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Chemical and stable carbon isotopic composition of $PM_{2.5}$ from on-road vehicle emissions in the PRD region and implications for vehicle emission control policy

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Experimental details of chemical analysis

1. OC/EC

A punch (1.5×1.0 cm) of each filter was taken for the measurements of OC and EC using a thermal/optical transmittance aerosol carbon analyzer (Sunset Laboratory) with the NIOSH method for diesel soot (NIOSH, 1999).

2. Water soluble organic carbon

An additional four punches were taken from each filter and extracted in 10 mL of 18.2-Mohm MilliQ water and sonicated for 60 min. After filtration, the extract was analyzed for WSOC with a Sievers Model TOC-V CPH TOC analyzer (Shimadzu Corporation, Japan). Method detection limit (MDL) of 0.08 μg C m^{-3} for WSOC is estimated by three times of the standard deviation of field blanks.

3. Water soluble inorganic ions

Sample preparation for water soluble ions was the same as that for WSOC which has been described above. The extract was analyzed for Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} using ion chromatography (Metrohm, Herisau, Switzerland). The corresponding MDL were 0.008, 0.010, 0.012, 0.026, 0.015, 0.036, 0.005, 0.015, 0.015, 0.020, 0.030, 0.030 and 0.030 μg m^{-3}, respectively. The reproducibility tests showed that the relative standard deviation of each ion was generally lower than 5%.

4. Metal elements

The extraction and instrumental analyses were executed according to the method in previous study (He et al., 2008) with minor modifications. Briefly, four punches

(1.5×1.0 cm) of each filter were first extracted in a XP-1500 digestion bomb (CEM Corp., USA) with a mixture of 4 ml of HNO_3 (Merck Corp., Germany), 1 ml of HCl (Guangzhou Chemical Reagent Factory, China), and 0.2 ml of HF (Guangzhou Chemical Reagent Factory, China), and digested by a MARS5 microwave digestion unit (CEM Corp., USA). The digestion was carried out at 175 °C for 25 min. The resulting solution was diluted to 50 ml with ultra-pure water generated from a Milli-Q system (Millipore Corp., USA). The final solutions were measured by an Agilent 7700X ICP-MS instrument equipped with a Babington nebulizer (Agilent Corp., USA). The MDL (in ng m^{-3}) were Li (1.89), Be (0.056), Na (1.57), Mg (0.413), Al (0.582), K (12.8), Ca (4.92), V (0.33), Cr (0.127), Mn (0.362), Fe (59.5), Co (0.033), Ni (1.10), Cu (0.314), Zn (0.831), Ga (0.005), As (0.014), Se (0.174), Rb (0.009), Sr (0.009), Ag (0.009), Cd (0.014), Cs (0.005), Ba (0.188), Tl (0.005), Pb (0.198), and U (0.005). A certified reference soil material (GBW07403 (GSS-3), China National Institute of Metrology) was analyzed to evaluate the accuracy of the method. In result, all elements showed small relative deviations of <30% from the standard values. The precisions of analysis for the elements quantified were all less than 10%. All the results were then corrected for filter blanks.

5. Organic compounds

Filters were extracted with 30 mL dichloromethane (DCM) using ultrasonic agitation under 30 °C and filtered. The procedure was repeated three times. The combined extracts were filtered and concentrated by rotary evaporation under vacuum. Each sample was concentrated to about 0.5 mL. Interfering compounds were removed by liquid-solid chromatography using 2:1 silica-alumina column. Two fractions were eluted. Fraction I (40 mL of hexane) contained n-alkanes, hopanes and steranes, while fraction II (100 mL of DCM-hexane (1:1)) contained the priority PAHs. Then under a gentle stream of nitrogen, fraction I and fraction II were reduced almost to dryness and redissolved with 100 μL n-hexane. Then, the two fractions were analyzed on GC-MS according to the previous study (Wu et al., 2005).

6. Stable carbon isotopic composition

A small punch which contain about 0.3 mg carbon of each filter was taken for the measurements of isotope abundance with a Finnigan MAT-252 mass spectrometer (Thermo Electron Corporation, USA). The carbon isotope composition (δ13C) is calculated using a reference standard material (GBW04408, China National Institute of Metrology), which standard value is -36.91 ±0.10 $\delta^{13}C_{VPDB}\times10^{-3}$. $\delta^{13}C$ in samples are usually expressed as:

$$\delta^{13}C = ((13C/12C_{sample})/(13C/12C_{standard}) - 1) \times 1000$$

Samples were analyzed at least in duplicate with a maximum allowable difference of 0.1‰.

Table S1. Vehicle counts and meteorological parameters during the 10 sampling periods

Test #	Time	Vehicle Number	DV Percent (%)	GV Percent (%)	LPGV Percent (%)	Ave. Temp. (℃)	Ave. R.H. (%)	Ave. Wind Speed (m s^{-1})
1	10/08/13 7:30-19:00	25654	20.1	51.6	28.2	35.88	45.99	3.80
2	10/08/13 19:30-7:00	13913	13.8	48.5	37.8	32.62	50.14	3.69
3	11/08/13 7:30-19:00	24791	11.6	69.5	18.9	34.03	46.64	3.81
4	11/08/13 19:30-7:00	11977	14.0	53.7	32.3	32.74	57.08	3.27
5	12/08/13 7:30-19:00	27555	13.6	68.8	17.6	36.13	42.69	3.95
6	12/08/13 19:30-7:00	13435	14.3	50.4	35.3	34.04	50.70	3.56
7	13/08/13 7:30-19:00	27606	13.2	69.6	17.3	34.58	50.62	3.96
8	13/08/13 19:30-7:00	13661	14.0	54.7	31.3	31.51	59.31	3.33
9	14/08/13 7:30-19:00	26947	13.4	68.9	17.8	30.50	51.41	3.99
10	14/08/13 19:30-23:30	6756	9.4	61.9	28.7	28.63	60.22	3.80

Table S2. Average concentrations of species and stable carbon isotopic composition at the inlet and the outlet sampling locations in $PM_{2.5}$ in the Zhujiang tunnel.

Species	Inlet	Outlet	Species	Inlet	Outlet
Mass	71	204	OC	20.0	44.7
EC	6.89	30.3	WSOC	6.21	8.00
$\delta^{13}C$, ‰	-26.089	-25.384			
Water soluble ions					
F^-	0.023	0.045	Li^+	BDL	BDL
Cl^-	0.664	6.86	Na^+	0.724	4.92
NO_2^-	BDL[b]	BDL	NH_4^+	0.787	1.02
Br^-	BDL	BDL	K^+	0.182	0.271
NO_3^-	0.603	0.756	Mg^{2+}	0.058	0.314
PO_4^{3-}	ND	0.036	Ca^{2+}	0.601	1.93
SO_4^{2-}	2.44	3.30			
Metal elements					
Li	0.0048	0.0077	Zn	0.299	0.516
Be	0.0002	0.0006	Ga	0.0432	0.0938
Na	3.00	8.79	As	0.0339	0.0344
Mg	1.04	1.79	Se	0.0064	0.0078
Al	1.92	6.19	Rb	0.0154	0.0291
K	0.658	1.09	Sr	0.0234	0.0604
Ca	2.53	4.97	Ag	0.0050	0.0051
V	0.0107	0.0195	Cd	0.0032	0.0035
Cr	0.0413	0.0635	Cs	0.0011	0.0022
Mn	0.0235	0.139	Ba	0.236	0.552
Fe	0.707	5.96	Tl	0.0005	0.0007
Co	0.0005	0.0025	Pb	0.0593	0.0700
Ni	0.0008	0.0107	U	0.0003	0.0007
Cu	0.0348	0.157			
Organic compounds					
C11	1.49	1.98	CHR	0.22	1.31
C12	2.09	2.70	BbF	0.34	0.84
C13	0.71	1.11	BkF	0.13	0.31
C14	2.60	3.52	BaP	0.24	0.81
C15	2.49	3.71	IcdP	0.34	0.62
C16	5.26	7.28	DBahA	0.05	0.08
C17	4.39	6.43	BghiP	0.63	1.46
C18	4.19	6.66	Ts	0.21	1.94
C19	2.59	5.99	Tm	0.27	2.30
C20	2.23	7.43	HP29	1.05	8.99
C21	2.18	10.3	HP30	1.92	14.5
C22	2.74	16.0	HP31S	0.70	5.06
C23	3.94	23.3	HP31R	0.49	3.48
C24	4.23	28.6	HP32S	0.46	3.34
C25	4.97	25.0	HP32R	0.35	2.61
C26	4.97	19.6	HP33S	0.32	2.50
C27	8.29	22.8	HP33R	0.21	1.67
C28	5.39	15.9	HP34S	0.21	1.67
C29	9.62	16.3	HP34R	0.12	1.06
C30	5.08	11.2	HP35S	0.13	1.17
C31	14.6	17.0	HP35R	0.08	0.72
C32	4.67	8.51	27αααS	0.08	0.71
C33	6.46	7.37	27αββR	0.13	1.07
C34	1.70	4.68	27αββS	0.10	0.85
C35	1.12	2.37	27αααR	0.12	0.87
C36	0.58	1.08	28αααS	0.08	0.49
ACY	0.01	0.06	28αββR	0.13	0.93
ACE	0.01	0.02	28αββS	0.11	0.77
FLO	0.07	0.14	28αααR	0.13	0.87
PHE	0.28	0.84	29αααS	0.20	1.36
ANT	0.03	0.13	29αββR	0.22	1.56
FLA	0.18	0.96	29αββS	0.19	1.34
PYR	0.22	1.54	29αααR	0.19	1.17
BaA	0.11	0.93			

[a] The concentrations are in μg m^{-3} except those for organic compounds in ng m^{-3}. [b] BDL, below detection limit.

Table S3 Average emission factors (mg vehicle^{-1} km^{-1}) of species in $PM_{2.5}$ in the Zhujiang tunnel

Species	Emission factor	SD[a]
$PM_{2.5}$ mass	92.4	8.9
OC	16.7	1.9
EC	16.4	2.1
WSOC	1.31	0.3
WSII		
F^{-}	0.02	0.008
Cl^{-}	4.17	0.9
NO_3^{-}	0.10	0.03
PO_4^{3-}	0.02	0.02
SO_4^{2-}	0.61	0.1
Na^{+}	2.88	0.5
NH_4^{+}	0.17	0.06
K^{+}	0.06	0.02
Mg^{2+}	0.18	0.02
Ca^{2+}	0.95	0.3
Metal elements		
Li	0.002	0.001
Be	0.0002	0.0001
Na	3.53	0.4
Mg	0.50	0.08
Al	3.15	0.3
K	0.34	0.04
Ca	1.93	0.3
V	0.007	0.0004
Cr	0.01	0.0008
Mn	0.08	0.02
Fe	3.91	0.2
Co	0.002	0.003
Ni	0.008	0.002
Cu	0.09	0.01
Zn	0.16	0.02
Ga	0.04	0.003
As	0.005	0.001
Se	0.0009	0.0003
Rb	0.01	0.002
Sr	0.03	0.003
Ag	0.0001	0.00002
Cd	0.0003	0.00004
Cs	0.0008	0.0002
Ba	0.25	0.03
Tl	0.0001	0.00001
Pb	0.01	0.0007
U	0.0003	0.0002

[a] SD: standard deviation

Table S4. Average emission factors (EF, μg vehicle^{-1} km^{-1}) of organic compounds in PM$_{2.5}$ in the Zhujiang tunnel

Species	Abbr.[a]	EF	SD[b]	Species	Abbr.	EF	SD
n-Alkanes				chrysene	CHR	0.761	0.08
n-hendecane	C11	0.27	0.12	benzo[b]fluoranthene	BbF	0.351	0.05
n-dodecane	C12	0.33	0.15	benzo[k]fluoranthene	BkF	0.133	0.02
n-tridecane	C13	0.22	0.04	benzo[a]pyrene	BaP	0.416	0.05
n-tetradecane	C14	0.50	0.15	indeno[cd]pyrene	IcdP	0.209	0.04
n-pentadecane	C15	0.66	0.17	dibenzo[ah]anthrathene	DBahA	0.023	0.003
n-hexadance	C16	1.10	0.33	benzo[ghi]perylene	BghiP	0.622	0.09
n-heptandecane	C17	1.12	0.23	Hopanes			
n-octadecane	C18	1.35	0.20	22,29,30-trisnorhopane	Ts	1.25	0.09
n-nonadecane	C19	1.85	0.18	17αH-22,29,30-trisnorhopane	Tm	1.49	0.11
n-eicosane	C20	2.84	0.24	norhopane	HP29	5.75	0.42
n-heneicosane	C21	4.46	0.40	hopane	HP30	9.14	0.68
n-docosane	C22	7.22	0.65	22S-homohopane	HP31S	3.13	0.22
n-tricosane	C23	10.6	0.91	22R-homohopane	HP31R	2.17	0.16
n-tetracosane	C24	13.3	1.11	22S-bishomohopane	HP32S	2.06	0.14
n-pentacosane	C25	10.9	0.87	22R-bishomohopane	HP32R	1.61	0.10
n-hexacosane	C26	7.98	0.54	22S-trishomohopane	HP33S	1.54	0.09
n-heptacosane	C27	7.94	0.62	22R-trishomohopane	HP33R	1.02	0.06
n-octacosane	C28	5.76	0.51	22S-tetrahomohopane	HP34S	1.02	0.07
n-nonacosane	C29	3.62	0.59	22R-tetrahomohopane	HP34R	0.65	0.04
n-triacontane	C30	3.36	0.45	22S-pentahomohopane	HP35S	0.73	0.04
n-hentriacontane	C31	1.35	0.88	22R-pentahomohopane	HP35R	0.46	0.03
n-dotriacontane	C32	2.10	0.36	Steranes			
n-tritriacontane	C33	0.50	0.38	C27ααα-cholestane(20S)	27αααS	0.46	0.04
n-tetratriacontane	C34	1.63	0.24	C27αββ-cholestane (20R)	27αββR	0.69	0.05
n-pentatriacontane	C35	0.68	0.14	C27αββ-cholestane(20S)	27αββS	0.55	0.04
n-pexatriacontane	C36	0.27	0.08	C27ααα-cholestane (20R)	27αααR	0.56	0.05
PAHs				C28ααα-ergostane (20S)	28αααS	0.31	0.03
acenaphthylene	ACY	0.028	0.01	C28αββ-ergostane (20R)	28αββR	0.60	0.05
acenaphthene	ACE	0.006	0.001	C28αββ-ergostane (20S)	28αββS	0.49	0.05
fluorene	FLO	0.047	0.004	C28ααα-ergostane (20R)	28αααR	0.55	0.05
phenanthrene	PHE	0.374	0.04	C29ααα-stigmastane(20S)	29αααS	0.85	0.07
anthracene	ANT	0.068	0.01	C29αββ-stigmastane(20R)	29αββR	0.97	0.07
fluoranthene	FLA	0.523	0.06	C29αββ-stigmastane(20S)	29αββS	0.84	0.06
pyrene	PYR	0.890	0.10	C29ααα-stigmastane(20R)	29αααR	0.72	0.06
benz[a]anthracene	BaA	0.568	0.06				

[a] Abbr.: abbreviation [b] SD: standard deviation

Table S5. Average emission factors (mg vehicle^{-1} km^{-1}) of species in PM$_{2.5}$ in this study and comparisons with other tunnel studies

Species	Zhujiang tunnel 2013, China [a]	Zhujiang tunnel 2004, China	Chung-Liao tunnel, Taiwan	Kaisernuhlen tunnel, Austria	Sepulveda tunnel, USA	Howell tunnel, USA
Mass	92.4(8.9)	110	38	26	52	39.3
OC	16.7(1.9)	24.3	4.67	5.4	19.3	12.9
EC	16.4(2.1)	49.6	15.1	17.8	25.5	10.8
WSOC	1.31(0.3)					
F^-	0.02(0.008)					
Cl^-	4.17(0.9)	0.98	0.09		0.67	
NO_2^-	BDL[b]		0.027			
Br^-	BDL					
NO_3^-	0.10 (0.03)	1.37	0.374		3.27	
PO_4^{3-}	0.02(0.02)					
SO_4^{2-}	0.61 (0.1)	3.87	0.917		1.77	
Li^+	BDL					
Na^+	2.88(0.5)		0.201			
NH_4^+	0.17(0.06)	0.80	0.151		1.61	
K^+	0.06 (0.02)		0.029			
Mg^{2+}	0.18(0.02)		0.031			
Ca^{2+}	0.95(0.3)		0.162			
Li	0.002(0.001)					
Be	0.0002(0.0001)					
Na	3.53(0.4)	0.37	1.05		0.3	0.038
Mg	0.50(0.08)	0.22	0.112	0.08	0.26	0.044
Al	3.15(0.3)		0.405	0.47		
K	0.34(0.04)	0.14	0.379		0.08	0.065
Ca	1.93(0.3)	0.64	0.428	0.27	0.3	0.43
V	0.007(0.0004)	0.0015	0.013	0.002	0.05	0.0004
Cr	0.01(0.0008)	0.0054	0.072		0.02	0.0018
Mn	0.08(0.02)	0.019	0.152	0.006	0.02	0.006
Fe	3.91(0.2)	1.12	0.582	0.77	2.79	0.55
Co	0.002(0.003)	0.00013	0.015			0.0004
Ni	0.008(0.002)	0.0034	0.009		0.01	0.009
Cu	0.09(0.01)	0.034	0.037	0.041	0.17	0.012
Zn	0.16(0.02)	0.078	0.149	0.034	0.14	0.028
Ga	0.04 (0.003)					
As	0.005(0.001)	0.002	0.015			0.00045
Se	0.0009(0.0003)		0.049			
Rb	0.01 (0.002)					
Sr	0.03(0.003)		0.008	0.001		
Ag	0.0001(0.00002)					
Cd	0.0003(0.00004)	0.00049	0.001		0.02	0.00005
Cs	0.0008(0.0002)					
Ba	0.25 (0.03)		0.04	0.015		
Tl	0.0001(0.00001)	0.00004				
Pb	0.01(0.0007)	0.014	0.292		0.03	0.001
U	0.0003(0.0002)	0.00004				
Reference	this study	(He et al., 2008)	(Chiang and Huang, 2009)	(Handler et al., 2008)	(Gillies and Gertler, 2000)	(Lough et al., 2005)

[a] Values in parentheses indicate associated uncertainties (standard deviation); [b] BDL, below detection limit.

Table S6. BaPeq emission factors (μg vehicle^{-1} km^{-1}) of vehicle from Zhujiang tunnel 2004 and 2013

PAH	TEF[a]	Zhujiang tunnel 2004	Zhujiang tunnel 2013
ACY	0.001		0.00003
ACE	0.001		0.00001
FLO	0.001		0.00005
PHE	0.001	0.003	0.00037
ANT	0.01	0.002	0.00068
FLA	0.001	0.002	0.00052
PYR	0.001	0.003	0.00089
BaA	0.1	0.175	0.05679
CHR	0.01	0.022	0.00761
BbF	0.1	0.510	0.03508
BkF	0.1	0.139	0.01334
BaP	1	3.500	0.41558
IcdP	0.1	0.247	0.02093
DBahA	0.1		0.00232
BghiP	0.01	0.094	0.00622
total		4.70	0.561

[a] TEF: toxic equivalency factors, proposed by (Nisbet and Lagoy, 1992).

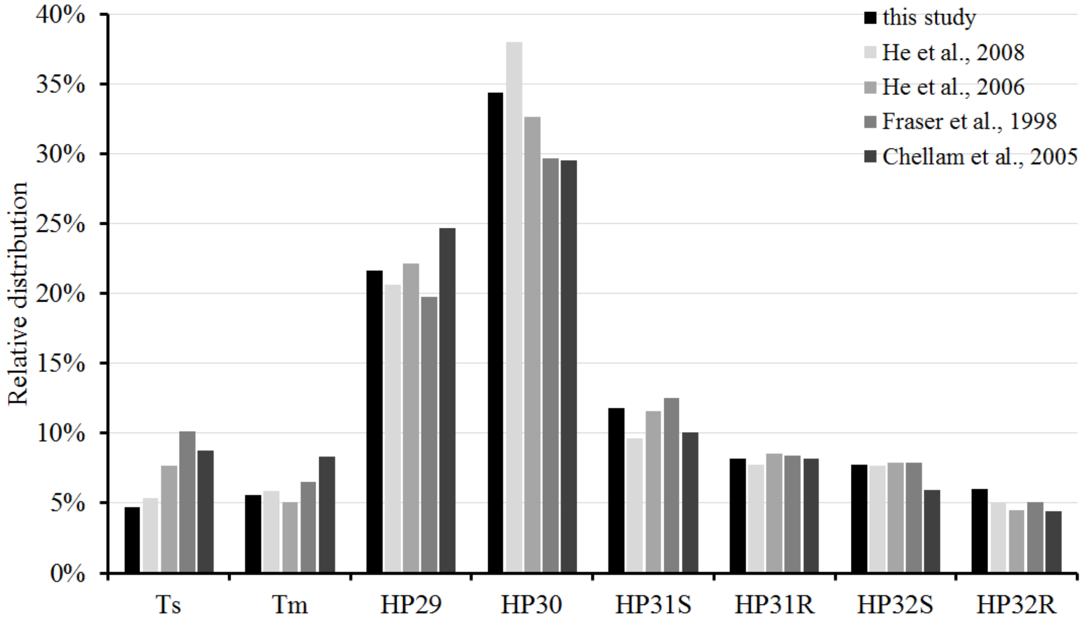

Fig. S1. Relative distributions of hopanes in different studies (this study; (He et al., 2008);(He et al., 2006);(Fraser et al., 1998);(Chellam et al., 2005)).

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