Bull Environ Contam Toxicol (2009) 82:332–337
DOI 10.1007/s00128-008-9560-0

Measurements and Characteristics of Nitrogen-Containing Compounds in Atmospheric Particulate Matter in Beijing, China

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Received: 10 March 2008 / Accepted: 1 September 2008 / Published online: 20 September 2008

Abstract The total nitrogen (TN) and water-soluble nitrogenous ions were determined by using CHN Elemental Analyzer and ion chromatography method, respectively, from November 24, 1998 to February 12, 1999 in Beijing. The average concentrations of TN, NH_4^+ and NO_3^- were 10.62 μg N m^{-3}, 6.67 μg m^{-3} and 10.01 μg m^{-3}, respectively. The total inorganic nitrogen (IN) calculated from NH_4^+ and NO_3^- was 7.45 μg N m^{-3}, accounting for 70% of TN, i.e., 30% of TN existed as organic nitrogen form (ON). The correlation between ON and other pollution tracers showed that, coal combustion, biomass burning, soil humic matter and secondary formation were the important sources of ON in particulate matter in Beijing.

Keywords Particulate matter · CHN elemental analysis · Total nitrogen · Organic nitrogen

Atmospheric particulate matter (PM) has attracted global attentions because of its adverse impacts on human health, air quality, climate change as well as visibility. Nitrogenous compounds are the important constituent of urban PM that can be classed into two main categories: inorganic nitrogen (IN) and organic nitrogen (ON). The former mainly includes nitrate (NO_3^-), ammonium (NH_4^+) and nitrite (NO_2^-) and exists as water-soluble ions; the latter, by definition, is a part of organic carbon (OC) in PM. Many previous studies have indicated IN as one kind of the major components in urban aerosols in China (e.g., Duan et al. 2003; Yao et al. 2002). It can be emitted either directly from the anthropogenic sources such as fossil fuel combustion, vehicle exhaust and industrial process, or formed as secondary organic aerosol (SOA) through atmospheric chemistry from gas precursors such as NO, NO_2 and NH_3. The ambient nitrogenous compounds may cause many environmental problems such as acid rain, soil and aquatic acidification, and so on.

In the past decades, the studies of particulate nitrogenous compounds mainly focused on IN species, including their concentration characteristics, sources and transport, while seldom were related to ON species, especially their analytical methods and pollution characteristics. It is well-known that each category of component in PM (e.g., inorganic multi-elements, carbonaceous species and water-soluble ions) might provide important information of the sources. It is necessary to determine as much species as possible so as to get enough pollution information. However, the quantity of PM samples collected on the filter is usually small, which will limit the further investigation of more components. Therefore, methods can realize direct and multicomponents measurement once will be helpful for saving samples. Previous studies have carried out on the dissolved organic nitrogen (DON)in precipitation. The measurement methods adopted (Jassby et al. 1994; Cornell et al. 1995, 1998, 1999) mainly included Kjeldahl, persulfate oxidation, high temperature catalytic oxidation, as well as UV photolysis. Recently, measurements of

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individual ON compounds were reported (Cheng et al. 2006). However, data of total amount of ON are of importance for air quality management and aerosol research as well.

In China, the integration effects of rapid economic growth, urbanization process, energy structure and meteorological factors result in complex pollution characteristics of urban air. Developing a rapid and direct analytical method for particulate ON and investigating its pollution characteristics and sources will be of scientific significance. In this study, on the basis of optimizing the analytical conditions, an elemental analytical method has been developed for direct and simultaneous measurements of total carbon (TC) and total nitrogen (TN) in PM. At the same time, water-soluble IN is determined by using ion chromatograph (IC). Based above, the chemical characteristics and concentration level are discussed; the preliminary investigation of the pollution sources is carried out.

Materials and Methods

Samples of total suspended particles (TSP, with aerodynamic diameter less than 100 μm) were collected during the period from November 24, 1998 to February 12, 1999. A high volume air sampler (SHIBATA HV-1000 N) was deployed and installed on the building roof of the Sino-Japan Friendship Center for Environmental Protection, which is about 30 m above ground level. This site is located near the northeastern ring road, which is one of the main traffic avenues in the Beijing urban area. The sampling duration was 24-h with stochastic dates. Samples were collected on Pallflex quartz fiber filters (20×25 cm^2) at a flow rate of 1000 L min^{-1}. These quartz filters were prefired at 850°C for 3 h to remove any absorbed carbon. After sampling the quartz filters were stored in the refrigerator with a temperature of −4°C. Prior to analysis the samples and blank filter were put in a vessel at the room temperature and relative humidity of approximately 25% to condition for 24 h, and then weighted with a MT-5 electric balance (Mettler-Toledo Inc.).

A CHN Elemental Analyzer (MT-5 YANACO New Science Corporation) was adopted for the determination of particulate TC and TN. The work principle is as follows: when the filter sample is sent to the combustion tube, it will decompose in the mixture gas of He/O_2 (8%) under high temperature. The decomposed products then converted to CO_2, NO_x and H_2O quantitatively by catalyst in oxidation tube. The disturber products will be absorbed by the special absorbent in the oxidation tube. The NO_x is deoxidized by copper in the reductive tube and redundant oxygen reacts with the copper. The target components mixed well by pump and then are sent to three thermal conductivity detector (TCD) by carrier gas. The concentration of each component can be obtained by differential thermal conductivity method. The operational parameters of instrument are shown in Table 1.

CHN elemental analytical method was traditionally used for measurements of pure organic compounds. The loss or error of pretreatment can be reduced because the filter samples can be determined directly and thus avoiding the destructive procedure of sample preparation. In our previous work this method was applied successfully to determine carbonaceous species (Chi et al. 1999; Duan et al. 2004). In this study, the mixture of 8% pure O_2 in pure He is still used as the carrier gas; and Antipyrine (N%: 14.88%) is used as the standard reagent to verify the method performance.

The result of parallel 7-time measurements showed that N% averaged 14.87%, with standard deviation (SD) and relative standard deviation (RSD) of 0.19% and 1.28%, respectively. The R^2 of standard curve based on 7-time parallel determination was 0.9995, and the limit of detection (LOD) can be obtained according to the method reported by Niosh Manual of Analytical Methods (1996), i.e.,

$$\begin{aligned}\mathrm{LOD} &= 3 \times \mathrm{SD}/R^2 = 3 \times 0.0019/0.9995 \\ &= 0.005703\,\mathrm{mg\,N} = 5.70\,\mu\mathrm{g\,N}\end{aligned}$$

Hitachi L-4000 ion chromatography was employed for ionic measurement. Before analysis, a small fraction of each sample was cut and submerged into 10.0 mL high pure water then extracted twice with ultrasonic shaking for 15 min. Then the solution was filtered by micro-filter and the filtrate was united for IC analysis. The blank sample was treated as the same procedure as above to monitor the probable contamination during the whole process. Among the ions, concentration of NO_2^- was too low to detect therefore it will not be discussed in the following part.

Table 1 Operational parameters of CHN Elemental Analyzer

Parameters	Values and units
Flow of He	180 mL min^{-1}
Flow of O_2	15 mL min^{-1}
Combustion tube	950°C
Oxidation tube	850°C
Reductive tube	550°C
Detector	100°C
Pump	55°C
Bridge current	H 85 mA
	C 65 mA
	N 120 mA

Results and Discussion

Two methods were adopted to judge the feasibility of TN measurement in this study. First, the known N-containing compounds (e.g., Antipyrine) was selected as the unknown sample, and the analytical conditions thus can be chosen by comparison the measured value with the theoretical value. In our previous work (Chi et al. 1999; Duan et al. 2004), TC in PM sample can be determined when the combustion temperature was set as 950°C. Considering the limit quantity of each filter sample, and in order to detect TN and TC simultaneously, the instrument conditions were kept unchanged, i.e., 950°C for combustion tube and He/O_2 (8%) mixture as the carrier gas.

The further experiment was carried out according to the following considerations: (1) the ON compounds are usually with weak thermal stability and are easy to be determined. Therefore, the entire determination of IN compounds becomes the key of this work. (2) Nitrate, ammonium and nitrite are the main forms of particulate IN. Based on the chemical valance of N and the thermal stability of ammonium compounds, we hypothesis that the particulate ammonium can decompose entirely at 950°C. On basis of above considerations, only $NaNO_3$ and $NaNO_2$ were selected as unknown samples to conduct the thermal decomposition test with the instrumental conditions mentioned above. *N* percentage can be calculated based on the standard sample of Antipyrine. Seven times parallel tests showed that the SD of measured *N*% was 0.21% and 0.19% for $NaNO_3$ and $NaNO_2$, respectively. The recoveries were further determined by above two standard N compounds, 97.2 ± 6.9% and 95.4 ± 3.3% ($n = 3$), respectively. It meant that with the same operational conditions as TC measurement, particulate TN can also be determined.

Second, results comparison between two analytical methods might provide useful information. As described above, IN can be calculated from the sum N of NH_4^+ and NO_3^-, i.e., $IN = (NH_4^+\text{-N}) + (NO_3^-\text{-N})$. The relation between TN and IN is shown in Fig. 1. It presents obvious correlation with the coefficient R^2 of 0.8909. It indicated that two methods adopted in this study for particulate *N* measurement are feasible and the further discussion on their results is as following.

Times series of the concentrations of TSP, OC, NH_4^+, NO_3^- and TN are shown in Fig. 2. TN average concentration was 10.62 ± 6.26 μg N m^{-3}, accounting 2.93% for TSP. Concentration of NH_4^+ and NO_3^- averaged 6.67 ± 5.43 and 10.01 ± 7.18 μg m^{-3}, accounting 2.13% and 3.20% for TSP, respectively. IN concentration calculated from NH_4^+ and NO_3^- was 7.45 ± 5.71 μg N m^{-3}, accounting 70% for TN. That was, ON contributed 30% to TN. This percentage was comparable to that of WSON (water-soluble organic N) in TN in $PM_{2.5}$ reported by Zhang et al. (2002). ON average concentration in this study was 3.17 ± 2.02 μg N m^{-3}, also approximating to 3.6 μg N m^{-3} reported by Zhang et al. (2002). It can be seen that either ON or IN, their percentage in TSP was low. It was likely ascribed to the fine mode existence of particulate nitrogenous compounds (Spokes et al. 2000; Cornell et al. 2001). In North California, average percentage of ON in $PM_{2.5}$ was 18%, and in winter it reached as high as 31% (Zhang et al. 2002).

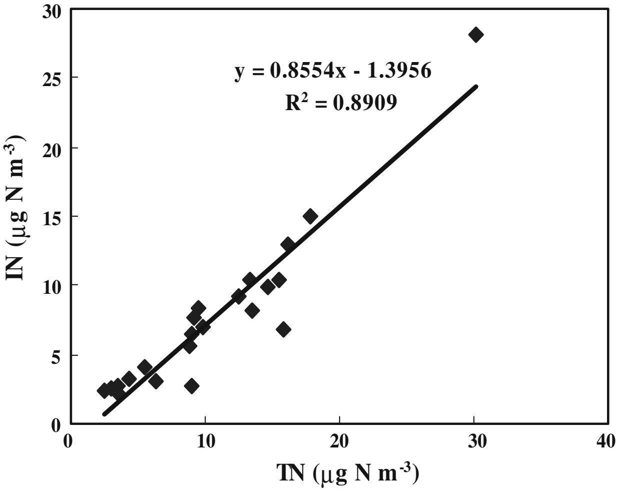

Fig. 1 Correlation between TN and IN

Studies in the past decades focused on the sources of inorganic ionic species (i.e. NH_4^+, NO_3^-) demonstrated that they were mainly formed through the gas precursors in atmosphere (Seinfeld and Pandis 1998). However, seldom studies were related to the source of ON. ON sources can be deduced indirectly by means of comparison between ON and other diagnostic parameter or components of ambient sample such as OC, tracer metal, ionic species, C/N ratio, and so on, which will be discussed in detail as follows.

As mentioned above, ON sources are inevitably related to those of OC since it exists in the form of organics. Combustion process is the important source of OC and accordingly, it is also one important source of ON. Cornell et al. (2003) estimated that the global ON emitted from combustion was about 0.2–0.7 Tg $year^{-1}$. In this study, ON presents correlation with OC as shown in Fig. 3, with R^2 of 0.5938. EC is usually considered a tracer of coal burning emission. The correlation between ON and EC was good, with R^2 of 0.6393. Those indicated that combustion especially coal combustion was the important source of ON in Beijing.

Water-soluble K^+ is considered as one of the tracers of biomass burning (Duan et al. 2004). Biomass burning can occurred in many ways such as forest fire, grassland fire, agricultural burning and wood burning for heat supply, and

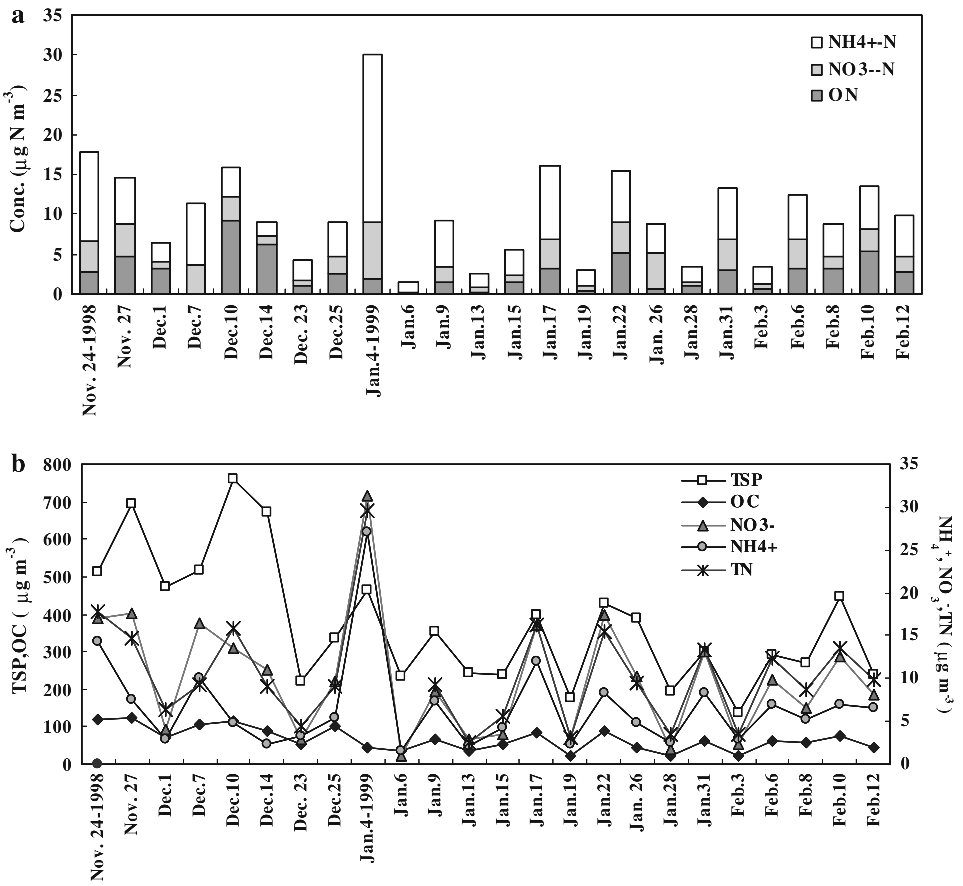

Fig. 2 Time series of TSP (**a**) and chemical components (**b**)

so on. Plentiful organic pollutants are emitted during those processes. Our previous work (Zheng et al. 2005) showed that contributions of biomass burning to particulate matter were seasonal and periodic in Beijing. OC emitted from fall leaves accounted as high as 50% for the total OC in TSP. In this study, there is weak correlation between ON and K^+ with the R^2 of 0.5293 (Fig. 3). It indicated biomass burning as one of the important sources of ON. Studies (Cornell et al. 2003) showed that N-containing PAHs, PAN, amine, amino acid and urea are all the possible existence form of ON. Al is one of main tracers of crustal matter, and usually taken as the reference element in enrich factor analysis works (Gao et al. 2002). In this study, strong correlation can been observed as shown in Fig. 4, with the R^2 of 0.76. It indicated the contribution of crustal matter to ON. For urban particulate matter, crustal sources include several categories: agricultural soil, road dust, construction dust, as well as dust schlepped by long-distance transportation from arid area. Nitrogenous species in crustal sources likely come from rotted plant materials existing as macromolecule compounds such as humic matter, or from nitrogenous fertilizer (e.g., urea) for agricultural activities. Studies showed that those soil organics were the important sources of DON in precipitation (Cornell et al. 2003).

Furthermore, C/N ratio is the important parameter for indicating soil or biology sources. Studies showed that in temperate location C/N ratio of soil organic matter ranges from 10 to 14:1 (Holland et al. 1997), and C/N ratio of humic matter is about 20:1 (Schwarzenbach et al. 2000). In this work, C/N ratio averaged 31.5, with a range of 14.6–57.8. C/N ratios of more than 1/3 samples were $\leq$20, as shown in Fig. 4. It is obvious that Al presents negative correlation with C/N ratio and strong correlation with TSP (R^2: 0.87). For these data points with high Al concentration (>10 μg m^{-3}), the TSP concentrations are also high, exceeding 400 μg m^{-3} (as marked with hollow in upper ellipse); while the C/N ratios present low (<30) as marked with triangle solid in bottom ellipse. These characteristics demonstrated that soil were the important factor resulting in heavy pollution in wintertime in Beijing, and soil organics such as humic acid were the important sources of particulate ON. Additionally, urban road dust is another kind source of PM. It is likely consisted of various pollutants coming from vehicle exhaust, tyre abrasion, and pitch ground surface weathering and so on. The direct emission of industrial process is probably one kind source of ON, and can even reach remote areas by long-distance transportation and existed as fine particulate matter (Cornell et al. 2003). However, identification of those sources might

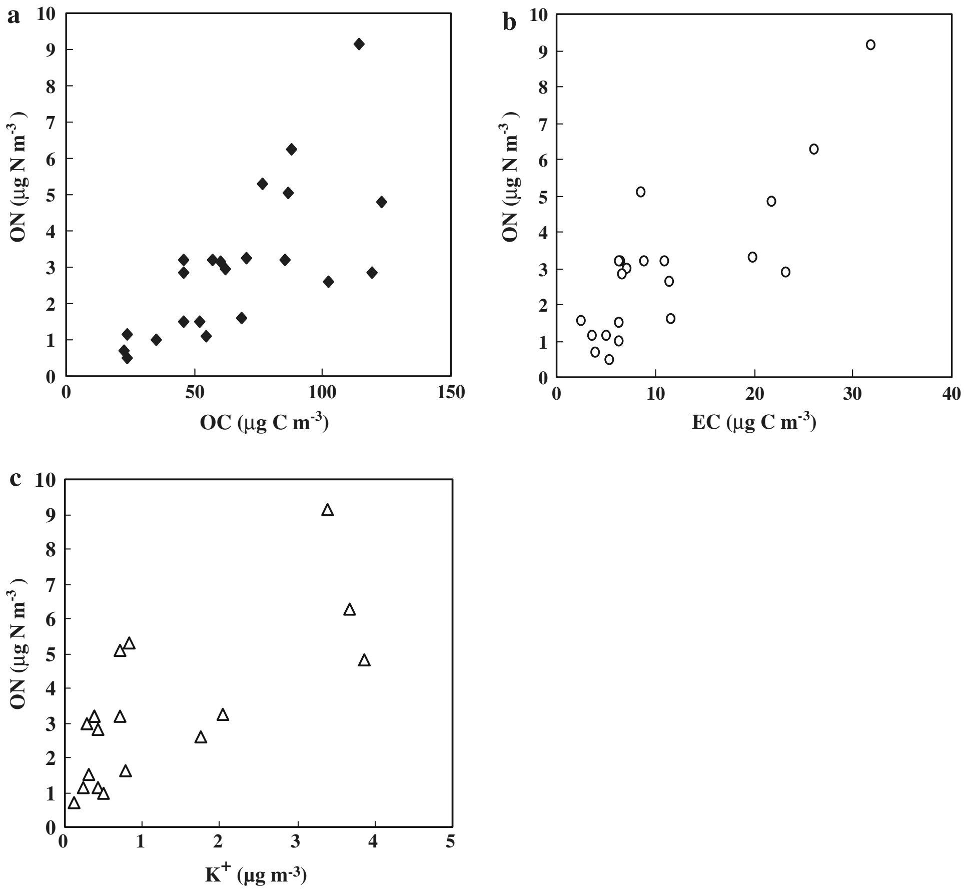

Fig. 3 Correlation of ON with OC (**a**), EC (**b**) and K^+ (**c**)

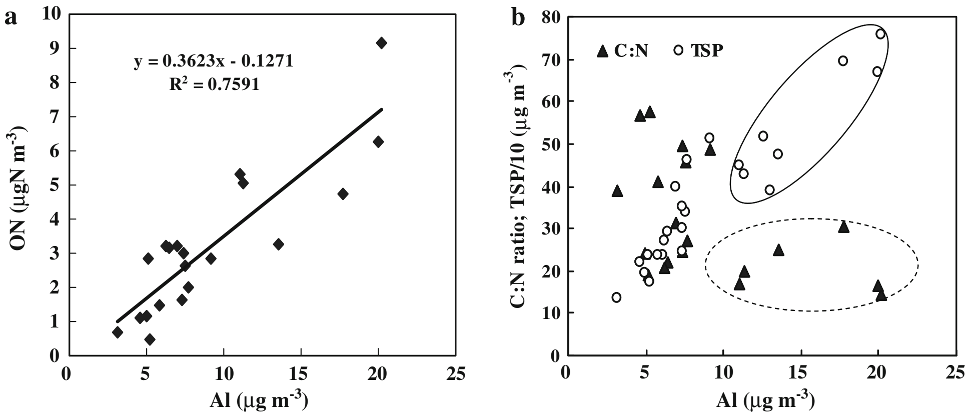

Fig. 4 Correlation of Al with ON (**a**), C/N and TSP (**b**)

resort to multifold information such as source characteristics or biological marker.

As mentioned above, SO_4^{2-} mainly exists as secondary particle formed by SO_2 through homogeneous or heterogeneous atmospheric reaction (Seinfeld and Pandis, 1998). In this work, there is no obvious correlation between ON and SO_4^{2-} for the whole sampling period, as shown in Fig. 5. It is caused by several dispersive data points. The sampling days of the right four points in Fig. 5 are November 24 and 27, January 4 and 17, respectively, of which SO_4^{2-} presents high concentration level. The R^2 of ON vs. SO_4^{2-} could be improved to 0.84 if above four scatter points were excluded. That means strong correlation between ON and SO_4^{2-} for most of the sampling period, indicating the secondary conversion in atmosphere as the important source of ON. Among the four scatter points, TSP presented high concentrations on November 24 and 27, 511.26 µg m^{-3} and 693.37 µg m^{-3}, respectively; and concentrations of Al were also high, 9.14 µg m^{-3} and 17.7 µg m^{-3}, respectively. It implied the dominant contribution of crustal matter to TSP effected by the high wind speed (>2 m s^{-1}). Contrarily, on January 4 and 7, the

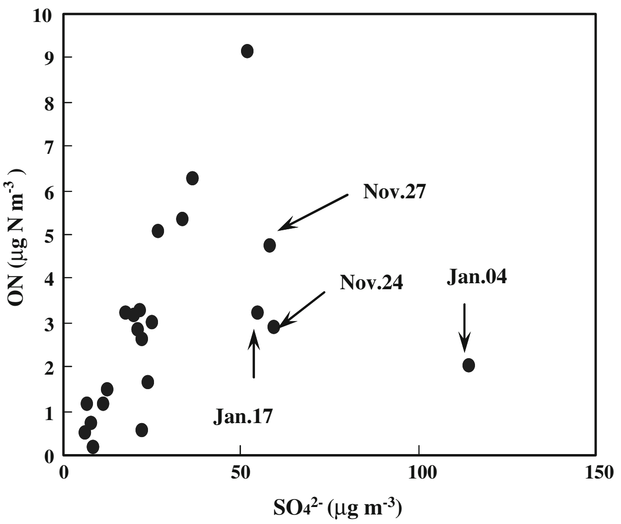

Fig. 5 Correlation of ON with SO_4^{2-}

concentrations of TSP and Al were relatively low, 462.98 and 398.23 μg m^{-3}, and 6.95 μg m^{-3}, respectively. At the same time, the meteorological conditions characterized with low wind speed (averaged 1 m s^{-1}) and high relative humidity (averaged 79%). This kind of meteorological condition would be favorable for the accumulation of gas pollutants and thus likely accelerate the formation of both organic and inorganic secondary aerosols in those two sampling days.

Acknowledgment This study was supported by the National Science Foundation of China (20177036, 20477042).

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