

Assays	Amine	Aliquot (g) Amine salt	Correc. Factor	Aliquot (g)	H <sub>2</sub> O volume (mL)	Stock standard solution ( $\mu\text{g mL}^{-1}$ )	Aliquot ( $\mu\text{L}$ )	H <sub>2</sub> O volume (mL)	Working std solution ( $\mu\text{g mL}^{-1}$ )
Serie I	MA	0,09591	0,46060	0,04418	50,34	878	100	10	8.78
	DMA	0,10409	0,55286	0,05755	50,34	1143	100	10	11.43
Serie II	MA	0,02586	0,46060	0,01191	10	1191	100	10	11.91
	DMA	0,0095	0,55286	0,00525	10	525	100	10	5.25
Serie III	MA	0,0939	0,46060	0,04325	10	4325	100	10	4.33
	DMA	0,0991	0,55286	0,05479	10	5479	100	10	5.48
Serie IV	MA	0,11623	0,46060	0,05354	10	5354	100	10	5.35
	DMA	0,10083	0,55286	0,05574	10	5574	100	10	5.57
Series V-IX (std MeOH, 2M)	MA					62200	160	100	99.5
	DMA					90160	110	100	99.2

Table 1S – Calculations for the preparation of standards from hydrochloride salts and solution in Methanol (2M).

- Correction Factor, corresponding to the molecular weight ratio of "*amine / amine-Fmoc.Cl derivative*"
- MA and DMA, which correspond to the abbreviations for methylamine and dimethylamine, respectively

	Final concentration	Peak Area	Final concentration	Peak Area
	(ng mL <sup>-1</sup> )	Methylamine salt	(ng mL <sup>-1</sup> )	Dimethylamine salt
<b>Serie I</b>	Blank	6.2	Blank	37
		3.8		31
		3.6		32
	29	48	38	202
		60		208
<b>Serie II</b>	Blank	9.9	Blank	45
		6.5		30
		6.1		41
		4.9		26
	15	41	19	146
		35		137
		26		115
	29	49	38	238
		53		238
	40	80		235
		94		224
	79		209	
	202			
<b>Serie III</b>	Blank	9.5	Blank	47
		9.9		41
		7.3		32.5
	15	25	18	155
		17		123
		13		131
	30	50	37	218
	32		217	
	26			
<b>Serie IV</b>	BL	3.6	BL	11
	24	33	24	110
		26		97
	48	56	48	260
	34		192	
<b>Serie V</b>	Blank	3.2	Blank	37
		3.0		43.6
	38	79	45	231
		72		233
			67	150
				274
				233
			217	
<b>Serie VI</b>	Blank	2	Blank	37.4
		3.5		41
	38	73	45	231
		103		244
		87		237
<b>Serie VII</b>	Blank	2.9	Blank	30
		1.7		41
	38	75	89	495
		96		361
	71			
<b>Intermediate Precision</b>		0.33		0.12

Table 2S –Chromatographic peak area obtained from the analyses of blanks and standard solutions prepared in different days from hydrochloride salt standards. The data has been grouped according to the final concentration of the standard, and the intermediate precision derived from this is included.

	Final concentration (ng mL <sup>-1</sup> )	Peak Area	
		Methylamine	Dimethylamine
<b>Serie I</b>	<b>Blank</b>	4.3	55
		3.9	52
		4.5	55
	<b>66</b>	105	325
		133	374
		129	359
<b>Serie II</b>	<b>Blank</b>	6.6	47
		4.2	42
		3.7	38
	<b>66</b>	103	323
		90	290
		95	324
<b>Serie III</b>	<b>BL</b>	12	36
		9.2	44
	<b>34</b>	63	255
		50	190
	<b>66</b>	44	178
		106	214
		84	222
		100	239
<b>Serie IV</b>	<b>Blank</b>	11	23.5
		7.6	11
		48	196
	<b>27</b>	38	185
		29	181
	<b>33</b>	63	257
		36	221
	<b>66</b>	59	200
		85	392
139		432	
<b>Serie V</b>	<b>Blank</b>	7.2	35
		4.0	35.7
		11	92.8
	<b>17</b>	11.6	93.8
		13.2	103.8
	<b>33</b>	87	211.8
		91	215.8
		80	203.8
	<b>66</b>	124	463
131		475.8	
<b>Intermediate Precision</b>		0.28	0.24

Table 3S –Chromatographic peak area obtained from the analyses of blanks and standard solutions prepared in different days from standard solution in methanol (2M). The data has been grouped according to the final concentration of the standard, and the intermediate precision derived from this is included.

Blanks	Peak Area	Peak Area
	Methylamine	Dimethylamine
<b>Serie I</b>	7.3	29.6
	7.8	33.0
<b>Serie II</b>	9.9	41.0
	7.3	32.5
<b>Serie III</b>	6.1	48.2
	4.9	41.0
<b>Serie IV</b>	10	44.5
	6.5	30.0
<b>Serie V</b>	6.2	37.0
	8.9	26.2
	6.8	24.8
<b>Serie VI</b>	7.0	20.3
	6.3	26.6
	4.1	24.6
	3.4	23.1
<b>Serie VII</b>	6.2	37.0
	3.8	31.3
	3.6	32.0
<b>Serie VIII</b>	9.9	44.5
	6.5	30.0
	6.1	48.2
	4.9	41.0
<b>Serie IX</b>	9.5	47.0
	9.9	41.0
<b>Mean</b>	7 ± 2.1	35 ± 8.5
<b>Intermediate Precision</b>	0.21	0.16

Table 4S –Chromatographic peak area obtained from the analyses of blanks in a work area that was free of standards. The data has been grouped according to the day of preparation, and the intermediate precision derived from this is included.

### Estimation of the limits of detection (LOD) and quantification (LOQ)

These values were considered as the concentrations corresponding to the area calculated as the sum of the background plus three (LOD) and ten times (LOQ) multiplied this value by the pooled relative standard deviation ( $RSD_{pooled}$ ) of the blank solutions. Limit values were then calculated as follows:

$$LOD = (\bar{A}_{blank} + 3 * \bar{A}_{blank} * RSD_{pooled}) * (CC_{stand} / \bar{A}_{stand})$$

$$LOQ = (\bar{A}_{blank} + 10 * \bar{A}_{blank} * RSD_{pooled}) * (CC_{stand} / \bar{A}_{stand})$$

Where:

- $\bar{A}_{blank}$  corresponds to the average area obtained from the measured blank solutions,
- $RSD_{pooled}$  is the pooled relative standard deviation derived from the measured blank solutions from the equation (1),
- $CC_{stand}$  is the concentration of the standard solution at low levels (around 30 ng mL<sup>-1</sup> was chosen as concentration level)
- $\bar{A}_{stand}$  is the mean area obtained from the analysis of the standards. This mean value was calculated from the peak area corrected peak areas previously corrected with respect to the background measurements obtained in the analysis batch.

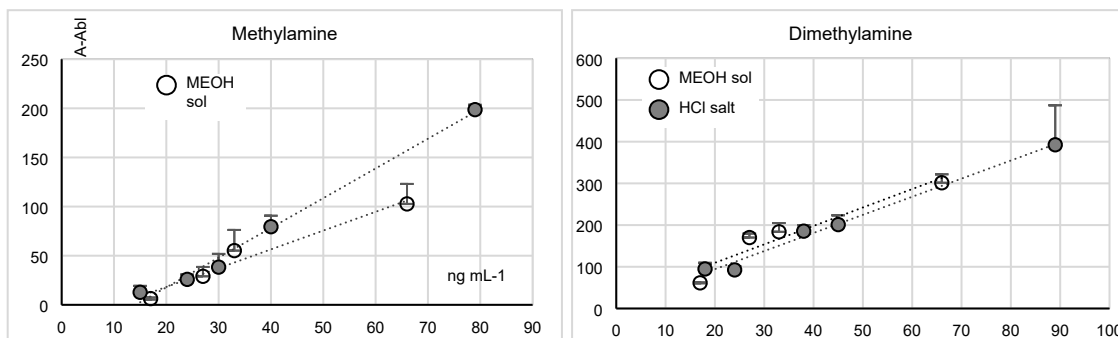


Figure 1S – Calibration adjustment for methylamine and dimethylamine from the results after analysis of hydrochloride salt standards. The areas of the peaks were corrected by the corresponding blank areas of the blanks in each batch measured.

### Chromatographic analysis of BTEX

Samples were taken into commercial sorbent tubes supplied by Markes International Ltd (UK) filled with Tenax TA/Carbograph 1TD/Carboxen 1003 (C3-AAXX-5266). Sampling flow was 80 mL min<sup>-1</sup> for 2 hours respectively. After sampling, the tubes were capped and stored at 4°C until transportation to the laboratory. Analysis were performed before one week.

Samples were subsequently analyzed using a gas chromatograph/mass spectrometer, GC/MS (Agilent 6890/5975B, Santa Clara, USA) coupled to a thermal desorption, TD (Unity, Markes). The thermal desorption system worked as follows: pre-purge 6 min at a flow rate of 50 mL min<sup>-1</sup>, primary desorption at 280°C for 5 min with a flow rate of 30 mL min<sup>-1</sup>, no inlet split, cold trap low 25°C, pre-trap fire purge 3 min at 50 mL min<sup>-1</sup>, cold trap high at 300°C for 6 min, outlet split 10 mL min<sup>-1</sup>, and flow path temperature 200°C. The cold trap “Air Toxic Analyser” (Markes) was used.

Separation was achieved using a DB-624-MS column (60 m x 0.25 mm i.d. x 1,40 µm film thickness) (J&W Scientific, USA). The column oven temperature was maintained at 40 °C for the initial 5 min, then increased at 6 °C min<sup>-1</sup> up to 220 °C and held for 3 min. The injector port was set at 250°C and the transfer line from TD to GC at 300°C. Samples were injected in splitless mode, using helium as carrier gas with a flow rate of 1.0 mL min<sup>-1</sup>. MS was operated in EI mode at 70 eV. The ion source temperature was 230°C and the quadrupole temperature 100°C, operating in the SCAN mode (50-250 uma).

Calibration was achieved using liquid standards in methanol, 5 µL of which were injected in clean sorbent tubes through a calibration loading rig (Markes) while purging with nitrogen for 3 min. A standard including 18 VOCs (n-C10 to n-C14, BTEX, α- and β-pinene, camphene, limonene benzyl alcohol 3-isopropyltoluene, 1,2,3-trifluorobenzene and propionic acid) in methanol was custom prepared and used for calibration at both laboratories LM24-CUS-72074 (Labmix, Hamminkein, Germany).

The standard was diluted to inject solutions in the range 0.4-150 ng per tube for each compound. Field blanks were taken each day of campaign, and data were blank corrected. The method detection limits (MDLs) were calculated as three times the standard deviation for each target compound concentration in spiked samples (n=7, spiked amount 0.5 ng), and were in the range 0.2-0.5 ng.

Precision, determined from five replicates analysis of a standard of 2 ng was within 3% for α-pinene to 16% for n-C14.

	12/07/2022	13/07/2022	14/07/2022	15/07/2022	16/07/2022	17/07/2022	18/07/2022	19/07/2022	Intermediate Precision
PM	38,52	34,84	58,46	44,48	48,00	35,89	49,65	26,87	
Methylamine	2,3±0.50	3.0±0.26	2,3±0.22	1,9±0.11	1,3±0.16	0,8±0.17	2,6±0.16	1,08±0.014	0.13
Dimethylamine	7,1±0.95	4,16±0.027	2,3±0.51	3,7±0.29	3,3±0.52	1,6±0.54	1,87±0.089	1,4±0.29	0.18
Formaldehyde	7,3±0.69	6,6±0.31	3,89±1.05	2,14±0.074	2,1±0.13	1,65±0.041	3,32±0.065	2,12±0.071	0.11
Acetaldehyde	2,43±0.092	2,4±0.11	1,56±0.14	1,4±0.34	1,5±0.11	1,63±0.047	1,5±0.12	1,06±0.085	0.10
Acetone	4,3±0.13	6,1±0.18	3,89±0.043	4,2±0.26	4.0±0.18	3,5±0.24	4,7±0.29	1,94±0.047	0.04
Propionaldehyde	0,26±0.010	0,23±0.017	0,16±0.020	0,10±0.022	0,13±0.026	0,13±0.015	0,17±0.013	0,11±0.023	0.13
Metacrolein	0,22	0,35	0,23	0,10	0,12	0,09	0,18	0,06	
Butanone	0,47	0,35	0,26	0,68	0,78	0,60	0,29	0,07	
Butanal	0,53	0,36	0,26	0,42	0,50	0,46	0,10	0,08	
Benzaldehyde	0,70 ±0,081	1,8±0,13	1,6±0,16	0,83±0,052	1,2±0,17	1,1±0,15	0,8±0,10	0,53±0,070	0.10
Hexanal	0,20	0,17	0,18	0,11	0,14	0,12	0,15	0,15	
Heptanal	0,23	0,13	0,15	0,03	0,04	0,04	0,04	0,04	
Octanal	0,41	0,64	0,13	0,14	0,07	0,06	0,08	0,08	
Nonanal	0,64	0,28	0,27	0,12	0,15	0,13	0,17	0,15	
Decanal	0,55	0,18	0,13	0,04	0,07	0,05	0,11	0,06	
Bencene	0,332	0,510	0,371	0,316	0,351	0,292	0,323	0,262	
Toluene	0,818	1,492	0,913	0,585	0,348	0,269	0,809	0,673	
Ethylbencene	0,165	0,321	0,212	0,108	0,087	0,056	0,224	0,147	
m+p-xilene	0,422	0,624	0,533	0,306	0,226	0,188	0,582	0,454	
o-xilene	0,187	0,308	0,229	0,124	0,095	0,075	0,243	0,166	
a-pineno	0,048	0,048	0,066	0,043	0,031	0,039	0,234	0,161	

Table 5S – Variation of concentrations of PM ( $\mu\text{g m}^{-3}$ ), methylamine and dimethylamine ( $\text{ng m}^{-3}$ ), and thirteen carbonyl compounds ( $\mu\text{g m}^{-3}$ ) measured during a week-long sampling period at CIEMAT in July, 2022.

Results are given as the “*mean ± standard deviation*” obtained from duplicate analyses. Some carbonyl measurements could only be performed once. The intermediate precision was deduced from the relative standard deviations for each compound from the eight analysis batches.

	MA	DMA	Formald	Acetald	Aceton	Propionald	Hexanal	Heptanal	Octanal	Nonanal	Decanal	Isoprene	Benzene	Toluene	Ethyl- benzene	m+p- xylene	o- xylene	$\alpha$ - pinene
Dimethylamine	0,4392																	
Formald	<b>0,7603</b>	<b>0,7796</b>																
Acetald	0,6183	<b>0,7898</b>	<b>0,9038</b>															
Aceton	<b>0,8087</b>	0,454	0,6175	<b>0,7373</b>														
Propionald	0,6925	<b>0,7352</b>	<b>0,9624</b>	<b>0,919</b>	0,5968													
Hexanal	0,5833	0,4947	<b>0,8068</b>	0,5697	0,2293	<b>0,7954</b>												
Heptanal	0,5535	<b>0,7424</b>	<b>0,894</b>	<b>0,7693</b>	0,3357	<b>0,8587</b>	<b>0,8757</b>											
Octanal	0,6866	0,6665	<b>0,8844</b>	<b>0,8776</b>	<b>0,7177</b>	<b>0,7976</b>	0,5205	0,6607										
Nonanal	0,4604	<b>0,8494</b>	<b>0,8712</b>	<b>0,776</b>	0,2757	<b>0,8824</b>	<b>0,8046</b>	<b>0,9398</b>	0,6039									
Decanal	0,4378	<b>0,8665</b>	<b>0,8484</b>	<b>0,7637</b>	0,2661	<b>0,8727</b>	<b>0,7508</b>	<b>0,8902</b>	0,582	<b>0,9917</b>								
Isoprene	0,5813	-0,2053	0,1657	0,1114	0,497	0,2526	0,0817	-0,16	0,1552	-0,1262	-0,0867							
Benzene	<b>0,7124</b>	0,337	0,6318	0,6821	0,8513	0,5447	0,3796	0,4051	<b>0,8057</b>	0,2309	0,172	0,275						
Toluene	<b>0,8559</b>	0,3041	<b>0,7606</b>	0,5786	0,6456	0,6386	0,6088	0,547	<b>0,822</b>	0,3832	0,3346	0,4242	<b>0,7969</b>					
Ethyl-benzene	<b>0,8802</b>	0,1734	0,6895	0,4918	0,6391	0,6057	0,6188	0,4643	0,7038	0,3055	0,2601	0,5884	<b>0,7564</b>	<b>0,9701</b>				
m+p-xylene	<b>0,8161</b>	0,0525	0,5872	0,2942	0,4217	0,5118	0,6447	0,4208	0,512	0,2797	0,2415	0,6155	0,5193	<b>0,8872</b>	<b>0,9495</b>			
o-xylene	<b>0,8862</b>	0,1689	0,693	0,4664	0,5913	0,6169	0,6581	0,4937	0,661	0,3419	0,2984	0,5997	0,6876	<b>0,9537</b>	<b>0,9934</b>	<b>0,9746</b>		
$\alpha$ -pinene	0,1643	-0,4657	-0,1599	-0,408	-0,2078	-0,0892	0,0803	-0,2827	-0,3077	-0,2158	-0,1721	<b>0,7156</b>	-0,3243	0,1042	0,2817	0,5115	0,3456	

Table 6S - Coefficient of correlation among compounds measured. Statistically significant at the 95 % confidence level

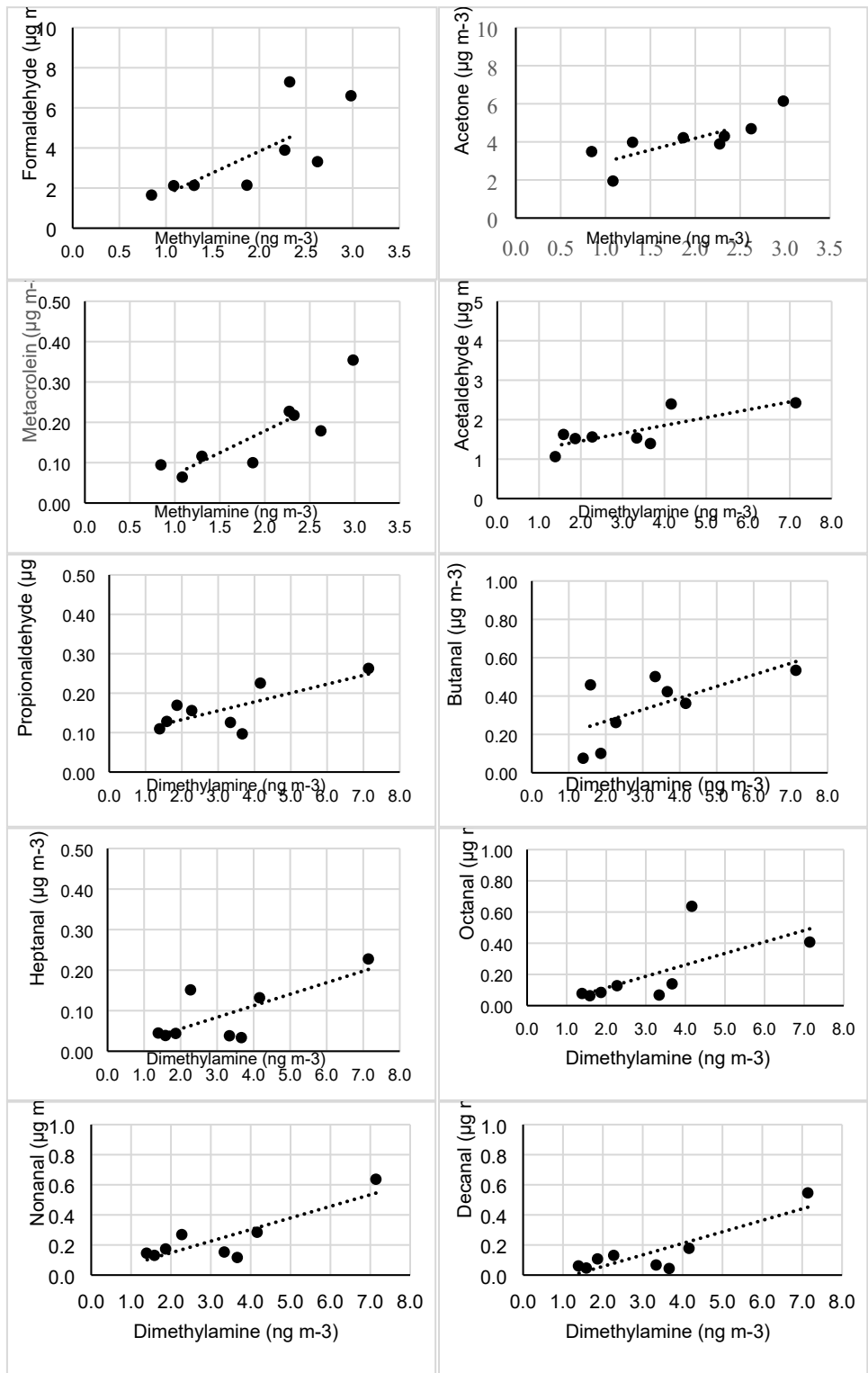


Figure 2S – Correlations between the concentration of methylamine and dimethylamine and some of the carbonyls measured during one week July (2021).



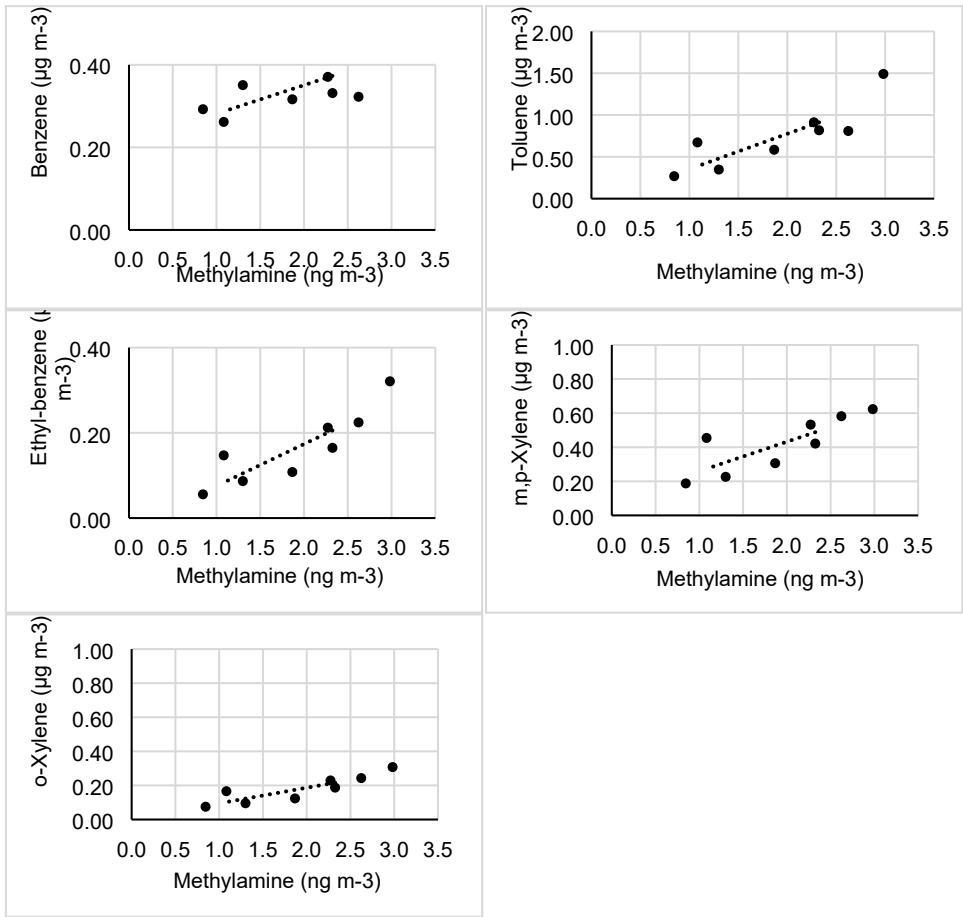


Figure 3S – Correlations between the concentration of methylamine and dimethylamine and benzene, toluene, ethylbenzene and xylenes measured during one week July (2021).