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Variation of airborne quartz in air of Beijing during the Asia-Pacific Economic Cooperation Economic Leaders' Meeting

Gang Li[1], Yingming Li[1], Hongxing Zhang[2], Honghua Li[1], Guanjun Gao[1], Qian Zhou[1], Yuan Gao[1], Wenjuan Li[1], Huizhong Sun[1], Xiaoke Wang[2], Qinghua Zhang[1,3,*]

1. State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: gangli@rcees.ac.cn

2. Beijing Urban Ecosystem Research Station, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

3. Institute of Environment and Health, Jianghan University, Wuhan 430056, China

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ABSTRACT

Quartz particles are a toxic component of airborne particulate matter (PM). Quartz concentrations were analyzed by X-ray diffraction in eighty-seven airborne PM samples collected from three locations in Beijing before, during, and after the Asia-Pacific Economic Cooperation (APEC) Leaders' Meeting in 2014. The results showed that the mean concentrations of quartz in PM samples from the two urban sites were considerably higher than those from the rural site. The quartz concentrations in samples collected after the APEC meeting, when the pollution restriction lever was lifted, were higher than those in the samples collected before or during the APEC meeting. The quartz concentrations ranged from 0.97 to 13.2 $\mu g/m^3$, which were among the highest values amid those reported from other countries. The highest quartz concentration exceeded the Californian Office of Environmental Health Hazard Assessment reference exposure level and was close to the occupational threshold limit values for occupational settings. Moreover, a correlation analysis showed that quartz concentrations were positively correlated with concentrations of pollution parameters PM_{10}, $PM_{2.5}$, SO_2 and NO_x, but were negatively correlated with O_3 concentration. The results suggest that the airborne quartz particles may potentially pose health risks to the general population of Beijing.

Introduction

Quartz is the most thermodynamically stable form of silica. It has been suggested in a number of studies that quartz is a lung carcinogen that poses considerable risks to human health (Hessel et al., 2000; Lynge et al., 1986). Studies in Sweden (Westerholm and Scand, 1980), Ontario in Canada (Finkelstein et al., 1982), and elsewhere (Begin et al., 1987; Emerson and Davis, 1983) published in the 1980s showed that there is a probable relationship between exposure to crystalline silica and the occurrence of lung cancer. The International Agency for Research on Cancer (IARC) classified quartz as a Group 2A chemical (*i.e.*, probably carcinogenic to humans) in 1987 (IARC, 1987). The agency later concluded, from epidemiological data and the results of animal model studies, that there was sufficient evidence for inhaled quartz to be

* Corresponding author.
E-mail: qhzhang@rcees.ac.cn (Qinghua Zhang).

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classified as a carcinogen to humans exposed to certain occupational sources (IARC, 1996). The agency classified quartz as a Group I chemical (carcinogenic to humans) in 2012 (IARC, 2012).

A great deal of research into the carcinogenic properties of quartz has been performed, but there is still some disagreement about the mechanism through which quartz causes cancer. Borm et al. (2011) suggested that quartz could primarily be genotoxic directly by interacting with target cells or indirectly by causing inflammation (the inflammatory cell-derived oxidants being genotoxic). It has also been suggested in some publications that quartz particles can be phagocytized by cells and accumulate in the perinuclear regions of the cells. The presence of quartz within a cell could interfere with the segregation of the chromosomes when the cell undergoes mitosis, causing anaphase abnormalities to occur (Barrett et al., 1989).

Most systematic carcinogenic risk assessments for quartz have been focused on occupational exposure. For example, it has been suggested that the presence of highly reactive radicals on the surfaces of fractured silica that may be present in certain workplaces make the fractured silica highly cytotoxic (Castranova et al., 1996; Clouter et al., 2001). Dobias et al. (2006) suggested that quartz dust is genotoxic and is an important contributor to the genotoxicity of complex mixtures of fibrogenic respirable airborne particles in ambient air in certain workplaces. Westberg et al. (2013) measured cancer morbidity in Swedish iron foundry workers exposed to quartz. They found significant overall risks of the foundry workers developing lung cancer. However, it has been shown in *in vivo* and *in vitro* toxicological studies (Balduzzi et al., 2004; Porter et al., 2002) that environmental quartz particles may also have important inflammatory effects. A clear association between exposure to quartz and the development of active tuberculosis has been found not only among silicotic individuals but even in people exposed to quartz dust over long periods of time (Mason and Thompson, 2010; Solomon et al., 2000). The risks associated with exposure of the general population to quartz cannot therefore be ignored; but, until now, very few measurements of quartz concentrations in ambient air have been available.

Environmental pollution in China, especially air pollution in some Chinese mega-cities, has been increasing in severity in recent years (Sun et al., 2015; He et al., 2015). For example, several serious haze events occurred in Beijing in January 2013 (Zhang et al., 2014). It has been suggested in many publications that exposure to haze could cause a variety of respiratory diseases (Pavagadhi et al., 2013; See et al., 2006; Tie et al., 2009). Inhalation is the main pathway through which humans are exposed to quartz (US EPA, 1996); therefore, the relationship between quartz concentrations and the occurrence of haze should be investigated. Most previous literature reports on haze have been concerned with black carbon (Wang et al., 2015), heavy metals (Zhou et al., 2014) and aerosols (Sun et al., 2014). To the best of our knowledge, no studies of the exposure of humans to quartz in haze have been published to date.

In the work described here, we collected inhalable particulate fraction (PM_{10}) samples at three sites in Beijing between 2 November and 30 November 2014. The Asia-Pacific Economic Cooperation (APEC) Economic Leaders' Meeting took place in Beijing entirely within the study period. In order to guarantee the air quality of the 2014 APEC meeting, Beijing and its neighboring regions, including Hebei, Tianjin, Shandong and Inner Mongolia, imposed temporary restrictions, included halting emission-heavy production and limiting cars on the streets based on their license plates (Chen et al., 2015). The aim of the study was to determine the quartz concentrations in the air and to assess how effectively the emission-control measures that were taken decreased atmospheric quartz concentrations during the APEC meeting. The potential risks posed to humans exposed to airborne quartz in Beijing were then discussed.

1. Materials and methods

1.1. Sample collection

Airborne PM_{10} samples were collected using TH-150a air samplers (Wuhan Tian Hong Instruments Co., Ltd., Wuhan, China). The flow rate of the sampler is 100 L/min. Silver membrane filters (25-mm diameter, 0.45-μm pore size) were available from Sterlitech Corp (Kent, WA, USA). In total, 87 air samples were collected at an interval of 24 hr in November 2014, which included about 1 week before and 2 weeks after the APEC meeting. The prevailing wind direction for most of the sampling period was northwest. Samples were collected at two urban sites, Haidian District (HD) and Dongcheng District (DC), and one rural site, Changping District (CP). HD is in northwest Beijing, DC is in southeast Beijing, and CP is in north Beijing. Meteorological data were obtained from the Beijing Urban Ecosystem Research Station (part of the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences). Other meteorological data (including whether or not sampling periods had been affected by haze) were obtained from www.nmc.cn/publish/forecast/china.html.

1.2. Sample analysis

The samples were quantitatively analyzed using NIOSH method 7500 (NIOSH, 2003). The samples contained significant amounts of calcite, so quartz may have been lost through the formation of $CaSiO_3$. We therefore removed the calcite using the following procedure. A new filter was placed in a filtration apparatus, then the sample filter was removed from the sampling cassette, folded, and placed on top. A mixture of 25% (*V*/*V*) HCl and 2-propanol was added to the filter funnel and allowed to stand for 5 min, then a vacuum was applied and the acid and alcohol were slowly drawn through the filter. The filter was then washed with 10 mL distilled water three times before the vacuum was released. Both filters were then placed in a porcelain crucible, which was then loosely covered and baked at 800°C in a muffle furnace for 2 hr. A 10-mL aliquot of 2-propanol was added to the ash, then a glass rod was used to loosen the residue, and all of the residue was transferred to a beaker. The crucible was washed three times, and the washings were added to the beaker; then 2-propanol was added to the beaker. The beaker was covered with a