



**Technical report on ACTION 3.2.2:  
COMPARISON STUDY OF PM<sub>2.5</sub> CHEMICAL COMPOSITION  
BY USING MV AND LV SAMPLERS**

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**Introduction**

A study of PM<sub>2.5</sub> mass concentration and chemical composition has been carried out during the preliminary campaign (action 3.2.2) in the framework of the research project “EXPAH” (Population Exposure to PAH). The study was preparatory to the field campaigns to be carried out during the winter of 2011-2012 and the summer of 2012 (action 3.3); it was aimed to obtain a data set of the chemical composition of PM<sub>2.5</sub> samples collected in indoor and outdoor environments by using different sampling devices (low-volume and medium-volume samplers) and to evaluate their performances. In addition, the study was aimed to provide preliminary information about the indoor-outdoor differences of the daily concentration of PM mass, water-soluble inorganic compounds, elements, organic carbon (OC) and elemental carbon (EC).

The study was performed at two different sites, one in the urban area of Rome (the infant school “Don Paolo Albera”), the other one in the peri-urban site of Montelibretti (the Institute of Atmospheric Pollution, CNR-IIA), about 25 km from the centre of the city. At each site indoor and outdoor daily PM samplings were carried out by using medium volume (MV) and low volume (LV) PM<sub>2.5</sub> samplers equipped with Teflon or with quartz fiber filters.

The comparison study was scheduled over two weeks (from 28<sup>th</sup> July to 11<sup>th</sup> August, 2011); the results discussed in this report were obtained during the first week; the second week was addressed to PAH determination.

The sampling strategy was set up in order to provide information about:

- comparison of MV and LV performances in determining EC and OC in outdoor PM samples;
- performance of LV samplers in determining EC and OC in indoor PM samples;
- comparison of indoor and outdoor PM composition.



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In general, the study was aimed to provide information about the reliability of the sampling strategy to be used in future EXPAH field campaigns, in particular about the possibility to perform daily sampling of PM with low-volume devices.

### **Experimental**

#### ***1. Indoor and outdoor sampling: Montelibretti site (ML)***

Sampling time was 24h, starting at 11:00 a.m. of each day (from Thursday 28/7 to Wednesday 3/8). On 30<sup>th</sup> and 31<sup>st</sup>, LV samplings lasted for 48 hours.

The outdoor sampling site was located in the EMEP monitoring station of CNR-IIA, inside the Research Area RM1 in Montelibretti; the indoor sampling was carried out inside a disused laboratory of the CNR-IIA building, at a distance of about 100 meters from the outdoor site.

Outdoor samplings were carried out by using a MV device operating at a flow rate of 38 l/min (SWAM Dual Channel, FAI Instruments, Fonte Nuova - RM) set side-by-side with a LV sampler operating at a flow rate of 6 l/min (Asbesto, TCR TECORA, Corsico – Mi). The dual channel MV was equipped with filters 47 mm in diameter; Teflon membranes were used in one channel (TEFLO Pall Co., USA, 2 µm pore size) and quartz membranes in the other one (PALLFLEX, Pall Co., USA). The LV was equipped with 37 mm quartz filters (PALLFLEX, Pall Co., USA).

Three identical LV samplers (Asbesto, TCR TECORA, Corsico – Mi) were operated indoor; two of them were equipped with quartz filter, the third one with Teflon membranes.

All the devices were equipped with PM<sub>2.5</sub> sampling heads following the requirements of UNI EN 12341:2001.

#### ***2. Indoor and outdoor sampling: Don Bosco site (DB)***

As for the ML site, sampling time was 24h, starting at 11:00 a.m. of each day (from Thursday 28/7 to Wednesday 3/8). On 30<sup>th</sup> and 31<sup>st</sup>, LV samplings lasted for 48 hours.

The sampling was performed at the “Don Paolo Albera” primary school, located in the south-east area of the city. Outdoor samplers were placed at first floor, on the roof above the entrance of the building; this position was the best choice from the point of view of avoiding possible obstructions in the vicinity of the sampler (buildings, trees).

Outdoor samplings were carried out by using two MV samplers operating at a flow rate of 38 l/min (Skypost, TCR TECORA, Corsico – Mi) set side by side with a LV sampler operating at a



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flow rate of 6 l/min (Asbesto, TCR TECORA, Corsico – Mi). Two identical LV samplers (Asbesto, TCR TECORA, Corsico – Mi) were operated indoor; the instruments were sited at the end of a corridor, normally used by the children to enter the classroom, at the same floor of the outdoor site, 20 meters away. Both outdoor and indoor, the pair of instruments was equipped with one Teflon and one membrane filters (47 mm in diameter for outdoor instruments, 37 mm for indoor instruments).

The sampling was carried out during summer vacation and only the personnel of the school was allowed to enter the sampling site.

### 3. *Chemical analysis*

The Teflon membranes used in the comparison study were weighted before and after the sampling; the quartz membranes were pre-fired at 600°C for 6 hours before use.

The Teflon filters were first analysed by energy dispersion X-ray fluorescence (X-Lab 2000, Spectro, Mi) for determining their elemental content (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb). Then they were water extracted in an ultrasonic bath and analysed by means of ion chromatography (ICS-90, Dionex Co., USA); the instrument was equipped with Ionpac AS14 column for anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and Ionpac CS12A column for cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ).

The quartz filters were punched and each punch (1.5 cm<sup>2</sup>) analysed for its EC/OC content by means of a thermal-optical analyser (OCEC Carbon Aerosol Analyser, Sunset Laboratory, OR-U.S.A.). The instrument operates in two phases: during the first step the sample is heated up to 870°C in helium atmosphere (evolution of organic compounds); then, during the second step, after a cooling-off period, it is heated again up to 900°C in oxidant atmosphere (evolution of elemental carbon). Both the evolved organic and elemental compounds are converted from CO<sub>2</sub> to CH<sub>4</sub> and determined by a flame ionization detector. Pyrolytic conversion is taken into account through laser monitoring.

The limits of detection for all the analysed species are reported in Table I.

### 4. *Mass closure*

For a better evaluation of the day-to-day PM variations, we considered the following PM macro-sources: soil, sea-spray, combustion (traffic, domestic heating, industries), inorganic secondary species, organic matter.

PM fraction due to soil (SOIL) was estimated by the following equation, which takes into



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account the main elements that are considered as components of the earth's crust:

$$[\text{SOIL}] = (1.89 [\text{Al}] + 2.14 [\text{Si}] + 1.42 [\text{Fe}] + 1.35 [\text{Na}_{\text{ins}}] + 1.2 [\text{K}_{\text{ins}}] + 1.67 [\text{Mg}_{\text{ins}}] + 1.4 [\text{Ca}_{\text{ins}}] + \text{Mg}_{\text{sol}} + \text{Ca}_{\text{sol}} + \text{CO}_3^{\ominus})$$

Aluminium, silicon and iron were determined by XRF. The insoluble fraction (<sub>ins</sub>) of Na, K, Mg and Ca was calculated as the difference between the XRF determination (total) and the IC determination (soluble fraction only). As we assume that these seven elements are in the form of oxides, their concentration was multiplied by the ratio between the molecular weight of the oxide and the molecular weight of the element. Calcium and magnesium carbonates were calculated as the soluble (<sub>sol</sub>) fractions of Ca and Mg (determined by IC) plus  $\text{CO}_3^{\ominus}$ , which was estimated as:

$$\text{CO}_3^{\ominus} = 2.5 \text{Mg}_{\text{sol}} + 1.5 \text{Ca}_{\text{sol}}$$

Sea-spray (SEA) was estimated by the following equation, which takes into account sodium and chloride and estimates the minor constituents (S, Mg, Ca, K):

$$[\text{SEA}] = ([\text{Na}^+] + [\text{Cl}^-]) * 1.176$$

Combustion sources (COMB) were estimated as the elemental carbon concentration plus an amount of organic matter equivalent to the elemental carbon multiplied by 1.1:

$$[\text{COMB}] = [\text{EC}] + [\text{EC}] * 1.1$$

Organic matter (OM) was estimated as the remaining amount of organic carbon content multiplied by a factor  $\alpha$  that takes into account the non-carbon component of organic molecules; this factor was set to 1.6 for the urban station DB and 1.8 for the peri-urban station of ML:

$$[\text{OM}] = \alpha ([\text{OC}] - 1.1[\text{EC}])$$

Inorganic secondary species (ISS) were estimated as the sum of ammonium, nitrate and non-sea-salt sulphate:

$$[\text{ISS}] = [\text{NH}_4^+] + [\text{NO}_3^-] + n_{\text{SS}}[\text{SO}_4^{\ominus}]$$



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To verify the mass closure, the gravimetric determination of the PM mass was compared with the reconstructed mass (sum of the PM amounts from the five macro-sources).

### **Results**

Figure 1 reports the comparison between the gravimetric determination of PM<sub>2.5</sub> mass at the urban site DB and the sum of the analytical determinations (mass closure), calculated as detailed in the Experimental section. The results are very satisfactory, in spite of the very low concentrations recorded during the period (average value: 13.5 µg/m<sup>3</sup>): the regression analysis between the two series of data shows a Pearson's coefficient better than 0.87, a slope of 1.05 and an intercept of 0.72 µg/m<sup>3</sup>.

These good results allow the calculation of the day-by-day (Figure 2) and average (Figure 3) composition of PM<sub>2.5</sub> during the campaign. The data show that outdoor PM<sub>2.5</sub> is mainly composed of organic matter (40%) and secondary inorganic species (34%) and that a relevant contribution comes from combustion sources (17%). Natural sources (soil and sea-spray) show a lower contribution, as expected for the fine fraction of PM.

The comparison with the average composition at the ML site (Figure 4) shows, as expected, that at the peri-urban site the contribution of the combustion sources (mainly traffic) was lower and that of organic matter was slightly higher.

These results, all obtained by using certified medium-volume samplers, constitute a reliable starting point for the evaluation of the performances of low-volume samplers. Figure 5 shows the comparison of the results obtained when analysing OC and EC sampled outdoor with the LV and the MV, while in Figure 6 we report, for the only site of ML, the comparison of the results obtained when analysing OC and EC sampled indoor with two identical LVs. The data shows a good consistence of the results obtained by two co-located LV samplers (Figure 6) for both OC and EC (the per cent difference between the pairs of values ranges from -2% to +3% for OC and from -18% to +4% for EC, whose concentration is much lower).

When comparing LV and MV (Figure 5), however, a good consistence is obtained only for EC, in spite of its very low concentration. The EC per cent difference between the pairs of values ranges from -4% to +20%, with an average value of +3.1% at BD and from -11% to +7%, with an average value of -1.2% at ML. In the case of OC, instead, the per cent differences are not only higher, but also take always positive values (the data obtained by using LVs are higher than those



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obtained by using MVs). The OC per cent difference between the pairs of values ranges from -1% to +13%, with an average value of +6.7% at BD and from +0.7% to +25%, with an average value of +11.3% at ML. To explain this bad performance of the LVs, we must consider that the sampling of particulate organic species suffers from the artifact due to the retention of organic vapors, which may adsorb on the filter media and on the collected dust. The extent of this artifact is in inverse proportion to the face velocity, which is lower for the LVs than for the MVs (13.3 cm/s against 54.7 cm/s).

Figures 7-11 report the comparison of indoor and outdoor results in the determination of PM mass (Figure 7) and of some selected PM components (Figures 8-11). In Figures 8 and 9 we also report a comparison of the results obtained by different analytical techniques (XRF and IC). The data show that the difference between indoor and outdoor PM<sub>2.5</sub> mass concentration was very small, ranging from 0.3% to 11% at DB (average 0.5%) and from 1.4% to 13.2% at ML (average 4.2%). Small difference between indoor and outdoor values were observed also for sulphate, nitrate and ammonium. As these species have no direct emission sources and are produced by secondary atmospheric reactions, it is not surprising that indoor and outdoor concentration levels are quite similar.

The variable behavior which is shown by the other species (Cl, K, EC and OC) may, in principle, depend both on the day-to-day variability in the relative strength of the sources and on the uncertainty associated to the sampling and analytical steps. For the considered species, these errors are generally not higher than some percents of the measured amount. Moreover, the comparison between XRF and IC analyses of some components allows a direct estimation of an upper limit for the analytical uncertainty (XRF determines the total amount of the elements, while IC determines only the water-soluble fraction). In the case of Cl and K, for example, the difference between XRF and IC determination is much lower than the difference between indoor and outdoor results. Also, it is worth noting that the errors associated to the sampling step would influence at the same extent all the determinations carried out on the same membrane. The great variability which is observed in the indoor/outdoor ratios for the different components during different days indicate that the errors due to the uncertainty in the sampling step cannot be the cause of the observed differences, as well as the uncertainty in the analytical phases. This implies that the analyses highlight a real difference in the indoor-outdoor concentration of the analysed PM components.

As far as EC and OC are concerned, the graphs reported in Figure 11 show that their indoor and outdoor levels are similar, particularly at the ML site: moreover, a variability in the sign of the small differences is observed, making the evaluation of the infiltration coefficient a very difficult



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task. For OC, a further source of uncertainty in the evaluation of the indoor/outdoor ratio when using LVs is constituted by the adsorption of organics, which themselves show a variable distribution between indoor and outdoor environments.

### **Conclusions and suggestions**

The results of the comparison study of PM<sub>2.5</sub> chemical composition lead to the following preliminary conclusions:

- LV samplers seem to exhibit good performances in sampling atmospheric PM as far as mass concentration and inorganic components are concerned;
- a positive artifact in the collection of organics, due to the retention of vapors, makes the use of LV samplers scarcely reliable for OC daily determinations;
- some PM components (e.g.: Cl, K) showed reliable differences in indoor-outdoor concentration, while for other components (e.g.: S, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) the differences were negligible;
- low and variable indoor-outdoor differences were observed also for EC and OC, making the evaluation of the infiltration coefficient a very difficult task.

These results were obtained in conditions of very low PM concentration (13.5 µg/m<sup>3</sup>). It is likely that during the winter campaign the concentration will increase substantially, leading to a substantial increase in the reliability of the results. Anyway, to increase the collected PM amounts and to obtain a further improvement of the quality of the results we suggest:

- to increase the flow rate of the low-volume samplers to 10 l/min;
- to decrease the area of sampling surface of quartz filters when using LVs; for example, by inserting a reduction plate with an open area of about 2 cm<sup>2</sup> inside the filter holder, the linear velocity across the membrane would increase to values of the same order of magnitude as the MVs (about 50 cm/s), strongly reducing the extent of the positive artifact due to organic vapors;
- to increase the sample time from one to five days in case of low PM concentration (e.g. advection meteo condition).



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Table I: Limits of detection (LOD) and limits of quantification (LOQ) expressed in  $\mu\text{g}/\text{m}^3$  for the chemical species analysed during the intercomparison.

	<b>MV</b>		<b>LV</b>	
	<b>LOD</b>	<b>LOQ</b>	<b>LOD</b>	<b>LOQ</b>
<b>Al</b>	0.02	0.07	0.09	0.28
<b>Si</b>	0.02	0.07	0.09	0.28
<b>Fe</b>	0.01	0.01	0.02	0.06
<b>Na</b>	0.02	0.07	0.09	0.28
<b>K</b>	0.01	0.04	0.05	0.14
<b>Mg</b>	0.02	0.07	0.09	0.28
<b>Ca</b>	0.01	0.04	0.05	0.14
<b>Cl<sup>-</sup></b>	0.002	0.006	0.013	0.038
<b>NO<sub>3</sub><sup>-</sup></b>	0.005	0.015	0.031	0.094
<b>SO<sub>4</sub><sup>=</sup></b>	0.010	0.030	0.063	0.19
<b>Na<sup>+</sup></b>	0.002	0.006	0.013	0.038
<b>NH<sub>4</sub><sup>+</sup></b>	0.002	0.006	0.013	0.038
<b>K<sup>+</sup></b>	0.005	0.015	0.031	0.094
<b>Mg<sup>2+</sup></b>	0.005	0.015	0.031	0.094
<b>OC</b>	0.4	1.2	1.6	4.8
<b>EC</b>	0.1	0.3	0.4	1.2



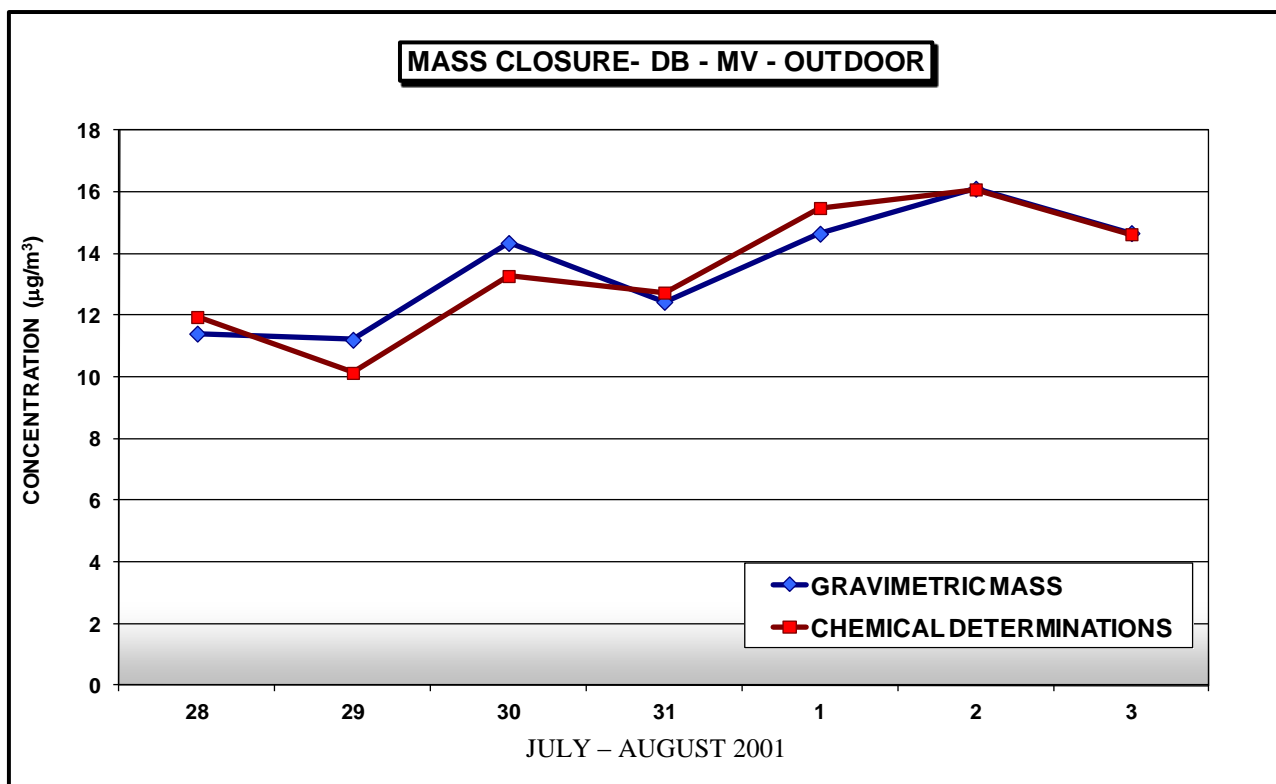
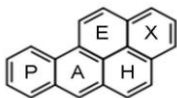


Figure 1: Comparison between gravimetric determinations and reconstructed mass at the DB site.

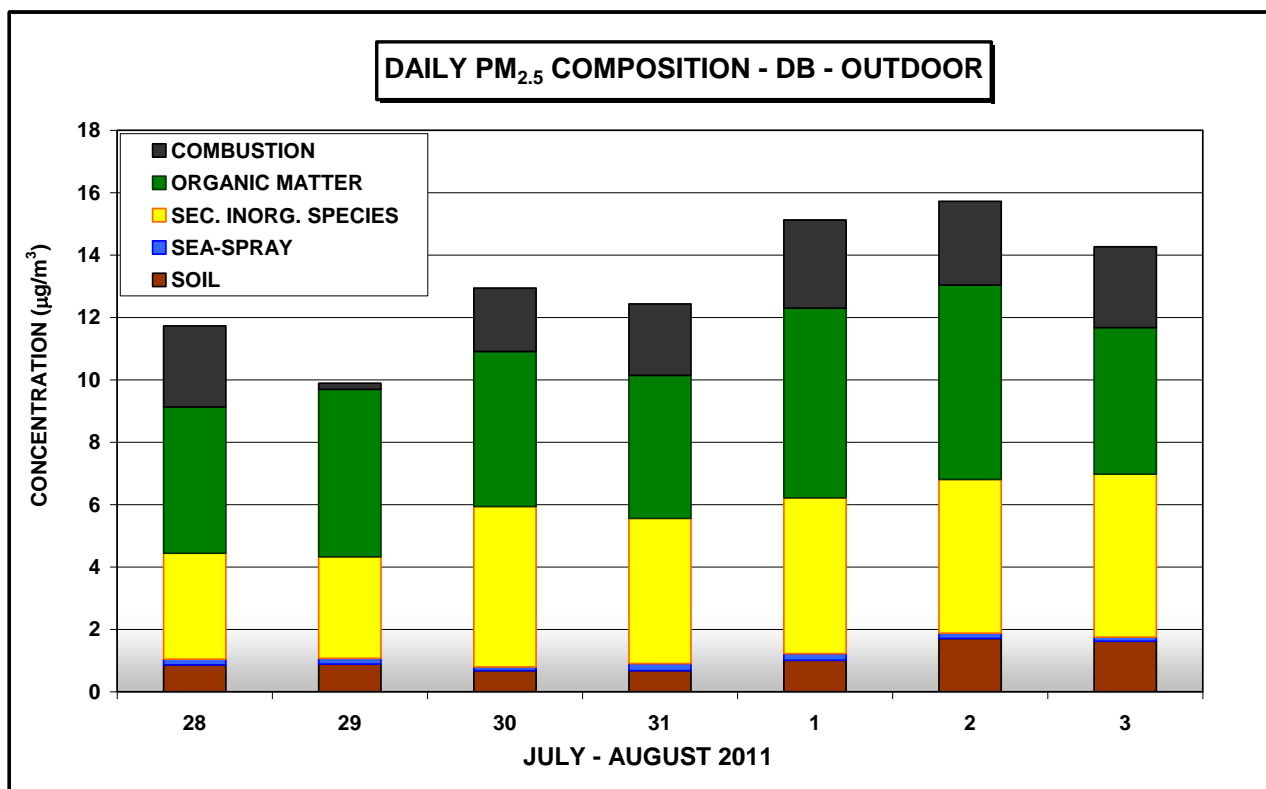


Figure 2: Daily composition of outdoor PM<sub>2.5</sub> at the DB site (MV samplers).

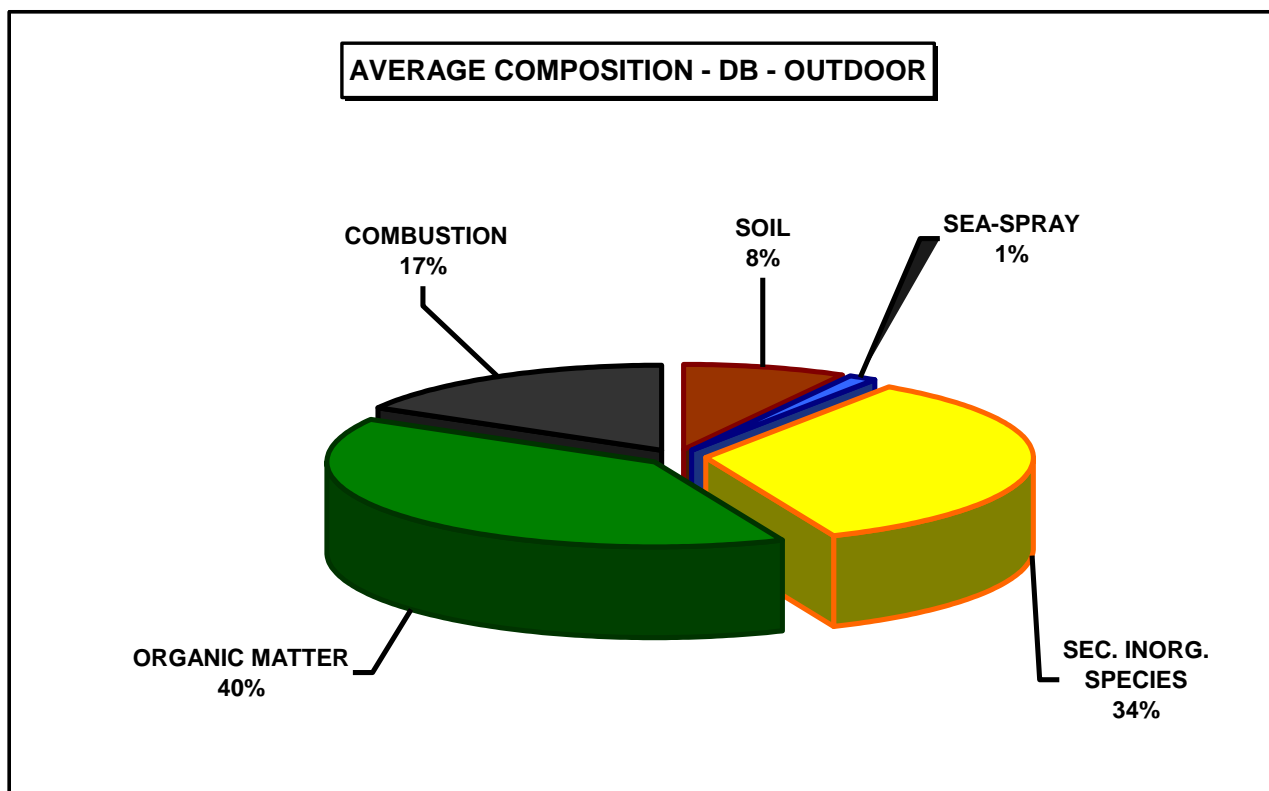


Figure 3: Average composition of outdoor PM<sub>2.5</sub> at the DB site (MV samplers).

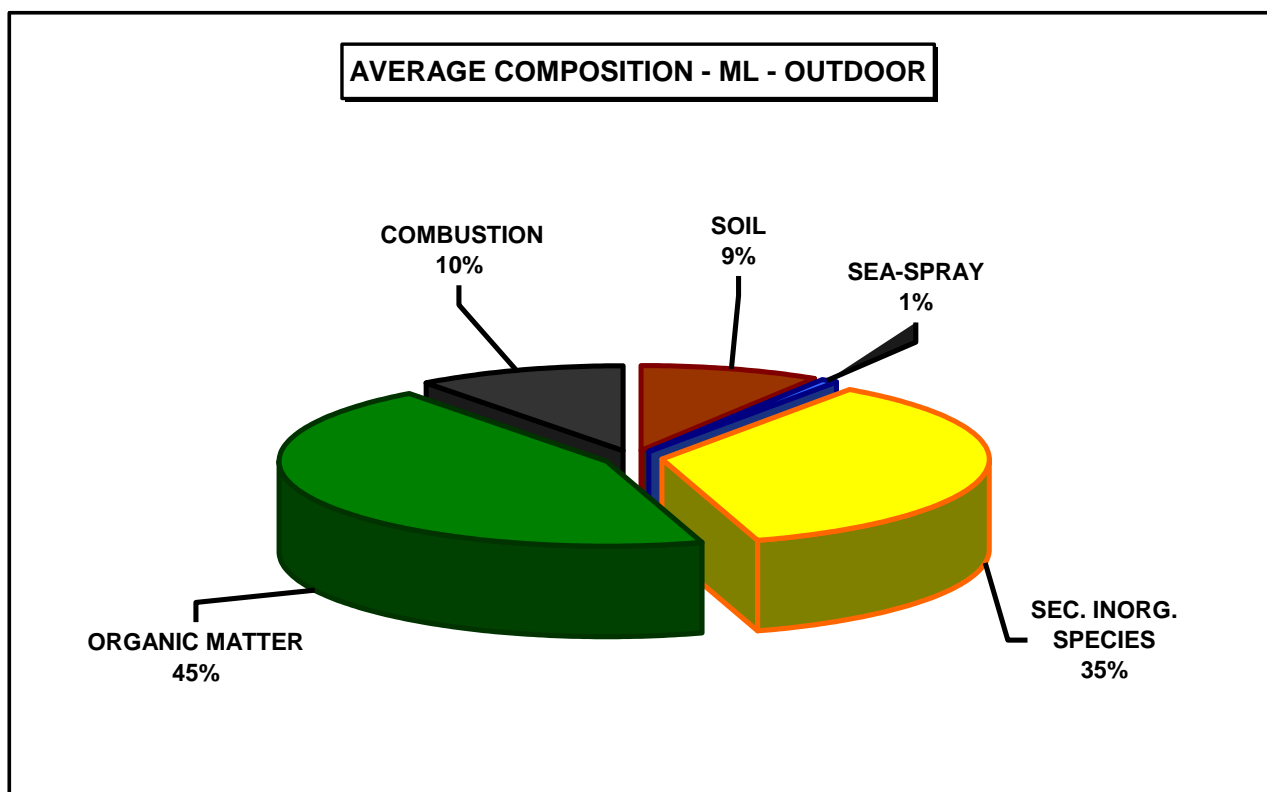
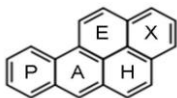


Figure 4: Average composition of outdoor PM<sub>2.5</sub> at the ML site (MV samplers).



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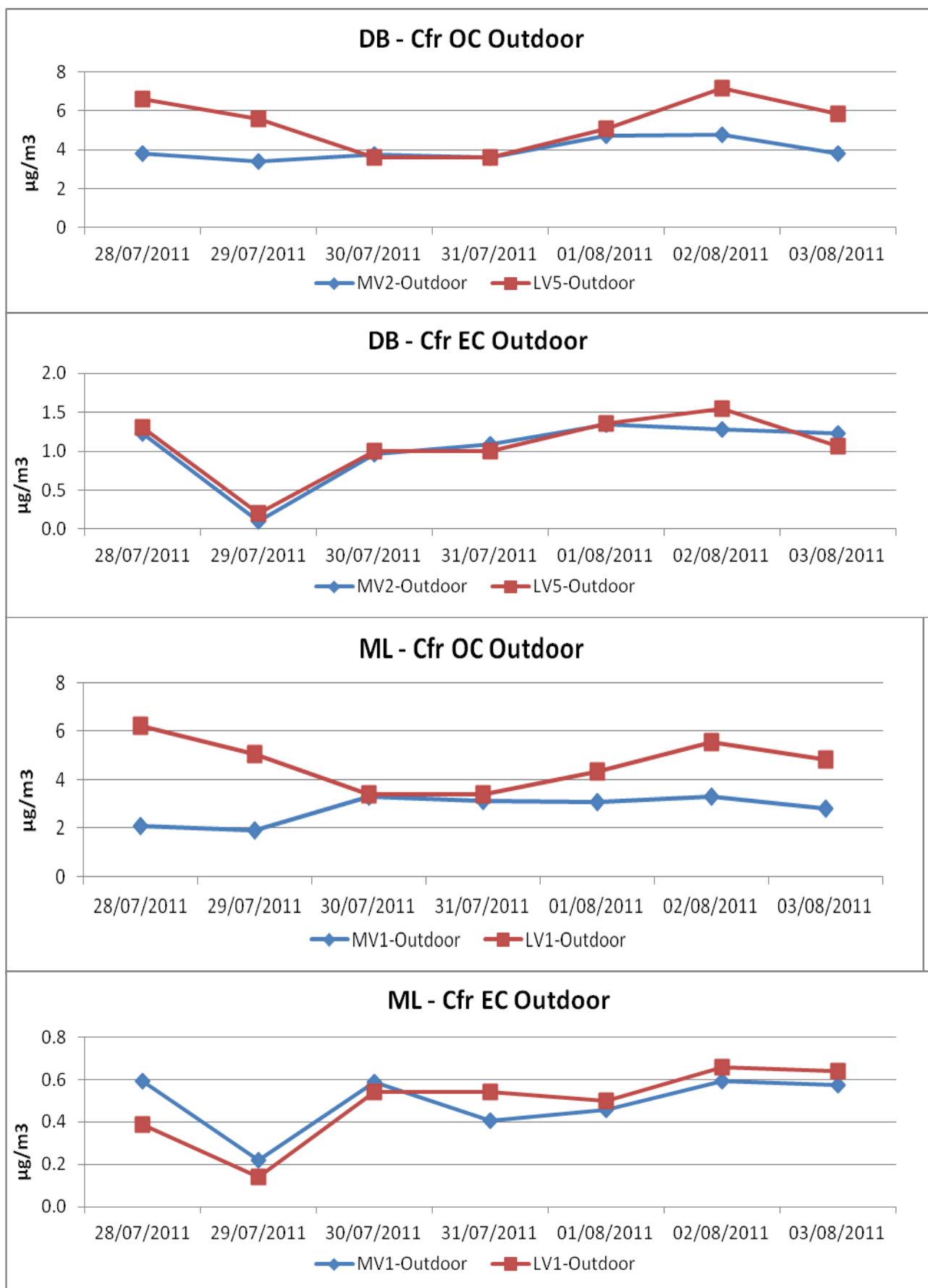
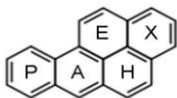


Figure 5: Comparison of MV and LV results in determining OC and EC at the two sites.



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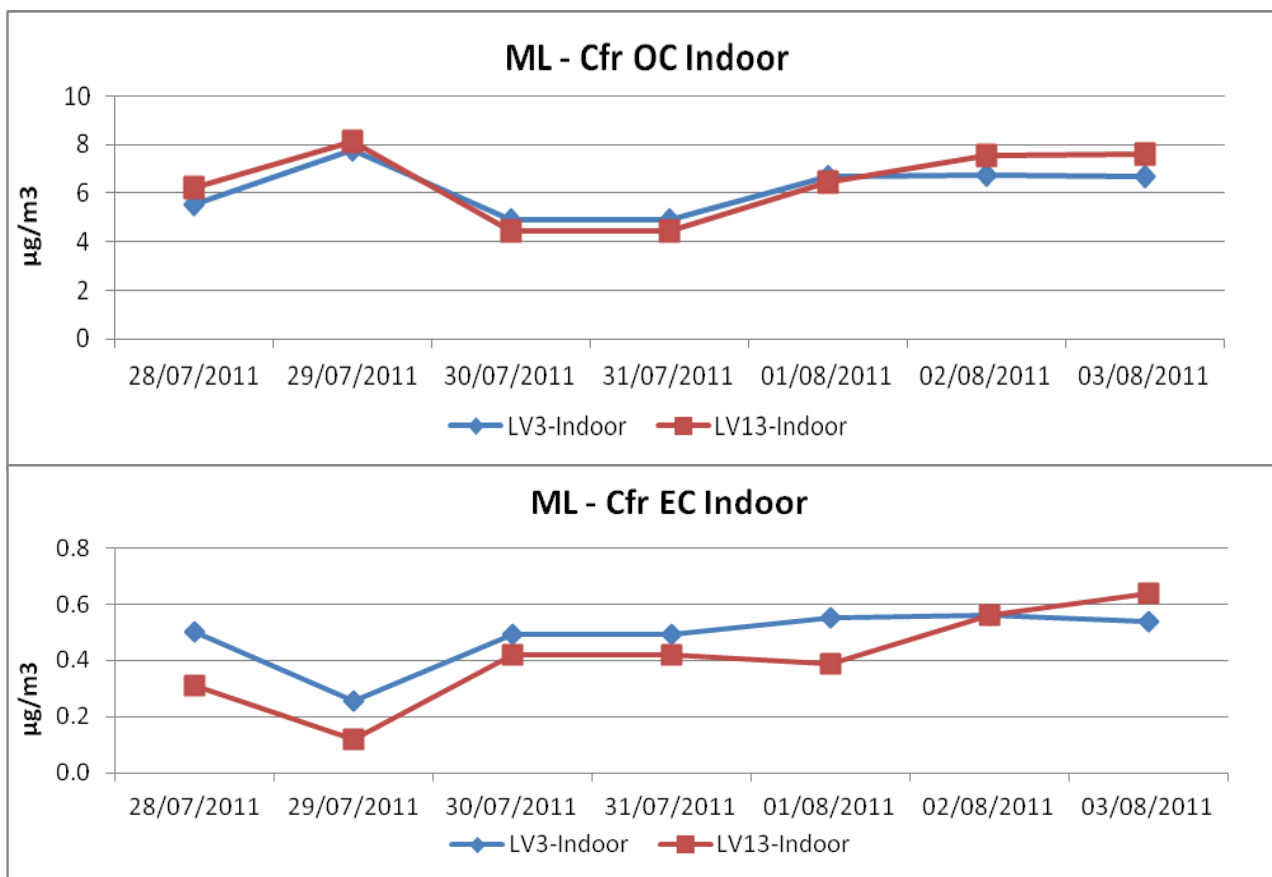


Figure 6: Comparison of two LV samplers in determining OC and EC at the ML site.

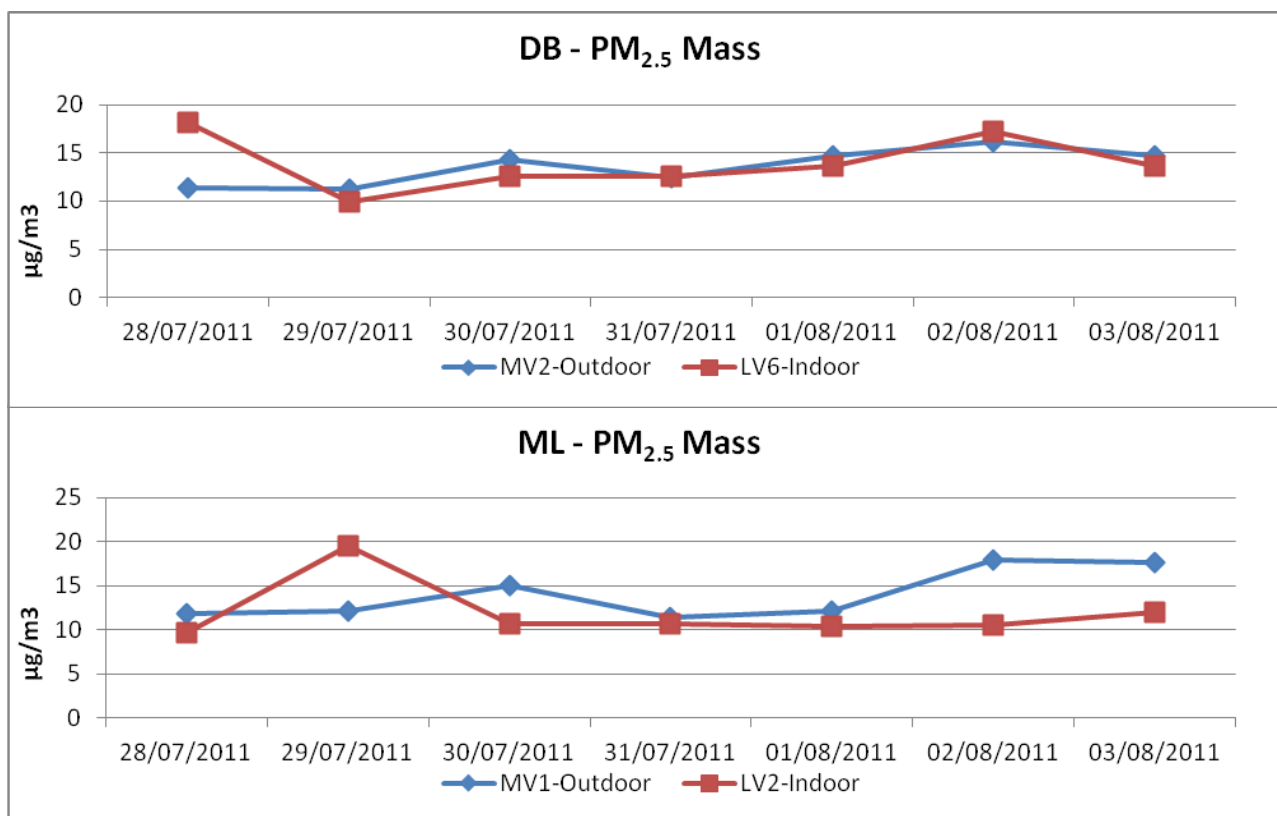
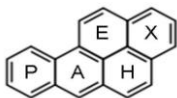


Figure 7: Comparison of MV and LV samplers in determining PM<sub>2.5</sub> mass at the two sites.



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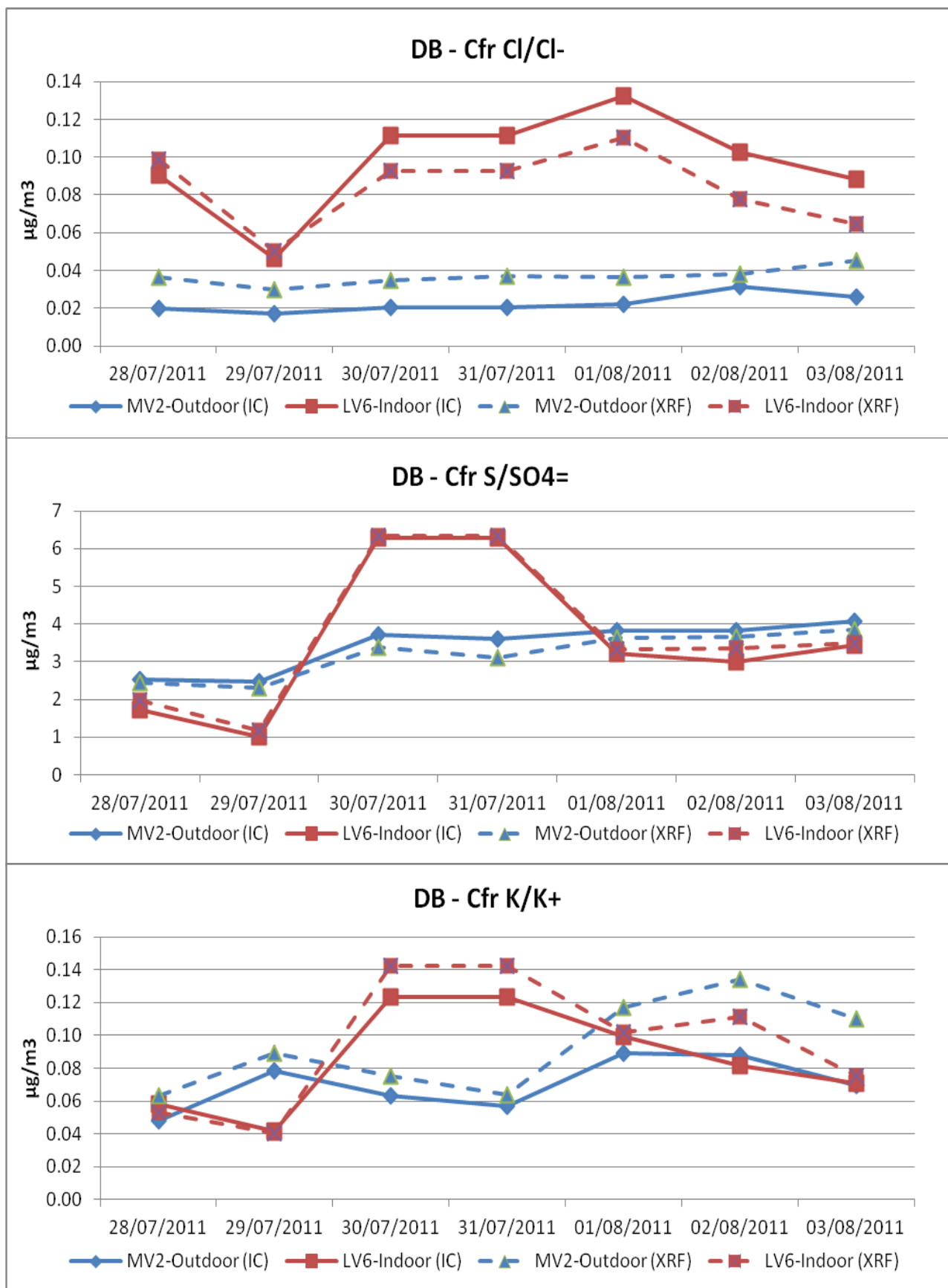


Figure 8: XRF and IC determination of Cl, S, K and Na in PM<sub>2.5</sub> sampled by MV and LV at DB.



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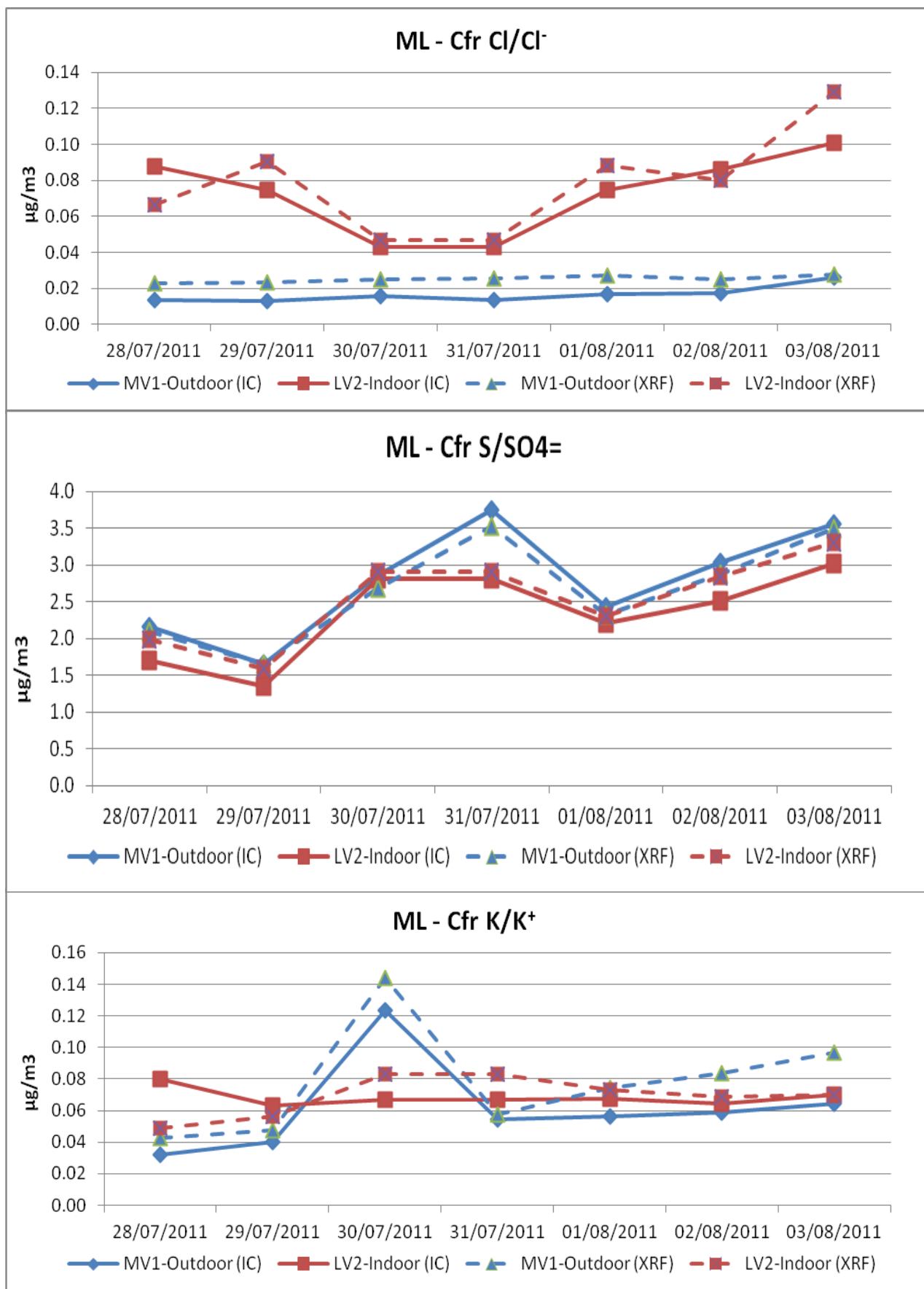


Figure 9: XRF and IC determination of Cl, S, K and Na in PM<sub>2.5</sub> sampled by MV and LV at ML.



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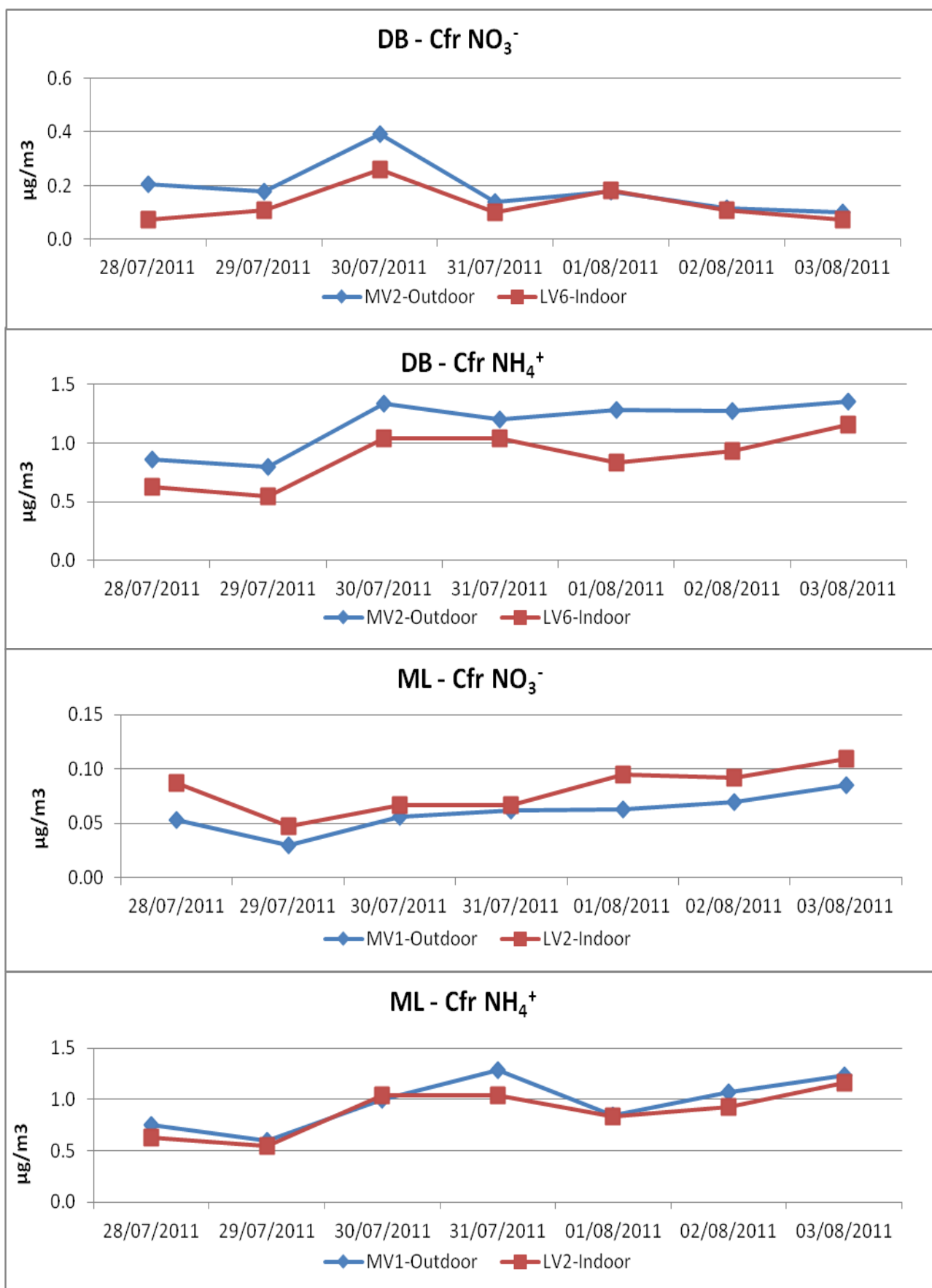
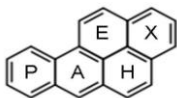


Figure 10: Determination of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  sampled by MV and LV at DB and ML



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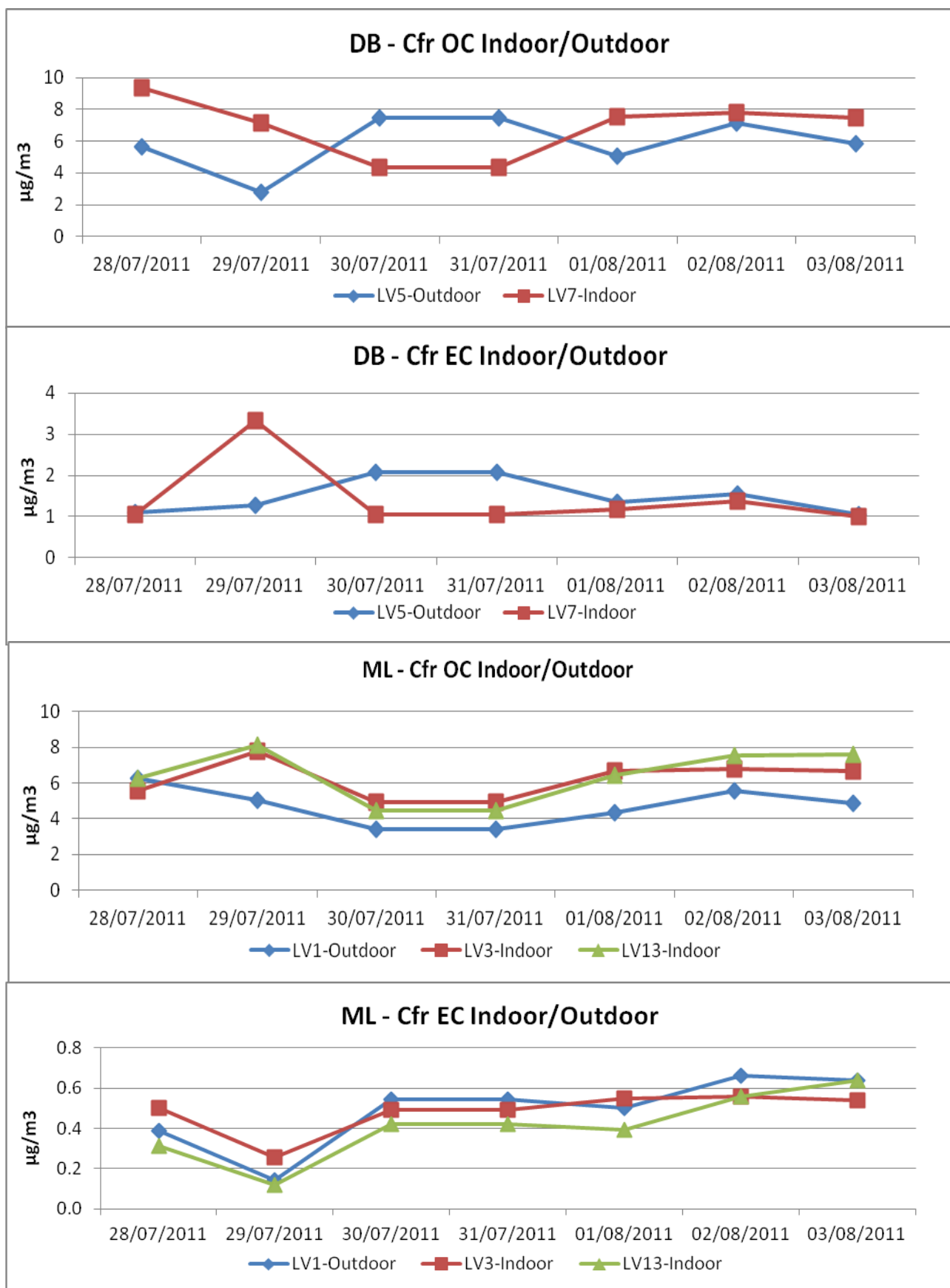


Figure 11: Determination of OC and EC in PM<sub>2.5</sub> sampled by MV and LV at DB and ML.