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Original Article

Chinese vehicle emissions characteristic testing with small sample size: Results and comparison



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ABSTRACT

Mobile emissions represent a main source of fine particulate matter (PM_{2.5}) in China, however, few studies have tested the mobile source profiles of Chinese vehicles due to the high cost. In this study, the exhaust emissions of 21 Chinese vehicles, which were divided into five groups according to weight and fuel type, were sampled using the chassis dynamometer–dilution tunnel method. PM_{2.5} mass, organic carbon (OC), elemental carbon (EC) and 190 compounds of organic matter were measured to compare emission characteristics with published mobile profiles. In this study, PM_{2.5} emission factors are higher for high mileage vehicles than new vehicles (255 and 115 mg/km). Among all vehicle emissions, OC averaged 55.4 ± 15.5% of PM_{2.5} mass while quantified organic carbon (QOC) averaged 4.5 ± 3.0% of PM_{2.5} mass. N-alkanes were the predominant species within QOC, averaging 57.0 ± 22.1% of QOC by mass. Normal-aliphatic acids, which are products of catalysis, were observed in the highest concentrations in light-duty gasoline cars. Concentrations of polycyclic aromatic hydrocarbons with more than five rings (large PAHs) differed between gasoline and diesel vehicles, suggesting that large PAHs like benzo[ghi]perylene and coronene could be used to distinguish between fuel types. Hopanes and steranes made up a relatively small fraction of QOC compared with other species (1.1%–16.7% of the total QOC mass) but the relative concentrations of hopanes were similar among different vehicle types. The observed emission characteristics in this study are comparable with a US mobile source profiles published by Lough et al. (2007).

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1. Introduction

Vehicle exhaust is a ubiquitous pollution source in urban areas and many studies have shown its adverse health effects (Pearson et al., 2000; Vette et al., 2013). In recent years, fine particulate matter (PM_{2.5}) pollution has received increased attention as a global problem. Previous research has found that automotive pollutants occupy 12.6–44% of total airborne particulate matter

pollution (Maykut et al., 2003; Almeida et al., 2005; Lee and Hopke, 2006; Huang et al., 2015), which showed the significance in mobile source studies. Rapid economic progress and urbanization in China in recent decades has led to a dramatic increase in the number of vehicles in China. For example, the vehicular population in Beijing almost doubled from 2007 to 2012, going from 2.73 million vehicles to more than 5 million (Wang et al., 2014). Moreover, China has relatively high single-vehicle emissions factors due to vehicle design (i.e. lack of aftertreatment) as well as urban space limitations, which concentrate serious traffic pollution in specific areas. A recent source apportionment study in Beijing showed that vehicle emissions contributed to 63.0% of the carbonaceous mass of PM_{2.5} (Wang et al., 2015).

Because the measurement methods are expensive and complex, there are few mobile source profile studies that quantify mobile

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sources in China, especially for source profiles containing organic molecular markers. A chemical mass balance model (CMB), widely used in source apportionment studies, uses ambient data and source profiles to quantify each source's contribution to particulate matter (Coulter, 2004). However, without local source profiles, the CMB source apportionment model results in non-ignorable errors (Lee et al., 2008; Taiwo et al., 2014). Most source apportionment studies in China which used the CMB model, used non-local traffic profiles (Zheng et al., 2005, 2011). Although the results of these studies seem reasonable, emissions discrepancies exist between vehicles in China and developed countries, which limit the generalizability of these studies. It is necessary to understand the emissions factors of Chinese motor vehicles because of their design, which causes the average automotive emissions rate in China to be much higher than in industrialized countries. Motor vehicle emissions factors are affected by several features, such as fuel type, starting mode, ambient temperature and maintenance conditions (Rogge et al., 1993). The diversity of vehicle weights, aftertreatment and fuel injection techniques is pronounced in Chinese vehicles given the fast development of the automobile industry in recent years. Measuring source profiles of each type of vehicle rather than a unitary traffic profile is there more useful in source apportionment studies.

There are usually three ways to collect automotive emission samples: the dilution tunnel–chassis dynamometer method, field sampling and traffic tunnel sampling (Pant et al., 2014). In this paper, to achieve accurate and comparable emissions measurement results for individual vehicles, the dilution tunnel–chassis dynamometer method was selected as the preferable method. There are two goals in this study. One is to report the emissions factors of different types of vehicles as references for traffic control and environmental policy setting. Another is to compare vehicle emission characteristics between a small sample fleet (our results) and a published mobile profiles (we call them CN and US profiles in the following parts), which provides the basis for future mobile profiles measuring. We will display the vehicle emission characteristics tested in this study first then do the following comparison.

2. Methods

2.1. Sampling

Vehicles are usually classified by environmental agencies according to engine fuel types since this is usually regarded as the main factor impacting $PM_{2.5}$ emissions. Gasoline and diesel powered vehicles were tested in this study because of their prevalence in China. In addition to fuel type, vehicle design and vehicle mass also significantly influence vehicle emissions. Considering the complexity of the combustion-control technique combinations, we first classified the vehicles into two classes: heavy-duty (>3.5 ton) and light-duty (<3.5 ton). We then divided the vehicles into different groups according to their combustion-control techniques, including electronic fuel injection (EFI), carburetor (Cbtr) and catalyst (Cat). Two-wheel motorcycles were considered as an individual class given the fact that China produces and maintains the biggest motorcycle population in the world. A total of 21 vehicles were selected for testing. They were common in China with large vehicle amounts and were randomly selected to represent the real situation in China. Table S1 lists detailed information for all the vehicles tested in this study. Light vehicles and heavy vehicles produced after April, 2001 and September, 2000, respectively, follow the Chinese National Standard (GB18352.2-2001). In the test fleet, seven vehicles did not follow this standard and others did (Table S2).

2.2. Chassis dynamometer tests

All the chassis dynamometer tests in this study were conducted following the Chinese National Standard (GB18352.2-2001). Some cycles were modified as indicated in Table S1. To simulate the heavy traffic pressure in China, all the tests were conducted with a warm start. Briefly, there are two sections included in the procedure (Fig. S1). The first section is an ECE cycles which simulates low speed urban driving conditions; the second is an EUDC cycle which simulates high speed driving conditions in suburban areas. Before measuring, the owners of the vehicles were inquired the activity areas to determine the cycles used in the tests. Vehicle tests were started with 40 s of idle engine operation, followed by four 195 s cycles as illustrated in Fig. S1. Emissions were collected by a constant-volume sampling procedure (Fig. S2). To meet the wide range emission volume from motorcycle to heavy diesel vehicles, three venturi tube (6, 9 and 12 m^3/min) and a secondary ten times dilution system were used in this study (Wang et al., 2005). A blank sample would be taken to correct the background influence after every five vehicle emissions samples finished.

Test cycles are usually repeated many times in most gasoline powered vehicle tests because one standard test usually does not produce enough particulate matter to exceed detection limits (Schauer et al., 2002). Therefore, strict QA/QC is important for the PM tests and the steps followed are outlined below:

- 1) All the sampling parts which came into contact with filters or diluted smokes were clean and wrapped with clean aluminum foil for storage.
- 2) Aluminum foil and quartz filters were baked at 550 °C for at least 6 h prior to use in order to remove background organics.
- 3) A loading blank and a system blank were inserted into the sampling sequences. Details of blank samples have been described elsewhere (Lough et al., 2007).

2.3. Chemical analysis

47 mm Teflon filters (GE Whatman 7592-104) were equalized in a superclean room (25 °C, 50% RH) for 48 h before and after sampling, then weighed by a microbalance (Mettler AE204). Each of them was weighed until three continuous measurements agreed within 60 μg . The average of the three masses was used. The organic carbon (OC) and elemental carbon (EC) concentrations were tested by a thermal-optical method using a Sunset Laboratory laboratory-based instrument (Sunset Laboratory Inc., NIOSH, 1996).

Particulate organic matter was collected on quartz filters and analyzed by an updated method reported by He et al. (2004). Details of the extraction and GC–MS analysis methods are described by Zhang et al. (2007). Briefly, the filters were spiked with an isotopically-labeled internal standard solution then ultra-sonicated three times with 30 ml dichloromethane/methanol (3/1 v/v) at room temperature. The extract was concentrated to ~5 ml using a rotary evaporator at 37 °C then evaporated to 1 ml under a stream of nitrogen (ultra purified, $>99.9\%$). The concentrate was split into two fractions. Polar compounds were analyzed using an Agilent GC–MS (6890-5973N) after being derivatized with BSTFA (BSTFA/TMCS, 99:1, Supelco); non-polar and moderately polar compounds were directly measured by GC–MS.

3. Results and discussion

The $PM_{2.5}$ emissions factors are listed in Table S2 and the Chinese mobile source profiles are listed in Table S3. The average $PM_{2.5}$ emissions factors for gasoline-powered cars, diesel powered cars

and motorcycles are 213, 266 and 79 mg/km. Note that the average PM_{2.5} emissions factor for light-duty gasoline cars is 32 mg/km, a value which demonstrates the difference between different types of vehicles. In the mobile source profiles published by Lough et al. (2007), the PM_{2.5} emission factor of nonsmokers ranged from 1.68 ± 0.05 to 11.7 ± 0.51 mg/mile and that of smoker vehicles ranged from 6.56 ± 0.92 to 270 ± 13.7 mg/mile.

The median odometer value of the test fleet is 37,476 km. Average emission factors are 115 and 255 mg/km for vehicles with odometer values respectively smaller and larger than the median. This difference shows the influence from the degradation of vehicles. Vehicles followed National Standard have smaller emission factor than those not following the standard, with averages of 149 and 325 mg/km, respectively, which shows the impact of emission standards on emissions. Considering the sample size, vehicles were not sub-classified here.

3.1. OC/EC and mass balance

OC, a general metric used to assess gasoline vehicle pollution levels, had the highest proportion of PM_{2.5} mass in vehicles emission. The percentages of mass attributable to OC for light-duty and heavy-duty gasoline cars were $31.7 \pm 3.2\%$ and $54.9 \pm 4.6\%$, respectively. In this study, catalyst-equipped gasoline vehicles had an OC/PM_{2.5} ratio of 0.416 ± 0.135 while the ratio of non-catalyst-equipped vehicles was 0.540 ± 0.062 . These numbers agreed with a study by Schauer et al. (2002). Given the lower OC/PM_{2.5} ratios among vehicles with catalytic converters, equipping future vehicles with catalytic converters would greatly reduce OC emissions attributable to automobiles. Motorcycles were considered as an independent group in this study because of their high pollution emissions and prevalence in China. Motorcycles showed the highest percentage of OC among all vehicle types with $68.6 \pm 15.4\%$, suggesting that the aftertreatment technique in motorcycles needs to be improved. The average percentage of OC in diesel cars was $56.9 \pm 11.2\%$, lower than that in motorcycles. However, the average PM_{2.5} emissions factor for diesel cars was more than three times larger than for motorcycles, suggesting the total OC emissions are higher among diesel cars than motorcycles. It is effective to control PM_{2.5} and OC emissions by improving aftertreatment of diesel vehicles. EC may be used as tracer of diesel vehicle emissions due to the high concentration of EC in diesel car exhaust (Cadle et al., 1999). The EC/PM_{2.5} ratios of light-duty and heavy-duty diesel vehicles were $17.6 \pm 20.9\%$ and $17.7 \pm 7.0\%$, respectively, both higher than the gasoline vehicles' average of 8%. EC was considered to be a product of incomplete combustion of carbonaceous fuel (Bond et al., 2004), thus a higher EC ratio might appear in older gasoline cars or gasoline cars with poor aftertreatment (Fig. 1c, d). Schauer et al. (2002) found the EC/PM_{2.5} ratio of gasoline and diesel vehicles was 8.7% and 30.8%, respectively, showing a large difference between two diesel results. Cadle et al. (1999) tested the emissions of gasoline powered vehicles and found the EC/TC ratio ranged from 8% to 90%. This suggests that vehicle conditions impact the emissions composition significantly. It is therefore necessary to measure more than one vehicle because the results from a single vehicle might contain a large amount of uncertainty.

Different burning sources show various EC/OC ratios in the emissions. The average EC/OC ratio of all vehicles in this study is 0.21 ± 0.25 . Zhang et al. (2008) measured the industrial coal burning source profile and found the EC/OC ratio was 0.25 ± 0.11 . Schauer et al. (2001) tested various wood burning emissions and found the EC/OC ratio ranged from 0.03 to 0.06. The ratio can be used to determine the pollution sources in some cases.

Although 190 organic compounds were quantified in this study, QOC only represented an average of $4.5 \pm 3.0\%$ of overall PM

mass in all measured vehicles. Heavy-duty cars showed higher QOC percentage (1.90 times larger) than light-duty vehicles. Among all vehicles except light-duty gasoline vehicles, the most abundant species in QOC were normal-alkanes (n-alkane), ranging from 28.1% to 87.2% and averaging $57.0 \pm 22.1\%$. N-alkanes in all the diesel cars represented more than three-quarters of total QOC. In the heavy-duty gasoline cars (Cbtr), n-alkanes averaged $60.1 \pm 20.2\%$ of all QOC. Catalysts are effective at removing CO, NO_x and hydrocarbon, so the high levels of n-alkanes likely resulted from the lack of a catalytic cracking unit (Masui et al., 2000). Other abundant species were branched alkanes, n-alkanols, n-aliphatic acids, aromatic acids, polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes. N-aliphatic acids represented the largest proportion of QOC among the light-duty gasoline vehicles emissions with an average of $33.0 \pm 3.0\%$. The percentage of n-alkanols ($13.3 \pm 1.3\%$) in light-duty gasoline vehicles was much higher than that in other types of vehicles. Different QOC compositions showed the influence that emissions control methods caused.

3.2. N-alkanes

N-alkanes are a main component of petroleum and lubricate oil, and are pollutants in vehicle emissions. All n-alkanes measured among particles emissions in this study showed clear characteristics of fossil fuels (Fig. 2). The dominant compound was heptadecane (C17) in all gasoline-powered vehicles. However, positive deviation might exist in C17 test due to the disturbance of pristane and the low respond values of its internal standard C15–D32. Parallel results measured by similar method at the University of Wisconsin showed lower C17 values. This suggested C17 values may be exaggerated in this study so they were omitted from the following discussion.

The dominant n-alkanes carbon number (C_{max}) among vehicle emissions ranged from 18 to 25. The carbon preference index (CPI) of gasoline vehicles, diesel vehicles and motorcycles were 0.93, 1.07 and 0.72, respectively. The distribution of n-alkanes carbon numbers among vehicle emissions did not show an obvious odd or even predominance. CPI values reported by other researchers ranged from 0.93 to 1. The low observed CPI of motorcycles might be caused by the removal of C17 in the CPI calculation (Simoneit, 1985; Rogge et al., 1993). The carbon numbers of n-alkanes in fuels were low (C4–C14) so the fuel's volatility was not the only source of n-alkanes. Although most of the n-alkanes had been removed during lube oil production, cycloalkanes and aromatic cyclanones can undergo ring opening to generate n-alkenes when the engine temperature exceeds 250 °C (Rogge et al., 1993). N-alkanes emissions of some gasoline vehicles demonstrated bimodal distributions of n-alkanes (C20, C25), suggesting multiple sources (Fig. 2a, c, d). Unimodal distributions were more common in both light-duty and heavy-duty diesel cars due to the different types of engine (Fig. 2e, f).

3.3. N-aliphatic acids

N-aliphatic acids also represented a large proportion of the QOC for each vehicle type, especially light-duty gasoline cars. N-aliphatic acids with carbon numbers from 6 to 30 (F6–F30) were quantified in this study. The emissions factors of N-aliphatic acids for gasoline vehicles, diesel vehicles and motorcycles were found to be 10,270, 1536 and 2822 ng/mg PM_{2.5}, respectively. The order of the proportion of n-aliphatic acids to QOC for different gasoline types was: light-duty gasoline (Cat/EFI, $30.0 \pm 3.0\%$), heavy-duty gasoline (Cat/Cbtr, $6.8 \pm 0.7\%$), heavy-duty gasoline (Cat/EFI, $6.1 \pm 0.6\%$) and heavy-duty gasoline (Cbtr, $6.0 \pm 4.6\%$). This result

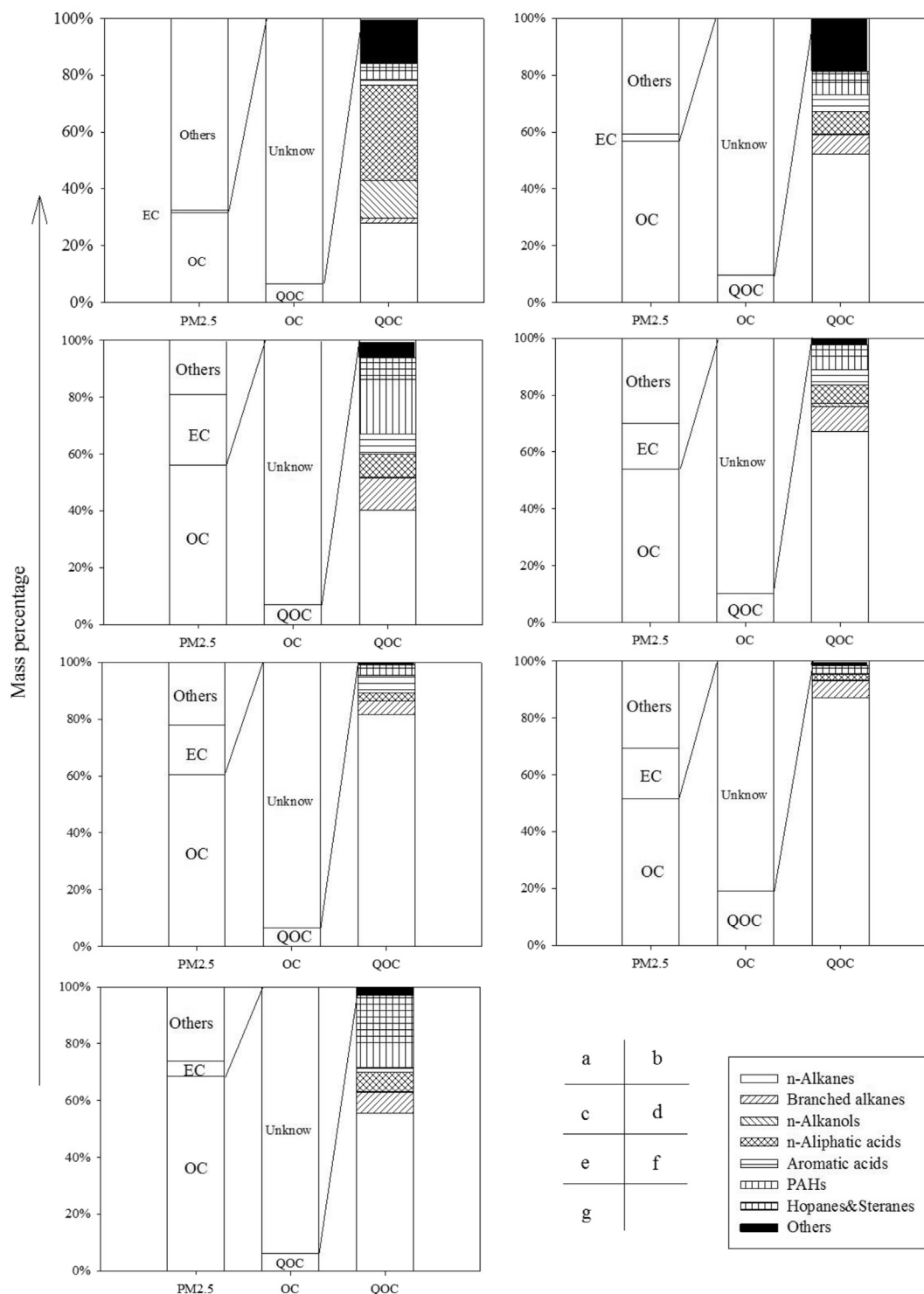


Fig. 1. Mass balance of PM_{2.5} emission of different types of vehicles. (a) Light-duty gasoline; (b) Heavy-duty gasoline (Cat/EFI); (c) Heavy-duty gasoline (Cat/Cbri); (d) Heavy-duty gasoline (Cbri); (e) Light-duty Diesel; (f) Heavy-duty Diesel; (g) Motorcycle. PAHs: polycyclic aromatic hydrocarbons.

agreed with other vehicle emissions studies (Rogge et al., 1993; Schauer et al., 2002), suggesting that catalysis generates the n-aliphatic acids. The catalytic equipment of the vehicle contains metallic oxides and metal salts that can speed up the conversion from alkanes to fatty acids when temperatures are between 100 and 160 °C. F6, F9 and F16 were the most prevalent compounds among the n-aliphatic acids. Compounds F6–F10 accounted for

more than half of the n-aliphatic acids in both gasoline and diesel vehicles. Compounds F5–F10 were not detected in either engine lube oil or the fuel, which supports the notion that the n-aliphatic acids are generated in the process of combustion and catalysis. There was no catalytic unit on the diesel vehicles in this study, so the n-aliphatic acids emissions for these vehicles were relative low compared to gasoline cars.

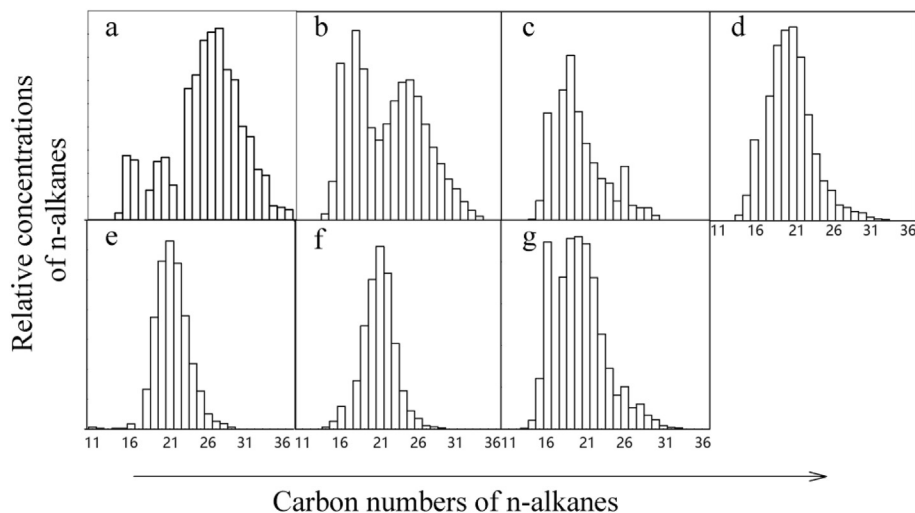


Fig. 2. Relative concentration of n-alkanes of different types of vehicles. (a) Light-duty gasoline; (b) Heavy-duty gasoline (Cat/EFI); (c) Heavy-duty gasoline (Cat/Cbtr); (d) Heavy-duty gasoline (Cbtr); (e) Light-duty Diesel; (f) Heavy-duty Diesel; (g) Motorcycle. The bars were arrayed by carbon numbers.

3.4. Branched alkanes

Six branched alkanes were measured in this study. They were nor-pristane, pristane, phytane, 2-Methylnonadecane, 3-Methylnonadecane and squalene. These six alkanes with isoprenoid structures naturally arise in petroleum. They are hard to separate in petroleum refining so they can be found in gasoline, diesel and lube oils. Branched alkanes can be used to judge the combustion source because they are rarely found in biomass burning emissions. In this study, the emissions factors for branched alkanes from particle emissions were determined to be 3169, 3454 and 2958 ng/mg PM_{2.5} in gasoline cars, diesel cars and motorcycles, respectively.

The ratio of pristane to phytane (PR/PH ratio) was available for inferring different petroleum products in geochemistry (Hughes et al., 1995). In this study, there was a good linear relationship between pristane and phytane concentrations with an R^2 of 0.85. The average PR/PH ratio was 0.5 (Fig. 3). Schauer et al. (2002) found pristane and phytane in only the gas phase. They reported PR/PH ratios of 0.9 and 2.4 in noncatalyst-equipped and catalyst-equipped

gasoline powered vehicles, respectively. The difference in ratios reflects differences in vehicle conditions. The ratio of octadecane to phytane (O/PH ratio) was used to judge the maturity degree of fossil fuels and high O/PH ratio meant high maturity. Linear regressions of octadecane on phytane in all types of vehicles showed high correlation with an R^2 of 0.84 and the slope was 1.84 in this study, with each type of vehicle yielding similar O/PH ratio (Fig. 3).

3.5. N-alkanols

N-alkanols with 14–30 carbon atoms (O14–O30) were quantified in this study. Their total concentration was relatively low in vehicle emissions, except in emissions from light-duty gasoline cars. The average n-alkanols emissions factor among all vehicle types was 1578 ng/mg PM_{2.5}. The highest emissions factor was observed among gasoline cars (3424 ng/mg PM_{2.5}), followed by motorcycles (134 ng/mg PM_{2.5}) and diesel cars (70 ng/mg PM_{2.5}). The same trend was observed among emissions factors of aliphatic acids. It was inferred that n-alkanol is generated in the catalysis process.

O16, O18 and O20 were the dominant compounds in n-alkanols in this study. Together, they averaged 69.4% of the mass of n-alkanols among all vehicles. The distribution of their concentrations showed a strong even predominance with the average CPI_{even} of 17.4. Oros and Simoneit (2000) studied coal smoke and found the CPI_{even} of alkanols ranged from 3.2 to 16.1. Rogge et al. (1994) measured alkanols in cigarette smoke but found no even predominance. This suggests that alkanol generation was related to fuel maturity. Distinguishing combustion sources by alkanol distribution requires further study.

3.6. PAHs

PAHs represented a small proportion of organic particles but are still relevant for emissions regulation because of their high teratogenicity and carcinogenicity (Baek et al., 1991). PAHs are generated in working engines. Their production is influenced by many factors including fuel quality, lube quality and engine loading. A main PAHs generation process is the rearrangement of the hydrocarbon radical to create small PAHs, which then may react with other hydrocarbon radicals to produce larger PAHs.

Thirty-two unique compounds of PAHs, ranging from two to seven rings, were quantified in this study. Heavy-duty cars emitted

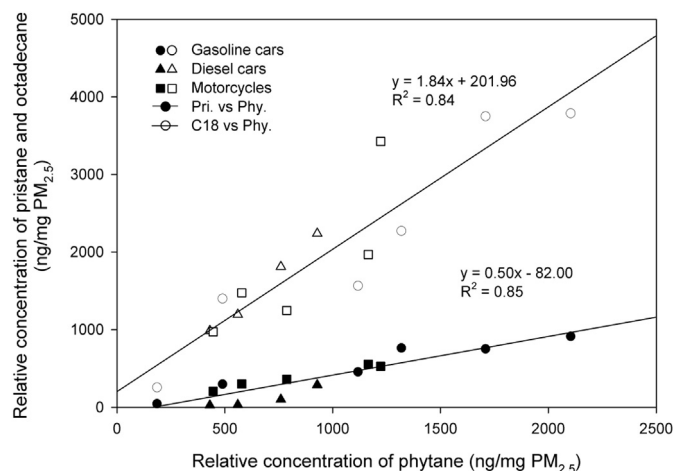


Fig. 3. Correlations among pristane, n-octadecane and phytane in PM_{2.5} emission of measured vehicles. Circles, triangles and squares meant gasoline cars, diesel cars and motorcycles, respectively. Solid and hollow symbols represented pristane vs phytane and n-octadecane vs pristane, respectively.

more PAHs than light-duty cars. The concentration of PAHs observed in heavy-duty gasoline (Cat/Cbrt) vehicle exhaust was 7471 ng/mg PM_{2.5}. The emissions of the other two types of heavy-duty gasoline vehicles both showed higher PAHs concentrations (Cat/EFI: 2353 ng/mg PM_{2.5}, Cbrt: 2650 ng/mg PM_{2.5}) than light-duty gasoline cars (2010 ng/mg PM_{2.5}). Diesel cars followed the same trend, with PAH emissions factors of 1003 and 1727 ng/mg PM_{2.5} in light-duty and heavy-duty diesel cars, respectively. Because the PM_{2.5} emissions factors of heavy-duty gasoline and diesel cars are high, PAHs emissions for these vehicles could be considerable and should be monitored in the future. The average PAHs concentration among motorcycles was 3656 ng/mg PM_{2.5}, which was raised by an extremely high value for one motorcycle in this study (10,307 ng/mg PM_{2.5}). Yang et al. (2005b) found a positive correlation between PAHs and CO in motorcycles emissions with an R² of 0.51 and concluded that both compounds were the products of incomplete combustion. As we focused on the particle mobile source profiles, gaseous pollutants such as CO were not measured in this study. However a strong positive correlation between PAHs and EC (another product of incomplete combustion) was discovered in gasoline-powered vehicles (Cat) emissions with an R² of 0.83 (Fig. S3).

The concentrations of PAHs observed in this study are higher than those observed for cereal straw burning (2697–270 ng/mg PM_{2.5} in average), suggesting that the mobile source may pose a higher health risk from PAHs inhalation than the biomass burning source (Zhang et al., 2007). The high PAHs concentration was related to incomplete combustion in the engine. Fig. 4 shows the PAHs' compositional distributions of gasoline and diesel powered vehicles. Two-ring PAHs concentrations were low relative to other

PAHs. High 2-Methylphenanthrene and pyrene concentrations were found in both fuel types of vehicles. PAHs of 3 and 4 rings were the most common type of PAHs emissions. Gasoline vehicles, especially large gasoline cars (Cat/Cbrt), showed high emissions of large PAHs (more than five rings) while large PAHs concentrations were low in diesel cars and some large PAHs were not detected at all in diesel exhaust. Different emission characteristics allowed us to identify the contributions to PM_{2.5} pollutions of gasoline and diesel vehicles. For example, the average benzo[ghi]perylene concentrations in gasoline and diesel vehicles were 399.7 and 20.1 ng/mg PM_{2.5}, respectively. Furthermore, coronene was not detected in diesel emissions, although it was present in gasoline emissions. These differences could be used to distinguish between emissions from gasoline and diesel cars. In addition to these differences, indeno[1,2,3-cd]pyrene (IncdP) concentrations between gasoline and diesel vehicle emissions also differed significantly, from 118.7 to 3.1 ng/mg PM_{2.5}, respectively, though it is not clear whether this difference can be used to distinguish gasoline and diesel vehicles. Rogge et al. (1993) and Schauer et al. (1999, 2002) did not detect IncdP in diesel emissions but found high IncdP concentrations in gasoline exhaust, observations which agree with results in this study. However, Venkataraman and Friedlander (1994) suggested that IncdP was a common tracer for all vehicles. Further emissions comparisons to other sources are needed to define tracers of all vehicles.

3.7. Hopanes and steranes

Simoneit (1985) was the first to suggest using hopanes and steranes as tracers of vehicle exhaust and demonstrated their utility

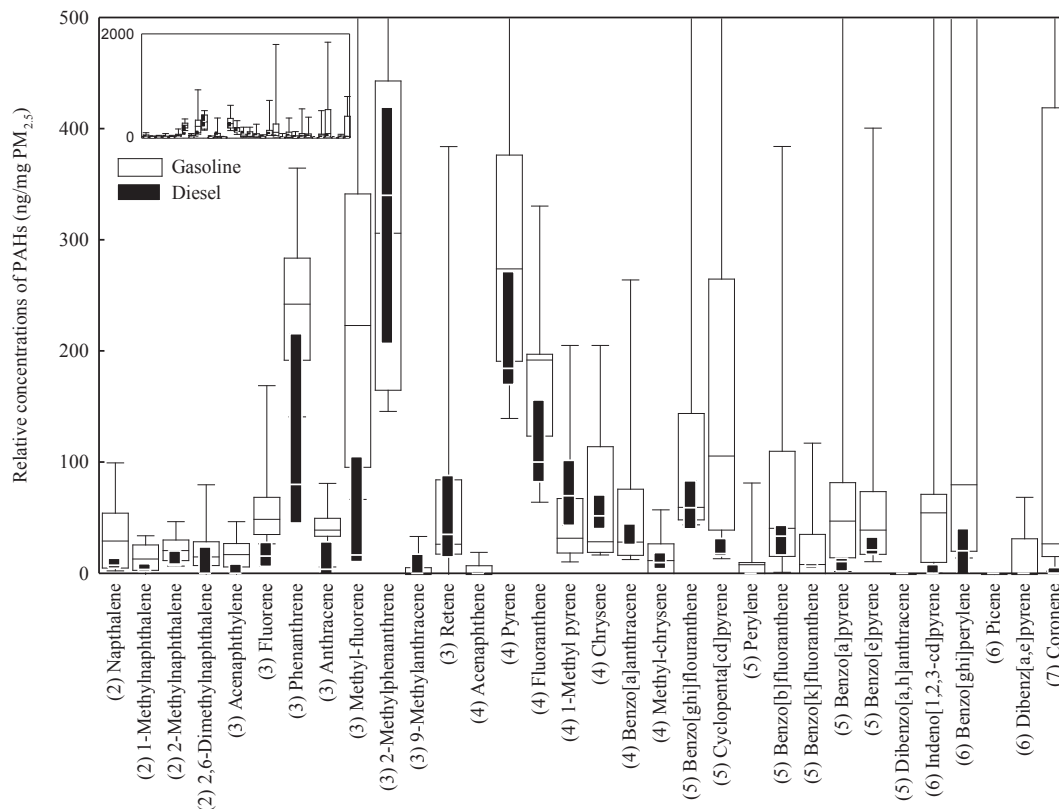


Fig. 4. Relative concentrations of PAHs in PM_{2.5} emission of gasoline (include motorcycles) and diesel vehicles. Box plot: the 25th–75th percentile of the relative concentrations; Solid line inside of the box plot (white line inside of the black box): the median of the relative concentrations; Short horizontal line: the 5th and 95th percentiles of the relative concentrations. The scale of y-axis was set as 500 to display the details of most box and the small screen in the top left showed some extremely high values. The numbers in the brackets meant the numbers of rings of PAHs.

in several studies (Schauer et al., 1996; Yang et al., 2005a). Eight hopanes and four steranes were quantitatively analyzed in this study (Table S3). Hopanes and steranes concentrations comprised 6.67% of QOC, where hopanes concentrations were higher than steranes. Average hopanes concentrations in motorcycle, gasoline and diesel vehicles were 5698, 1732 and 594 ng/mg PM_{2.5}, respectively, with heavy-duty cars emitting higher hopanes concentrations than light-duty cars. The ratio of steranes to hopanes was similar across vehicle types and these results agree with those obtained by Rogge et al. (1993).

It is generally recognized that the precursor of several kinds of hopanes in fuels is 17 β (H),21 β (H)-hopanes with an R configuration at C22. As the fuel age increases, the stereochemistry at C17, C21 and C22 changes to form a more thermodynamically stable configuration. Thus, the relative concentrations of hopane homologues could be used to estimate the fuel age. The most common hopanes species we observed across fuels was 17 α (H),21 β (H)-hopanes (HP30). Fig. 5 displays different hopanes concentrations across vehicle types with data collected from other published papers added for comparison (Rogge et al., 1993; Schauer et al., 1999, 2002; Phuleria et al., 2006). The hopanes concentrations were normalized to HP30 to best represent the emissions characteristics. The relative concentrations of specific hopanes were consistent across vehicle types in this study, with the highest concentration of HP30, followed by norhopane (HP29). The concentrations of 17 α (H),21 β (H)-22,29,30-Trisnorhopane (Ts) was also found to be consistently above those of 17 α (H)-22,29,30-Trisnorhopane (Tm). The fact that the S configuration in 17 α (H),21 β (H)-Homohopane (HP31) and 17 α (H),21 β (H)-Bishomohopane (HP32) was more prevalent than the R configuration suggested that the gasoline was mature. The results agreed with the emission characteristics of gasoline cars in other studies, except the catalyst-equipped cars tested by Schauer et al. (2002). Hopanes emissions characteristics of diesel cars in this study were similar to gasoline vehicles, which meant that both diesel and gasoline had similar degrees of fuel maturity. Hopanes are also detected in lube oil, which suggests that they might come from the combustion and volatilization of

lubes. This could help explain why some others observed high HP29 concentrations in a tunnel test (Phuleria et al., 2006).

Hopanes are thought as desirable tracers of mobile sources due to their stability in the atmosphere. Steranes are not detected in gasoline and diesel fuels but exist in lube oil. Like with hopanes, the proportion of R and S configurations of steranes reflects the degree of fuel maturity. In this study, the average 20R-5 α (H),14 β (H),17 β (H)-Cholestane/20S-5 α (H),14 α (H),17 α (H)-Cholestane ratio was 0.863 in all vehicles and this ratio was expected to be a marker of vehicle emission.

3.8. Dicarboxylic acids and aromatic acids

Ten dicarboxylic acids were quantitatively analyzed in this study. The concentrations of dicarboxylic acids in motorcycles, gasoline and diesel vehicles were 91, 449 and 337 ng/mg PM_{2.5}, respectively. The average concentration of dicarboxylic acids among heavy-duty gasoline cars (711 ng/mg PM_{2.5}) was higher than that of light-duty gasoline cars (13 ng/mg PM_{2.5}) while the opposite trend was observed among diesel cars, with concentrations of 433 and 193 ng/mg PM_{2.5} for light-duty and heavy-duty diesel cars, respectively. Dicarboxylic acids were thought of as the products of alkane combustion. Kawamura and Kaplan (1987) found that traffic emissions were a primary source of dicarboxylic acids in Los Angeles ambient air.

Eight aromatic acids, including benzoic acid, four benzene dicarboxylic acids and three benzene tricarboxylic acids, were quantified in this study. Similar to dicarboxylic acids, the highest concentrations of aromatic acids for each fuel type were found among heavy-duty gasoline cars and light-duty diesel cars. The dominant aromatic acid in light-duty gasoline cars was benzoic acid while benzene dicarboxylic acids were the primary compounds in other types of vehicles. Kawamura et al. (1985) studied organic acids in engine oils and they found benzoic acid only in used engine oils. This implies that benzoic acid is generated in the combustion process in the engine.

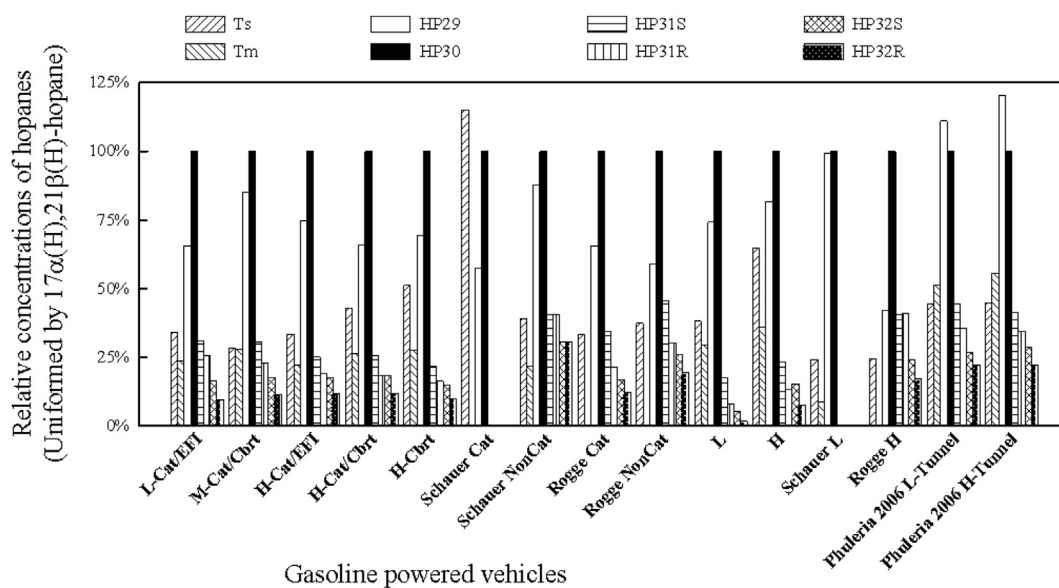


Fig. 5. Relative concentration of hopanes in each type of vehicles, including vehicles in other published mobile source profiles. The last six columns represented diesel vehicles. Ts: 17 α (H),21 β (H)-22,29,30-Trisnorhopane; Tm: 17 α (H)-22,29,30-Trisnorhopane; HP29: norhopane; HP30: 17 α (H),21 β (H)-hopanes; HP31: 17 α (H),21 β (H)-Homohopane; HP32: 17 α (H),21 β (H)-Bishomohopane; S: S configuration; R: R configuration.

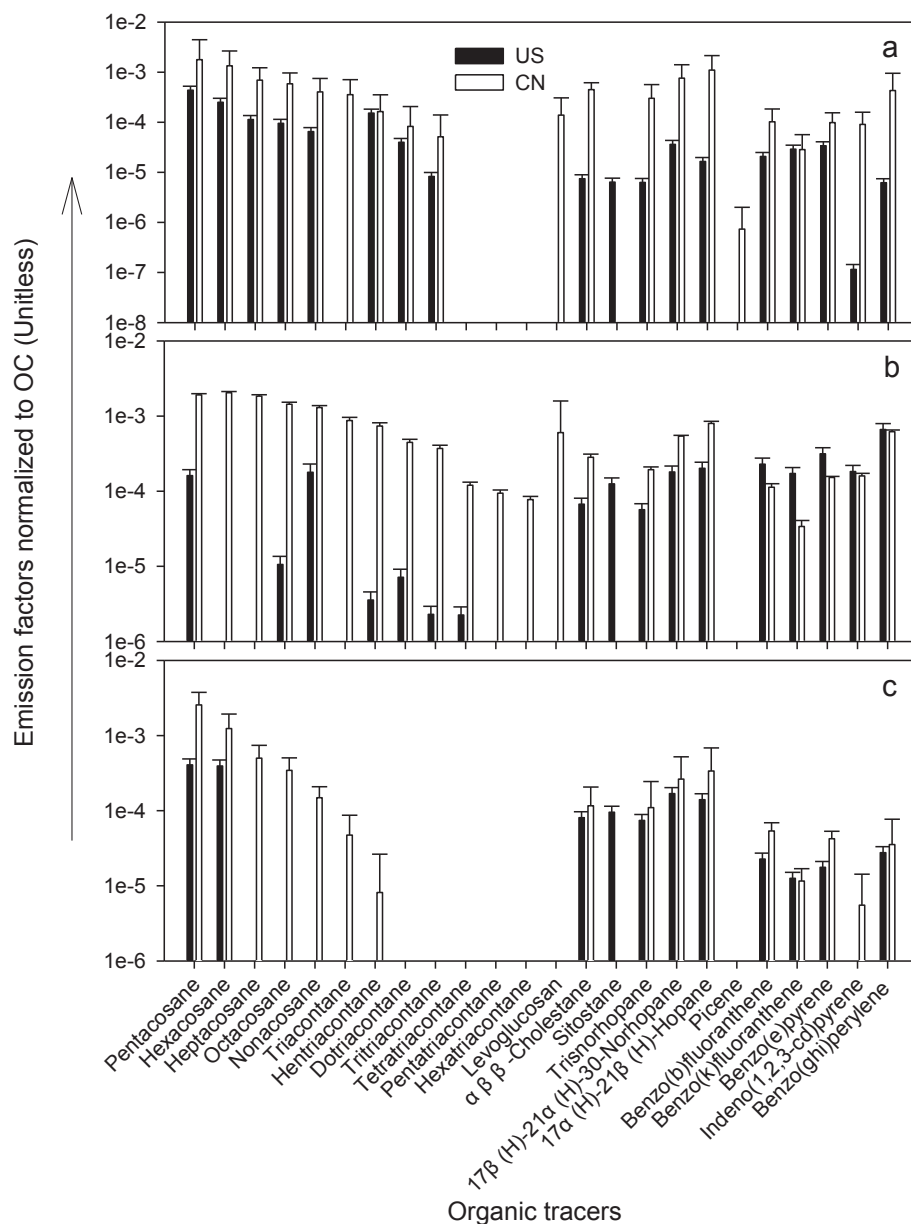


Fig. 6. Emission characteristics of common organic tracer comparison between the (a) diesel cars; (b) gasoline cars; (c) smoking vehicles in two tested fleets. The black bars are published mobile profiles (US) and the white bars are results in this study (CN). Y axis is logarithmic coordinates and the error bars show the uncertainties of emission factors. Species with no bar mean that they are under detection limits.

3.9. Other compounds

Many species with low concentrations were classified as “others,” such as cycloalkane, sterols and nicotine. Alkylcyclohexanes exist exclusively in petroleum products such as gasoline, diesel and lube oil. Simoneit (1985) demonstrated alkylcyclohexanes was one of the primary compounds in vehicles emissions. Average alkylcyclohexanes concentrations in exhaust from motorcycles and gasoline and diesel cars were 290, 305 and 569 ng/mg PM_{2.5}, respectively. These results were lower than those reported in Schauer et al. (2002) because only three alkylcyclohexanes were quantified in this study. Some species in “others”, which might come from the experiment operation, are unrelated to mobile emission and therefore cannot be used for source apportionment or to distinguish gasoline and diesel emission.

3.10. Emission characteristics comparison

A widely used US mobile profile is used to compare to the vehicle emission characteristics above (Lough et al., 2007). To match its published form, tested vehicles without motorcycles are re-classified to three categories – diesel, gasoline and smoking vehicles. Diesel and gasoline cars are both consist of three light-duty and two heavy-duty cars and smoking vehicles are those without exhaust catalytic device. Fig. 6 shows the comparison of common organic tracers between each type of vehicles. The emission factors are generally higher in the CN profile than the US profile. Emission factor of n-alkanes in the CN profile are significantly larger than that in the US profile, especially in gasoline and smoking vehicles. In opposite, Hopananes and cholestane are more similar in gasoline and smoking vehicles, while in diesel shows

large discrepancy. PAHs are the products of fuel combustion and they are quite similar in all types of vehicles. Although n-alkanes present huge differences, they are not tracers of mobile source so it may cause slight impact if using it in source apportionment. Hopanes and cholestane are significant organic markers of mobile source so the CN profile shows certain similarities in emission characteristics with the US profile.

4. Conclusion

In this study, twenty-one Chinese vehicles were tested by the dilution tunnel–chassis dynamometer method. They were classified to five groups by fuel type and weight: motorcycles, light-duty gasoline cars, heavy-duty gasoline cars, light-duty diesel cars and heavy-duty diesel cars. PM_{2.5} in vehicle exhaust was sampled and mass, OC/EC and speciated organic compounds were measured. Emission characteristics of our results and a published mobile source profile were compared. In this study, PM_{2.5} emission factors are larger in aged cars. OC and EC averaged $55.4 \pm 15.6\%$ and $10.7 \pm 12.1\%$ of total PM mass and ranged from 31.7% to 68.6% and 0.7%–24.8%, respectively. 190 organic compounds were quantified and n-alkanes was observed as the predominant species in QOC. There was no obvious odd or even predominance in n-alkanes with an average CPI of 0.91, although n-alkanols in this study did show a strong even predominance. Similar to n-alkanols, n-aliphatic acids were thought of as the products of catalysis, and they represented a large proportion of the QOC ($9.4 \pm 1.1\%$ on average). Six branched alkanes were quantified and the average PR/PH ratio was 0.50, which showed a high degree of vehicle fuel maturity. PAHs were considered to be the products of incomplete combustion. Gasoline vehicles emitted more large PAHs, which suggests that benzo[ghi]perylene and coronene can be used as tracers to distinguish between gasoline and diesel vehicles. Although hopanes and steranes represented only $7.4 \pm 11\%$ of QOC by mass, they were the most effective tracers of the mobile source due to the similarity of emissions characteristics in all types of vehicles. The configuration ratio in hopanes and steranes suggested that the fuels were mature. The results of this study suggest that installing catalytic converters in all vehicles and implementing strict PM_{2.5} emissions standards for heavy-duty gasoline and diesel cars would help reduce PM_{2.5} emissions from automobiles in China.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apr.2016.08.007>.

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