Presentation
The combination of activities carried out during the preliminary step of EXPAH project allowed to draw a set of recommendations to fulfill in order to obtain reliable results and products from the laboratory tests and in-field experiments.

Collection of PM2.5 from indoor air
The procedure adopted for PAHs monitoring in the frame of EXPAH project is based on the active sampling of airborne particulates. The following instructions/suggestions/remarks have to be considered:

- If at a first look the soot does not appear uniformly distributed over the filter surface, the collection performed has been unreliable since the gas flow through the filter was irregular. That can give rise to marked differences between two samples formally collected in parallel and the not-representativeness of sample.

- When PM$_{2.5}$ are collected indoors, it is mandatory that sampling does not alter the micro-environment (e.g., by remixing air volume or modifying the ambient temperature). On the other hand, the sample amounts collected must be sufficient to perform chemical characterizations. Thus, the best compromise seems that of collecting PM at low-volume conditions (up to ~10 L/min, depending on the room size and shape), and of lasting collection for 24-120h. Lower collection times are allowed only in special sites (e.g., industrial plants, kitchens, chemical laboratories).

- The filtering membranes to be used for collecting PM can be made in quartz or Teflon. Anyway, special care must be paid for: a) the cleanliness of substrate; b) the flow impedance.
  - For the first purpose, quartz filters are baked at 350-400°C, or Teflon filters at 60-70 °C, for 12-16 h, then are stored in a dryer bottle and finally sealed into plastic boxes and wrapped with aluminum foils.
  - As for the flow impedance, the porosity of membranes plays a key role. When PTFE filters are adopted, the choice porosity is 2 µm (lower porosities are allowed for atmospheres poor of humidity).

- A special care must be paid to the (quality of) performances of the PM sampling devices: in particular, the precise volume sampled is mandatory for calculations, while the constancy and accuracy of the aspiration flow is important with regard to the true particle size cut-off of the inlet. Consequently the fine control of aspiration and collection parameters prevents for differences in the PM size cut-off and for uncertainty in the air volume really sampled. Well trained people must conduct each step of the procedure.
PAH characterization in PM.

The procedure adopted for PAHs monitoring in the frame of EXPAH (described in the Technical Report on preliminary activity of the project) is based on the gas chromatography/mass spectrometry instrumental analysis. The following instructions/suggestions/remarks have to be considered:

- Capillary columns are used for the analyte separation, while the MS detection is operated in EI-SIM mode.
- Solvents must be of high-purity grade.
- The use of the internal standard method is mandatory for quantitative assays.
- The concern is focused on the non-volatile PAH congeners recognized as certain, probable or possible carcinogens. They are benz(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene. In addition, the procedure can be applied to evaluate some mutagenic PAHs, namely: chrysene, benzo(e)pyrene and benzo(ghi)perylene.
- The following analytical method parameters have been evaluated: sensitivity; range of linearity (qualitative evaluation); accuracy; precision.
  - The method sensitivity is expressed in terms of the limit of detection (LOD) and the lower limit of quantification (LOQ) defined as three and ten time the standard deviation of the appropriate blank baseline value, respectively. These values are expressed as mass of analyte for each sample (ng/sample).
  - The range of linearity has been evaluated in terms of the “best fit” obtained in the range experimented, because of the low levels of the PAHs of concern in the EXPAH project.
- All the target analytes must be well separated. This usually occurs with silicone gum GC stationary phases, except for benzo(b)fluoranthene, benzo(j)fluoranthene and benzo(k)fluoranthene.
- Often two of the three congeners co-elute (b+j, k; or b, j+k, depending on the phase polarity). Thus, in most cases their content is expressed as the sum of the three congeners. It is worth noting that the detector responses are a bit different for the three isomers, which introduces some uncertainty in their estimate. Whereas the three compounds require to be determined individually, only special dedicated GC phases must be used in instrumental analysis.
- A problem observed sometimes comes out from the GC phase inertness; in fact, molecular fragments negatively influencing the PAH identification and quantification appear as long as the number of analyses run increases and/or traces of air and water reach the column. These fragments contain “silane” group(s) and come out from column degradation and/or from the injector septum. Special care must be spent to cut off air and water traces from the carrier gas.
- The use of PTFE or quartz filters to collect particulate PAHs from air seems irrelevant, when 24h or shorter periods are programmed for individual samplings. Nevertheless, the choice of material is influenced by the need of weighting filters to determine the PM concentration. Special care must be paid to cleanness, which cuts-off the use of glass fiber membranes in the case of quite small equivalent volumes of air sampled and/or of rural sites.

Project modulation/management

The set of stations where PAHs are concurrently measured is increased. By consequence, by modulating the true burden of toxicants across the domain of study, probably the exposition of
population to PAHs and the corresponding health impact can be better estimated. Although the indoor/outdoor concentration ratios change with site and are expected to change also with year time and with congeners (i.e., they differ for the sole BaP and total PAHs), nevertheless the knowledge of PAH burdens and profiles in more than three sites (the minimum required by the project) appears as a suitable improvement of the project. Thus, it is suggested of repeating this “wide scale” investigation to the “regular” campaigns, or at least to portions of the corresponding periods. The knowledge of the “environmental contour” (namely, of concentrations reached by other regulated pollutants like PM, O$_3$ and NO$_2$) is also important to cut off the corresponding impacts on health. Thus, all ambient air data must be collected, whenever available, to discriminate the neat impact of PAHs.

VOCs sampling and analysis
Volatile hydrocarbons, namely benzene, toluene, ethylbenzene, m/p-xylene and o-xylene (BTEX), have been monitored by applying the diffusive sampling approach to enrich them from air, and GC-FID for the instrumental analysis. The following instructions/suggestions/remarks have to be considered:

- The diffusive sampling device must be suitable for the timing of in-field experiment; if the collection period is some hours to a few days, the “radiello-type” is reliable, whilst the “Analyst-type” well runs for timing between 1 to 12 weeks.
- To control the overall quality of measurements, at each site in each run the samplers are displayed in duplicate or triplicate, and are accompanied by a blank device.
- The samplers require to be exposed to air in locations free from close walls, surfaces or obstacles, and facing the ground.
- The transport to/from the sampling sites must be made in glass drying containers, stored in the dark at room temperature (20°C).
- The devices are sealed soon in aluminum cartridges at the end of the VOC sampling and analyzed for VOC within 15 days.
- Using the internal standard method instead of the external standard method, the quality of the analyte quantification results a bit improved. For this purpose, dioxane (dietylendioxide) or chlorobenzene can be used as internal reference compound. Suitable amounts of internal standard must spiked both in the calibration standards of analytes and sample extracts, providing that the reference compound reaches equal concentration (i.e.,1.0 ng/µL) in all solutions.
- The solvent used to extract VOCs must be tested for the contamination by benzene. This is important overall for carbon disulphide.
- If diethylendioxide spiked into the extracting solution is adopted as internal standard compound for analysis, chlorobenzene can be used as “injection control”.
- The calibration curves must be set up just before analyzing the sample extracts, and test runs with pure solvent and standard solutions must be replicated to check for overall method uncertainty. This latter must result better than 12% for all analytes.
- Since BTEX tend to evaporate from CS$_2$ even at low temperature, it is important that standard solutions are freshly prepared and calibration is repeated for each set of samples.
Chemical Composition of PM

The determination of the main PM components requires the simultaneous collection of PM on two membrane filters: quartz filters for the determination of EC/OC by thermo-optical techniques, and Teflon filter for the determination of inorganic species (elements by XRF and ions by ion chromatography). The main problems are encountered when sampling elemental and organic carbon: elemental carbon is generally present at very low concentration, making LV samplers inadequate to reliably determine its daily indoor concentrations, the determination of organic carbon is affected by a positive artifact due to organic vapour retention, the extent of the artifact inversely proportional to the face velocity during the collection phase. The good sensitivity of XRF and IC techniques, joined to the very low blank levels of Teflon membranes, make, instead, daily sampling of inorganic species feasible also when low volumes samplers are used.

On these basis, the following recommendations should be applied to sampling operations in the framework of the EXPAH project.

- Quartz filters preparation must include pre-baking of filters for 6 hours at 600°C and conservation of clean filters in desiccator; this procedure assures the reduction of blank values.
- Teflon filters can be used as such.
- The results of the comparison study of PM$_{2.5}$ chemical composition confirmed that LV samplers operating at a flow rate of 6 l/min on Teflon membranes exhibit acceptable performances in sampling atmospheric PM as far as mass concentration and inorganic components are concerned.
- LV samplers operating at a flow rate of 6 l/min on quartz membranes are scarcely reliable for daily OC determinations as the low face velocity (about 13 cm/s) favours the retention of organic vapours.
- To improve the reliability of daily OC measurements by using LV samplers a reduction plate must be inserted immediately over the filter membrane. The reduction plate has an open area of about 2 cm$^2$, allowing the increase of the face velocity to 50 cm/s, a value that is comparable with the face velocity of MV samplers operating at 2.3 m$^3$/h.
- LV samplers operating at a flow rate of 6 l/min on quartz membranes are scarcely reliable for daily EC determinations particularly when outdoor concentration is expected to be low (e.g.: summer periods or periods of strong advection). In these cases the sampling time for the determination of EC/OC should be increased from one day to two days or even to five days.
- In any case, in order to increase the sampled amount, it is strongly suggested to increase the flow rate of indoor LV samplers to 10 l/min.