Supporting Information

Environmental and biological monitoring of exposures to PAHs and ETS in the general population

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Number of Pages: 9

Number of Tables: 6

Number of Figures: 1

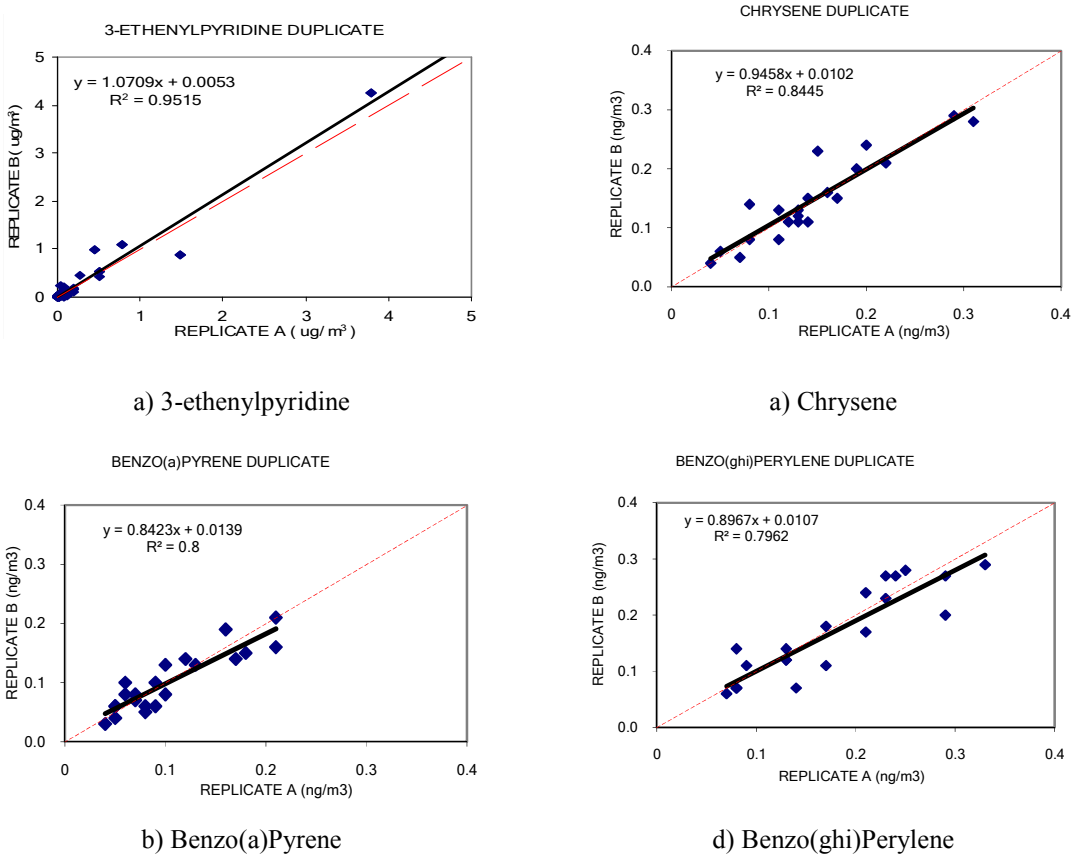
Quality Assurance – Quality Control on Sampling

For the quality assurance and quality control (QA-QC) on PAH sampling, 6% of the samples were taken as Field Blanks (FB) and Travel and Exposure Blanks (TEB). A FB was defined as a filter or sorbent tube blank that has been connected to the pump and undergone through the calibration process, has been subsequently disconnected from the pump and placed back in a metal tin (filter) or capped with Swagelok caps (sorbent tube), and carried to the sampling site, exposed to the sampling conditions without opening the metal tin (filters) or caps (sorbent tubes). A TEB was defined as a clean filter or sorbent tube sample enclosed in a metal tin (filter) or capped with Swagelok caps (sorbent tube), carried to the sampling site and returned to the lab without opening the metal tin (filters) or Swagelok caps (sorbent tubes) and treated as an environmental sample. In both occasions, FB and TEB, the filter enclosed in a metal tin or sorbent tube capped, was placed in the sampler during the travel time, left in the sampler during the sampling period and was returned to the lab without being opened at all. The difference between both blanks is that the FB sample was connected to the pump and underwent also the calibration with the rotameter. The average and standard deviation of the different types of blanks are shown in Table S1.

Table S1: Analytical limits - Sampling blanks

Compound	Travel and Exposure Blank		Field Blank	
	Average	STD	Average	STD
GAS PHASE VOCS (ng)				
3-Ethenylpyridine	0.56	1.0	0.73	0.82
Naphthalene	5.69	3.6	6.05	3.49
1,3-Butadiene	0.65	0.90	1.22	2.46
PARTICULATE PHASE PAHS (pg/µL)				
Acenaphthylene	27.9	23.9	6.6	2.1
Acenaphthene	36.1	18.8	24.9	16.8
Fluorene	104.3	98.1	29.9	15.4
Phenanthrene	139.2	49.1	30.6	5.4
Anthracene	10.6	7.3	4.7	1.9
Fluoranthene	11.4	1.1	4.1	0.9
Pyrene	36.4	5.9	4.8	3.3
Benz(a)anthracene	1.6	0.4	1.4	1.3
Chrysene	5.8	0.2	1.9	0.3
Benzo(b)fluoranthene	2.1	1.5	0.8	0.7
Benzo(k)fluoranthene	1.6	0.9	0.9	0.3
Benzo(a)pyrene	3.5	1.8	4.0	2.2
Indeno(1,2,3-cd)pyrene	4.9	2.4	3.8	2.2
Dibenz(ah)anthracene	1.1	0.2	0.9	0.4
Benzo(ghi)perylene	7.2	1.3	2.6	0.8
Coronene	2.4	1.4	0.5	0.3

To assess the precision of the measurements, duplicates equivalent to 3% of the samples were taken; these refer to two samples taken in the same environment for the same time period. The duplicate samples were also analysed altogether in the same batch to assess the total variance of the sampling and analytical procedure. Figure S1 shows the correlation of some representative compounds for PAH and VOC and illustrates that duplicate samples show an excellent agreement within 15% between concurrently collected samples.



a) 3-ethenylpyridine

a) Chrysene

b) Benzo(a)Pyrene

d) Benzo(ghi)Perylene

Figure S1: Field duplicate samples for (a) 3-ethenylpyridine, (b) chrysene, (c) benzo(a)pyrene and (d) benzo(ghi)perylene

The flow rates of all the pumps were calibrated with rotameters, covering the appropriate range of flow rate values, before and after the sampling period. The average value of both measurements was used in calculations. The sample was considered invalid when there was a deviation of greater than 30% between the start and the end flowrate. The average deviation between the start and the end of the sampling period was 6±17% for the VOC sampling and 8±10% for the1,3-butadiene sampling train. All the rotameters were calibrated regularly using a Gilian II Gilibrator which in turn was annually serviced

and calibrated. The pumps were also calibrated annually by the supplier. In general, the agreement between flow rates recorded with rotameters and the Gilibrator was very satisfactory with an average correlation coefficient of 0.92 ± 0.10. The calibration of the rotameters showed a percentage deviation less than 15% from the Gilibrator.

Analysis of ETS Urinary Biomarkers- Cotinine and trans-3'-hydroxycotinine

Deuterium-labeled internal standards, cotinine-d9 and *trans*-3'-hydroxycotinine-d9 are used as internal standards. Chromatography is carried out using a 4.6 X 150 mm Phenomenex Synergi Polar RP (embedded phenoxypropyl group) column using a water-to-methanol gradient with 10 mM ammonium acetate/0.1% acetic acid buffer. The retention times are 7.1 minute for trans-3'-hydroxycotinine and 8.5 minute for cotinine and they are baseline separated. Analytes and internal standards are all distinguished by unique mass transitions. The mass spectrometer is operated in the positive ion mode using atmospheric pressure chemical ionization. Quantitation is achieved using selected reaction monitoring (SRM) of the transitions m/z 177 to m/z 80 for cotinine, m/z 193 to m/z 80 for *trans*-3'-hydroxycotinine and the transitions m/z 186 to m/z 84 and m/z 202 to m/z 84 for the respective internal standards. Calibration curves were constructed from peak area ratios of the analyte to its internal standard using linear regression. Standard curves were linear over the concentration ranges 0.05 to 10 ng/mL for cotinine, and 0.1 to 10 ng/mL for *trans*-3'-hydroxycotinine. For cotinine, between-run precision (percent coefficient of variation, n = 6) ranged from 0.7% to 7.4%, and accuracy (percent of expected values, n = 6) ranged from 101% to 103% for concentrations ranging from 0.05 to 5 ng/mL. For trans-3'-hydroxycotinine, between-run precision (percent coefficient of variation, n = 6) ranged from 0.5 to 3.5%, and accuracy (percent of expected values, n = 6) ranged from 96% to 103% for concentrations ranging from 0.10 to 10 ng/mL. The limits of quantitation are 0.05 ng/mL (0.29 nmol/L) for cotinine, and 0.10 ng/mL (0.58 nmol/L) for *trans*-3'-hydroxycotinine.

Table S2: Number of samples of urine, VOC and PAH in all the selected subjects and for ETS and No ETS subjects. The number of concurrent

No of Samples	All subjects (ETS + No ETS)	No ETS subjects [(b)]	ETS subjects		
			All ETS (Low + High ETS)	Low ETS [(c)]	High ETS [(d)]
Urine & VOC & PAH concurrent	62	41	19	12	9
Urine & VOC without PAH concurrent	24	14	10	5	5
Total urine samples [(a)]	86	55	31	19	12

(a) Total urine samples considered for data analysis is 86 from the original analysed 100. This number results from excluding the results of 8 smokers, and considering the mean value for 6 subjects whose urine from two different days was analysed.

(b) No ETS subjects were those who declared his/her No ETS status in the screening questionnaire, no ETS events were registered in the time-activity diaries and whose levels of 3-ethenylpyridine (3-EP) in air samples were <0.25 $\mu g/m^3$ (maximum 3-EP concentration measured in the No-ETS subpopulation).

(c) ETS subjects were those who reported ETS events in the time-activity diary in the day were urine was collected. Those subjects whose 3-ETS was 0.25<3-EP<1.4 $\mu g/m^3$ were classified as low ETS. The value of 1.4 $\mu g/m^3$ was selected as the frequency distribution of 3-ethenylpyridine in the ETS population appears to be bimodal, with the value of 1.4 $\mu g/m^3$ as the cutpoint between both modes (See main document for further details).

(d) ETS subjects were those who reported ETS events in the time-activity diary in the day were urine was collected. Those subjects whose 3-ETS was >1.4 $\mu g/m^3$ were classified as high ETS.

Table S3: Instrument Limits of Detection

Compound	Instrument Limit of Detection
	Average
VOC COMPOUNDS	**(ng)**
n-Hexane	0.030
Benzene	0.044
Toluene	0.053
Ethylbenzene	0.037
p-Xylene	0.074
m-Xylene	0.071
Pyridine	0.273
o-Xylene	0.056
1,3,5-Trimethylbenzene	0.056
Styrene	0.042
p-Isopropyltoluene	0.024
1,2,4-Trimethylbenzene	0.035
3-Ethenylpyridine	0.620
Naphthalene	0.024
1,3-Butadiene	0.030
PAH COMPOUNDS	**(pg/µL)**
Acenaphthylene	1.0
Acenaphthene	5.0
Fluorene	5.0
Phenanthrene	6.7
Anthracene	1.4
Fluoranthene	0.6
Pyrene	0.5
Benzo(a)anthracene	0.2
Chrysene	0.3
Benzo(b)fluoranthene	1.0
Benzo(k)fluoranthene	0.3
Benzo(a)pyrene	0.3
Indeno(1,2,3-cd)pyrene	0.6
Dibenz(a,h)anthracene	0.3
Benzo(ghi)perylene	0.7
Coronene	0.1
URINARY BIOMARKERS	**(pg/µL)**
Cotinine	0.05
Trans-3'-Hydroxycotinine	0.10
2-Naphthol	0.50
1-Hydroxyfluorene	0.10
2-Hydroxyfluorene	0.025
3-Hydroxyfluorene	0.10
1-Hydroxyphenanthrene	0.025
2-Hydroxyphenanthrene	0.010
3- + 4-Hydroxyphenanthrene	0.20
1-Hydroxypyrene	0.025

Table S4: Subject characteristics description

Characteristic	Percentage of cases MATCH Project	Percentage of cases analyzed urine (%)
Gender		
Female	57	55
Male	43	45
Age		
18-25	18	18
26-35	31	28
36-45	15	16
46-55	13	14
56-65	17	18
66+	6	6
Occupation category		
Administration/office worker	48	49
Cleaning	1	1
Education	6	6
Food/Hospitality	7	7
Health	7	7
Housewife	4	4
Manufacturing	1	1
Police	1	1
Research and development	7	6
Retired	7	7
Student	10	10
Unemployed	1	1
Time spent per microenvironment		
Indoors at home	62	64
Indoors at work	16	15
Other indoors	12	12
Outdoors	4	4
In transit	6	6
Time spent traveling to workplace		
Not applicable	17	17
Less than 5 minutes	47	48
Less than 30 minutes	32	31
More than 30 minutes	4	4
ETS exposure		
ETS exposed at least 1 day	43	43
ETS exposed at home	12	16
Not ETS exposed at home	88	84
ETS exposed at work	8	9
Not ETS exposed at work	92	91
Activities relevant to VOC and PAH concentrations		
Cleaning	61	62
Aerosol/Perfume use	55	55
Solvent use	8	7
Candle burning	13	13
Photocopier/Printer	41	41
Lighted fire in fireplace	11	11
Other fossil fuel use	4	4
Refueling car	23	23
DIY-Hobbies	12	12
Cooking characteristics		
Natural gas	47	48
Electricity	53	52
Use of cooker hood	36	35
No use of cooker hood	64	65
Geographical location		
London	11	12
West Midlands	79	78
Wales	10	10
Home location		
Urban	38	36
Suburban	42	43
Rural	20	21
Other		
Living in houses with attached garages	16	20
Living in trafficked roadsides	44	43

Table S5: Concentrations of Urinary Biomarkers (ng mL^{-1} and µmol mol^{-1} creatinine), Selected VOC (µg.m^{-3}), Parent PAH (ng m^{-3}) and Non-Parent PAH (ng m^{-3}) Personal Exposure Concentrations by Key Determinant

	% Cases < LOD	All subjects							Non ETS subjects							ETS subjects						
		Min/Max			Arithmetic		Geometric		Min/Max			Arithmetic		Geometric		Min/Max			Arithmetic		Geometric	
		No Cases	Min	Max	Mean	SD	GM	GSD	No Cases	Min	Max	Mean	SD	GM	GSD	No Cases	Min	Max	Mean[a]	SD	GM[a]	GSD
Urinary Biomarker concentrations																						
Cot	0	86	0.10	35.0	3.30	6.39	0.88	5.28	55	0.10	6.7	0.59	0.97	0.33	2.70	37	0.10	35.0	**7.33**	8.60	**3.72**	4.01
Cot/Creat	0	86	0.03	35.43	2.51	5.57	0.56	0.65	6.22	0.03	2.93	0.36	0.50	0.21	0.32	4.19	0.05	35.43	**5.70**	7.77	**2.41**	0.54
T3HCot	0	86	0.20	63.3	9.09	14.32	3.13	4.60	55	0.20	31.9	2.84	4.86	1.41	3.12	37	0.50	63.3	**18.37**	18.29	**10.20**	3.47
T3HCot/Creat	0	86	0.10	61.03	5.25	8.80	1.84	0.50	6.22	0.10	10.66	1.51	2.19	0.83	0.31	4.19	0.24	61.03	**10.80**	11.64	**6.03**	0.40
2-Nap	0	86	0.30	33.2	4.58	5.57	2.92	2.52	55	0.50	33.2	5.17	6.60	3.13	2.64	37	0.30	15.4	3.71	3.45	2.64	2.34
2-Nap/Creat	0	86	0.51	26.04	3.10	3.31	2.28	0.24	6.22	0.63	26.04	3.48	4.00	2.43	0.25	4.19	0.51	9.20	2.52	1.77	2.08	0.21
1-HFl	87	11	0.10	0.7	0.23	0.21	0.17	2.08	6	0.10	0.7	0.28	0.29	0.19	2.63	5	0.10	0.2	0.16	0.05	0.15	1.46
1-HFl/Creat	87	11	0.03	0.36	0.12	0.11	0.08	0.25	0.68	0.03	0.36	0.14	0.14	0.09	0.32	0.57	0.06	0.17	0.08	0.05	0.07	0.18
2-HFl	0	86	0.00	3.3	0.36	0.40	0.28	2.07	55	n.d.	3.3	0.41	0.49	0.30	2.17	37	n.d.	0.9	0.29	0.21	0.25	1.90
2-HFl/Creat	0	86	0.05	2.02	0.21	0.27	0.16	0.22	6.22	0.05	2.02	0.23	0.32	0.16	0.23	4.19	0.06	0.90	0.19	0.18	0.15	0.21
3-HFl	56	38	n.d.	1.0	0.21	0.19	0.18	1.77	24	0.10	1.0	0.22	0.23	0.16	1.92	14	n.d.	0.5	0.21	0.11	0.21	1.42
3-HFl/Creat	56	38	0.02	0.60	0.11	0.12	0.08	0.24	2.71	0.02	0.60	0.11	0.13	0.08	0.24	1.58	0.02	0.38	0.12	0.10	0.09	0.24
1-HPhe	1	85	n.d	1.4	0.30	0.31	0.22	2.21	54	n.d.	1.3	0.29	0.27	0.22	2.08	37	n.d.	1.4	0.32	0.37	0.22	2.43
1-HPhe/Creat	1	85	0.03	0.90	0.15	0.15	0.12	0.23	6.11	0.03	0.71	0.15	0.14	0.12	0.22	4.19	0.05	0.90	0.16	0.16	0.12	0.24
2-HPhe	1	85	n.d.	0.5	0.12	0.12	0.14	1.66	55	n.d.	0.5	0.12	0.11	0.14	1.63	37	n.d.	0.5	0.12	0.13	0.14	1.72
2-HPhe/Creat	0	86	0.01	0.52	0.06	0.06	0.05	0.21	6.22	0.01	0.52	0.06	0.07	0.05	0.22	4.19	0.02	0.25	0.06	0.05	0.05	0.20
3+4-HPhe	1	85	n.d	2.7	0.30	0.38	0.22	2.16	54	n.d.	0.7	0.26	0.19	0.22	1.98	37	0.10	2.7	0.36	0.54	0.21	2.43
3+4HPhe/Creat	1	85	0.03	1.28	0.16	0.18	0.12	0.23	6.11	0.03	0.70	0.14	0.13	0.11	0.22	4.19	0.05	1.28	0.18	0.24	0.12	0.24
1-HPyr	1	85	n.d.	1.2	0.13	0.15	0.14	1.66	54	n.d.	0.4	0.13	0.11	0.14	1.62	37	n.d.	1.2	0.14	0.19	0.13	1.72
1-HPyr/Creat	1	85	0.01	0.34	0.06	0.05	0.05	0.19	6.11	0.01	0.34	0.06	0.05	0.05	0.20	4.19	0.02	0.29	0.06	0.05	0.05	0.19
Selected VOC Personal Exposure Concentrations																						
3-EP	2	84	0.01	6.92	0.60	1.04	0.16	5.50	53	0.01	0.26	0.07	0.06	0.05	2.15	37	0.01	6.92	**1.37**	1.29	**0.78**	3.95
Naph	2	84	0.06	165.01	2.77	17.39	0.64	2.63	53	0.06	14.21	0.95	1.96	0.57	2.29	37	0.22	165.01	5.39	27.02	0.76	3.08
But	1	85	n.d.	5.73	0.58	1.01	0.22	4.28	54	n.d.	5.73	0.50	1.03	0.16	4.41	37	n.d.	5.48	**0.69**	0.99	**0.35**	3.63
Parent PAH Personal Exposure Concentrations																						
Fl	91	6	0.02	1.32	0.56	0.53	0.23	6.21	3	0.03	1.32	0.54	0.68	0.22	6.70	3	0.02	0.90	0.58	0.49	0.25	8.77
Phe	31	47	0.02	2.32	0.39	0.52	0.20	3.18	35	0.02	2.03	0.38	0.49	0.21	3.06	12	0.02	2.32	0.40	0.63	0.18	3.72
Pyr	21	54	n.d.	2.34	0.38	0.49	0.22	2.87	38	0.04	1.89	0.40	0.45	0.25	2.57	16	n.d.	2.34	0.35	0.58	0.17	3.67
Non Parent PAH Personal Exposure Concentrations																						
Ac	46	37	n.d.	3.21	0.45	0.65	0.20	4.19	25	n.d.	3.21	0.42	0.66	0.18	4.27	12	0.02	2.25	0.51	0.66	0.23	4.22
Ace	47	36	n.d.	3.69	0.42	0.62	0.24	3.43	28	n.d.	3.69	0.43	0.68	0.25	3.17	8	0.01	1.07	0.41	0.39	0.20	4.72
Ant	34	45	n.d.	0.6	0.09	0.13	0.04	3.28	34	n.d.	0.53	0.09	0.12	0.05	3.28	11	0.01	0.60	0.09	0.17	0.04	3.36
Fluo	22	53	0.02	3.7	0.61	0.76	0.37	2.80	39	0.02	3.64	0.60	0.70	0.37	2.74	14	0.03	3.70	0.64	0.94	0.35	3.10
BaA	6	64	n.d.	0.97	0.13	0.21	0.06	3.27	46	n.d.	0.97	0.10	0.18	0.05	3.03	18	0.02	0.78	**0.19**	0.25	**0.09**	3.69
Chry	1	67	n.d.	2.94	0.37	0.52	0.22	2.72	48	0.02	1.47	0.26	0.29	0.18	2.34	19	n.d.	2.94	**0.66**	0.80	**0.38**	3.23
BbF	3	66	0.01	2.24	0.28	0.38	0.16	2.94	47	0.02	1.49	0.23	0.31	0.14	2.69	19	0.01	2.24	**0.41**	0.51	**0.22**	3.41
BkF	0	68	n.d.	1.59	0.24	0.31	0.15	2.50	49	n.d.	1.37	0.21	0.29	0.13	2.41	19	n.d.	1.59	**0.31**	0.36	**0.21**	2.56
BaP	4	65	n.d.	1.19	0.18	0.27	0.09	3.03	46	n.d.	1.19	0.16	0.28	0.08	2.89	19	0.02	0.80	0.23	0.23	0.13	3.25
Ind	0	68	0.01	1.48	0.17	0.23	0.10	2.84	49	0.01	1.48	0.17	0.26	0.09	2.84	19	0.01	0.50	0.16	0.13	0.11	2.88
BghiP	21	54	n.d.	0.2	0.03	0.05	0.03	2.54	38	n.d.	0.19	0.03	0.04	0.02	2.43	16	n.d.	0.20	0.05	0.05	0.04	2.60
DahA	0	68	0.01	2.01	0.25	0.35	0.14	2.90	49	0.02	2.01	0.25	0.39	0.13	2.84	19	0.01	0.82	**0.26**	0.22	**0.17**	3.08
Cor	12	60	n.d.	0.94	0.15	0.20	0.09	2.57	42	0.02	0.94	0.16	0.24	0.09	2.80	18	n.d.	0.39	0.14	0.10	0.12	1.93
Σ Low MW [Naph - An]	0	68	n.d.	5.71	0.92	1.34	0.69	3.07	49	n.d.	5.71	0.84	1.24	0.60	3.06	19	n.d.	4.84	**1.12**	1.59	**1.12**	2.80
Σ Medium MW [Fluo - Chry]	0	68	n.d.	8.75	1.27	1.58	0.65	3.76	49	n.d.	5.8	1.14	1.34	0.61	3.62	19	0.03	8.75	1.62	2.07	0.75	4.25
Σ High MW [B(b)F - Cor]	0	68	0.03	8.27	1.26	1.66	0.71	2.94	49	0.03	8.27	1.15	1.74	0.62	2.90	19	0.10	5.74	1.55	1.44	0.98	2.91
Σ 16 [Naph - B(ghi)P]	0	69	n.d.	15.02	3.27	3.40	2.00	2.92	50	n.d.	13.7	2.93	3.20	1.82	2.79	19	0.13	15.02	4.15	3.80	2.54	3.24

(a) Bold figures indicate that concentrations in ETS subset are significantly different than the non ETS subset at the 0.05 level.

Table S6: Correlation of Urinary Biomarkers with ETS Selected VOC Compounds, Parent PAH and Non-Parent PAH Personal Exposures (Pearson R, logged database) (Sample Size VOC≤86, PAH ≤68)

	Cotinine / Creatinine	Trans-3'-Hydroxycotinine / Creatinine	2-Hydroxyfluorene / Creatinine	1-Hydroxypyrene/ Creatinine
VOC Selected Compounds				
3-Ethenyl Pyridine	**0.74**$^{(**)}$	**0.68**$^{(**)}$	0.12	0.1
Naphthalene (gas phase)	0.05	-0.03	0.12	0.01
1,3-Butadiene	**0.43**$^{(**)}$	**0.42**$^{(**)}$	0.1	**0.23**$^{(*)}$
PAH Parent Compounds				
Fluorene	-0.26	0.07	-0.33	0.3
Phenanthrene	0.13	0.09	0.22	0.24
Pyrene	0.02	0.03	0.24	0.26
PAH Non Parent Compounds				
Benzo(a)anthracene	**0.28**$^{(*)}$	**0.25**$^{(*)}$	0.13	0
Chrysene	**0.44**$^{(**)}$	**0.43**$^{(**)}$	0.21	0.12
Benzo(b)fluoranthene	**0.36**$^{(**)}$	**0.34**$^{(**)}$	0.18	0.2
Benzo(k)fluoranthene	**0.38**$^{(**)}$	**0.38**$^{(**)}$	0.21	0.19
Benzo(a)pyrene	**0.3**$^{(*)}$	**0.29**$^{(*)}$	0.23	0.18
Indeno(1,2,3-cd)pyrene	0.04	0.07	0.18	0.14
Dibenz(a,h)anthracene	**0.29**$^{(*)}$	**0.25**$^{(*)}$	0	-0.12
Benzo(ghi)perylene	**0.23**$^{(*)}$	**0.26**$^{(*)}$	0.12	0.12
Coronene	0.19	0.19	0.06	0.07
Sum of low MW PAH [Naph - An]	0.16	0.14	0.18	0.12
Sum of medium MW PAH [Fluo - Chry]	0.18	0.23	**0.25**$^{(*)}$	0.17
Sum of high MW PAH [B(b)F - Cor]	**0.28**$^{(*)}$	**0.31**$^{(*)}$	0.15	0.09
Sum of 16PAH [Naph - B(ghi)P]	0.17	0.22	**0.24**$^{(*)}$	0.2

(a) Bold figures represent that both variable significantly correlate at the 0.05 level.