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Composition and variability of gaseous organic pollution in the port megacity of Istanbul: source attribution, emission ratios, and inventory evaluation

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SUPPLEMENT MATERIAL

Large gaseous organic pollution in the port megacity of Istanbul during the TRANSEMED/ChArMEx experiment: variability, source attribution and emission ratios

1. Uncertainties calculation

The concentration uncertainty σ_{ij} of a species j for the sample i measured by the GC-FID was calculated as follow:

$$\sigma_{ij} = \sqrt{\left(\frac{DL}{3} + u * x_{ij}\right)^2 + \left(\frac{w}{2} * x_{ij}\right)^2} \qquad (1)$$

WhereDL is the detection limit of the GCFID (in ppt). It equals 20 ppt for all the compounds except for n-heptane (4 ppt) (Baudic et al., 2016).

u is the repetability of the measurement (in %), obtained from the repeated injection of the NPL standard of 4 ppb. It ranges between 5 and 12 % depending on the compounds.

w is the expanded uncertainty of the NPL standard (2 % for all the compounds).

x_{ij} is the concentration of species j in sample i.

The uncertainties of VOCs measured by the PTRMS were computed as follow:

$$\sigma_{ij} = \sqrt{\left(\frac{DL}{3} + u * x_{ij}\right)^2 + \left(\frac{\sigma}{C_{STD}} * x_{ij}\right)^2} \qquad (2)$$

DL value ranges from 21 (C9-aromatics) to 1192 ppt (methanol).

The repeatability u ranges between 1.7 % (toluene) and 30.5 % (c9-aromatics).

C_{STD} is the diluted concentration (5 ppb) from the Gas Calibration Unit and the Ionimed standard (1 ppm).

σ is the uncertainty of the 5 ppb-diluted C_{STD} concentration calculated using Equation 3:

$$\sigma_{ij}{}^2 = \left(\frac{F_{STD}}{F_{STD} + F_{ZERO}}\right)^2 * u_{CSTD}{}^2 + \left(\frac{-F_{STD}}{(F_{STD} + F_{ZERO})^2}\right)^2 u_{FSTD}{}^2 + \left(\frac{-1}{(F_{STD} + F_{ZERO})^2}\right) u_{FZERO}{}^2 \quad (3)$$

- F_{STD} is the standard air flow (10 mL/min).
- F_{ZERO} is the air zero flow (2000 mL/min).
- U_{CSTD} is the error on the 1 ppm-Ionimed standard as indicated by the manufacturer (50 ppb).
- U_{FSTD} is the error on the generated standard air flow determined at the laboratory (±0.08 mL/min).
- $U_{F_{ZERO}}$ is the error on the generated dilution air flow determined at the laboratory (±197 mL/min).

The uncertainty of the PTRMS ranges between 5 % (toluene) and 59 % (acetaldehyde) of the concentrations while the uncertainty for the GC-FID ranges between 4 % (2-methyl-pentane) and 17 % (o-xylene) of the concentration.

For compounds which have a percentage of missing data exceeding 40 %, the uncertainty equals 4 times the median the measurement as suggested in Paatero et al. (2014). For compounds that have a percentage of missing data below 40 %, the uncertainty was equal to 4 times the interpolated value.

This method of uncertainty calculation enables to strongly weight those particular values and to limit their impact on the model result.

In order to better judge the general quality of the chemical compound data, Paatero & Hopke, (2003) have developed a method based on the signal to noise ratio (S/N) which is computed directly by the PMF model according to the equation 4:

$$\frac{S}{N} = \sqrt{\frac{\sum_{j=1}^{n}\left(x_{ij} - s_{ij}\right)^2}{\sum_{j=1}^{n} {s_{ij}}^2}} \qquad (4)$$

This ratio indicates whether the variability in the measurements is real or within the noise of the data. The species have been categorized as bad and strong according to the following criteria:

- S/N≥1: strong quality
- S/N ≤1: bad quality

All the compounds have a S/N ratio higher than 1 showing the high quality of the input dataset. S/N ratio ranges between 1.23 (1, 3-butadiene) and 9.46 (n-butane) for compounds measured by the GCFID and ranges from 2.00 (acetonitrile) to 9.96 (toluene) for PTRMS species.

2. Figures and tables

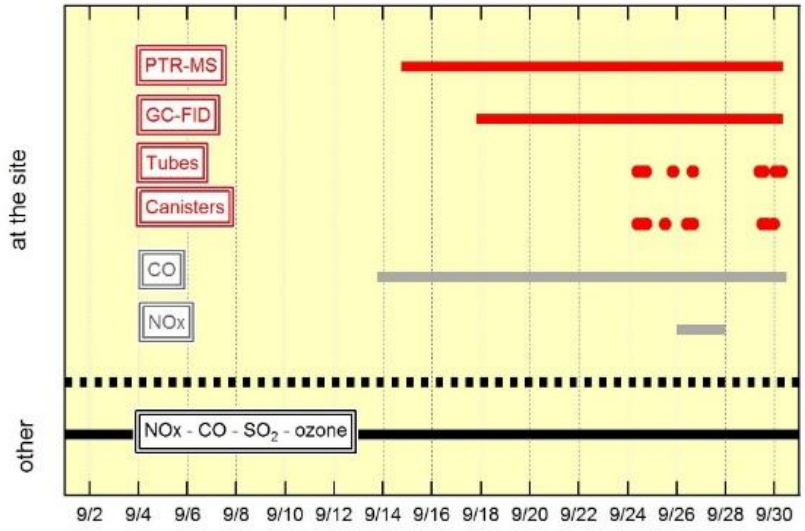

Figure S1: Atmospheric data used for this study and availability during September.

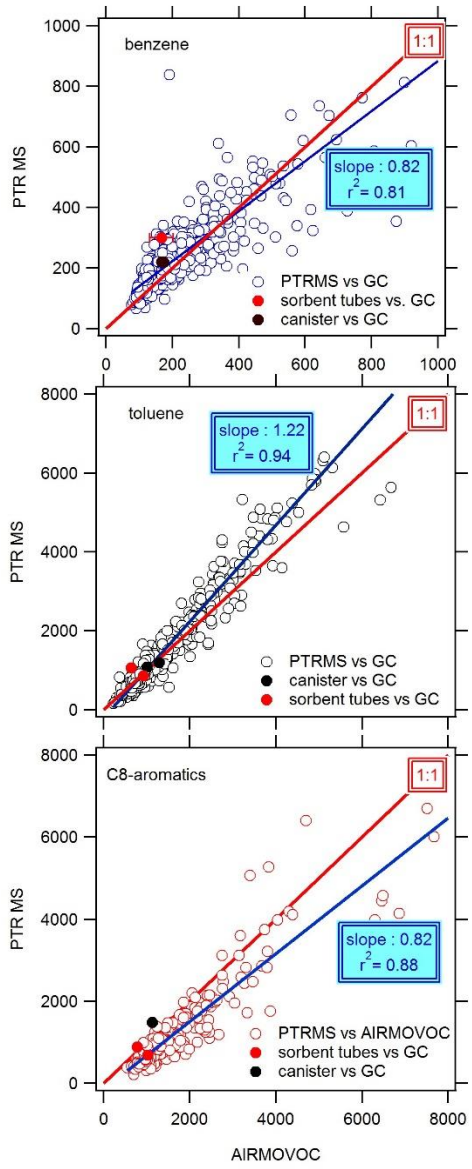

Figure S2: Comparison of PTRMS, tubes and canister concentrations with GC-FID (AIRMOVOC) for aromatic compounds

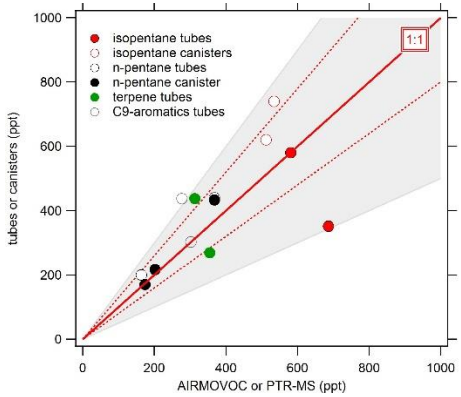

Figure S3: Comparison of tubes and canisters with GC-FID for pentanes, terpenes and trimethylbenzenes (C9-aromatics). The red full line is the one-to-one slope. The red dashed line is the ±20% and the grey area is the ±50%.

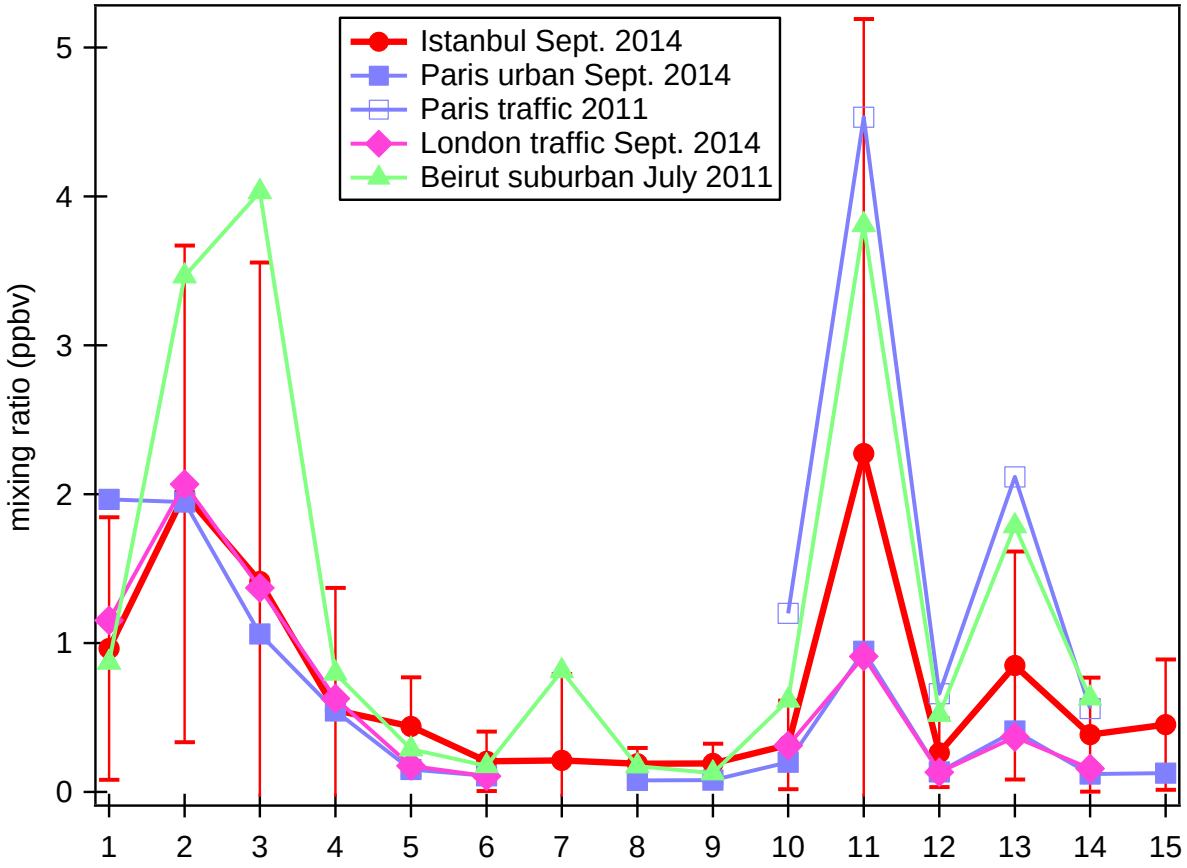

Figure S4: Comparison of mean concentrations of selected VOCs observed in different megacities: Istanbul (our supersite in Besiktas, Paris (urban and traffic) (Borbon et al., 2018), London (traffic) (Borbon et al., 2018), and Beirut (suburban in summer) (Salameh et al., 2015). Each number represents: 1: Isobutane, 2:nbutane, 3:isopentane, 4:npentane, 5:n hexane, 6:n heptane, 7:2-methyl-pentane, 8:1,3-butadiene, 9:1- pentene, 10:benzene, 11:toluene, 12:ethylbenzene, 13:m+p xylenes, 14:o xylene, 15: C9 aromatics.

Table S5: Off-line VOC concentrations (in ppbv) collected with canisters (C) and sorbent tubes (T). N stands for the number of samples

Families	Species	Mean (ppbv)	σ (ppbv)	N/Instrument
Alkanes	Ethane	5.58	9.44	14/ C
	Propane	4.15	4.82	14/ C
	isooctane	0.28	0.07	8/ T
	octane	0.63	0.23	8/T
	nonane	0.62	0.53	8/T
	decane	0.90	1.02	8/T
	undecane	0.73	0.88	8/T
	dodecane	1.33	2.46	8/T
	tridecane	3.05	7.49	8/T
	tetradecane	3.66	8.14	8/T
	pentadecane	2.34	3.41	8/T
	hexadecane	1.80	1.60	8/T
Aldehydes	nonanal	2.26	1.00	8/T
	heptanal	1.11	0.40	8/T
	decanal	2.17	0.68	8/T
	undecanal	1.86	2.95	8/T
Alkenes	Ethylene	2.89	1.95	14/ C
	Propene	1.02	1.05	14/ C
	Trans-2-butene	1.42	2.92	14/ C
	But-1-ene	0.46	0.77	14/ C
	isobutene	1.01	1.83	14/ C
	Cis-2-butene	0.82	1.66	14/ C
Alkyne	Acetylene	1.51	0.95	14/C
Terpenes	β-pinene	0.95	1.83	8/T
	123tmb+α-terpinene	0.61	0.78	8/T
	Limonene	0.28	0.18	8/T
	Camphene	2.13	0.64	8/T
	α-pinene+benzaldehyde	0.40	0.38	8/T

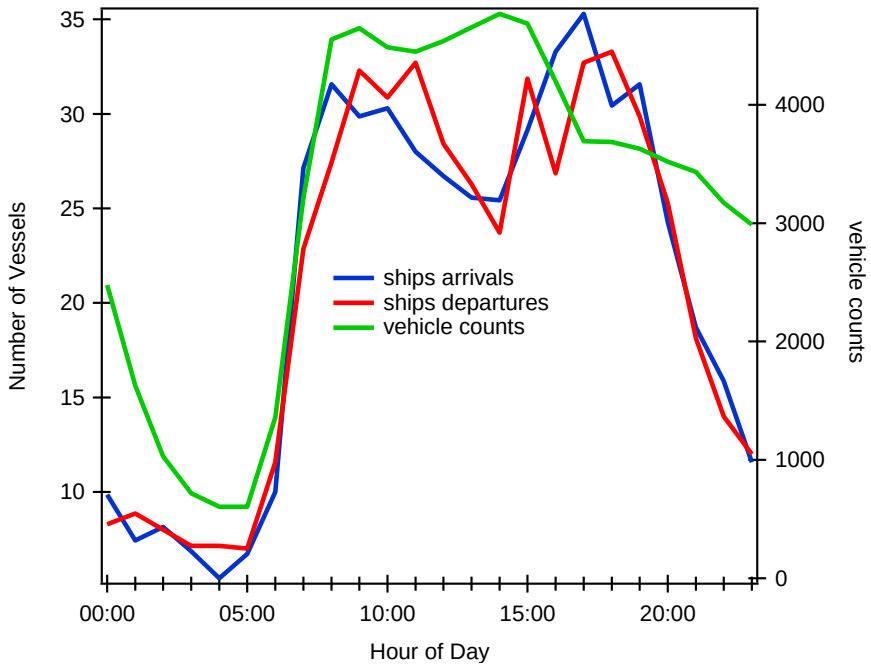

Figure S6: Local traffic counts for ships and road transport in Istanbul.

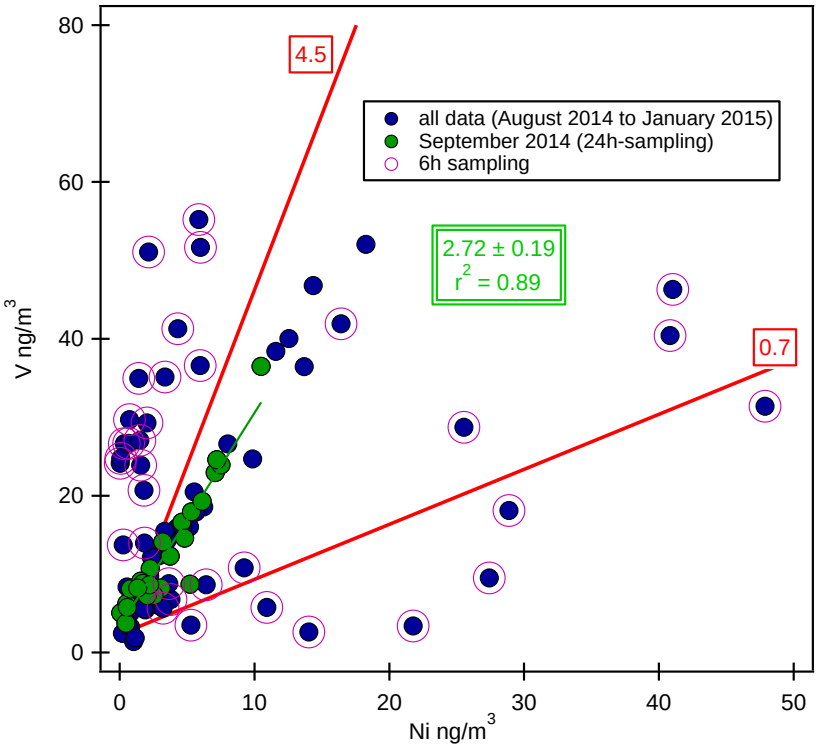

Figure S7: V versus Ni concentrations

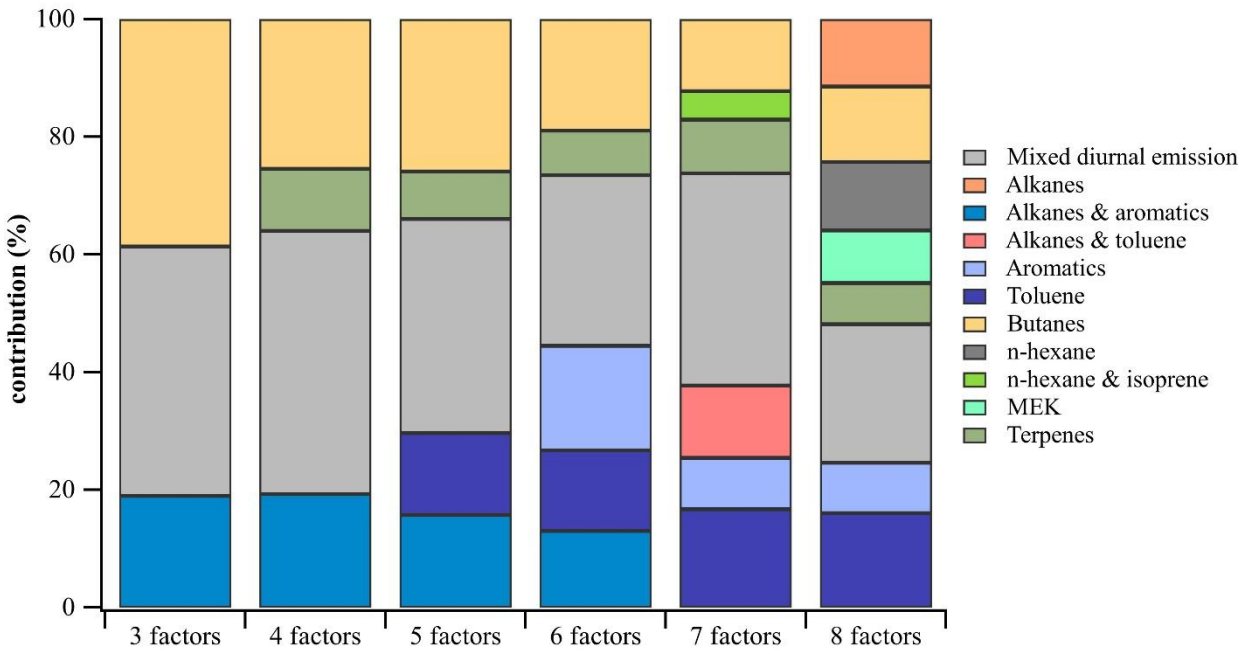

Figure S8: contribution concentration fraction from various factors in different PMF solutions. Alkanes here refer to all the alkanes in this study except for butanes.

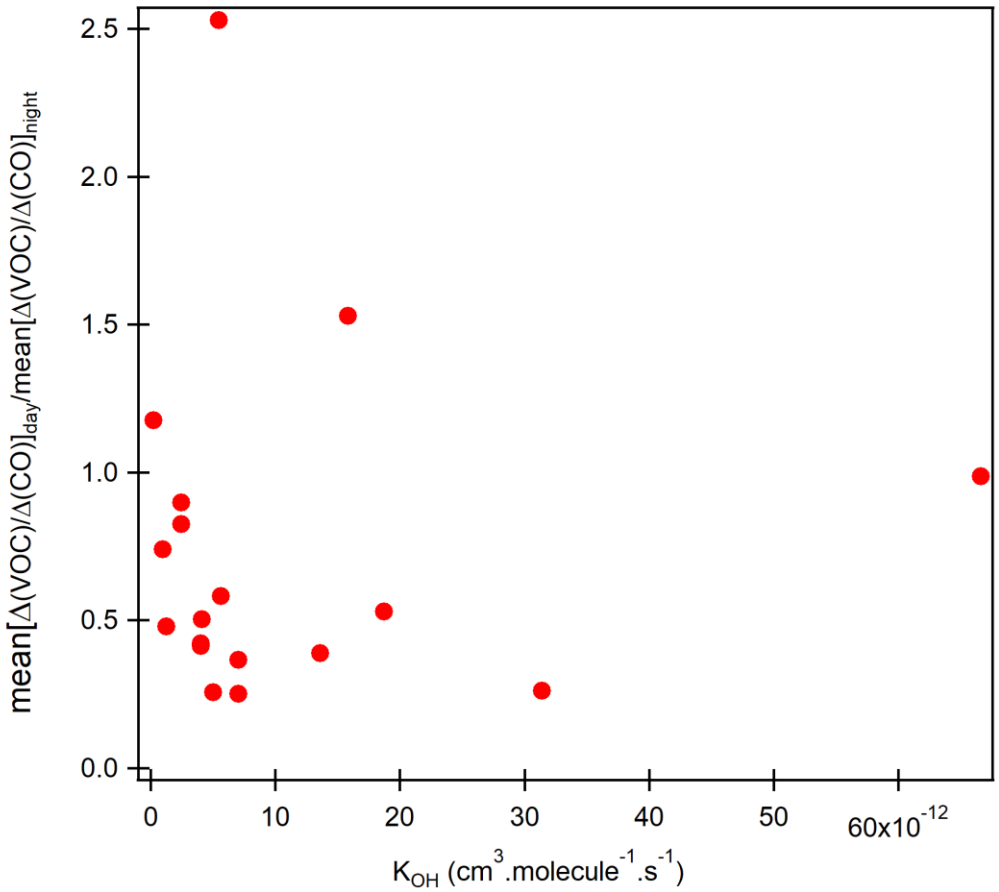

Figure S9: Scatterplot of the ratio of the mean VOC-to-CO ratio at day over the mean VOC-to-CO ratio at night vs the OH kinetic constants of each VOC in this study.

Table S10: Comparison of estimated VOC and PMF road transport emissions with EDGAR, MACCity and ACCMIP global emissions inventories.

	EDGAR						MACCity			ACCMIP					
	ALL SECTORS			ROAD TRANSPORT			ALL SECTORS			ALL SECTORS			ROAD TRANSPORT		
	inventory	estimation	ratio	inventory	Estimation from PMF	ratio	inventory	estimation	ratio	inventory	estimation	ratio	inventory	Estimation from PMF	
butanes										8118.8	17292,2	2,1			
pentanes	964.4	8157.65	8.5	509.3	6182.3	12.1				7233.2	20251.3	2.8	4494.2	14558.7	3.2
c>=4 alkanes							5376.1	12449.4	2.3						
c>=6 alkanes	4492.37	5059.45	1.1							15589.2	12560.1	1.2			
benzene	1450.1	1023.8	0.7	563.6	324.7	1.7				3746.0	2541.7	1.5	817.8	764.6	0.9
toluene	793.4	11402.84	14.4	67.8	2808.1	41.4				6141.5	28307.5	4.6	1439.0	6612.8	4.6
xylenes	3838.4	5595.77	1.5	296.2	2855.5	9.6				14613.2	13891.5	0.95	1227.7	6724.4	5.5
C9 aromatics	170.0	2457.80	14.5	123.1	890.8	7.2				1358.6	6101.5	4.5	1284.0	2097.7	1.6
aromatics							5897.7	13332.3	2.3						
methanol	10106.5	4620.34	0.5				52.1	2850.0	54.7						
acetone							37.6	2181.0	58.0						
other ketone							46.7	1035.9	22.2						
ketones	919.1	5215.2	5.7							408.8	12946.6	31.7			
CO	112493.0			29724.1						279263.5			69997.4		