

Supplement of

A field intercomparison of three passive air samplers for gaseous mercury in ambient air

Attilio Naccarato^{1*}, Antonella Tassone¹, Maria Martino¹, Sacha Moretti¹, Antonella Macagnano², Emiliano Zampetti², Paolo Papa², Joshua Avossa², Nicola Pirrone¹, Michelle Nerentorp³, John Munthe³, Ingvar Wängberg³, Geoff W. Stupple⁴, Carl P. J. Mitchell⁵, Adam R. Martin⁵, Alexandra Steffen⁴, Diana Babi⁶, Eric M. Prestbo⁶, Francesca Sprovieri¹, Frank Wania^{5*}

¹CNR-Institute of Atmospheric Pollution Research, Division of Rende, UNICAL-Polifunzionale, I-87036 Arcavacata di Rende, CS, Italy;

²CNR-Institute of Atmospheric Pollution Research, Research Area of Rome 1, Via Salaria km 29,300, 00016 Monterotondo, Italy;

³IVL Swedish Environmental Research Institute, Gothenburg, 41133, Sweden;

⁴Air Quality Processes Research Section, Environment and Climate Change Canada, Toronto, M3H 5T4, Canada;

⁵Department of Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, M1C 1A4, Canada;

⁶Tekran Instruments Corporation, 330 Nantucket Boulevard, Toronto, Ontario, M1P 2P4, Canada;

*Correspondence to: Attilio Naccarato (attilio.naccarato@iia.cnr.it), Frank Wania (frank.wania@utoronto.ca)

Table S1 Detailed sampler deployment plan. Dates refer to 2019.

Site	Deployment	1w	2w	3w	4w	5w	6w	7w	8w	9w	10w	11w	12w	Sampling start and stop
Rende	1 st 2-week													5 Feb to 19 Feb
	2 nd 2-week													19 Feb to 5 Mar
	3 rd 2-week													5 Mar to 19 Mar
	4 th 2-week													2 Apr to 16 Apr
	1 st 4-week													5 Feb to 5 Mar
	2 nd 4-week													5 Mar to 2 Apr
	3 rd 4-week													2 Apr to 30 Apr
	1 st 6-week													5 Feb to 19 Mar
	2 nd 6-week													19 Mar to 30 Apr
	1 st 8-week													5 Feb to 2 Apr
	1 st 12-week													5 Feb to 30 Apr
Toronto	1 st 2-week													5 Feb to 19 Feb
	2 nd 2-week													19 Feb to 5 Mar
	3 rd 2-week													5 Mar to 20 Mar
	4 th 2-week													2 Apr to 16 Apr
	1 st 4-week													5 Feb to 5 Mar
	2 nd 4-week													5 Mar to 2 Apr
	3 rd 4-week													2 Apr to 30 Apr
	1 st 6-week													5 Feb to 20 Mar
	2 nd 6-week													20 Mar to 30 Apr
	1 st 8-week													5 Feb to 2 Apr
	1 st 12-week													5 Feb to 30 Apr

Figure S2 Photographs of the deployment set up in Toronto (left) and Rende (right).



Figure S2. Concentration of gaseous mercury (5 minutes resolution) at Rende and Toronto using active instrumentation. Gaps in sampling data are due to automatic calibrations, maintenance operations and power failure.

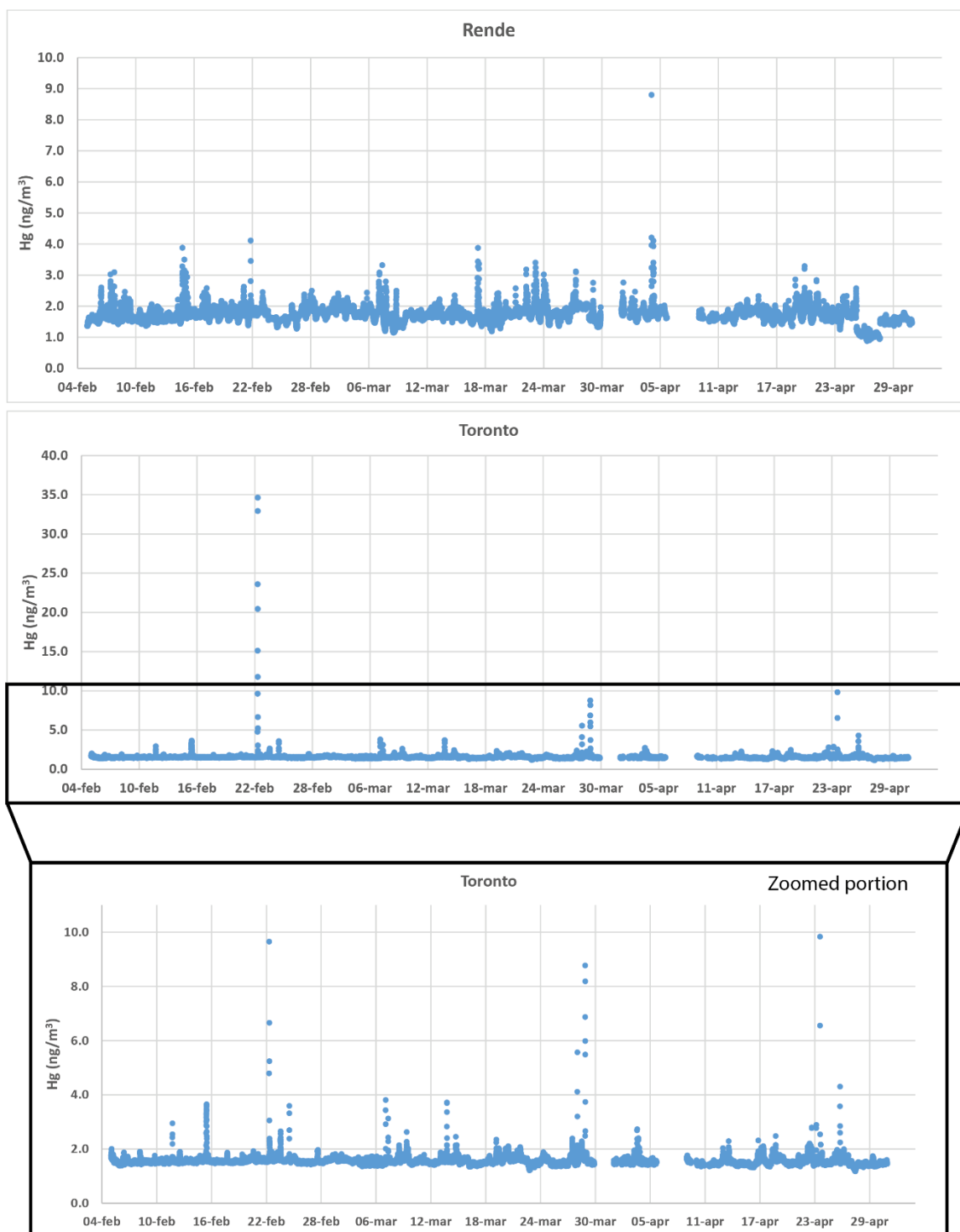


Table S2. Mean, standard deviation (SD) and percentage relative standard deviation (%RSD) of mercury levels (nanograms) in field blanks for *MerPAS*[®], IVL-PAS, and CNR-PAS. The values are reported for each deployment period at both exposure sites. In Toronto the field blanks of the IVL-PAS were not deployed alongside the exposed samplers. *n* designates the number of field blanks of a certain deployment length. The average values for each location (in bold font) are used for the blank correction of the amount of mercury measured in exposed passive air samplers.

	Length	<i>n</i>	<i>MerPAS</i> [®]		IVL-PAS		CNR-PAS	
			Mean ± SD	RSD	Mean ± SD	RSD	Mean ± SD	RSD
Rende	2 weeks	4	0.228 ± 0.012	5%	0.495 ± 0.079 ^b	16%	0.144 ± 0.014	10%
	4 weeks	3	0.244 ± 0.014	6%	0.482 ± 0.110 ^c	23%	0.155 ± 0.029	19%
	6 weeks	2	0.263 ^a	-	0.576 ± 0.072	12%	0.151 ± 0.014	9%
	8 weeks	1	0.213	-	0.440	-	0.175	-
	12 weeks	1	0.315	-	0.390	-	0.174	-
	all	11	0.229 ± 0.055	24%	0.490 ± 0.090	18%	0.154 ± 0.019	12%
Toronto	2 weeks	4	0.200 ± 0.041	21%	-	-	0.136 ± 0.052	38%
	4 weeks	3	0.258 ± 0.040	16%	-	-	0.275 ± 0.053	19%
	6 weeks	2	0.240 ± 0.068	28%	-	-	0.231 ± 0.023	10%
	8 weeks	1	0.243	-	-	-	0.211	-
	12 weeks	1	0.322	-	-	-	0.195	-
	all	11	0.238 ± 0.052	22%	0.430 ± 0.077^d	18%	0.203 ± 0.070	34%

^a *n*=1 only, ^b *n*=3 only, ^c *n*=2 only, ^d *n*=12

Table S3. Method detection limit (MDL), practical quantification limit (PQL) and limits of detection (LOD) and quantification (LOQ) for mercury for the three passive air samplers used in this study. Because the field blank levels were different in the two deployment locations, these method performance metrics are given for Rende and Toronto separately.

	Length of Deployment (days)	<i>MerPAS</i> [®]		IVL-PAS		CNR-PAS	
		Rende	Toronto	Rende	Toronto	Rende	Toronto
MDL (ng)		0.17	0.16	0.27	0.23	0.06	0.21
PQL (ng)		0.55	0.52	0.90	0.77	0.19	0.70
LOD (ng m ⁻³)	14	0.11	0.10	0.64	0.55	0.28	1.02
	28	0.05	0.05	0.32	0.27	0.14	0.51
	42	0.04	0.03	0.21	0.18	0.09	0.34
	56	0.03	0.03	0.16	0.14	0.07	0.26
	84	0.02	0.02	0.11	0.09	0.05	0.17
LOQ (ng m ⁻³)	14	0.35	0.33	2.14	1.82	0.92	3.40
	28	0.18	0.17	1.07	0.91	0.46	1.70
	42	0.12	0.11	0.71	0.61	0.31	1.13
	56	0.09	0.08	0.54	0.46	0.23	0.85
	84	0.06	0.06	0.36	0.30	0.15	0.57

Table S4. Field blanks expressed as percentage of the amount of mercury in exposed samplers. The average of triplicate deployments is given in the top panel. The bottom panel shows the percentages averaged over deployment length.

Deployment	<i>MerPAS</i>[®]		IVL-PAS		CNR-PAS	
	Rende	Toronto	Rende	Toronto	Rende	Toronto
1 st 2-week	8%	8%	43%	37%	31%	42%
2 nd 2-week	8%	8%	43%	36%	31%	32%
3 rd 2-week	8%	8%	40%	29%	30%	28%
4 th 2-week	8%	9%	43%	36%	30%	47%
1 st 4-week	4%	4%	28%	23%	18%	37%
2 nd 4-week	4%	4%	23%	21%	16%	32%
3 rd 4-week	4%	4%	27%	23%	17%	33%
1 st 6-week	3%	3%	21%	17%	13%	18%
2 nd 6-week	3%	3%	21%	17%	13%	19%
1 st 8-week	2%	2%	16%	15%	11%	13%
1 st 12-week	1%	1%	10%	10%	7%	11%
2-week (n=8)	7.9 ± 0.4 %		38 ± 5 %		34 ± 7 %	
4-week (n=6)	4.2 ± 0.1 %		24 ± 3 %		26 ± 9 %	
6-week (n=4)	2.7 ± 0.1 %		19 ± 2 %		16 ± 3 %	
8-week (n=2)	2.1 ± 0.1 %		15.2 ± 0.7 %		12.0 ± 1.2 %	
12-week (n=2)	1.38 ± 0.01 %		10.0 ± 0.2 %		9 ± 2 %	

Table S5. Mean, standard deviation (SD) and percentage relative standard deviation (%RSD) of the amounts of mercury quantified in the deployed passive air samplers (prior to blank correction) for each of the 22 deployments. All values are for triplicates unless otherwise noted.

Location	Deployment	<i>MerPAS</i> [®]		IVL-PAS		CNR-PAS	
		Mean \pm SD (ng)	RSD (%)	Mean \pm SD (ng)	RSD (%)	Mean \pm SD (ng)	RSD (%)
Rende	1 st 2-week	2.99 \pm 0.11	4	1.15 \pm 0.09	8	0.50 \pm 0.02	3
	2 nd 2-week	3.00 \pm 0.06	2	1.15 \pm 0.09	8	0.50 \pm 0.02	4
	3 rd 2-week	2.92 \pm 0.27	9	1.21 \pm 0.09	7	0.51 \pm 0.03	5
	4 th 2-week	3.02 \pm 0.11	4	1.15 \pm 0.09	8	0.52 \pm 0.01	3
	1 st 4-week	5.72 \pm 0.29	5	1.74 \pm 0.15	8	0.84 \pm 0.12	14
	2 nd 4-week	5.72 \pm 0.14	2	2.10 \pm 0.62	29	0.96 \pm 0.02	2
	3 rd 4-week	5.44 \pm 0.18	3	1.82 \pm 0.32	17	0.89 \pm 0.03	3
	1 st 6-week	8.71 \pm 0.23 ^a	3	2.39 \pm 0.26	11	1.15 \pm 0.11	9
	2 nd 6-week	8.69 \pm 0.11	1	2.38 \pm 0.24	10	1.20 \pm 0.05	4
	1 st 8-week	11.41 \pm 0.43	4	3.12 \pm 0.25	8	1.38 \pm 0.15	11
	1 st 12-week	16.61 \pm 0.30	2	4.80 \pm 0.33	7	2.13 \pm 0.35 ^a	16
Toronto	1 st 2-week	2.84 \pm 0.14	5	1.17 \pm 0.05	4	0.48 \pm 0.04	7
	2 nd 2-week	3.12 \pm 0.11	4	1.19 ^b		0.64 \pm 0.06	10
	3 rd 2-week	2.90 \pm 0.20	7	1.49 \pm 0.20	13	0.73 \pm 0.07	10
	4 th 2-week	2.80 \pm 0.10	4	1.18 \pm 0.01 ^a	1	0.43 \pm 0.03	6
	1 st 4-week	5.50 \pm 0.05	1	1.91 \pm 0.10	5	0.55 \pm 0.01	3
	2 nd 4-week	5.64 \pm 0.30	5	2.09 \pm 0.27	13	0.63 \pm 0.01	2
	3 rd 4-week	5.67 \pm 0.14	2	1.89 \pm 0.13	7	0.62 \pm 0.03	4
	1 st 6-week	8.28 \pm 0.33	4	2.52 \pm 0.21	8	1.10 \pm 0.09	9
	2 nd 6-week	8.48 \pm 0.23	3	2.54 \pm 0.32	13	1.05 \pm 0.08	7
	1 st 8-week	11.12 \pm 0.15	1	2.91 \pm 0.04	1	1.59 \pm 0.26	16
	1 st 12-week	17.11 \pm 0.27	2	4.36 \pm 0.11	2	1.91 \pm 0.10 ^a	5

^a duplicate only, ^b no replication

Table S6. Mean, standard deviation (SD) and relative standard deviation (RSD) of the amount of mercury quantified in the deployed passive air samplers (after blank correction) for each of the 22 deployments. All values are for triplicates unless otherwise noted. Standard deviations are calculated by propagating the standard deviation of both the amounts in Table S4 and the field blank levels in Table S1.

Location	Deployment	<i>MerPAS</i> [®]		IVL-PAS		CNR-PAS	
		Mean \pm SD (ng)	RSD (%)	Mean \pm SD (ng)	RSD (%)	Mean \pm SD (ng)	RSD (%)
Rende	1 st 2-week	2.76 \pm 0.12	4	0.66 \pm 0.13	19	0.34 \pm 0.02	7
	2 nd 2-week	2.77 \pm 0.08	3	0.66 \pm 0.13	20	0.35 \pm 0.03	8
	3 rd 2-week	2.69 \pm 0.28	10	0.72 \pm 0.13	18	0.36 \pm 0.03	9
	4 th 2-week	2.79 \pm 0.12	4	0.66 \pm 0.13	19	0.36 \pm 0.02	7
	1 st 4-week	5.49 \pm 0.30	5	1.25 \pm 0.17	14	0.69 \pm 0.12	18
	2 nd 4-week	5.49 \pm 0.15	3	1.61 \pm 0.62	39	0.81 \pm 0.03	4
	3 rd 4-week	5.21 \pm 0.19	4	1.33 \pm 0.33	25	0.73 \pm 0.04	5
	1 st 6-week	8.48 \pm 0.24 ^a	3	1.90 \pm 0.28	15	1.00 \pm 0.11	11
	2 nd 6-week	8.46 \pm 0.12	1	1.89 \pm 0.26	14	1.05 \pm 0.05	5
	1 st 8-week	11.18 \pm 0.43	4	2.63 \pm 0.27	10	1.23 \pm 0.15	12
	1 st 12-week	16.38 \pm 0.31	2	4.31 \pm 0.34	8	1.97 \pm 0.35 ^a	18
Toronto	1 st 2-week	2.60 \pm 0.15	6	0.74 \pm 0.09	12	0.28 \pm 0.08	28
	2 nd 2-week	2.88 \pm 0.12	4	0.76 \pm 0.08 ^b	10	0.43 \pm 0.09	21
	3 rd 2-week	2.66 \pm 0.21	8	1.06 \pm 0.21	20	0.53 \pm 0.10	19
	4 th 2-week	2.56 \pm 0.11	4	0.75 \pm 0.08 ^a	10	0.23 \pm 0.07	33
	1 st 4-week	5.26 \pm 0.07	1	1.48 \pm 0.13	9	0.35 \pm 0.07	20
	2 nd 4-week	5.40 \pm 0.33	6	1.66 \pm 0.28	17	0.43 \pm 0.07	17
	3 rd 4-week	5.43 \pm 0.15	3	1.46 \pm 0.15	10	0.42 \pm 0.08	18
	1 st 6-week	8.04 \pm 0.33	4	2.09 \pm 0.22	11	0.90 \pm 0.12	13
	2 nd 6-week	8.24 \pm 0.24	3	2.11 \pm 0.33	16	0.85 \pm 0.10	12
	1 st 8-week	10.88 \pm 0.16	1	2.28 \pm 0.09	3	1.38 \pm 0.27	19
	1 st 12-week	16.87 \pm 0.27	2	3.93 \pm 0.13	3	1.70 \pm 0.12 ^a	7

^a duplicate only, ^b no replication

Table S7. Average replicate precision (in %) of the amount of mercury quantified in a PAS (m_{PAS}) and of the blank-corrected amount of mercury in a PAS ($m_{PAS-m_{FB}}$). n designates the number of deployments of a certain type.

	n	MerPAS[®]		IVL-PAS		CNR-PAS	
		m_{PAS}	$m_{PAS-m_{FB}}$	m_{PAS}	$m_{PAS-m_{FB}}$	m_{PAS}	$m_{PAS-m_{FB}}$
2-week deployments	8	4.7	5.5	7.0	16	6.0	17
4-week deployments	6	3.3	3.6	13	19	4.8	14
6-week deployments	4	2.7	2.8	11	14	7.3	10
8-week deployments	2	2.6	2.7	4.7	6.8	13.4	16
12-week deployments	2	1.7	1.7	4.7	5.7	10.7	12
Rende deployments	11	3.5	4.0	11	18	6.9	9.3
Toronto deployments	11	3.4	3.8	6.8	11	7.2	19
all deployments	22	3.5	3.9	9.1	15	7.0	14

Table S8. Mean, standard deviation (SD) and relative standard deviation (RSD) of the volumetric concentrations of mercury in air for each of the 22 deployments as derived by the three passive air samplers. All values refer to triplicates unless otherwise noted. Standard deviations are calculated by propagating the standard deviation of the amounts in Table S5 and the assumed uncertainty of the sampling rates.

Location	Deployment	<i>MerPAS</i> [®]		IVL-PAS		CNR-PAS	
		Mean \pm SD (ng/m ³)	RSD (%)	Mean \pm SD (ng/m ³)	RSD (%)	Mean \pm SD (ng/m ³)	RSD (%)
Rende	1 st 2-week	1.78 \pm 0.16	9	1.66 \pm 0.20	12	1.67 \pm 0.09	5
	2 nd 2-week	1.78 \pm 0.15	9	1.66 \pm 0.21	13	1.69 \pm 0.10	6
	3 rd 2-week	1.71 \pm 0.18	10	1.84 \pm 0.19	10	1.74 \pm 0.10	5
	4 th 2-week	1.80 \pm 0.16	9	1.67 \pm 0.20	12	1.76 \pm 0.08	4
	1 st 4-week	1.77 \pm 0.16	9	1.57 \pm 0.15	10	1.68 \pm 0.18	10
	2 nd 4-week	1.77 \pm 0.15	9	2.05 \pm 0.39	19	1.96 \pm 0.06	3
	3 rd 4-week	1.68 \pm 0.15	9	1.70 \pm 0.25	15	1.78 \pm 0.07	4
	1 st 6-week	1.82 \pm 0.15 ^a	8	1.60 \pm 0.16	10	1.61 \pm 0.12	8
	2 nd 6-week	1.82 \pm 0.15	8	1.61 \pm 0.15	9	1.69 \pm 0.07	4
	1 st 8-week	1.80 \pm 0.15	9	1.67 \pm 0.12	7	1.49 \pm 0.13	9
	1 st 12-week	1.76 \pm 0.15	9	1.83 \pm 0.10	5	1.60 \pm 0.18 ^a	12
Toronto	1 st 2-week	1.65 \pm 0.16	10	1.77 \pm 0.18	10	1.35 \pm 0.28	21
	2 nd 2-week	1.87 \pm 0.16	8	1.86 \pm 0.17 ^b	9	2.12 \pm 0.22	10
	3 rd 2-week	1.60 \pm 0.17	11	2.42 \pm 0.24	10	2.40 \pm 0.20	8
	4 th 2-week	1.67 \pm 0.16	9	1.90 \pm 0.17 ^a	9	1.11 \pm 0.33	30
	1 st 4-week	1.69 \pm 0.15	9	1.79 \pm 0.16	9	0.85 \pm 0.21	25
	2 nd 4-week	1.73 \pm 0.16	9	2.03 \pm 0.22	11	1.04 \pm 0.17	17
	3 rd 4-week	1.76 \pm 0.15	9	1.84 \pm 0.17	9	1.03 \pm 0.18	18
	1 st 6-week	1.68 \pm 0.16	9	1.65 \pm 0.17	10	1.42 \pm 0.14	10
	2 nd 6-week	1.82 \pm 0.15	8	1.80 \pm 0.20	11	1.41 \pm 0.13	9
	1 st 8-week	1.74 \pm 0.15	9	1.51 \pm 0.13	9	1.67 \pm 0.20	12
	1 st 12-week	1.81 \pm 0.15	8	1.61 \pm 0.13	8	1.38 \pm 0.08 ^a	6

^a duplicate only, ^b no replication

Table S9. Variance decomposition analysis partitioning variability in the percent concentration differences between Tekran[®] and PASs, across four nested levels. Factors explaining the largest proportion of the variation are highlighted in bold.

Variable	Proportion explained
Site	0.4678
Period	0.0000
PAS ID	0.4834
Tekran ID	0.0474
Unexplained	0.0015

Table S10. Results of a mixed effects model predicting percent concentration differences between Tekran and PASs. Significant terms are highlighted in bold, and the model was fit while accounting for deployment time and location as random effects (where these random effects exerted a significant effect on concentration differences, $\chi^2=8.7$, $p=0.003$).

Term	Sum Sq.	Mean Sq.	Num D.F.	Den. D.F.	<i>F</i> value	<i>p</i> value
PAS ID	1903.6	951.8	2	83	5.37	0.006
Site	5036.6	5036.6	1	83	28.43	<0.001
PAS ID*Site	838.6	419.3	2	83	2.37	0.100

Table S11. Statistical comparison of least square mean differences in concentrations, across different passive sampler models, sites, and all passive air sampler (PAS) model-by-site combinations. Comparisons here are based on a linear mixed effects model (presented in Table 2) predicting concentration differences as a function of sampler, site, and a sampler-by-site interaction, while accounting for sampling location and time as random effects. Significant differences are highlighted in bold.

Factors compared	PAS 1	Site 1	PAS 2	Site 2	Estimated difference (%)	<i>t</i> value	<i>p</i> value
PAS	CNR-PAS	-	<i>MerPAS</i> [®]	-	5.5	1.59	0.116
PAS	CNR-PAS	-	<i>MerPAS</i>[®]	-	11.4	3.28	0.002
PAS	IVL-PAS	-	<i>MerPAS</i> [®]	-	5.9	1.69	0.095
Sites	-	Rende		Toronto	-15.1	-5.33	<0.001
PAS-by-Sites	CNR-PAS	Rende	IVL-PAS	Rende	-0.1	-0.01	0.992
PAS-by-Sites	CNR-PAS	Rende	<i>MerPAS</i> [®]	Rende	4.2	0.74	0.464
PAS-by-Sites	CNR-PAS	Rende	CNR-PAS	Toronto	-23.7	-4.81	<0.001
PAS-by-Sites	CNR-PAS	Rende	IVL-PAS	Toronto	-12.6	-2.56	0.012
PAS-by-Sites	CNR-PAS	Rende	<i>MerPAS</i> [®]	Toronto	-5.1	-1.03	0.307
PAS-by-Sites	IVL-PAS	Rende	<i>MerPAS</i> [®]	Rende	4.2	0.75	0.458
PAS-by-Sites	IVL-PAS	Rende	CNR-PAS	Toronto	-23.6	-4.8	<0.001
PAS-by-Sites	IVL-PAS	Rende	IVL-PAS	Toronto	-12.5	-2.54	0.013
PAS-by-Sites	IVL-PAS	Rende	<i>MerPAS</i> [®]	Toronto	-5	-1.02	0.312
PAS-by-Sites	<i>MerPAS</i>	Rende	CNR-PAS	Toronto	-27.8	-5.66	<0.001
PAS-by-Sites	<i>MerPAS</i>	Rende	IVL-PAS	Toronto	-16.7	-3.41	0.001
PAS-by-Sites	<i>MerPAS</i>	Rende	<i>MerPAS</i> [®]	Toronto	-9.2	-1.88	0.064
PAS-by-Sites	CNR-PAS	Toronto	IVL-PAS	Toronto	11.1	2.76	0.007
PAS-by-Sites	CNR-PAS	Toronto	<i>MerPAS</i>[®]	Toronto	18.6	4.64	<0.001
PAS-by-Sites	IVL-PAS	Toronto	<i>MerPAS</i> [®]	Toronto	7.5	1.87	0.065