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Occurrence, evolution and degradation of heavy haze events in Beijing traced by iodine-127 and iodine-129 in aerosols

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ABSTRACT

Heavy haze events have become a serious environment and health problem in China and many developing countries, especially in big cities, like Beijing. However, the factors and processes triggered the formation of secondary particles from the gaseous pollutants are still not clear, and the processes driving evolution and degradation of heavy haze events are not well understood. Iodine isotopes (^{127}I and ^{129}I) as tracers were analyzed in time series aerosol samples collected from Beijing. It was observed that the ^{127}I concentrations in aerosols peaked during the heavy haze events. The conversion of gaseous iodine to particular iodine oxides through photochemical reactions provides primary nuclei in nucleation and formation of secondary air particles, which was strengthened as the external iodine input from the fossil fuel burning in the south/southeast industrial cities and consequentially induced heavy haze events. Anthropogenic ^{129}I concentrations peaked during clean air conditions and showed high levels in spring and later autumn compared to that in summer. ^{129}I originated from the direct air discharges and re-emissions from contaminated seawaters by the European nuclear fuel reprocessing plants was transported to Beijing by the interaction of Westerlies and East Asian winter monsoon. Three types of mechanisms were found in the formation and evolution of heavy haze events in Beijing by the variation of ^{127}I and ^{129}I, *i.e.*, iodine oxides intermediated secondary air particles, dust storm and mixed mode by both secondary air particles and dust storm induced processes.

Atmospheric aerosols are originated from both anthropogenic releases (*e.g.*, motor vehicle exhaust, construction dust, coal and biomass burning and industrial emissions) and natural sources (*e.g.*, dust storms, sea salt spray, resuspension of soil particles, forest fires and volcano eruptions) [1]. Elevated concentrations of atmospheric aerosols could result in heavy haze event, which affect seriously on human health through the direct damage to the respiratory system and cardiovascular system [2]. The air quality in Beijing, the capital city of China with a population over twenty million has become quite worse in recent decades, and heavy haze events often occurred. Systematic monitoring of the air pollution and large numbers of investigation have suggested that besides the dust storm, increased emission of air pollutants from human activities was the main reason, and the formation of secondary particles through the reaction of gaseous pollutants in a certain climate and weather conditions trigged the aerosol blooming and resulted in heavy haze events [2,3]. With the implementation of restricted policy for reducing the releases of air pollution from industrial and civil activities, the frequency of heavy haze events decreased in the past few years. However, the factors and processes that triggered the formation of secondary air particles from the gaseous pollu-

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tants are still not clear, and the processes driving evolution and degradation of heavy haze events are not well understood.

Iodine is a volatile element and presents mainly as gaseous forms in atmosphere with small fraction associated on air particles. Ocean is the main reservoir of iodine on the earth, but iodine also widely presents in terrestrial environment. Emissions of gaseous iodine (*e.g.*, I_2 and alkyl iodide) from seawater, soil and vegetations are the main source of iodine in the atmosphere [4], human activities could also release iodine to the atmosphere through combustion of fossil fuel and biomass. An increased iodine concentration in urban atmosphere compared to rural areas has been observed [5,6], indicating significantly different sources of iodine in the urban area compared to the marine area. Due to the active chemical property, iodine has been reported to play an important role in the atmospheric chemistry, for example, destroying O_3 layer through reaction with I_2 and radical species of iodine, formation of primary nuclei of particles by production of iodine oxides through a series of photochemical reactions of gaseous iodine, changing OH concentrations, enhancing depletion of gaseous elemental mercury in atmosphere through reaction with iodine species [7,8]. The role of iodine oxides in the formation of ultrafine marine aerosols and cloud condensation nuclei has been reported in marine environment, such as in Antarctic, Arctic, North Sea, Gulf of Maine, and Cape Verde Islands [7,8], but no investigation on the role of iodine in the terrestrial aerosol formation is available. Iodine in the atmosphere might also play an important role in the formation of secondary air particles and the evolution of heavy haze events, but no investigation on this topic has been reported yet.

Although iodine has many isotopes, but only one stable isotope (^{127}I) and one long-lived isotope (^{129}I). ^{129}I ($t_{1/2} = 15.7$ Ma) in the environment was mainly released from human nuclear activities, dominantly from nuclear fuel reprocessing plants (NFRPs), although some amount of ^{129}I was also released from nuclear weapon tests and nuclear accidents, and a small fraction of ^{129}I was naturally produced by cosmic ray reactions with Xe in the atmosphere [9]. The two large NFRPs at La Hague (France) and Sellafield (UK) have released about 8000 kg ^{129}I to the English Channel and Irish Sea, which was then transported and dispersed to a large area in the European waters and the Arctic. Meanwhile these two NFRPs have also released about 230 kg ^{129}I directly to the atmosphere, mainly before 2000, and still remained at about 1 kg/y in the past 20 years [10]. Our recent investigations have demonstrated that ^{129}I discharged from the European NFRPs could be transported to China through re-emission to atmosphere from the contaminated seawater and long-distance transport and dispersion by westerlies wind [11]. Based on the features of the unique point source of ^{129}I and relatively long residence time of gaseous iodine in the atmosphere (>14 days) [4], ^{129}I has been used as an environmental tracer for investigating the source terms, transport pathways and transformation processes of air masses [11–14]. However, no application of ^{129}I in the formation and evolution of heavy haze event has been reported. The different source terms of stable ^{127}I and ^{129}I in the atmosphere, especially in the urban area, could provide complementary source and pathway information of the corresponding air masses in the formation and evolution of heavy haze events.

This work aims to investigate the formation, evolution and degradation of heavy haze events in Beijing using stable ^{127}I and anthropogenic ^{129}I as tracers by analysis of aerosol samples continuously collected in Beijing and comparison with the variation of other air pollution parameters such as $PM_{2.5}$ and PM_{10} levels, air quality index (AQI), humidity, wind speed and direction, in order to better understand the mechanism of the formation and evolution of heavy haze events and the role of iodine in these processes. This will be important for making suitable strategy for reduction or elimination of the harmful heavy haze events.

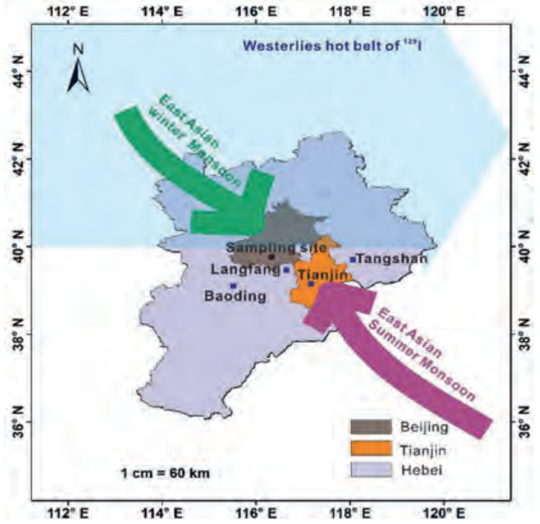

Fig. 1. Sampling site of aerosol in Beijing and nearby major industrial cities, as well as the direction of the major winds in this region.

The aerosol samples used in this study were collected in Beijing, a super-large city with a population of 21.5 million and located in the North China Plain. Beijing is located in the northern temperate zone with typical semi-humid continental climate, with predominant north or northwest East Asian winter monsoon in winter and south and southeast East Asian in summer. Beijing is surrounded by Taihang mountains in the west, Yanshan Mountains in the north and northeast, and 140 kms away from the Bohai Gulf in the southeast. Four big industrial cities Tianjin, Tangshan, Baoding and Langfang are in the south of Beijing within 150 km (Fig. 1).

The aerosol samples of total suspended particles (TSP) were collected on a polypropylene filter using an air sampler (Jiuding Hi-Tech Filtration Equipment Co., Ltd., Beijing, China). The flow rate of the sampler was 2.0 m^3/min and the filters were fixed to an aerosol collector and replaced every 4–48 h. The sampler was placed on the roof of No. 1 Hall of Institute of High Energy Physics, Chinese Academy of Sciences (39.92° N, 116.26° E) in Beijing, China.

From March 2017 to December 2018, 61 aerosol samples (non-uniform sampling duration) were collected for measurement of iodine isotopes. Methods for iodine separation from the aerosol filter and measurements of ^{127}I and ^{129}I were modified from Zhang *et al.* [15]. The separation procedure of iodine isotopes (^{127}I and ^{129}I) is given in Fig. S1 (Supporting information).

Aerosol filter (500–1500 m^3 air) was cut into small pieces (<3 mm) and weighed into a nickel crucible. ^{125}I tracer solution (100 Bq), 20 mL of 1 mol/L NaOH solution, and 2 mL of 1 mol/L $K_2S_2O_5$ solution were added and mixed with the sample. The sample mixture was dried on a hot plate at 80 °C, ashed at 350 °C for 30 min and then 600 °C for 2 h. The ashed filter sample was then leached with hot water and heated at 70 °C for 20 min. to extract iodine. The leachate was separated from the residue by filtration, and the residue was rinsed with hot water again, then the leachate and rinsing solution were combined. One milliliter leachate solution was taken to measure ^{125}I using a Gamma detector for calculating the chemical yield of iodine in this procedure, chemical yields of iodine were more than 70% for all samples. This leachate solution of 1.0 mL was then diluted with water and used to measure ^{127}I using ICP-MS (Agilent 8800, USA).

The remaining leachate was transferred into a separatory funnel, 0.5 mg ^{127}I carrier (Woodward Company, USA, with $^{129}I/^{127}I$ atomic ratio of less than 2×10^{-14}) and 1.0 mL of 1 mol/L $NaHSO_3$ solution were added. Then an appropriate amount of 6 mol/L HNO_3 solution was slowly added into the leachate to adjust the pH 1-

2 and convert all iodine species to iodide. About 15 mL CCl_4 and 1 mL of 1.0 mol/L $NaNO_2$ solution were added to oxidize iodide to I_2 and extract it into the CCl_4 phase. The extraction procedure was repeated and the CCl_4 phases were combined in a new separatory funnel. 0.5 mL of 0.01 mol/L $NaHSO_3$ solution and 10 mL H_2O were added to reduce I_2 to iodide and back extract it to water phase. The extraction and back extraction procedure were repeated, and iodine in final water phase was transferred into a 15 mL centrifuge tube. 1.0 mL of 0.5 mol/L $AgNO_3$ and 1 mL 3.0 mol/L HNO_3 were added to the solution to precipitate iodide as AgI. The AgI precipitate was separated by centrifuging, washed with deionized water, and finally dried at 60 °C. The procedural blank was prepared using a blank polypropylene filter (without aerosol) using the same procedure as for samples.

The prepared AgI precipitate was ground to fine powder, and mixed with Nb powder (99.9%, 325 mesh) in a mass ratio of 1:5 and pressed into copper target holders. $^{129}I/^{127}I$ atomic ratios were measured using a 3 MV accelerator mass spectrometry (AMS) at the Xi'an AMS center. Iodine ion was sputtered from the AgI target in the ion source, and +5 charge state was selected for measurement of $^{127}I^{5+}$ with Faraday Cup and $^{129}I^{5+}$ with ionization chamber. The measured $^{129}I/^{127}I$ ratios in the procedural blanks were lower than 5×10^{-13}, 2 orders of magnitude lower than that in samples, which was subtracted from the measurement result of the samples for correction of blank contribution.

^{127}I concentrations in the leachate of ashed filter samples were measured using ICP-MS (Agilent 8800, USA) under single quadrupole mode without collision-reaction gas. Cs^+ was used as an internal standard, and 1% $NH_3 \cdot H_2O$ solution was used as rinse solution. The detection limit of the method for iodine (^{127}I) was estimated to be 0.012 ng/mL, which is 2 orders of magnitude lower than the concentration of iodine in sample leachate. The linearity range of iodine measurement by ICP-MS is to be 0.1–100 ng/mL.

In this study, the observational data of the hourly mass concentration of $PM_{2.5}$ and PM_{10} and air quality index (AQI) were acquired from the National Environmental Monitoring Station close to our sampling site, which are available on the website of the China National Environmental Monitoring center [16]. AQI, $PM_{2.5}$ and PM_{10} values of each sample were the geomean values in the sampling period. The meteorological data observed every 3 h on ground, relative humidity, wind speeds and wind directions were obtained from Chinese Meteorological Science Data Sharing Service Network [17].

The concentrations of ^{127}I and ^{129}I in aerosol samples in Beijing, from March 2017 to December 2018, are shown in Fig. 2 and Table S1 (Supporting information). The concentrations of ^{127}I varied in 0.77–15.35 ng/m^3, seven extraordinary high ^{127}I events with more than double mean of ^{127}I were observed on 19 March 2017, 2–4 April 2017, 11 May 2018, 1 Nov. 2018, 13-14 Nov. 2018, 26 Nov. 2018 and 29 Nov.−2 Dec. 2018, marked as S1-S7 in Fig. 2d, respectively.

The concentrations of ^{129}I varied from 0.19×10^5 atoms/m^3 to 16.62×10^5 atoms/m^3 (Table S1). No significant correlation was found between ^{127}I and ^{129}I concentrations ($r < 0.01$). There are also seven high ^{129}I events with more than double of the mean value of ^{129}I observed, but not in the same date or season as that for ^{127}I. These seven events occurred 12–14, 22, 25–26 May 2018, 3 June 2018, 3 Nov. 2017, 28 Nov. 2017 and 19 Nov. 2018, identified as R1–R7 in Fig. 2e, respectively.

The measured ^{127}I concentrations (0.77–15.35 ng/m^3) in aerosol samples collected from Beijing fall in the reported ranges in urban areas in China and other countries [5,6,15,18–20]. There is not a clear trend of ^{127}I level with the distances from the sampling site to the ocean, where was supposed as the major source of iodine on the earth [5]. No distinct differences of ^{127}I level among marine, island and continental aerosols were also reported by Saiz-Lopez *et al.* [8]. However, the measured ^{127}I levels in aerosol in Beijing are significantly higher than that measured in rural and remote areas from human activities, such as 1.04–2.48 ng/m^3 at Risø, Denmark, 0.2–1.90 ng/m^3 in Alert, Canada, and 0.17–1.67 ng/m^3 in high altitude Alp stations [14,21,22]. This indicates that the anthropogenic derived iodine might be an important source in urban aerosols besides the naturally sourced iodine emitted from land and ocean.

The measured ^{129}I concentrations of $(0.19–16.62) \times 10^5$ atoms/m^3 in aerosol in Beijing are comparable with the values measured at the background sites that are remote from the nuclear facilities in Austria and inland Germany [22–25], but significantly lower than that measured in those sites directly affected by human nuclear activities, such as $(11.3–97.0) \times 10^5$ atoms/m^3 in Denmark and $(0.4–40.4) \times 10^5$ atoms/m^3 in Sweden, where the European reprocessing plants marine discharged ^{129}I was transported to the North Sea and Baltic Sea and re-emitted to the atmosphere [14,26]. The level is also of several orders of magnitude lower than that measured in the nearby areas of the NFRPs, such as $(500–50{,}000) \times 10^5$ atoms/m^3 nearby Karlsruhe and Hanford NFRPs [24].

To overcome the variations of ^{127}I concentrations among different kinds of environmental media, $^{129}I/^{127}I$ atomic ratios were widely applied to represent the level of ^{129}I in the environment. The $^{129}I/^{127}I$ atomic ratios in Beijing aerosols range in $(1.30–195) \times 10^{-9}$ with a mean value of 2.25×10^{-8}, which is around 4 orders of magnitude higher than the pre-nuclear background level (10^{-12}) [27], indicating the dominant anthropogenic sources of ^{129}I in the aerosol. This level is comparable with the ratios of 10^{-8} measured in atmospheric fallout samples (precipitation) in the background areas without direct contamination by human nuclear activities, such as in Tokyo, Xi'an, and Qingdao [28–30], but significantly higher than the ratios of 10^{-10}–10^{-9} measured in other surface environment media from similar regions, such as $(0.7–3.7) \times 10^{-9}$ in river water samples, $(0.1–2.8) \times 10^{-9}$ in surface soil samples, $(1.9–4.3) \times 10^{-9}$ in vegetation, and 0.2×10^{-9} in sediment [31–33]. Therefore, the atmospheric input/transport with atmospheric circulation might be the main source of ^{129}I in the studied area besides the emission from surface environment (such as local soil, vegetation), and the aerosol ^{129}I and $^{129}I/^{127}I$ variations could be used for explore the source of air masses.

The variation of ^{127}I concentrations in aerosol from Beijing shows a seasonal trend with relatively lower level (with mean of 2.44 ± 0.86 ng/m^3) in summer, increased level (mean of 4.00 ± 4.19 ng/m^3) in autumn and the highest level (mean of 4.49 ± 3.32 ng/m^3) in spring. Besides that, 7 high-level ^{127}I events were observed mainly in spring (March-May) and later autumn (November-December). This might be attributed to the change of sources and transporting pathways of iodine, or formation processes of particulate iodine in atmosphere.

The sources of iodine in air include gaseous releases from ocean and land (*e.g.*, I_2, HI, HOI and alkyl iodide) through chemical, biochemical and photochemical processes and human activities (including burning fossil fuel and biomaterials), and particulate releases including re-suspension of dust, pollen, and emissions and formation of particle associated iodine from human activities (low volatile RI, RIO_3, I_xO_y, HIO_x, IR, $C_xH_yI_z$, *etc.*) [1].

It was estimated that a total of $\sim 1.2 \times 10^9$ kg inorganic iodine (I_2) was emitted from ocean to atmosphere per year [8] through chemical (*e.g.*, O_3 reaction), biological and photochemical reactions, and higher emission occurs during summer with strong solar radiation, high temperature and bio-production compared to that in winter [4,34]. In addition, the southerly and southeasterly East Asian Summer Monsoon could bring gaseous iodine released from ocean (Pacific Ocean in the southeast of Beijing) to Beijing in China continent [3]. However, the measured iodine concentration in spring aerosol in Beijing was relatively lower compared to that

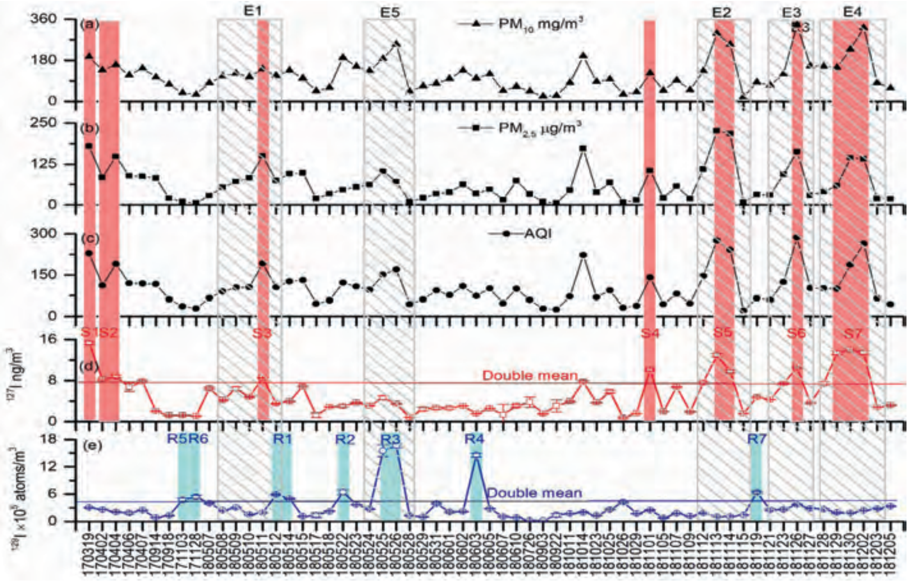

Fig. 2. Variation of concentrations of ^{127}I (d) and ^{129}I (e) in aerosol samples during March 2017 - December 2018 in Beijing, China, in comparison with PM_{10} and $PM_{2.5}$ concentrations and AQI values during the sampling intervals (a–c). Red bands indicate seven ^{127}I peak events (d) and light blue bands indicate seven ^{129}I peaks events (e).

in other seasons, this might indicate the source of iodine in aerosol in Beijing was not dominated by the marine emitted iodine. The species of iodine in atmosphere might change during its transport with air mass, but the conversion of gaseous iodine to particle associated iodine might be a slow process, and the marine emitted gaseous iodine might be less converted to particle associated form during its way from the Pacific to Beijing (140 km away to Bohai Gulf).

Iodine could also be released as gas forms from vegetation and land through biological and chemical processes. It was estimated that about 3×10^7 kg iodine is released to atmosphere mainly as alkyl iodide (*e.g.*, CH_3I) in mid-latitude areas per year and higher flux of CH_3I emission has been measured in summer than that in autumn and winter [35]. The observed lower ^{127}I level in the aerosol samples in summer compared to that in other seasons in Beijing in this work implies that the gaseous releases of iodine from vegetation and soil is not a major source of iodine in aerosol in Beijing, where has less soil and vegetation coverage compared to the rural areas. Weathering process of rocks might also release some fraction of iodine to the atmosphere, but it should only account for a small amount compared to the ocean, soil and vegetation because the very slow weather rate of rocks (0.002 mm/y) and relatively low iodine concentration in rock (*e.g.*, 1.5 μg/g sedimentary rock, 73% of coverage of earth crust) [36,37].

With the increasing consumption of fossil fuel in the past years (*e.g.*, 1×10^9 tons coal and 4×10^9 tons oil in 2017) [38], increased amount of iodine was released as gaseous form or particles (*e.g.*, fly ash) to the atmosphere (5×10^6 kg iodine in 2017) [5]. Although these releases are far less than that emitted from ocean, vegetation and soil, but a significant contribution to the urban atmosphere has been suggested due to the intensive consumption of fossil fuels in urban areas for heating, vehicles and industry activities compared to the rural area. Relatively high iodine level observed in aerosol in Beijing in Nov. to Dec. and March to April seems in an agreement with the heating season in mid-November to the next mid-March with higher combustion of fossil (although less samples in Dec. to Feb. were collected and analyzed). This might imply that the fossil fuel combustion was a source of iodine in aerosol in Beijing, or the relatively higher releases of fine particles from heating systems and the enhanced association and conversion of gaseous iodine to the air particles. Some big cities with heavy industry activities such as Tangshan, Tianjin, Langfang and Baoding are located in less than 150 km south and southeast of Beijing [39], the transport of the fossil fuel combustion released iodine from these surround industrial cities might be also an important contribution to the iodine in the atmosphere in Beijing. However, the prevailing south/southeast wind in summer compared to that in spring and winter in this region did not cause a high iodine concentration in aerosol in Beijing during the summer season. This might indicate that the direct transport of iodine released in the surround cities is not the main cause for the high iodine level in aerosol in Beijing.

All of these sources could not well interpret the observed higher iodine concentrations in aerosol samples in spring and autumn, as well as the observed seven events with extraordinary high iodine level. Transformation of new particulate iodine from gaseous forms in atmosphere, and stimulation of boosting of particle associated iodine by other processes are assumed to be responsible to this phenomenon.

High positive correlation ($r = 0.791$, $P < 0.01$) of ^{127}I concentrations measured in the aerosol samples with the mean AQI values of the corresponding days in Beijing was observed, and a slightly stronger correlation of ^{127}I concentrations with $PM_{2.5}$ values ($r = 0.807$, $P < 0.01$) compared to PM_{10} values ($r = 0.727$, $P < 0.01$) was also observed (Fig. S2 in Supporting information). The seven high ^{127}I events also match well with the heavy haze events in Beijing with the mean AQI values over 150. Meanwhile, relatively high humidity of 50%–90%, low wind speeds (<10 km/h) with south and southeast directions (where most industrial cities with high coal and oil consumption locate), and elevated $PM_{2.5}/PM_{10}$ ratios (fine particle contributions in PM_{10}) of 60%–100%, were recorded during the seven high ^{127}I events (https://www.cnemc.cn/) (Fig. S3 in Supporting information). This might indicate the favorable weather conditions (slow wind speed, and high humidity) in coupled with transport and accumulation of pollutants released from south and southeast industrial cities provoke the formation of the secondary air particles, which then induced heavy haze events in Beijing [2,3]. Iodine might play an important role in the formation of secondary particles and evolution of heavy haze events. A significantly reduced ozone concentrations was monitored in the periods of the peaked ^{127}I concentrations in aerosol in Beijing (Fig. S3), implying the occurrence of iodine associated aerosol might intermediated by O_3. Under the slow velocity of south- and southeast wind condition, iodine and other air pollutants produced from the heavy industrial activities in the cities located in south and southeast of Beijing were transported and accumulated in Beijing with those produced locally in Beijing. Gaseous iodine (inorganic: I_2, HI, HOI, and organic: $C_xH_yI_z$) accumulated in the steady atmosphere could be rapidly photolyzed to iodine radicals [40], which could be converted to iodine oxides (IO, OIO, I_2O_2, *etc.*) by O_3 [7] as primary nucleus of particles, and then stimulating the formation of secondary air particles.

The aerosol mass spectrometer analysis revealed that iodine associated particles are mainly composed of iodine oxides and iodine oxyacids, including I^+, HI^+, IO^+, HIO^+, IO_2^+, HIO_2^+, HIO_3^+, IO_5^+, I_2^+, I_2O^+ and I_2O^{3+} [7], indicating that iodine "enters into" particles through these processes. The chamber experiments under insolation and ozone conditions showed that the particle numbers and concentrations significantly increased within gaseous iodine input [41]. The ternary H_2SO_4–H_2O–NH_3 nucleation was proposed as a typical nucleation of thermodynamically stable clusters, and readily formed under atmospheric concentrations of H_2SO_4, which was considered as a major process in the secondary particle formation. But primary nuclei are still required for further production of secondary air particles. Iodine oxides formed through photolysis of gaseous iodine and reaction with O_3 provided the primary nuclei which triggered the formation and blooming of the secondary air particles (*e.g.*, $(NH_4)_2SO_4$) and by overcome the coagulation barrier of secondary air particles, resulting in the new air particles blooming [8]. The experimental measurements on new aerosol particle composition in the H_2SO_4–H_2O–NH_3 nucleation system showed that the $SO_4{}^{2-}$ dominated particles accompanied with iodine [7]. The chamber experiments also showed that significant numbers of particles were formed after gaseous iodine was injected into the mixed gas system of H_2O, SO_2, NH_3 and NO_x, and both the numbers and mass concentrations of the formed particles exceeded the values calculated from the iodine self-nucleation process [41]. The ternary H_2SO_4–H_2O–NH_3 nucleation was triggered by formed primary iodine oxides nuclei, and which was strengthened under high humidity conditions [41]. The elevated humidity observed during these high aerosol ^{127}I and heavy haze events indicate that the heavy haze events might results from multi-parameters including iodine, humidity, and other pollutants (*e.g.*, $SO_4{}^{2-}$, NH_3) (Fig. S3). High ^{127}I concentrations in aerosols collected in heavy air pollution events have also been observed in Xi'an, China [15].

Therefore, iodine accumulation in the atmosphere resulted from human activities including fossil fuel burning should be another important factor inducing the secondary particles formation and heavy haze event in Beijing. Iodine in aerosols as a tracer provides a key tool for investigating the "internal" processes of heavy haze events formation and evolution.

Significantly varied ^{129}I concentrations ($(0.19–16.62) \times 10^5$ atoms/m^3) in aerosol in Beijing were observed, but no correlation with ^{127}I concentrations ($R < 0.001$), indicating their different sources. Significantly higher ^{129}I concentrations were measured in aerosol samples collected in spring (with a mean of $(3.01 \pm 4.00) \times 10^5$ atoms/m^3) with prevailing northwest wind [3] compared to those in autumn (with a mean of $(1.95 \pm 1.40) \times 10^5$ atoms/m^3) and summer (with a mean of $(1.70 \pm 4.00) \times 10^5$ atoms/m^3). The seven high ^{129}I concentrations were observed in aerosol collected in spring (*i.e.*, 12–14, 22, 25, 26 of May, and 3 June 2018) and later autumn (*i.e.*, 3, 28 Nov. 2017 and 19 Nov. 2018). These days showed relatively clean air conditions with mean AQI values less than 106 (with an except on 25, 26 May 2018) and north- and northwest winds (Fig. 2). Additionally, the ^{127}I concentrations in the aerosol samples with these peak ^{129}I concentrations are significantly lower than the mean ^{127}I concentration of 3.96 ± 3.71 ng/m^3 (with an exception on 26 Nov. 2018, with ^{127}I concentration of (10.58 ± 0.16 ng/m^3)), further confirming the different sources and transport pathways of ^{129}I with ^{127}I in aerosol.

The highest ^{129}I concentration of 16.6×10^5 atoms/m^3 but low ^{127}I concentrations of (3.0~4.0) ng/m^3 in aerosol exceptionally occurred on 25, 26 May 2018 during a dust storm event with a peak AQI value of 170 [16]. The dust materials in this storm event were proposed to be transported from the Gobi Desert, Takla Makan Desert, Badain Jaran Desert located in the north and northwest China [5], and a relatively high ^{129}I deposition in the north and northwest of China were observed in surface soil samples [32], therefore, the high level of ^{129}I in aerosol in the dust storm event might be originated from the surface fine grain materials in the west and northwest China.

Since the ^{129}I level in fossil fuels ($^{129}I/^{127}I = 10^{-13}\sim10^{-10}$), rock ($^{129}I/^{127}I < 10^{-11}$), soil and vegetation ($^{129}I/^{127}I = 10^{-10}\sim10^{-9}$) are much lower than the level observed in aerosol in this work ($10^{-7}\sim10^{-9}$) [15,37]. The 9 burning of fossil fuel, rock weathering, emission from soil and vegetation could not be the sources of ^{129}I in aerosol in Beijing, and ^{129}I should be originated from other sources.

Compared to the natural inventory of ^{129}I in the earth surface and releases from nuclear weapons tests, nuclear accidents and operation of nuclear power plants, most ^{129}I in the environment was released from the spent fuel reprocessing plants, especially the releases from the two European reprocessing plants at La Hague (France) and Sellafield (UK), which account for more than 90% of ^{129}I in the current environment. The direct air release of ^{129}I from these NFRPs decreased to a relatively low and constant level of 1-2 kg/y since 1997. While, the annual marine discharges to English Channel and Irish Sea from the two NFRPs increased to 200-300 kg/y since 1995 and remained at a relatively constant high level afterwards [10]. The marine discharged ^{129}I was widely transported and spread to a large area in the European and Norwegian coast, induced a high level of ^{129}I ($^{129}I/^{127}I$ atomic ratios of $10^{-8}\sim10^{-6}$) in seawater in the North Sea, Norwegian coastal current, Baltic Sea and the Arctic [26,12]. The ^{129}I in the contaminated seawater could be re-emitted to atmosphere as gaseous ^{129}I through biological and photochemical process, which caused a high ^{129}I level in the atmosphere in North and Center Europe ($^{129}I/^{127}I$ atomic ratios of $10^{-8}\sim10^{-6}$ in rain water) [12,14]. The directly air released and re-emitted from seawater to atmosphere from the two Europe NFRPs should be one of the major original sources of ^{129}I in aerosol in Beijing, China, as demonstrated in the long-term records in tree-ring and sediment cores in North China, Yellow Sea and East China Sea [11,31,33].

The two European NFRPs and affected sea areas are mainly located in 49–70° N, 5° W-20° E. The released ^{129}I from the sea and the NFRPs could be gradually dispersed from ground to the middle troposphere and lower stratosphere by the intensive vertical motions, and then transported eastwards with the Westerlies (mainly located in 40–60° N, in middle troposphere to low stratosphere) to Asia, forming a significantly "hot belt" of ^{129}I in the atmosphere in 40–60° N, as recorded in rainwater samples collected from worldwide [42], surface soil samples from China [32], and atmospheric fallout samples from Japan [13]. The diffusion of ^{129}I in the "hot belt" southwards in China could then elevate ^{129}I concentrations in aerosols in Beijing (39° N) that located on the edge of the "hot belt".

In spring, when Siberian High (mainly existed in ground layer <3000 m) still entrenched in mid-high latitude of Central Asia (50–60° N), ^{129}I that falls into the lower atmosphere from the "hot belt" was controlled by the Siberian High. The northwest East Asian winter monsoon formed by the different air pressure between the Siberian High and the warm Pacific Ocean was reported

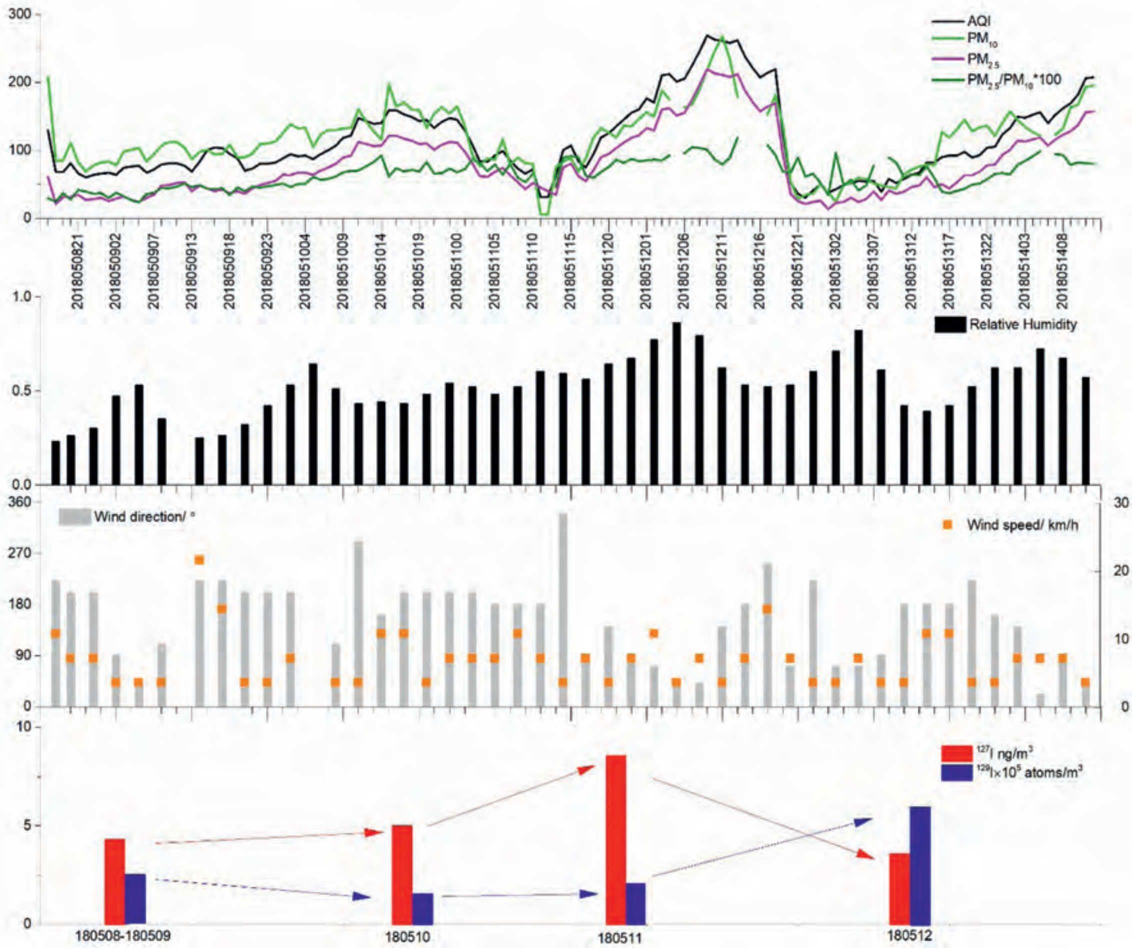

Fig. 3. Evolution of a popular secondary air particles induced heavy haze event (*e.g.*, 8–12 May 2018) in Beijing with the variation of pollution index, relative humidity, wind speeds, wind directions, and the combination patterns of ^{127}I and ^{129}I concentrations in aerosols.

to be the prevail wind in spring and winter in China, especially in North China [3], it transports air masses with high ^{129}I in "hot-belt" southwards, and enhanced the ^{129}I level in the atmosphere in Beijing.

In summer, as the degradation of Siberian High and northward lifting and westward intrusion of the subtropical high, southerly and southeasterly East Asian summer monsoon with low ^{129}I level air from the subtropic Pacific (^{129}I/^{127}I atomic ratio less than 1×10^{-9} in seawater in Pacific water) blows to the north and interacts with the local mountainous plain winds to reach to Beijing [3]. The air mass in the Westerlies with high ^{129}I level moves eastward straightforward, and hardly reaches to Beijing. In autumn, the circulation of mountainous plain winds start to weaken and disappear in November, accompanying with the formation of Siberian High and northwesterly East Asian winter monsoon in November [3,28], resulting in a relatively higher ^{129}I level in autumn compared to summer.

Beyond that, the occurrences of strong north and northwesterly cold air intrusion in the conversion of seasons, *e.g.*, the end of spring (12, 22, 25 May, 3 June 2018) and later autumn (3, 28 Nov. 2017 and 19 Nov. 2018), could also bring high ^{129}I air from the "hot-belt" to south and elevated ^{129}I level in the atmosphere in Beijing. This is supported by the observed high level of ^{129}I in the atmospheric deposition samples collected in Tokyo (35° N) and aerosol in Xi'an (34° N) in spring and winter compared to that in summer and autumn [15,28].

The high ^{129}I level and seven high events in aerosol occurred during northwest- and north wind prevailed seasons (winter and spring), the direct released and re-emitted ^{129}I from discharges of the two European NFRPs that transported eastward by the prevailing westerlies is the main source of ^{129}I in the atmosphere in North China, including Beijing. This agrees well with previous observation in tree ring in Qinghai-Tibet Plateau, aerosol and rain from Xi'an and sediment from the Yellow Sea and East China Sea [11,15,33,43]. The interaction of East Asian winter monsoon with the westerlies induced a high ^{129}I level in aerosol in Beijing in spring and winter compared to that in summer and early autumn. ^{129}I in aerosol in Beijing was therefore externally sourced from a long-distance transport in contrast with the internal formed ^{127}I.

Eight heavy haze events (defined by AQI values over 150, according to the Chinese ambient air quality standards GB3095–2012) occurred during the observation period from 19 March 2017 to 5 Dec. 2018. Among them, 6 events match well with the high ^{127}I events (S1–S3, S5–S7 in Fig. 2). In other two events, a higher ^{127}I concentration (7.74 ng/m^3) was observed in one heavy haze event on 14 Oct. 2018, and a high ^{129}I event (R3) in another heavy haze event in 25, 6 May 2018. A haze event with slight lower AQI (144) on 1 Nov. 2018 matched with one high ^{127}I event (S4) (Fig. 2). For exploring the evolution process of heavy haze events in Beijing, continuous aerosol sampling periods, including 8–12 May 2018, 12–15 Nov. 2018, 21–27 Nov. 2018, 28 Nov.–3 Dec. 2018 and 24–28 May 2018, with heavy haze events marked as E1–E5, were investigated.

In the periods of heavy haze events E1, E2, and E3 (Fig. 2), ^{127}I concentrations in aerosol quickly increased and ^{129}I concen-

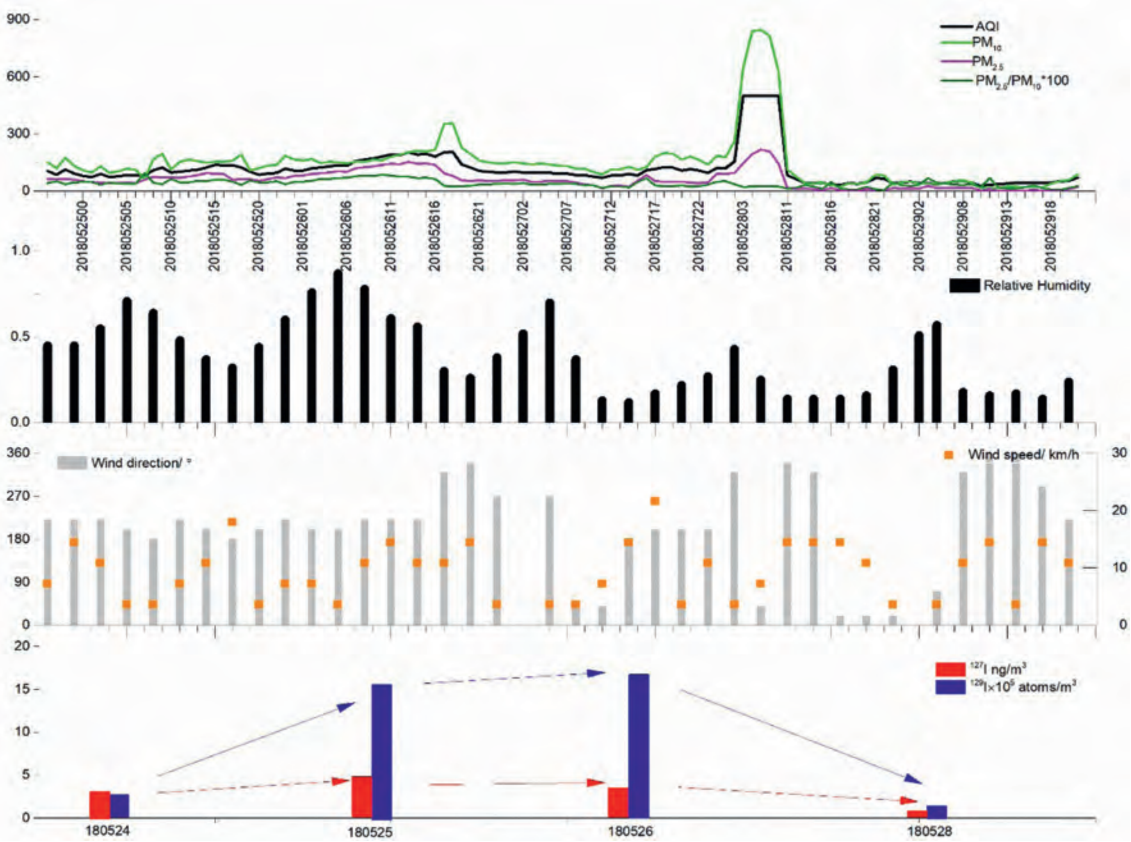

Fig. 4. Evolution of a typical dust storm induced heavy haze event (*e.g.*, 24–28 May 2018) in Beijing with variation of pollution index, relative humidity, wind speeds, wind directions, and the combination patterns of ^{127}I and ^{129}I concentrations in aerosols.

trations declined with time. During these periods, $PM_{2.5}$ concentrations increased to 100%–250% excessed the mean value of $PM_{2.5}$ concentrations, and PM_{10} concentrations increased to only 20%−150% of the excessed mean value PM_{10} concentrations, and the ratio of $PM_{2.5}/PM_{10}$ elevated to over 80% from ~50% excessed mean value. Meanwhile, the relative humidity soared to over 80% from ~20%, and wind speed lowered down to around 5 km/h with mainly south/east directions (Fig. 3). All these features and progresses showed a typical secondary particle blooming and heavy haze event evolution process [44]. It is therefore suggested that the secondary air particles were formed with the increased ^{127}I concentrations in aerosol as a consequence of the stimulation of iodine oxides primary nuclei. Meanwhile, ^{129}I concentrations declined with the reduced input of ^{129}I enriched air mass from remote north or northwest sites due to the steady air condition. With the degradation of heavy haze, ^{127}I concentrations in aerosol decreased, but ^{129}I concentrations elevated as the intrusion of a strong northwest wind that originated from the north "hot belt". Correspondingly, the relative humidity deceased down to 20%, wind speeds increased to over 10 km/h with north/west directions, and the ratios of $PM_{2.5}/PM_{10}$ decreased to less than 50% excessed value. The similar degradation process of haze events has been observed in the previous report, and this type of evolution process of haze events mainly induced by secondary air particle formation is the most popular one in Beijing (Fig. 3) [44].

In the period of heavy haze event E5 (24–28 May 2018), ^{129}I concentrations in aerosol firstly increased and then decreased, while ^{127}I concentration remained relatively constant (Fig. 4). During this period, PM_{10} concentrations increased to 100% exceeded the mean value of PM_{10} concentrations, $PM_{2.5}$ concentrations increased to only 50% exceeded the mean value of $PM_{2.5}$ concentration, and the ratio of $PM_{2.5}/PM_{10}$ deceased down to 20% with the time. Meanwhile, the relative humidity declined from ~50% to 20% and wind speed soared to over 10 km/h with prevailed north direction. All these well match with the reported characteristics of dust storms in Beijing [44,45]. Therefore, the ^{129}I concentrations rapidly increased with the occurrence and evolution of dust storms that transported ^{129}I enriched dust deposited in the surface environment in north and northwest China, as well as the air masses in "hot belt" with high-level ^{129}I that released from European NFRPs. Conversion and association of gaseous ^{129}I to the dust during the transport and formation of storm might be another contribution to the increased ^{129}I concentrations in aerosol during this period. The relatively constant and lower ^{127}I concentrations in aerosol during this period is attributed to the low ^{127}I concentration in the input dust and air. With the degradation of dust storms, ^{129}I concentrations decreased with the gradually increased $PM_{2.5}/PM_{10}$ ratios due to the slowed wind speeds to less than 5 km/h and significant removal of coarse particles by deposition, meanwhile the particles from north and northwest of China and ^{129}I from "hot belt" were reduced (Fig. 4). This type of heavy haze event is mainly storm induced, and often occurred in Beijing in spring.

In the period of heavy haze event E3 (21–27 Nov. 2018), ^{127}I concentrations firstly increased and ^{129}I remained at constant low level. In this period, $PM_{2.5}$ concentrations firstly increased to 40% excessed the mean value, the ratios of $PM_{2.5}/PM_{10}$ increased to over 60%, the relative humidity raised to 60% from ~20%, and wind speed lowered down to 3 km/h with south directions (Fig. 5), indicating a secondary air particle induced heavy haze event. The quickly increased ^{127}I concentrations in aerosol were resulted from the iodine oxides primary nuclei intermediated nucleation and integration process of secondary air particles during the evolution

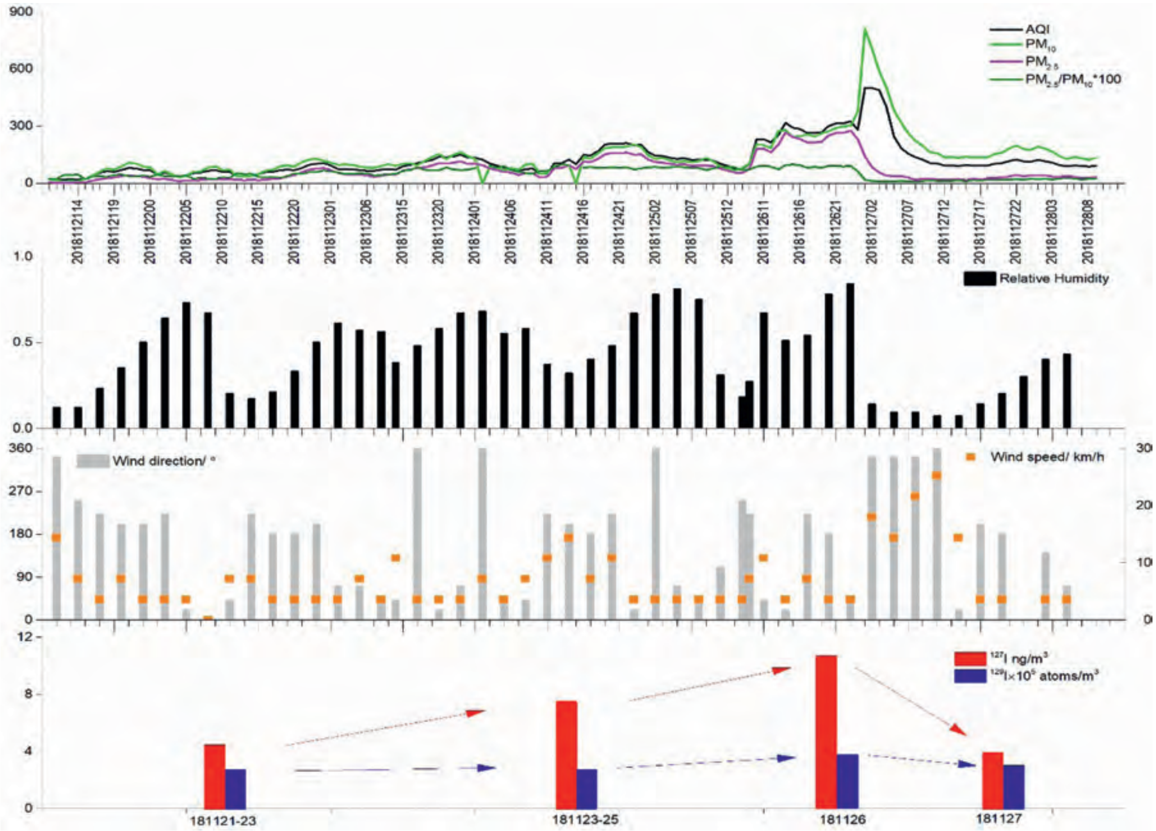

Fig. 5. Evolution of a mixed heavy haze event (*e.g.*, 21–27 Nov. 2018) induced by secondary air particle formation and dust storm in Beijing with variation of relative humidity, wind speeds, wind directions, pollution index, and the combination patterns of ^{127}I and ^{129}I concentrations in aerosols.

of heavy haze events. The constant low ^{129}I concentrations in this process was attributed to the prevail south wind without input of high ^{129}I air from the north/northwest areas and "hot belt". With the progress of the haze event, ^{127}I concentrations in aerosol further increased and ^{129}I concentrations started to increase significantly. Correspondingly, PM_{10} concentrations rapidly exceeded ~200% of the mean value, the relative humidity lowered down to 20%, wind speed elevated to over 15 km/h with north direction, and the ratios of $PM_{2.5}/PM_{10}$ decreased to 20%, clearly indicating a dust storm intrusion. With the degradation of haze event, ^{127}I and ^{129}I concentrations decreased together, accompanied with decreased $PM_{2.5}$ and PM_{10} concentrations, increased $PM_{2.5}/PM_{10}$ ratios and relative humidity and variable wind speeds (Fig. 5), indicating the cease of dust storm. This is therefore a mixed mode of secondary air particle and dust storm induced heavy haze event.

The evolution processes of heavy haze events are well revealed by the specific variation patterns of ^{127}I and ^{129}I concentrations in continuously collected aerosol samples from Beijing, and different mechanisms, *i.e.*, secondary air particles, dust storm, and a mixed secondary air particle and dust storm induced processes. This will improve our understanding on the evolution and formation of haze event and air pollution in other sites and will also be useful for controlling and management of the air quality.

Based on the variation of ^{127}I and ^{129}I levels in aerosol samples collected in Beijing and the investigation on their implications in the formation and evolution of heavy haze events in Beijing, it can be concluded that (1) The ^{127}I concentrations of 0.77–15.35 ng/m^3 are in the same range with the reported values in other urban areas, and the ^{129}I concentrations of $(0.19–16.62) \times 10^5$ atoms/m^3 are comparable with the values measured in background areas that far away from nuclear facilities; (2) Peaks of ^{127}I concentrations in aerosol matched well with the heavy haze events in Beijing, the conversion of gaseous iodine to particular iodine oxides in air through photochemical reaction provide primary nuclei in nucleation and formation of secondary air particles, and induced heavy haze event formation; highly released iodine from fossil fuel burning in the heavy industrial activities, was transported with prevailing south/southeast wind and accumulated in Beijing, promoting the formation of haze events with high ^{127}I concentrations in aerosols; (3) Both of the air discharges of European NFRPs and re-emissions of ^{129}I from contaminated European seawater contribute to the main source of ^{129}I in aerosols in Beijing, which was transported through Westerlies to middle - high altitude area in Asia, and diffused to south including Beijing by interaction of southerly East Asian winter monsoon in winter and spring, causing a high ^{129}I level in spring and later autumn compared to that in summer; (4) Three types of mechanisms were found in the formation and evolution of heavy haze events in Beijing by the variation of ^{127}I and ^{129}I in aerosl, *i.e.*, iodine oxides intermediated secondary air particles induced, dust storm induced and mixed mode by both secondary air particle and dust storm induced heavy haze.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.02.073.

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