s	84.4	0.0	15.1	16.8
1940s	45.7	0.0	17.0	12.9
1950s	115.2	0.0	17.8	20.3
1960s	332.5	0.0	32.9	55.6
1970s	113.8	0.0	23.7	27.2
1980s	310.2	0.0	24.6	49.2
1990s	26.3	0.0	8.2	7.0
20th century	332.5	0.0	18.6	28.6
1810s–1990s	332.5	0.0	13.7	22.1

extensively in the chemical industry (e.g. the medical, textile and metallurgical sectors) (Hong, 1997). Though the transportation and deposition for these industrial $C_2O_4^{2-}$ pollutants from source regions to mountain glaciers are not well known, the ice-core $C_2O_4^{2-}$ records from Mount Everest provide a unique opportunity to assess the contribution of anthropogenic emissions to the background $C_2O_4^{2-}$ concentration.

In the mid-20th century, industrial pollution by oxalate was very serious, and was less effectively controlled than today. More recently, strict controls have been imposed on industrial pollution, and many oxalate-producing factories have been closed around the world (Hong, 1997). This may be the reason for the lower $C_2O_4^{2-}$ concentrations in the 1990s. On the other hand, the $C_2O_4^{2-}$ concentrations start to increase around 1900, possibly related to the temperature increase (Fig. 1). In summary, the $C_2O_4^{2-}$ concentration during the 1950s–80s, which may mainly reflect anthropogenic emissions, is about three times higher than the background value in the 19th century.

ACKNOWLEDGEMENTS

This research is supported by the Chinese Natural Science Foundation (49871022, G1999043400), the Chinese Academy of Sciences (KZ951-A1-402, KZCX1-10-02, KZCX-2-301, 108), the Cold and Arid Regions Environmental and Engineering Research Institute (CACX210506, 210046), and a cooperative project between the Cold and Arid Regions Environmental and Engineering Research Institute and the Climate Change Research Center, University of New

Hampshire. We thank members of the 1997 Sino-U.S. Co-operative Glaciological Expedition to Mount Everest for assistance in the field, and S. Whitlow and Sun Weizheng for analyzing the samples.

Laboratory of Ice Core and
Cold Regions Environment,
Cold and Arid Regions Environmental
and Engineering Research Institute,
Chinese Academy of Sciences,
Lanzhou 730000, China

KANG SHICHANG*
QIN DAHE

Institute for Quaternary
and Climate Studies,
University of Maine,
Orono, Maine 04469, U.S.A.

PAUL A. MAYEWSKI

Climate Change Research Center,
Institute for the Study of Earth, Ocean and Space,
University of New Hampshire,
Durham, New Hampshire 03824, U.S.A.

CAMERON P. WAKE

26 January 2001

REFERENCES

- Andreae, M. O. and 14 others. 1988. Biomass-burning emission and associated haze layers over Amazonia. *J. Geophys. Res.*, **93**(D2), 1509–1527.
- Davidson, C. I., S. Lin, J. F. Osborn, M. R. Pandey, R. A. Rasmussen and M. A. K. Khalil. 1986. Indoor and outdoor air pollution in the Himalayas. *Environ. Sci. Technol.*, **20**(6), 561–567.
- Galloway, J. N., G. E. Likens, W. C. Keene and J. M. Miller. 1982. The composition of precipitation in remote areas of the world. *J. Geophys. Res.*, **87**(C11), 8771–8786.
- Hong Zhongling. 1997. [Organic industrial products.] In Hong Zhongling, ed. [*Deeply processing of organic industrial chemicals.*] Beijing, Chemical Industry Press, 421–438. [In Chinese.]
- Jacob, D. J. 1986. Chemistry of OH in remote clouds and its role in the production of formic acid and peroxyoxymonosulfate. *J. Geophys. Res.*, **91**(D9), 9807–9826.
- Kang Shichang, C. P. Wake, Qin Dahe, P. A. Mayewski and Yao Tandong. 2000. Monsoon and dust signals recorded in Dasuopu glacier, Tibetan Plateau. *J. Glaciol.*, **46**(153), 222–226.
- Keene, W. C. and J. N. Galloway. 1986. Consideration regarding sources for formic and acetic acids in the troposphere. *J. Geophys. Res.*, **91**(D13), 14,466–14,474.
- Legrand, M. and M. de Angelis. 1995. Origins and variations of light carboxylic acids in polar precipitation. *J. Geophys. Res.*, **100**(D1), 1445–1462.
- Legrand, M., M. De Angelis, T. Staffelbach, A. Nefel and B. Stauffer. 1992. Large perturbations of ammonium and organic acids content in the Summit-Greenland ice core: fingerprint from forest fires? *Geophys. Res. Lett.*, **19**(5), 473–475.
- Mayewski, P. A., W. B. Lyons and N. Ahmad. 1983. Chemical composition of a high altitude fresh snowfall in the Ladakh Himalayas. *Geophys. Res. Lett.*, **10**(1), 105–108.
- Qin Dahe and 9 others. 2000. Evidence for recent climate change from ice cores in the central Himalaya. *Ann. Glaciol.*, **31**, 153–158.
- Sun Junying, Qin Dahe, Yao Tandong and Li Zhongqin. 1998. [Preliminary analyses of biogenic organic acids in Guliya ice core.] *J. Glaciol. Geocryol.*, **20**(2), 163–166. [In Chinese with English summary.]
- Talbot, R. W., K. M. Beecher, R. C. Harriss and W. R. Cofer, III. 1988. Atmospheric geochemistry of formic and acetic acids at a mid-latitude temperate site. *J. Geophys. Res.*, **93**(D2), 1638–1652.

* Also at Institute for Quaternary and Climate Studies, University of Maine, Orono, Maine 04469, U.S.A.