

**European Network on New Sensing Technologies for Air Pollution
Control and Environmental Sustainability - *EuNetAir*
COST Action TD1105**

INTERNATIONAL WG1-WG4 MEETING on

New Sensing Technologies and Methods for Air-Pollution Monitoring

European Environment Agency - EEA

Copenhagen, Denmark, 3 - 4 October 2013

Action Start date: 01/07/2012 - Action End date: 30/06/2016 - Year 2: 2013-2014 (*Ongoing Action*)

**Air Quality Measurements in Republic of Macedonia
VOC Measurements**



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INTRODUCTION

Measurements in Republic of Macedonia

From 1998 till 2011:

- 17 automatic monitoring stations for air quality (SO₂, NO_x, PM₁₀, O₃, CO, BTEX)
- Calibration laboratory
- Balance room

In 2011:

- PM_{2.5} on two sites (Technical supply)
- **One year VOCs campaign on three measurement sites (Twinning project Strengthening the central and local level capacities for environmental management in the area of air quality):**

WHY VOCs measurements?

- ✓ Data from the BTEX instrument no reliable;
- ✓ To see if benzene concentration exceed limit value and assessment threshold;
- ✓ No equipment for VOCs analysis;

VOLATILE ORGANIC COMPOUND MEASUREMENTS IN SKOPJE

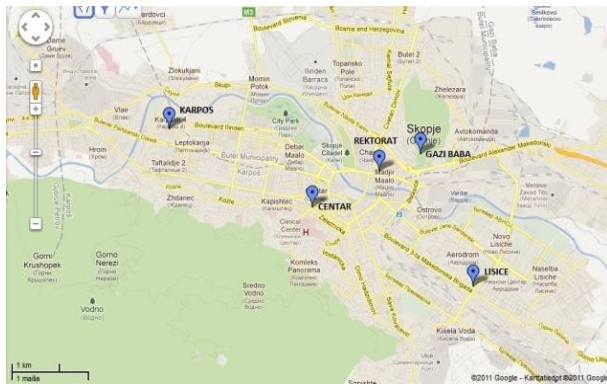
- Measurements for VOC diffusive two-week samples were carried from three stations, Rektorat, Ilinden – Miladinovci, Skopje Center
- Period - February 2011 to February 2012 and in station Skopje Center from March 2012 to May 2012
- Sampling time - two weeks simultaneously
- Adsorbent tubes filled with adsorbent carbopack-B from Perkin-Elmer



MEASUREMENT SITES

Skopje – Center

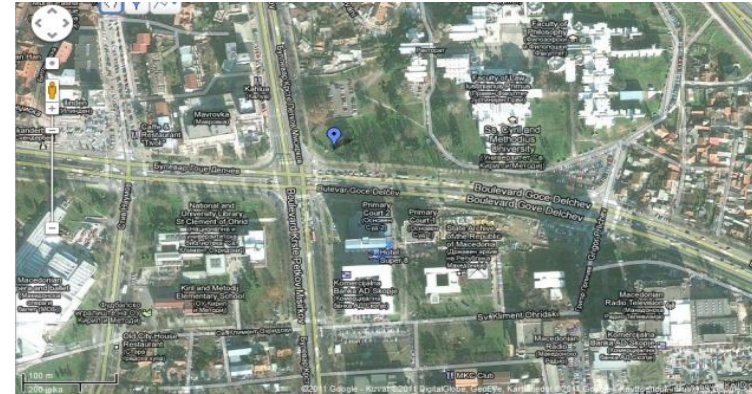
Center is a monitoring station in the capital of Skopje (500 000 inh.). It is classified as an urban – traffic station



MEASUREMENT SITES

Skopje - Rektorat

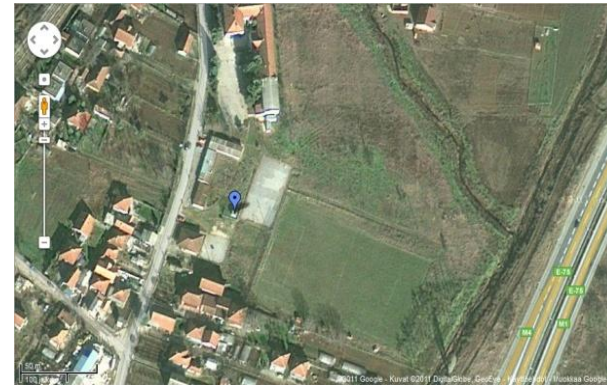
Rektorat is a monitoring station in the capital of Skopje (500 000 inh.). It is classified as an urban – traffic station. The station is located near a major junction.



MEASUREMENT SITES

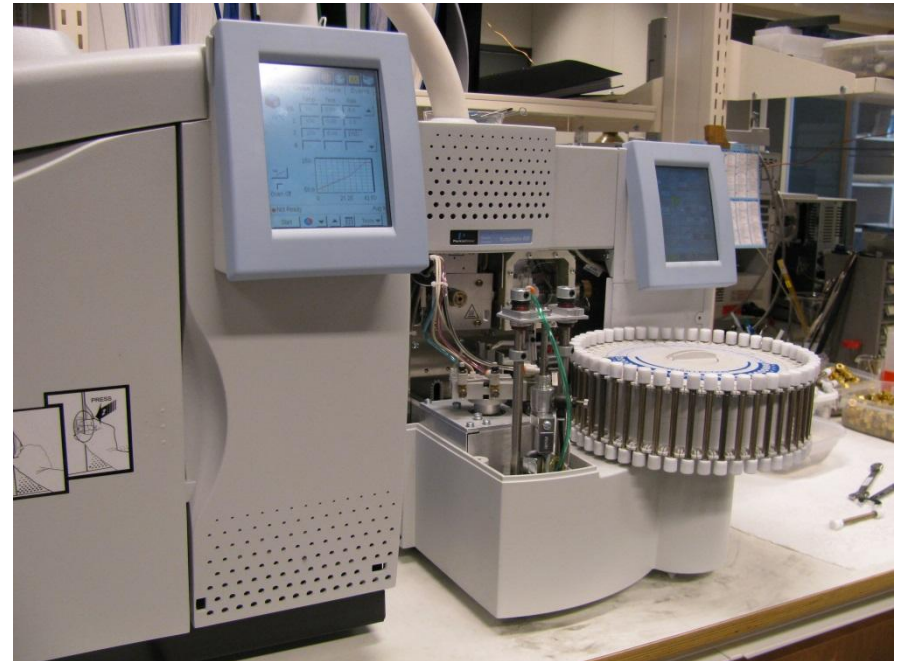
Ilinden– Miladinovci

Miladinovci is a station in the municipality of Ilinden. It is classified as a rural – industrial station. The station is meant to monitor the air quality effects of the OKTA refinery. The station is located approximately 0.5 km south from the refinery.



SAMPLING AND ANALYTICAL METHOD

- Samples were analyzed in the laboratory of Finnish Meteorological Institute FMI
- Measured compounds: benzene, toluene, ethylbenzene, m/p xylene, o-xylene, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene and styrene
- The uptake rates taken from standard *SFS-EN ISO 16017-2:2003* to benzene, toluene, xylenes and ethylbenzenes
- Samples analyzed using gas-chromatograph (Perkin-Elmer Clarus 600), with mass-selective detector (Perkin-Elmer Clarus 600T)
- Calibrations performed using liquid standards in methanol solutions.



RESULTS

Table 1 - Limit of detection (LOD), limit of quantification (LOQ) and measurement uncertainty (MU) for aromatic hydrocarbons.

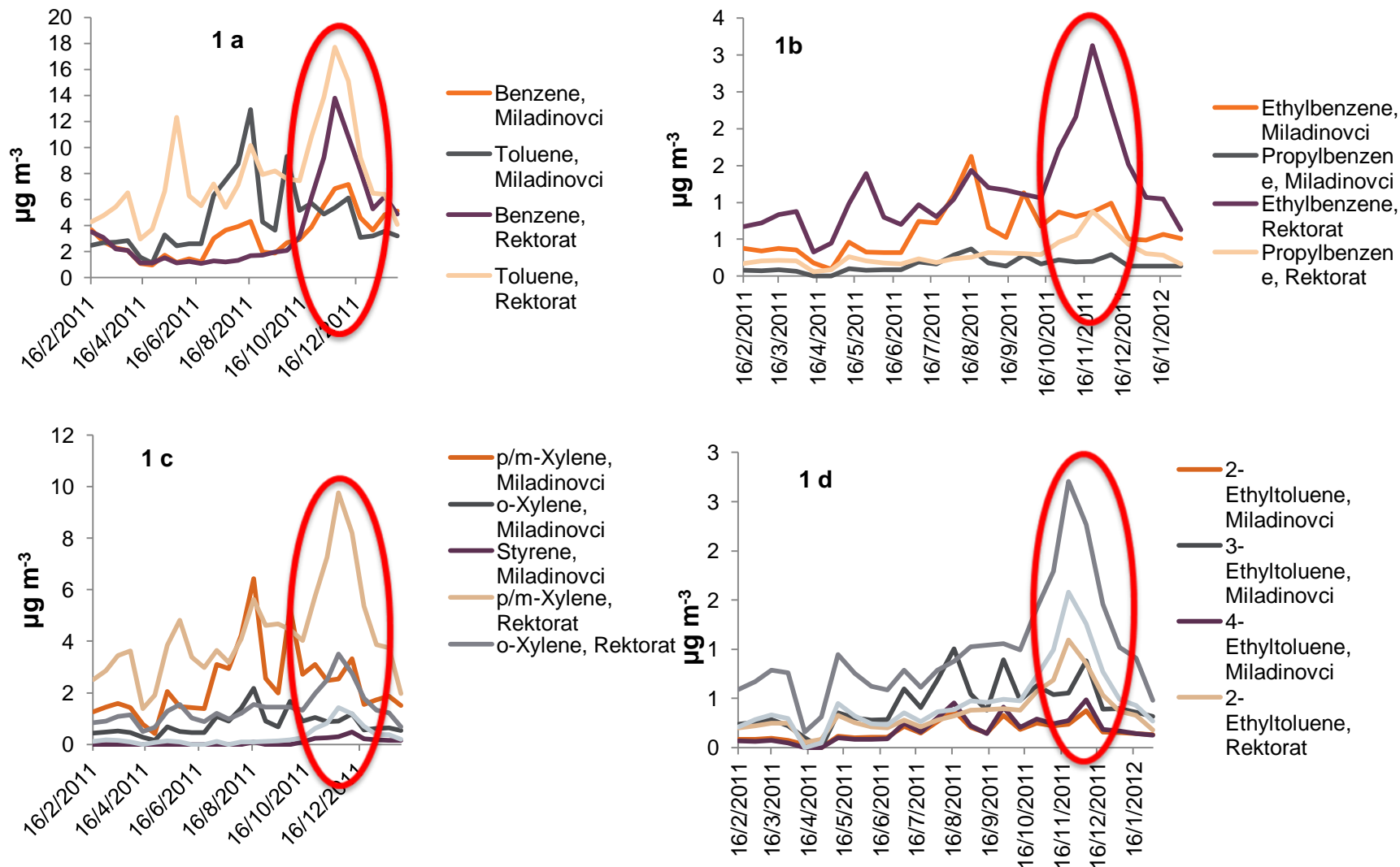
compound	LOD (ng/m ³)	LOQ (ng/m ³)	MU (%)
benzene	54	180	15
toluene	70	233	14
ethylbenzene	43	143	15
p/m-xylene	60	200	15
styrene	11	37	22
o-xylene	23	77	15
propylbenzene	9	30	16
2-ethyltoluene	8	27	19
3-ethyltoluene	16	53	18
4-ethyltoluene	7	23	19

RESULTS

Table 2 shows the annual means of all the measured compounds. The annual benzene concentrations **exceed the upper assessment threshold in Rektorat and the lower assessment threshold in Miladinovci stations**. The annual mean benzene concentrations were **3.73 and 3.24 $\mu\text{g}/\text{m}^3$** at Miladinovci and Rektorat stations, respectively. **Very high benzene concentrations, 9 - 14 $\mu\text{g}/\text{m}^3$ were measured at Rektorat in November and December 2011**. At the same time also other VOC concentrations were highest at both stations. Unit is $\mu\text{g}/\text{m}^3$.

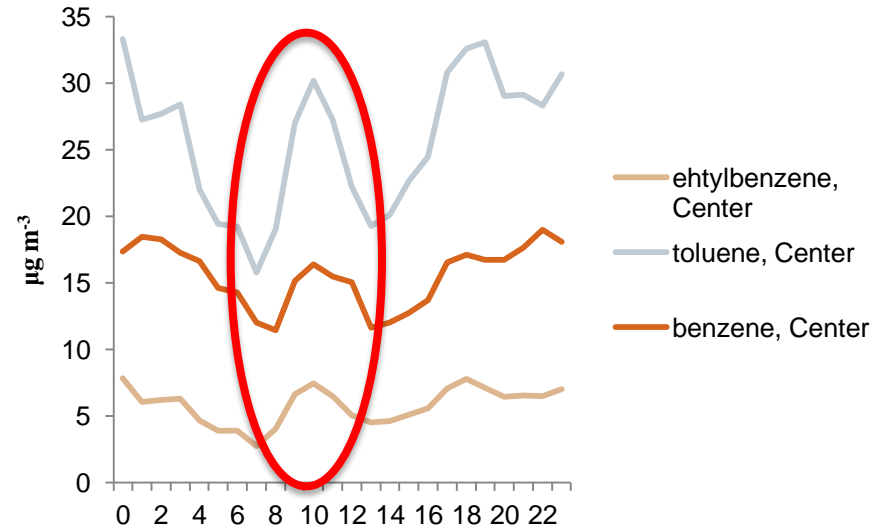
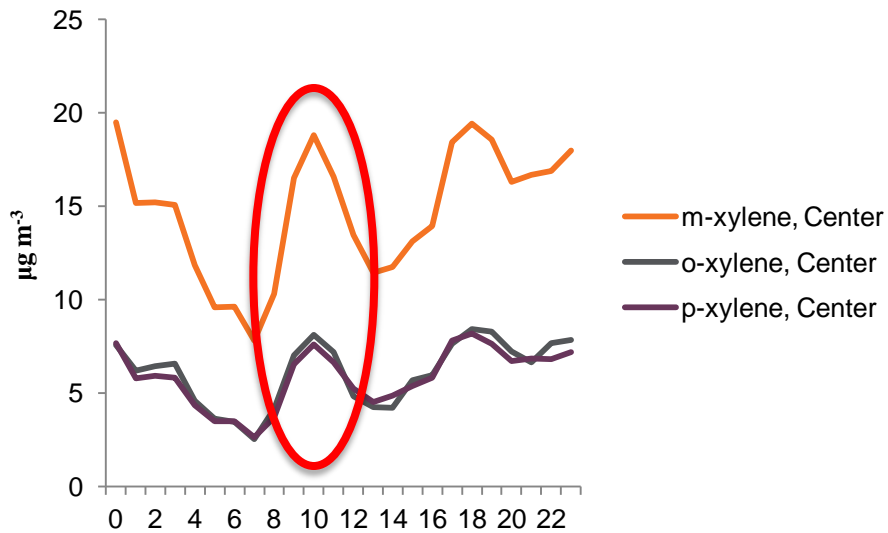
compound	Rektorat	Miladinovci	Centar
benzene	3.73	3.24	1.81
toluene	7.81	4.50	5.44
ethylbenzene	1.16	0.61	0.95
propylbenzene	0.29	0.16	0.26
p/m-xylene	4.27	2.33	3.28
o-xylene	1.39	0.79	1.22
styrene	0.34	0.22	0.14
2-ethyltoluene	0.36	0.17	0.32
3-ethyltoluene	0.98	0.46	0.84
4-ethyltoluene	0.49	0.19	0.38

DATA ANALYSIS



cost Figure 1 VOC measurements at Rektorat and Miladinovci sites.
 EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

DATA ANALYSIS



Diurnal variability of VOC concentrations in December 2011 (MEPP BTX monitor results) at Skopje Center

CONCLUSIONS AND FUTURE STEPS

- The concentrations of all the measured compounds were higher at Rektorat site than at Miladinovci showing that traffic is the main source of VOCs;
- The concentrations are higher in Skopje Center than in the other two stations for all other compounds except benzene;
- The EU assessment levels for benzene were exceeded at both stations, although the annual means were below the limit value ($5 \mu\text{g m}^{-3}$);
- The annual mean benzene concentrations were 3.73 and $3.24 \mu\text{g m}^{-3}$ at Miladinovci and Rektorat stations, respectively;
- Therefore, VOC measurement should be carried in Skopje agglomeration;
- No available equipment and budget to carry out VOCs indicative measurements in future;
- New BTEX analyser will be used for benzene measurements;
- Regular maintenance of the instrument and regular calibrations will lead to reliable results;
- New BTEX to be installed in 2015 in two other zones;



THANK YOU FOR YOUR ATTENTION

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