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Chemical and stable carbon isotopic composition of $PM_{2.5}$ from on-road vehicle emissions in the PRD region and implication 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 HNO3 (Merck Corp., Germany), 1 ml of HCl (GZRF Corp., China), and 0.2 ml of HF (GZRF Corp., 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 ℃ 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 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	Emission	Species	Inlet	Outlet	Emission
Mass	71	204	132	OC	20.0	44.7	24.8
EC	6.89	30.3	23.4	WSOC	6.21	8.00	1.79
$\delta^{13}C$, ‰	-26.089	-25.384	-25.012				
Water soluble ions							
F-	0.023	0.045	0.022	Li+	BLD	BLD	
Cl-	0.664	6.86	6.20	Na+	0.724	4.92	4.20
NO2-	BLD[b]	BLD		NH4+	0.787	1.02	0.231
Br-	BLD	BLD		K+	0.182	0.271	0.089
NO3-	0.603	0.756	0.153	Mg+	0.058	0.314	0.256
PO4-	ND	0.036	0.036	Ca+	0.601	1.93	1.33
SO4-	2.44	3.30	0.863				
Metal elements							
Li	0.0048	0.0077	0.0029	Zn	0.299	0.516	0.217
Be	0.0002	0.0006	0.0004	Ga	0.0432	0.0938	0.0506
Na	3.00	8.79	5.00	As	0.0339	0.0344	0.0005
Mg	1.04	1.79	0.752	Se	0.0064	0.0078	0.0014
Al	1.92	6.19	4.27	Rb	0.0154	0.0291	0.0138
K	0.658	1.09	0.436	Sr	0.0234	0.0604	0.0370
Ca	2.53	4.97	2.43	Ag	0.0050	0.0051	0.0001
V	0.0107	0.0195	0.0089	Cd	0.0032	0.0035	0.0003
Cr	0.0413	0.0635	0.0221	Cs	0.0011	0.0022	0.0011
Mn	0.0235	0.139	0.115	Ba	0.236	0.552	0.316
Fe	0.707	5.96	5.26	Tl	0.0005	0.0007	0.0001
Co	0.0005	0.0025	0.0020	Pb	0.0593	0.0700	0.0106
Ni	0.0008	0.0107	0.0099	U	0.0003	0.0007	0.0004
Cu	0.0348	0.157	0.122				
Organic compounds							
C11	1.49	1.98	0.49	CHR	0.22	1.31	1.10
C12	2.09	2.70	0.60	BbF	0.34	0.84	0.49
C13	0.71	1.11	0.41	BkF	0.13	0.31	0.18
C14	2.60	3.52	0.91	BaP	0.24	0.81	0.57
C15	2.49	3.71	1.21	INcdP	0.34	0.62	0.28
C16	5.26	7.28	2.02	DBahA	0.05	0.08	0.03
C17	4.39	6.43	2.04	BghiP	0.63	1.46	0.83
C18	4.19	6.66	2.47	Ts	0.21	1.94	1.73
C19	2.59	5.99	3.39	Tm	0.27	2.30	2.03
C20	2.23	7.43	5.20	HP29	1.05	8.99	7.94
C21	2.18	10.3	8.17	HP30	1.92	14.5	12.6
C22	2.74	16.0	13.22	HP31S	0.70	5.06	4.36
C23	3.94	23.3	19.32	HP31R	0.49	3.48	2.99
C24	4.23	28.6	24.34	HP32S	0.46	3.34	2.89
C25	4.97	25.0	20.02	HP32R	0.35	2.61	2.26
C26	4.97	19.6	14.61	HP33S	0.32	2.50	2.18
C27	8.29	22.8	14.54	HP33R	0.21	1.67	1.46
C28	5.39	15.9	10.54	HP34S	0.21	1.67	1.46
C29	9.62	16.3	6.63	HP34R	0.12	1.06	0.93
C30	5.08	11.2	6.15	HP35S	0.13	1.17	1.04
C31	14.6	17.0	2.46	HP35R	0.08	0.72	0.64
C32	4.67	8.51	3.84	27αααS	0.08	0.71	0.62
C33	6.46	7.37	0.91	27αββR	0.13	1.07	0.94
C34	1.70	4.68	2.98	27αββS	0.10	0.85	0.74
C35	1.12	2.37	1.25	27αααR	0.12	0.87	0.75
C36	0.58	1.08	0.50	28αααS	0.08	0.49	0.41
ACY	0.01	0.06	0.041	28αββR	0.13	0.93	0.80
ACE	0.01	0.02	0.008	28αββS	0.11	0.77	0.66
FLO	0.07	0.14	0.069	28αααR	0.13	0.87	0.73
PHE	0.28	0.84	0.553	29αααS	0.20	1.36	1.16
ANT	0.03	0.13	0.100	29αββR	0.22	1.56	1.34
FLA	0.18	0.96	0.775	29αββS	0.19	1.34	1.16
PYR	0.22	1.54	1.32	29αααR	0.19	1.17	0.98

BaA	0.11	0.93	0.82

[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 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^-	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^+	0.18(0.02)		0.031			
Ca^+	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 S4. Pearson correlation emission factors of metal elements with each other

	EC	Li	Be	Na	Mg	Al	K	Ca	V	Cr	Mn	Fe	Co
Li	.269												
Be	.829**	.382											
Na	.347	.964**	.46										
Mg	.397	.968**	.478	.927**									
Al	.538	.878**	.684*	.895**	.896**								
K	.366	.957**	0.445	.909**	.988**	.884**							
Ca	.445	.963**	0.517	.920**	.982**	.927**	.968**						
V	.905**	.234	.645*	.339	.297	.402	.277	.372					
Cr	-.732*	.249	-.649*	.11	.096	-.063	.169	.072	-.635*				
Mn	.683*	.213	.675*	.3	.305	.47	.366	.369	.696*	-.434			
Fe	.928**	.364	.791**	.443	.426	.611	.422	.508	.905**	-.531	.773**		
Co	.877**	.264	.533	.32	.401	.398	.38	.432	.888**	-.615	.576	.753*	
Ni	.074	-.028	-.373	-.047	-.089	-.202	-.142	-.023	.329	.005	-.287	.056	.372
Cu	.433	-.232	.221	-.234	-.242	-.116	-.28	-.206	.384	-.29	-.118	.382	.284
Zn	.462	-.633*	.268	-.546	-.587	-.378	-.582	-.511	.529	-.611	.39	.458	.316
Ga	.382	.974**	.495	.933**	.988**	.930**	.979**	.991**	.287	.128	.338	.457	.343
As	.241	.894**	.277	.815**	.940**	.754*	.969**	.891**	.152	.282	.278	.275	.325
Se	.402	.759*	.6	.784**	.702*	.725*	.698*	.723*	.406	.034	.447	.598	.169
Rb	.464	.928**	.502	.888**	.977**	.866**	.990**	.956**	.382	.079	.433	.501	.485
Sr	.361	.764*	.41	.666*	.769**	.794**	.815**	.846**	.316	.236	.524	.532	.313
Ag	.139	-.116	.006	-.176	-.072	-.099	.058	-.047	.214	.21	.527	.294	.143
Cd	.201	.924**	.253	.886**	.940**	.777**	.962**	.893**	.162	.286	.254	.239	.316
Cs	.515	.875**	.626	.869**	.927**	.881**	.931**	.885**	.355	-.007	.421	.551	.402
Ba	.411	.967**	.514	.929**	.991**	.933**	.983**	.992**	.311	.101	.364	.477	.376
Tl	.607	-0.32	.232	-0.231	-.213	-.226	-.206	-.198	.742*	-.637*	.457	.479	.752*
Pb	.576	.592	.341	.687*	.641*	.598	.619	.626	.63	-.252	.34	.498	.773**
U	.795**	.665*	.629	.715*	.707*	.744*	.678*	.772**	.845**	-.368	.577	.802**	.841**

** $p < 0.01$, * $p < 0.05$

(Continued) Table S4

	Ni	Cu	Zn	Ga	As	Se	Rb	Sr	Ag	Cd	Cs	Ba	Tl	Pb
Cu	.323													
Zn	.115	.593												
Ga	-.115	-.254	-.568											
As	-.143	-.341	-.647*	.912**										
Se	-.237	-.022	-.149	.748*	.581									
Rb	-.116	-.208	-.483	.957**	.960**	.704*								
Sr	-.078	-.187	-.303	.830**	.755*	.625	.797**							
Ag	-.163	.097	.376	-.054	.142	.136	.119	.355						
Cd	-.09	-.393	-.700*	.910**	.971**	.57	.944**	.700*	.018					
Cs	-.305	-.08	-.399	.913**	.881**	.781**	.943**	.690*	.073	.853**				
Ba	-.12	-.247	-.549	.999**	.917**	.740*	.966**	.830**	-.039	.913**	.922**			
Tl	.363	.397	.708*	-.284	-.204	-.161	-.071	-.206	.344	-.211	-.125	-.251		
Pb	.348	-.001	-.207	.578	.567	.269	.663*	.337	-.16	.671*	.572	.597	.379	
U	.328	.134	.019	.698*	.551	.547	.734*	.624	.01	.592	.639*	.713*	.391	.831**

** $p < 0.01$, * $p < 0.05$

Table S5. 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
INcdP	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).

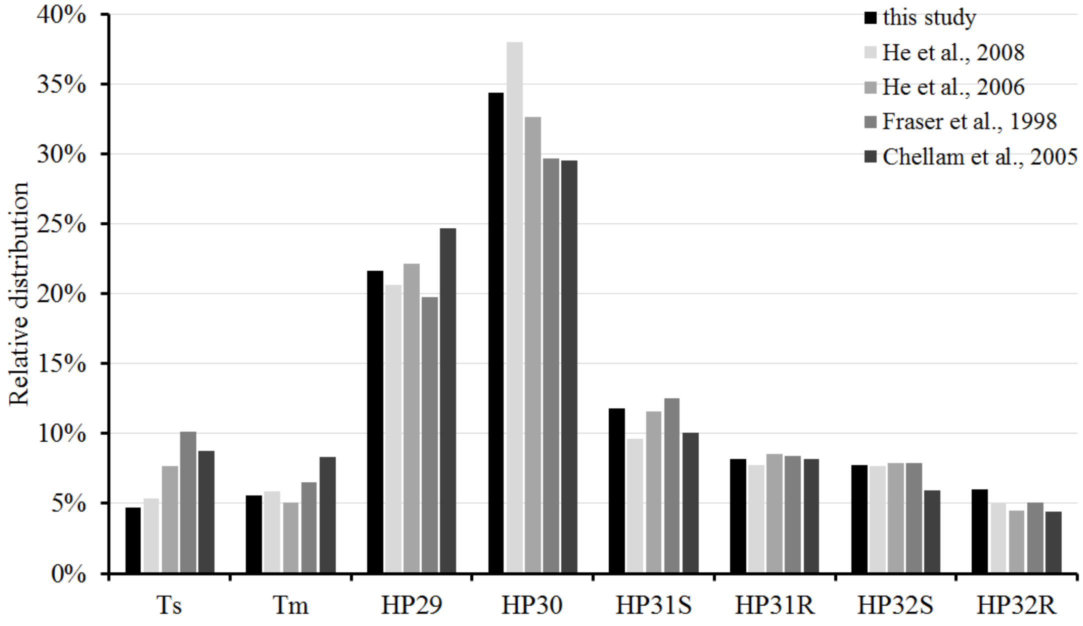

Fig. S1. Relative distributions of hopanes in different studies (this study; (He et al., 2008);(He et al., 2006);(Fraser et al., 1998);(Chellam et al., 2005)).

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