Notat: Status for Partikelprojektet 2011-2013

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Status for the Particle Project 2011-2013

The Particle Project 2011-2013 was granted ultimo 2011 by the Danish EPA, Miljøstyrelsen. Measurement activities involving particle size distributions started at urban background (H.C. Ørstedsinstituttet, HCOE) primo 2011 and have regularly been compared to the rural site RISOE (Risø peninsula at Roskilde Fjord) and an urban curbside station (H.C. Andersens Boulevard, HCAB). The first of two scheduled campaigns was initiated ultimo 2011. Method development for organic chemical analyses was finalized by February 2012, and the inorganic and organic analyses of the campaign data was completed at the end of 2nd quarter of 2013.

Measurement campaigns in 2011 and 2012

A winter season campaign was initiated in November-December 2011 in Copenhagen at HCOE and HCAB. Gaseous species, Volatile Organic Compounds (VOC) and filter samples for condensed species were sampled during the campaign (Annex ii). The sample program is illustrated in Table 1.

Table 1. Sample program during the field campaigns at urban background (HCOE) and at urban curbside (HCAB).

Parameter		**HCOE**	**HCAB**
$PM_{2.5}$	Inorganic ions	√	√
	Elements	√	√
	Organic compounds, incl. PAH	√	√
	^{14}C (carbon-14 isotope)	√	√
PM_{10}	Inorganic ions		√
	Elements		√
	PAH	√	√
DMPS	Particle size distributions 10-700 nm	√	√
Gasses	NO_X, O_3, CO, SO_2	√	√
VOC	C_4-C_9	√	

A winter campaign was conducted from November 14th to December 14th 2011 and involved three high-volume-samplers, 6 SM200 particulate monitors, one VOC sampler, and two monitors each for analysis of NO_X, O_3, CO and SO_2. In 2012, a summer campaign was conducted from June 28th to July 28th. More than 8 weeks of data has been collected and is currently evaluated. The sample matrix is comprehensive and is constructed to provide information on:

i) **Traffic source profile**. The contribution to particulate matter from traffic-related sources has been derived by subtraction of the urban background from the urban curbside measurements. A traffic source profile has previously been developed at the former Danmarks Miljøundersøgelser, which will now be updated on existing and new chemical species.

ii) **PAH**. Polycyclic Aromatic Hydrocarbons are formed during incomplete combustion, e.g. traffic and wood stove emissions. PAH from these sources are currently, or have been evaluated in the *Danish Air Quality Monitoring Program and additional air quality projects supported by The Danish EPA* , whereas no in-depth information on background levels exists. In the Particle Project 2011-2013, lumped weekday/weekend

measurements of 10 abundant PAH's serve to evaluate the traffic contribution to PAH's, the urban background level and the $PM_{2.5}/PM_{10}$ ratio.

iii) **Fossil fuel sources**. Soot and organic particulate matter that relates to human activities are expected to contribute significantly to atmospheric particles in the urban environment. Particulate carbon that relates to fossil fuel combustion is evaluated by measuring the carbon-14 isotope, ^{14}C in $PM_{2.5}$. Urban busy street levels are compared to background levels.

iv) **Natural sources**. In order to evaluate the fraction of atmospheric particles that origin from human activity, the natural contribution in the form of Primary Biological Aerosol Particles (PBAP) and Secondary Organic Aerosols (SOA) are evaluated. For this purpose, DCE - Danish Centre for Environment and Energy, Aarhus University has optimized methods for extraction and analysis of organic markers compounds for these aerosol classes.

v) **VOC**. Volatile organic compounds that relates to human activity are routinely measured in the urban background. Although they are in the opposite phase as particulate matter, most of the measured VOC's are precursors for particulate matter. Furthermore, the VOC's and atmospheric particles from traffic and industry have common sources, and will be evaluated together if possibly.

vi) **Particle size distribution**. Within the Particle Project, particle size distributions from 10-700 nm are continuously measured at HCOE.

vii) **Source apportionment**. The overall objective of the Particle Project is to provide the scientific machinery for evaluation of the $PM_{2.5}$ trend 2008-2020. The Particle Project 2011-2013 focuses on the chemical composition and sources to urban $PM_{2.5}$ during winter and summer 2011/2012. These will be evaluated from using two source-receptor model approaches, i.e. Positive Matrix Factorization (PMF) and the Constrained Physical Receptor Model (COPREM), on more than 60 chemical compounds. The reason for the comprehensive number of chemical and physical parameters in the receptor models is to provide a scientifically sound and detailed source apportionment analysis, which in combination with scenario calculations has the purpose to assist the political abatement strategy for $PM_{2.5}$ in 2013.

TEOM measurements

Within the new particle project 2011–2013, $PM_{2.5}$ and PM_{10} were measured using TEOM (Tapered Element Oscillating Microbalance). The TEOM instrument has a time resolution of ½ hour. Based on the measurement method, the sample is heated up to 50 degree Celsius implying that some of the volatile mass collected on the filter in the sensor unit may evaporate. Thus, it has to be considered that the mass reported by TEOM is lower than measured with the reference method (Massling et al., 2011).

$PM_{2.5}$ and PM_{10} were measured at RISOE and HCAB. In Table 2 the data coverages are summarized for 2011.

Table 2. Data coverages for TEOM-$PM_{2.5}$ and TEOM-PM_{10} measurements at regional background (RISOE) and urban curbside (HCAB) in 2011.

	RISOE	HCAB
TEOM-$PM_{2.5}$	55 %	93 %
TEOM-PM_{10}	60 %	87 %

The relatively low data coverage at RISOE is due to instrument service in the beginning of 2011 as the TEOM instruments were sent to the manufacturer in Sweden for general repair and calibration. Daily averages of the measured parameters are shown in Figure 1 and Figure 2.

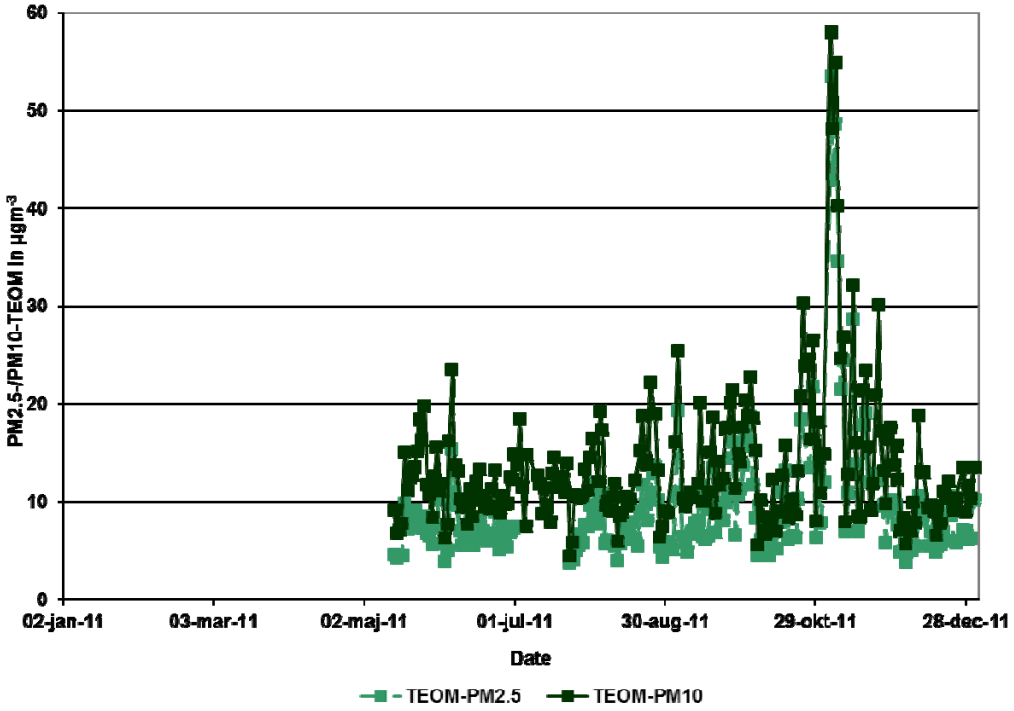

Figure 1: Time series of TEOM-$PM_{2.5}$ and TEOM-PM_{10} daily averages at regional background (RISOE) in 2011.

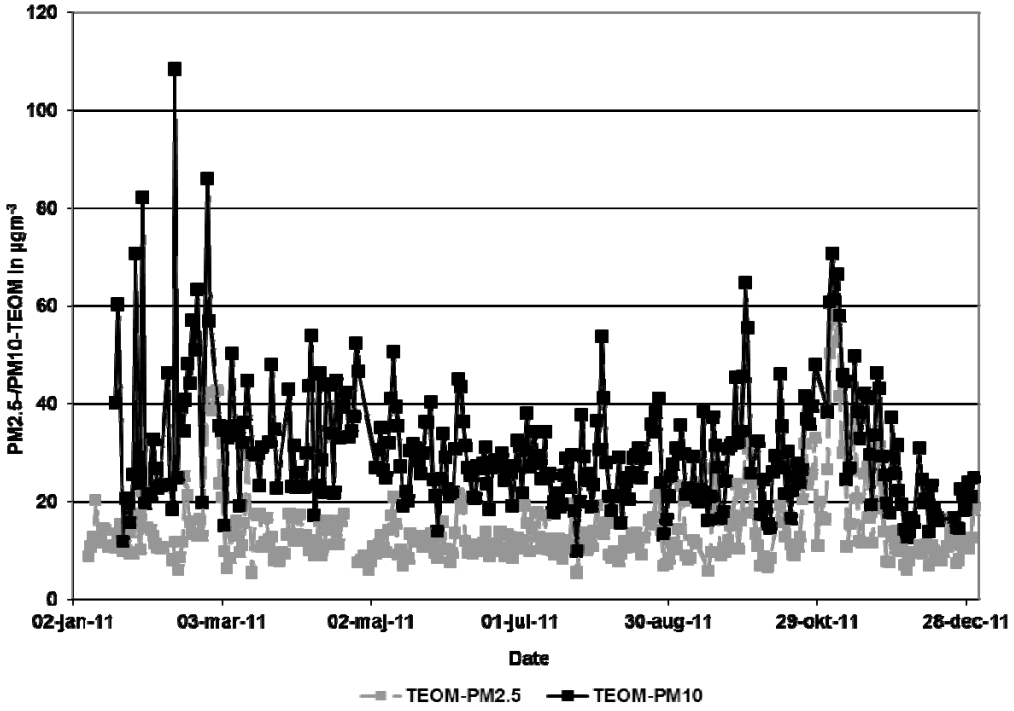

Figure 2: Time series of TEOM-$PM_{2.5}$ and TEOM-PM_{10} daily averages at urban curbside (HCAB) in 2011.

As expected, the mass concentrations of TEOM-PM_{10} at RISOE and HCAB are higher compared to TEOM-$PM_{2.5}$. At RISOE, TEOM-$PM_{2.5}$ and TEOM-PM_{10} is expected to be composed to a very large extent by long-range transported aerosols, which include a significant amount of inorganic nitrate, sulphate and ammonium. For some periods, local agricultural activities may contribute (seasonal variation), but also other regional emissions such secondary organic and inorganic aerosols may contribute to regional background (Massling et al., 2011). TEOM-$PM_{2.5}$ and -PM_{10} averaged 9.4 and 13.5 µg/m^3, respectively, at RISOE in 2011. In comparison, the 2008-2010 average for TEOM-$PM_{2.5}$ was 8.8 µg/m^3 at Lille Valby (LVBY), which was located about 3 km west of RISOE. The station is now closer to Roskilde Fjord and less influenced by the main Road, Frederiksborgvej. Please note that the present rural background at RISOE replaced the previous LVBY in summer 2010. TEOM-PM_{10} measurements were initiated at regional background in 2011.

Long-range transported aerosols as well as exhaust and non-exhaust traffic related emissions influence TEOM-PM2.5 at HCAB. In comparison, TEOM-PM_{10} at the urban curbside station is highly influenced by non-exhaust traffic related emissions from break dust and road dust in addition to road salt during the winter period (Massling et al., 2011). TEOM-$PM_{2.5}$ averaged 14.4 µg/m^3 at HCAB in 2011, which is in accordance with the 2008-2010 average of 12.7 µg/m^3. However, TEOM-PM_{10} increased to 30.7 µg/m^3 in 2011 compared to the 2008-2010 average of 25.7 µg/m^3. A general increase of several µg/m^3 was also observed in the SM200 measurements of $PM_{2.5}$ and PM_{10} at all Danish stations, and is most likely due to long-range transport episodes, which were observed in 2011.

As TEOM instruments were operated at some different parameter settings during 2011 (some of the systems were sent to service in 2010/2011), the uncertainty of the measured values is increased for this year. This predominantly affects the data sampled at the urban curbside station HCAB leading to an estimated uncertainty of 10 – 12 %.

Particle number size distribution measurements

Particle number size distributions were measured with a time resolution of ½ hour at RISOE, HCOE and HCAB using a DMPS system scanning the size regime between 6 and 700 nm. In Table 3 the data coverages are summarized for 2011.

Table 3. Data coverages for the DMPS measurements at rural background (RISOE), urban background (HCØ) and urban curbside (HCAB) in 2011.

	RISOE	HCOE	HCAB
DMPS	53 %	62 %	45 %

Yearly averages of the particle number size distributions at the three measurement stations for 2011 are shown in Figure 3.

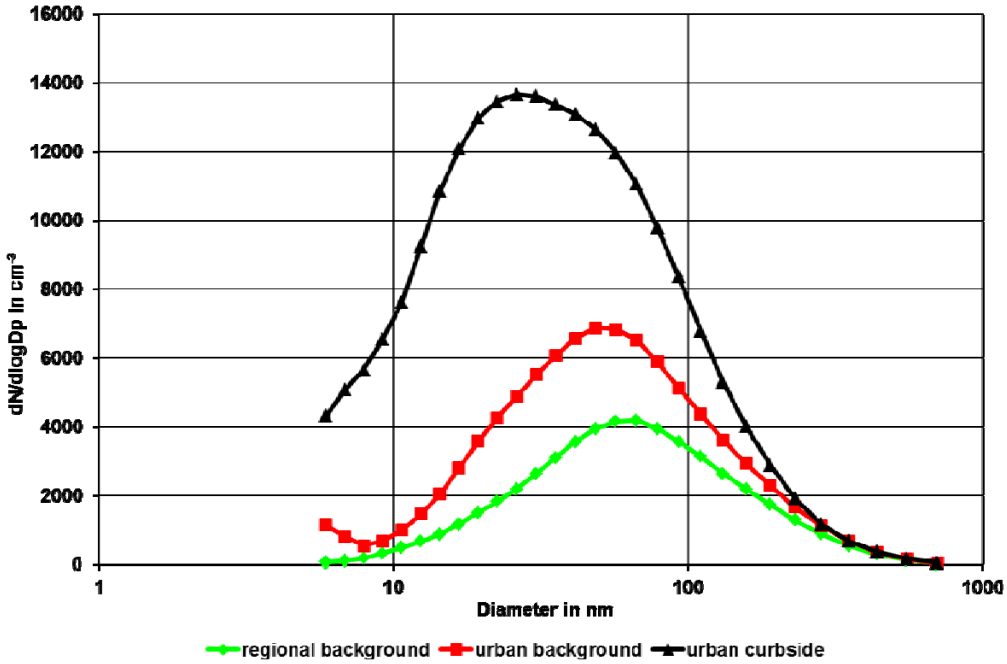

Figure 3: Yearly average particle number size distributions at regional background (RISOE), urban background (HCOE) and urban curbside (HCAB) in 2011.

In general, the total particle number concentrations increases from regional background to urban background and to urban curbside. The yearly average total number concentrations were 3700 cm^{-3}, 6300 cm^{-3}, and 14800 cm^{-3} in 2011 compared to 3800 cm^{-3}, 6800 cm^{-3} and 17000 cm^{-3} in 2010 at RISOE, HCOE, and HCAB, respectively. Hence, the particle number is notably lower in 2011 compared to 2010. However, the data coverage at HCAB was very poor in 2010 (32%), and the data was mostly collected during winter months, when the number concentrations are generally higher because of less turbulence. In 2011, a large fraction of the missing data is from the beginning of the year, which is expected to underestimate the yearly average.

The measured mean diameter of the particle number size distributions is about 50-70 nm at RISOE, 40-60 nm at HCOE, and 20-40 nm at HCAB, respectively. The 20-40 nm particles dominate the urban aerosol nearby busy streets, which is in full agreement with previous findings (Massling et al., 2011).

For a further analysis, the particle number concentrations were determined in specific size regimes, namely particles with diameters of Dp_{F1} = 6–40, Dp_{F2} = 40–110, and Dp_{F3} = 110–700 nm at all three stations. The results are presented in Figure 4.

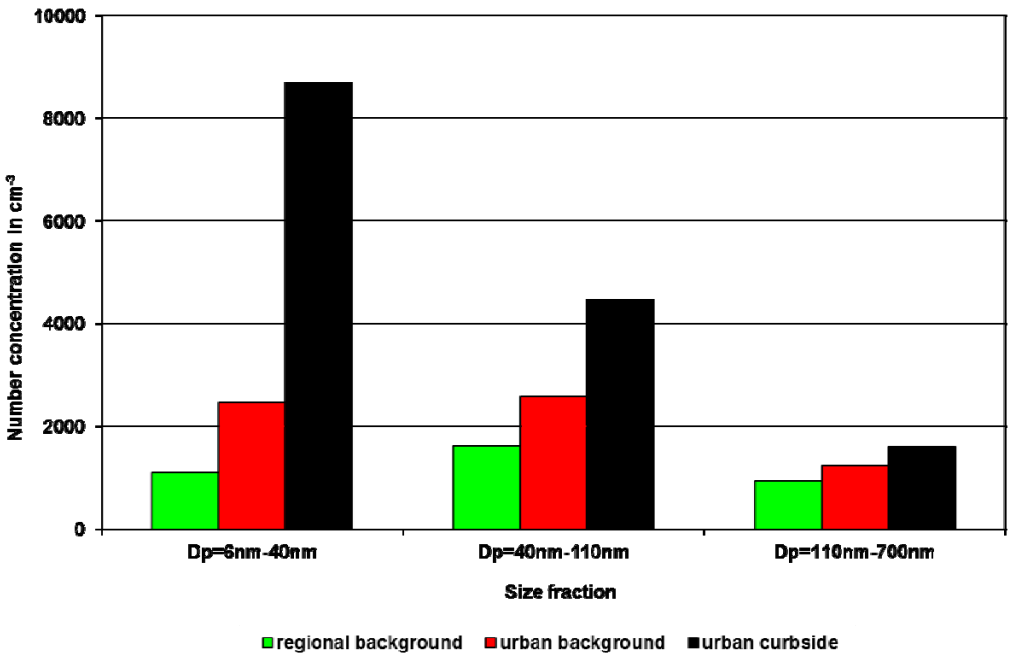

Figure 4: Yearly average particle number concentrations in specific size regimes Dp_{F1} = 6–40 nm, Dp_{F2} = 40–110 nm, and Dp_{F3} = 110–700 nm at regional background (RISOE), urban background (HCOE), and urban curbside (HCAB) in 2011.

In all three size regimes it is shown that particle number concentrations are elevated for the urban curbside compared to urban and regional backgrounds. RISOE represents in most cases long range transported aerosols except some episodes of e.g. intense local wood burning in private households during winter and other local activities as well as transported particles from urban emissions nearby. Number concentrations of Dp_{F1} = 6–40 nm particles are still more than 1400 cm^{-3} higher in the urban background compared to the regional background. The corresponding numbers are 1000 cm^{-3} and 300 cm^{-3} for the Dp_{F2} = 40–110 nm, and Dp_{F3} = 110–700 nm particles, respectively, for this comparison in 2011.

References

Massling, A., Nøjgaard, J. K., Ellermann, T., Ketzel, M., Nordstrøm, C. (2011) Particle project report 2008 – 2010: Particulate contribution from traffic in Copenhagen, NERI Technical Report No. 837, 62 p.

Appendix i: Measured species in the Particle Project 2011-2013

Physical parameters
$PM_{2.5}$, PM_{10}, DMPS (10-700 nm)

Chemical parameters (90+ compounds)
- *Gasses (4)*
NO_X, O_3, CO_2, CO

- *Volatile Organic Compounds (17)*

1-penten	n-pentan	trans-2-penten	isopren
2-methylheptan	n-hexan	benzen	n-heptan
isooctan	toluen	n-octan	ethylbenzen
m,p-xylen	o-xylen	1,2,3-trimethylbenzen	1,3,5-trimethylbenzen
1,2,4-trimethylbenzen			

- *Inorganic ions (8)*
Cl^-, NH_4^+, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}

- *Elements (24)*
Al, Mn, Ga, Pb, Sb, **K ,** Fe, As, **Na,** Ba, **Ca,** Ni, Se, Cd, **Mg**, Ti, Cu, Rb, Mo, **Cl**, V, Zn, Sr, Co, Cr, Mn, Ga, Pb

- *EC/OC analysis (2+)*
EC, OC, and thermal subcategories

- *Sugars (9)*

D-(+)-glucose	D-mannitol	D-arabitol
D-glycerol	D-(+)-trehalose	meso-erythritol
D-sorbitol	adonitol (ribitol)	myo-Inositol

- *Sugar anhydrides and other BB tracers (3)*

levoglucosan	mannosan	vanillic acid

- *PAH (10)*

chrysene	benzo(a)anthracene	dibenz(a,h)anthracene
benzo(ghi)perylene	indenopyrene	benzo(e)pyrene
benzo(a)pyrene	benzo(b+j)fluoranthene	benzo(k)fluoranthene
perylene		

- *Radioactive isotopes(1)*
^{14}C

- *Isoprenoids (3)*

2-methylglyceric acid	2-methylthreitol	2-methylerythritol

- *Monoterpenoids (7) and Sesquiterpenoids (1)*

pinic acid	cis-pinonic acid	3-hydroxyglutaric acid
3-methyl-1,2,3 butane	tricarboxylic acid	3-isopropylglutaric acid
3-(2-hydroxyethyl)-2,2-dimethylcyclobutane	carboxylic acid	3-hydroxy-2,2-dimethyl
glutaric acid	β-caryophyllinic acid	

- *Anthropogenic tracers (1)*
1,2-benzenedicarboxylic acid

Appendix ii: PM and DMPS measurements in 2011

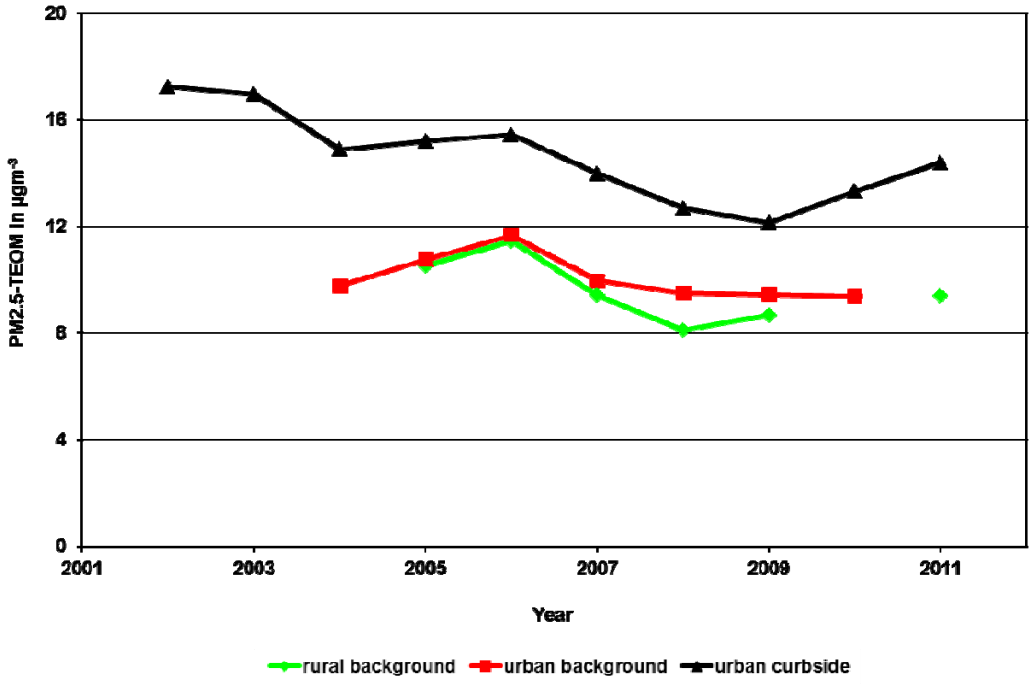

Figure A1: Yearly trend of TEOM-$PM_{2.5}$ at rural background (LVBY/RISOE), urban background (HCOE) and urban curbside (HCAB).

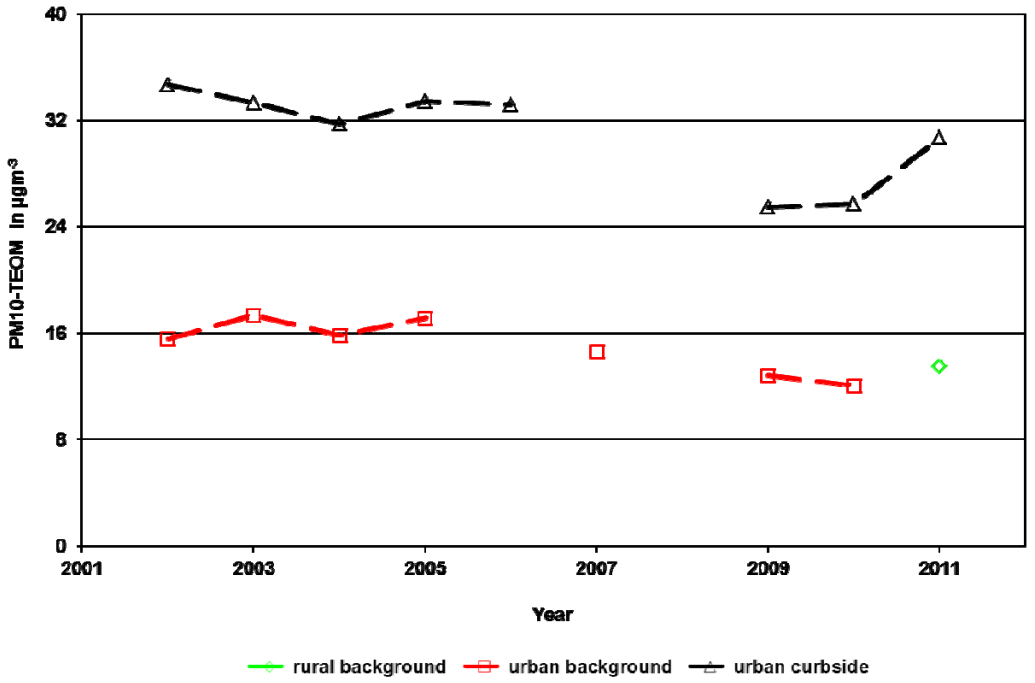

Figure A2: Yearly trend of TEOM-PM_{10} at rural background (LVBY/RISOE), urban background (HCOE) and urban curbside (HCAB).

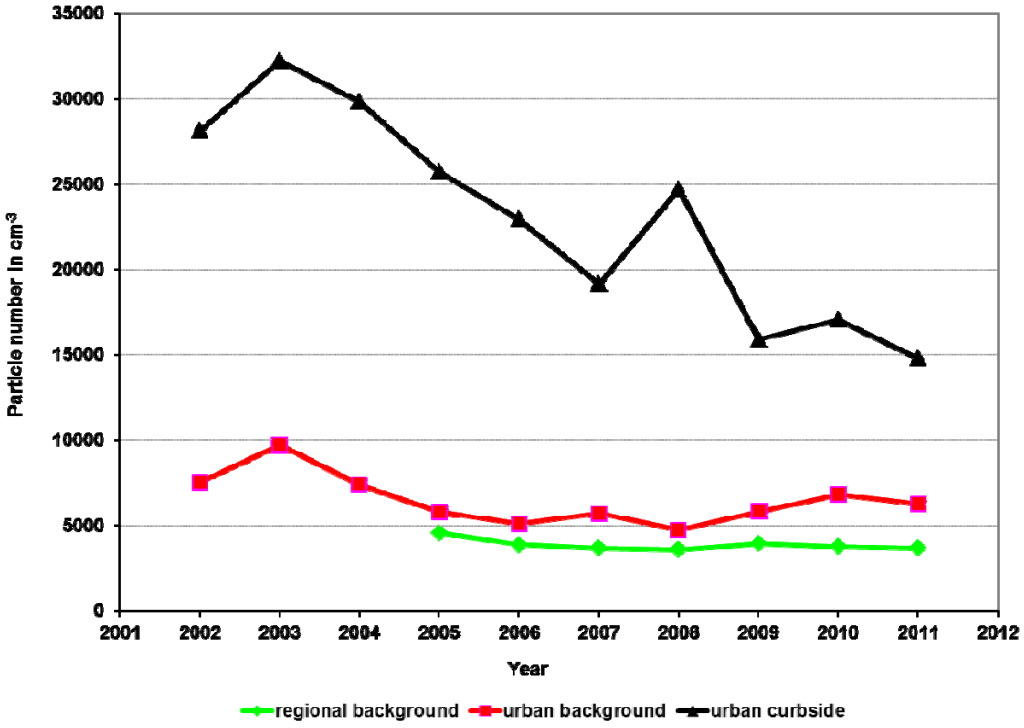

Figure A3: Yearly trend of DMPS particle number concentration at rural background (LVBY/RISOE), urban background (HCOE) and urban curbside (HCAB).