**Chapter 3 – Analysis of trace toxic pollutants in the particulate matter.**

### 3.1 Materials and Methods

The monitoring of particulate matter provides a great quantity of measured parameters data. Increasing importance is being given to the presence of organic micropollutants, particularly since some are known to be toxic or carcinogenic. As the number of measured parameters increases and their concentrations decrease proportionally to the minimum portion of particulate matter deposited on filters that could be analyzed, examining the data becomes more difficult. To overcome such difficulties, numerous mass spectrophotometric techniques have been introduced in environmental chemistry, such as GC-MS, LC-MS, LC-MS-MS. The use of these techniques has been applied to the interpretation of the quality of particulate matter, by measuring the concentration of numerous organic micropollutants (Oxy-PAHs, Nitro-PAHs and Bisphenol A), together with the classical pollution parameters (PAHs), in different sites and at different PM fractions.

#### 3.1.1 Sampling and Collecting System

The finality of an analysis of pollutants and a complex environmental matrix is to define the source of pollution and its fate in the environment. In the case of particulate matter this could mean to carry out the analysis of samples of different fractions of particulate matter sites coming from urban, rural and remote site, indoor or outdoor.

This target could be reached only performing in an atmospheric chemistry laboratory equipped for filter handling, conditioning and collecting, in order to create a filters bank.

So, from 2004 different campaigns were managed with low/high volume sampler and multistage impactor systems for this purpose. The final results are a samples archive of more than 8000 filters from which those processed in this study have been chosen.

Following is the main sample type used , in terms of time of sampling, fraction collected and system of treatment.

The high volume quartz fibber filters (GELMAN – A; 8x10 in.) were treated in a mitten oven at 400 °C for two hours, in order to remove the potential impurities present. Then, they were conditioned in a drier and finally weighed. Each filter was weighed with an analytical balance with at most 10 µg of discard. The day and night sampling was carried out for 12, 24 hours or 36 hours. Until the analysis, the filters were kept refrigerated at 4°C in a dark environment, to minimize the photochemical reactions, the loss of volatile compounds and the microbiological activity. At the same time, also camp bed white filters were performed that weren't usedfor sampling, but were treated as blank from beginning to end (conditioning, transport, weighting and maintenance). On these filters the contamination as detection limit (DL) was evaluated

$$DL = X_m + 3\sigma$$

Where $X_m$ = mean of contamination of white filters;

$3\sigma$ = standard deviation.

If $X_m$ is smaller than the particulate matter of black filters, their contamination is negligible.

In the 24 hour day sampling of PM1 and PM2.5 Teflon filters were used (Gelaman Laboratory, Teflon, Ø 47mm, 2 µm, PALL). Teflon is a material that allows a better precision and thoroughness of weighing: it is hydrophobic, not instable

at different humidity values and for the analysis of hydrophobic compounds like PAHs and derivatives, it minimizes the inclusion of gas–phase and other contaminants. These filters were weighted with a Sartorius M5P-000V001 and then preserved at about -20°C until the analysis. Each filter was weighed for three times, before and after the sampling, with at most 10 µg of discard. The average values were directly registered on a database.

If it is considered particulate mass (express in mg) like Mp (mean of black filter Mb minus mean of white filter Mw: Mp = Mb – Mw) could be obtained from concentration of PM in atmosphere (express in $\mu g/m^3$) with the equation:

$C_p = Mp/V_{air}$

Where $V_{air}$ = volume of the sucked up air

The concentration of PM in atmosphere could be expressed in two ways: at the temperature and pressure of sampling or at the standard condition (0 °C; 1 atm): from one way to the other the air volume changes. The conversion factor is expressed by the following equation:

$C_{st} = C_e (T_{st}/T_e) (p_e/p_{st})$

Where
$C_{st}$ = standard concentration in µg/m3
$C_e$ = environmental concentration in µg/m3
$T_{st}$ = standard temperature (273 K)
$T_e$ = environmental temperature (K)
$p_e$ = environmental pressure (atm)
$p_{st}$ = standard pressure (1 atm)

So,

$C_{st} = 273\ C_e (p_e/T_e)$

In this work the data is expressed as $C_e$, because it could directly represent the exposure level (in order to compare different sites, with different atmospheric conditions, it could be expressed in $C_{st}$).
For the PM10, sampling more than one night or day, the filters concentration of 48 hours could be expressed as:

$C_p = M_p/(flow^1 * \text{min I cycle} + flow^2 * \text{min II cycle} + flow^3 * \text{min III cycle})$

Where
$flow^{1-2-3}$ = mean l/min in the first cycle and l/min in the second cycle
min I-II-III cycle = the exact time (in minutes) of sampling.

### 3.1.2 Analysis of PAHs and Oxy-PAHs in the PM10 samples by HPLC-FLD and HPLC-MS.

LC-FLD is a technique that matches a high performance liquid chromatographic system (HPLC) of separation with a fluorimeter detector.

A fluorimeter is used to measure parameters of fluorescence: its intensity and wavelength distribution of emission spectrum after excitation by a certain spectrum of light.

These parameters are used to identify the presence and the amount of specific molecules in a medium. Modern fluorometers are capable of detecting fluorescent molecules, like PAHs, concentrations as low as few µg/l .

LC-MS is a technique that matches a high performance liquid chromatographic system (HPLC) of separation with a mass spectrometry analyzer.

This kind of Detector consists of three basic parts: an atmospheric pressure ion source, a mass analyzer and a detector system.

First in the source chamber the ions from the sample are produced; then the mass analyzer splits ions of different masses; finally the data is collected to generate the mass spectrum.

The ion source in use is an Atmospheric Pressure Chemical Ionization (APCI) chamber: the mobile phase containing eluting analyte, is heated at relatively high temperatures (above 400 degrees Celsius), sprayed with a flow of nitrogen and the entire aerosol cloud is subjected to a corona discharge needle that creates ions: proton transfer reactions and to a small amount fragmentation can occur.

Also, the solvent supports ions to gaseous state conversion.

Typically, APCI is a less "soft" ionization technique than ESI.

The formed positive or negative ions are directional to the analyzer under applied acceleration potentials.

Depending on the solvents, only molecular ions like $[M+H]^+$, $[M+Na]^+$ and $M^{+\cdot}$ (in the case of aromatics), and/or their fragments can be produced. Multiply charged molecules $[M+nH]^{n+}$, as in ESI, are not observed.

A portion of sample was treated with a fast sonication (SONICA Sweep System – 40 KHz and 70 Watt) in a vial of 35 ml with Dichloromethane.

The extract was collected and filtered with a PTFE fibber filter of 0.45 µm and dried up with $N_2$. The dry extract was recovered with 200-250 µl of $CH_3OH$ and analyzed.

The analytical experimental methods of analysis for PAH compounds by HPLC-FLD were one of the subjects of Perrone's PhD thesis [99].

For SIM analysis we must proceed to the construction of calibration fit function. The instrumental conditions are reported:

Column: Vydac C18; 3 µm – 100 Amstrong – 15 cm X 4.6 mm

Flow: 0.25 ml/min

Oven Temperature: 30°C

Injection Volume: 20 µl

Mobile Phase: $CH_3OH/H_2O$ Milliq

Gradient Program:

| Time (min) | Percentage |
|---|---|
| 0.0 | 55-45 |
| 3.0 | 60-40 |
| 15.0 | 70-30 |
| 30.0 | 75-25 |
| 40.0 | 80-20 |
| 50.0 | 95-5 |
| 55.0 | 95-5 |
| 60.0 | 100-0 |
| 65.0 | 100-0 |
| 68.0 | 55-45 |
| 85.0 | 55-45 |

Interface Temperature: 400°C

CDL Temperature: 250°C

Nebulisation Gas Flow (N2): 2.5 ml/min

Heat Block Temperature: 250 °C

SIM Mode: negative

Event Time: 1sec

Detector Voltage: 1.9 KV

Single Ion Monitoring:

| Start Time (min) | End Time (min) | SIM (m/z) | Compound |
|---|---|---|---|
| 5 | 30 | 208, 209 | 9,10-Phenanthraquinone; Anthraquinone |
| 30 | 45 | 282, 283 | 1,6; 3,6; 6,12-Benzo[a]pyrene diones |
| 45 | 60 | 258, 259 | Benzo[a]anthracene-7,12-dione |

The other instrumental parameters agreed with Tune ones.

In the graphs below (fig.51), standard chromatograms with the selected quantification ions are presented.

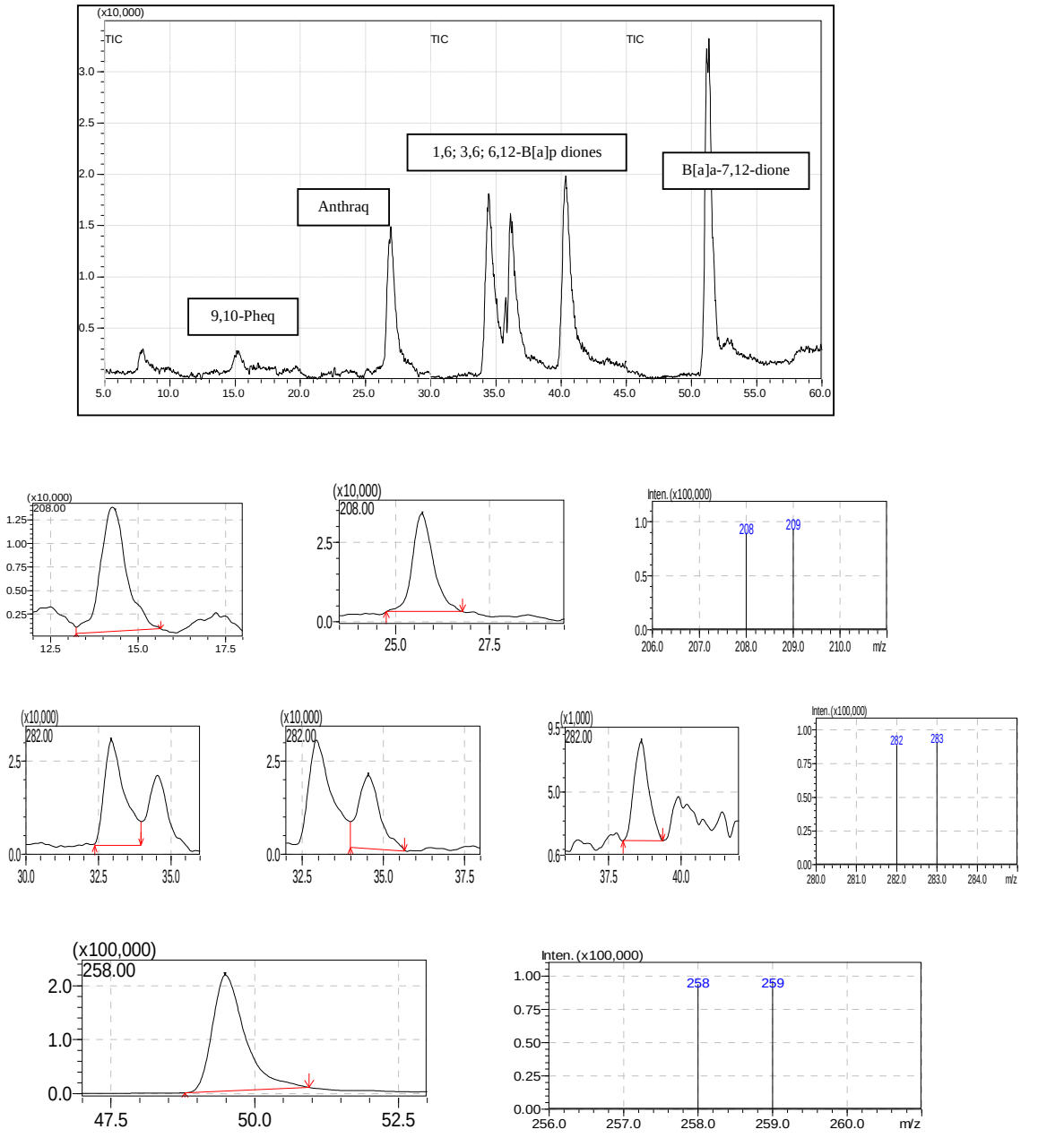



Fig.51 - A standard chromatogram (the total ion current) and the quantification of each Oxy-PAH (9,10-Phenanthraquinone; Anthraquinone; 1,6- Benzo[a]pyrene diones; 3,6- Benzo[a]pyrene diones; 6,12-Benzo[a]pyrene diones and Benzo[a]anthracene-7,12-dione respectively.

In order to evaluate the analytical method and to obtain a well-founded analytical data some recoveries were made. Two rates of a white filter were analysed: one tale qualis; the other previous a dosage of a standard of an Oxy-PAHs mixture at a concentration near the environmental samples. Both rates of filters were then processed as samples.
In the followed table, (tab.27), the obtained data is reproduced.

Tab.27 – Percentage data recovers; mean, maximum, minimum and standard deviation associated.

| Compound | Rec.1 % | Rec. 2 % | Rec. 3 % | Rec. 4 % | Mean % | DS% |
|---|---|---|---|---|---|---|
| 9,10-Phenanthraquinone | 36.0 | 76.2 | 41.1 | 64.0 | 54.3 | 19.0 |
| Anthraquinone | 79.5 | 98.5 | 87.1 | 105.3 | 92.6 | 11.5 |
| 1,6- Benzo[a]pyrene dione | 95.5 | 117.9 | 71.8 | 102.7 | 97.0 | 19.2 |
| 3,6- Benzo[a]pyrene dione | 99.0 | 115.0 | 63.9 | 95.6 | 93.4 | 21.4 |
| 6,12- Benzo[a]pyrene dione | 113.6 | 122.2 | 63.9 | 83.8 | 95.9 | 26.9 |
| Benzo[a]anthracene-7,12-dione | 112.8 | 126.9 | 66.8 | 101.9 | 102.1 | 25.7 |

As shown, for this data, there was a high variability. However, in general the recovery grows with the molecular weight and with the elution time.

For the evaluation of the interferences both the analysis of the white samples and some standard additions to a real black sample were made. In tab.28 the data results of the concentration found with the external calibration and with the standard additions calibration are compared.

Tab.28 - Concentration data for a black sample (Sample 7) in both cases, with a calibration with an external standard and with standard additions.

| Compound | Standard external calibration µg/l | Standard addition calibration µg/l | Standard external calibration ng/m$^3$ | Standard addition calibration ng/m$^3$ |
|---|---|---|---|---|
| **9,10-Phenanthraquinone** | 19.3 | 16.9 | 0.01 | 0.01 |
| **1,6- Benzo[a]pyrene dione** | 128.5 | 82.4 | 0.07 | 0.05 |
| **3,6- Benzo[a]pyrene dione** | 43.0 | 44.3 | 0.02 | 0.03 |
| **6,12- Benzo[a]pyrene dione** | 78.7 | 112.6 | 0.05 | 0.06 |
| **Benzo[a]anthracene-7,12-dione** | 111.1 | 156.0 | 0.06 | 0.09 |

As it could be seen the different data reflected the variability of the analysis and not systematic errors due to the presence of interferences.

Therefore it the external standard calibration for the analysis of samples could be used.

Even the precision was evaluated for the middle standard of the final linear squares fit function. The obtained results agreed with the reference manual UNICHIM 179/0 at the concentration used [100].

### 3.1.3 Analysis of PAHs; Oxy-PAHs and Nitro-PAHs in the PM1 and PM2 Samples by GC-MS.

GC-MS is a technique that matches a gas chromatographic system of separation with a mass spectrometry analyzer. This kind of Detector consists of three basic parts: an ion source, a mass analyzer and a detector system. First in the source chamber the ions from the sample are produced; then the mass analyzer separates ions of different masses; finally the data is collected to generate the mass spectrum. The ion source used is an Electron Impact (EI).

During instrument method development it may be common to first analyze test solutions in full scan mode to determine the retention time and the mass fragment fingerprint before moving to a SIM instrument method.

In our study we had to use both acquisition modes: SCAN to monitori the particulate matter's unknown low molecular weight compounds and SIM to quantify the compound of interest.

A half filter was extracted with a SONICA – Sweep System for ten minutes in a vial of 8 ml with $CH_3CN$. The extract was collected and filtered with a PTFE fibber filter of 0.45 µm and then dried up with $N_2$. The dry extract was recovered with 100-200 µl of Isooctane and analyzed.

After a preliminary screening of the Nitro-PAHs compound of interest by HPLC-MS (with both APCI and ESI ionization mode), the GC-MS system was chosen.

In fact Nitro-PAHs could not be ionized by HPLC-MS, i.e. with soft ionization mode, but only with an electron impact source set at 70 eV. After this first screening the same method was tried, correctly modified, for the analysis of Oxy-PAH. The conditions were good enough for the identification and quantification analysis. The instrumental parameters of the method set are shown: the analysis in the same injection and running of all the compound of interest (PAHs; Oxy-PAHs and Nitro-PAHs) can be allowed for the low concentration of PM1 and PM2.5 samples.

INLET PARAMETERS:

Inlet Heather (°C): 280

Carrier: Helium

Injection mode: Slitless

Inlet pressure (psi): 34,49

Total Flow (ml/min): 23,2

Purge Flow to Split Vent: 30 ml/min; 0.8 min

Gas Saver: 20.0 ml/min; 2 min

Injection Volume (ul): 2 µm

Mode: Constant Flow

COLUMN PARAMETERS:

Pressure (psi): 34,48

Flow (ml/min): 1

Average Velocity (cm/sec): 26

Installed Column DB-XLB; 55,5 m; 250 X 0,25 µm

Thermal Program:

| °C/min | Next°C | Run Time (min) |
|---|---|---|
| | 80 | 1 |
| 40 | 150 | 0 |
| 5 | 300 | 25,92 |
| | **Analysis Length Time** | 58,67 |

SOURCE PARAMETERS:

Solvent Delay: 6 min

EM Voltage: 1659 abs

MS Source: 230 °C

MS Quadrupole: 150 °C

SIM Program (IPONSIM.m method):

| Minute start | Minute end | m/z | NAME | $t_{rit}$ (min) |
|---|---|---|---|---|
| 6,00 | 10,20 | 128 | Naphthalene | 7,39 |
| 10,20 | 13,00 | 152 | Acenaphtilene | 11,58 |
| | | 153 | Acenaphtene | 12,17 |
| 13,00 | 17,00 | 166 | Fluorene | 14,24 |
| | | 173 | **1-Nitro-Naphthalene** | 14,80 |
| 17,00 | 21,00 | 178 | Phenanthrene | 18,52 |
| | | 178 | Anthracene | 18,83 |
| 21,00 | 23,80 | 208 | **Anthraquinone** | 22,84 |
| 23,80 | 30,00 | 202 | Fluoranthene | 24,38 |
| | | 202 | Pyrene | 25,50 |
| 30,00 | 32,25 | 228 | Benzo(a)Anthracene | 31,56 |
| | | 226 | Ciclopenta(c,d)pyrene | 31,62 |
| | | 228 | Chrysene | 31,76 |
| 32,25 | 33,50 | 230 | **Benzanthrone** | 32,62 |
| 33,50 | 35,00 | 258 | **B(a)Anthracene-7,12-dione** | 34,10 |
| | | 247 | **1-Nitro-Pyrene** | 34,53 |
| 35,00 | 49,00 | 252 | Benzo(b)Fluoranthene | 37,49 |
| | | 252 | Benzo(k)Fluoranthene | 37,62 |
| | | 252 | Benzo(e)Pyrene | 39,40 |
| | | 252 | Benzo(a)Pyrene | 39,88 |
| | | 273 | **6-Nitro-Chrysene** | 40,57 |
| 49,00 | 52,50 | 278 | Dibenzo(a,h)Anthracene | 50,65 |
| | | 276 | Indeno(1,2,3-c,d)Pyrene | 50,72 |
| 52,50 | 58,67 | 276 | Benzo(g,h,i)Perylene | 53,95 |

The other instrumental parameters agreed with Tune ones. In the graphs below (fig. 52) a standard Total Ion Chromatograms (TIC) with the quantification ions selected is presented. The quantification was worked on the single ion: in the time window containing more than one ion, each compound was quantified gleaned and integrated the ion of interest.

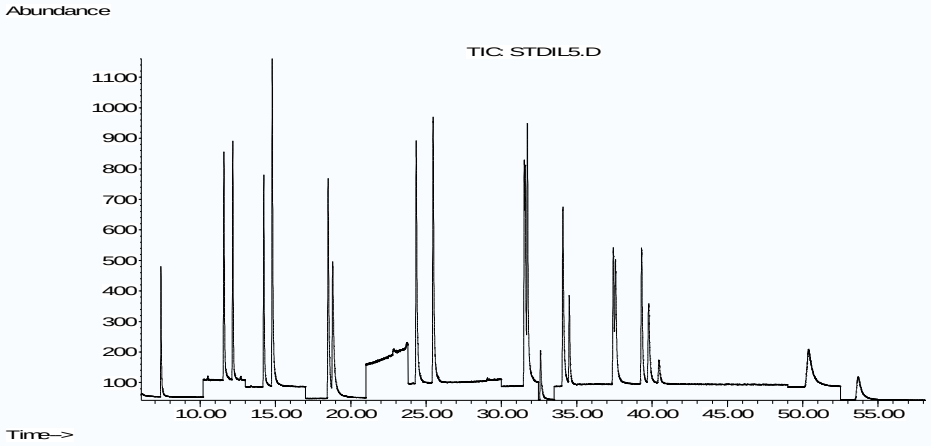


Fig.52- A Total Ion Current of a Mix Standard of PAHs; Oxy-PAHs and Nitro-PAHs.

After the set up of the method, a campaign of intercalibration was conduced between HPLC-FLD and GC-MS for the PAHs compound of an analytical session of black and white samples and SRMs 1649a, [101]. The obtained results had mustered a good correspondence of data.

The recoveries were calculated on the analytical resulting data obtained from the extraction and analysis of three aliquots of analyzed aliquots of SRM 1649a certified reference material for the Polycyclic Aromatic Hydrocarbons. The obtained data is reported in tab.29, as mean recoveries for each compound.

| | **Phe** | **Ant** | **Flnt** | **Py** | **B(a)A** | **Chr** | **B(b)F** | **B(k)F** | **B(a)P** | **D(a,h)A** | **I(123;cd)P** | **B(g,h,i)P** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **%rec** | 79,1 | 86,3 | 70,7 | 80,8 | 92,5 | 115,2 | 105,9 | 84,7 | 83,5 | 145,8 | 56,3 | 53,8 |
| **%rec** | 67,9 | 71,4 | 60,0 | 67,0 | 75,5 | 132,1 | 99,8 | 77,5 | 72,5 | 130,5 | 54,1 | 53,8 |
| **%rec** | 62,8 | 68,6 | 54,9 | 60,3 | 70,0 | 115,1 | 77,1 | 64,3 | 58,9 | 107,7 | 39,4 | 37,6 |
| **mean** | 69,9 | 75,4 | 61,9 | 69,4 | 79,3 | 120,8 | 94,2 | 75,5 | 71,7 | 128,0 | 49,9 | 48,4 |
| **DEV.STD** | 8,3 | 9,5 | 8,1 | 10,5 | 11,8 | 9,8 | 15,2 | 10,4 | 12,3 | 19,2 | 9,2 | 9,3 |

Tab.29 - Percentage of recoveries and their standard deviation for a set of aliquots of the reference material SRM 1649a.

### 3.1.4 Analysis of Bisphenol A by LC-MS-MS system.

Sample analysis was performed by using liquid chromatography/negative ion electrospray ionization – tandem mass spectrometry (HPLC/(-)ESI-MS/MS). An Agilent 1100 series HPLC system (Agilent, Waldbronn, Germany) with a binary pump, vacuum degasser, autosampler, and a thermostated column compartment was used. An API 4000 triple quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX, Toronto, Ontario, Canada) equipped with Turbo V source was used to determine bisphenol A in PM2,5.

Data was collected in negative ion mode by multiple reaction monitoring (MRM) with a 200 ms dwell time /transition. In the MRM acquisition mode the first quadrupole (Q1) and the third quadrupole (Q3), were set at unit resolution (a peak width of 0.7 ± 0.1 amu at 50% of maximum peak height) [102].

Instrumental conditions are reported in table 30, where an alternative ionization technique, atmospheric pressure chemical ionization (APCI), was tested and optimized for the heated nebulizer source, and the results were compared with the turbo ion spray source (ESI). The higher response was obtained with ESI rather than APCI.

Tab.30. Instrumental Conditions and Measurement Parameters for API 4000.

| Parameter | ESI | APCI |
|---|---|---|
| Curtain gas (psi) | 25 | |
| Nebulizer gas (psi) | 30 | |
| Auxiliary gas (psi) | 50 | |
| Source temperature (°C) | 550 | |
| Collision gas (psi) | 4 | |

Tab.31. Transition Monitored and Compound Parameter Collision Energy (CE) and Collision Cell Exit Potential (CXP) Settings for Bisphenol A and Labelled Bisphenol A.

| Compound | Q1 m/z | Q3 m/z |
|---|---|---|
| Bisphenol A | 227 | 211 |
| | | 212 |
| | | 133 |
| Bisphenol A $^{13}$C12 | 239 | 223 |
| | | 224 |
| | | 139 |

CE (the collision energy) and CXP (the collision cell exit potential), were optimized by direct infusion of a 500 ng/ml solution of bisphenol A in methanol into the ion source of the mass spectrometer [102]. A summary of the transitions monitored and the compound parameters CE and CXP is given in tab.31. The transition 227/239 m/z for bisphenol A and 133/139 for the $^{13}$C12 bisphenol A, given in figure 53, were used for the quantification of the sample.

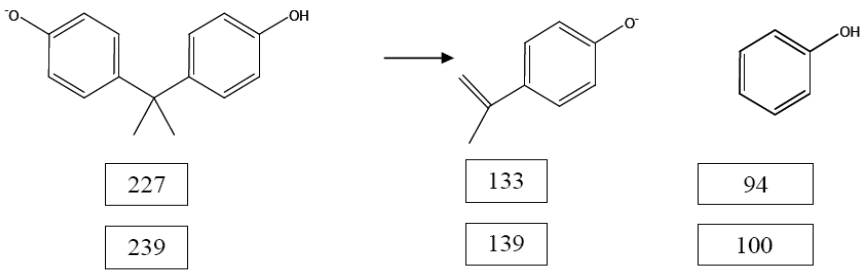



Figure 53. Transition (m/z) used for the quantification of Bisphenol A and Labelled bisphenol A.

For the chromatographic analysis, 50 µl of the sample was injected onto a AQ C18 4 x 3.0 mm security guard cardriges and a C18 Synergy 4 µm Hydro-RP 80 Å 50 x 4.6 mm Column, (Phenomenex, Torrance, CA), gradient elution, given in tab.32, was employed, at 500 µl/min using methanol and water.

Tab.32 - Gradient Elution for Agilent 1100 HPLC System.

| Time (min) | Ultrapure Water (%) | Methanol (%) |
|---|---|---|
| 0 | 50 | 50 |
| 2 | 0 | 100 |
| 7 | 0 | 100 |
| 9 | 50 | 50 |
| 15 | 50 | 50 |

The evaluation for the chromatogram signal of the transitions leading to the choice of the 227/239 m/z for the Bisphenol A and 133/139 m/z for the $^{13}$C12 Bisphenol A as could be seen in fig.54.

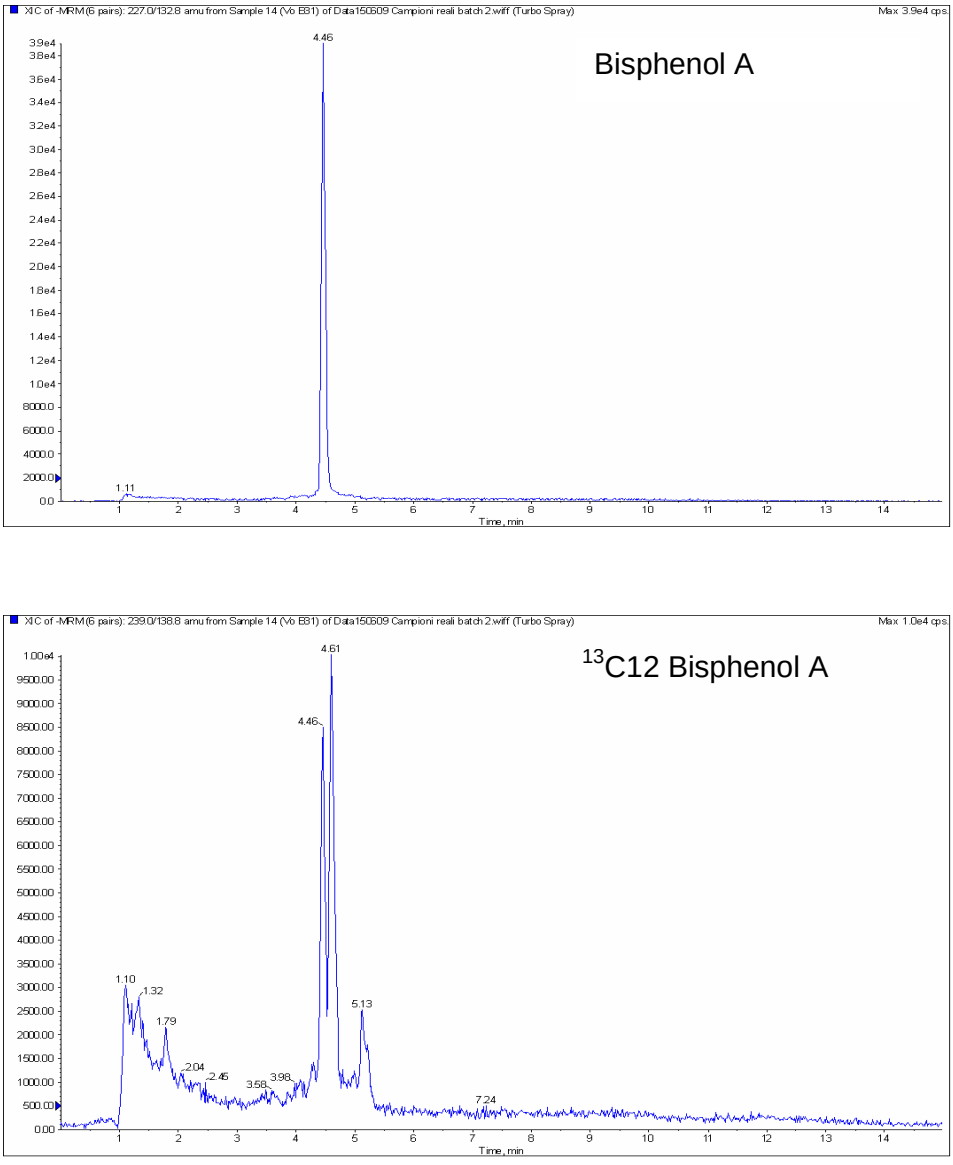



Fig.54 - HPLC/ESI-MS/MS chromatogram of the transition of quantification for bisphenol A (133 m/z) and $^{13}$C12 bisphenol A (139 m/z) respectively in a PM2,5 extract sample.

Procedural blanks were evaluated by analyzing the bisphenol A in white filters (six samples) treated as black ones during the drying up, the weighed step, sampling, collecting and storing of the analysis' steps. The obtained values were used to estimate the Detection Limit (LOD) and the Quantitation Limit (LOQ). The LOD is estimated as the standard deviation of the blank at three-confidence factor ($3SD_b$), and the LOQ at ten-confidence factor (2LOD). TheLOD was equal to 0,7 ng/ml (0,3 ng absolute amount injected). LOQ was equal to 1,4 ng/ml (0,7 ng absolute amount injected), lower than the minimum bisphenol A concentration detected in the particulate matter samples as shown in figure 55. The most recent study about air concentration of BPA reporting data about Detection Limit by GC-MS or LC-MS, showed respectively 20 ng and 10 ng, [78, 80, 103-105].

In this work, the internal standard method has been used for the determination of bisphenol A in PM2,5 PTFE samples. The internal standard method was performed by isotope dilution comparing the native compound peak area with that of

$^{13}$C12-labeled isotopomer. Results were corrected for the instrumental response factor, which was evaluated by analyzing a solution containing BPA at a concentration of 10 pg/ml and $^{13}$C-labeled BPA at 10 pg/ml concentrations in methanol.

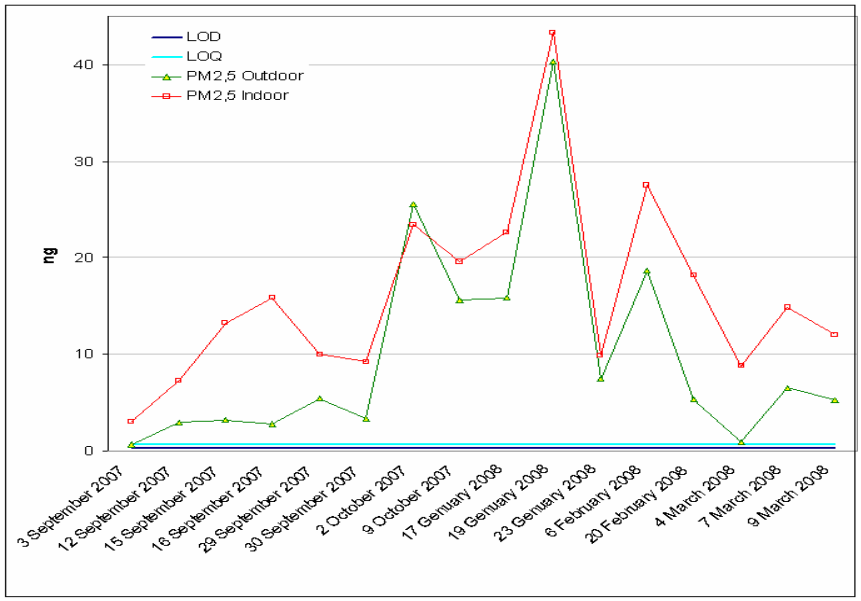
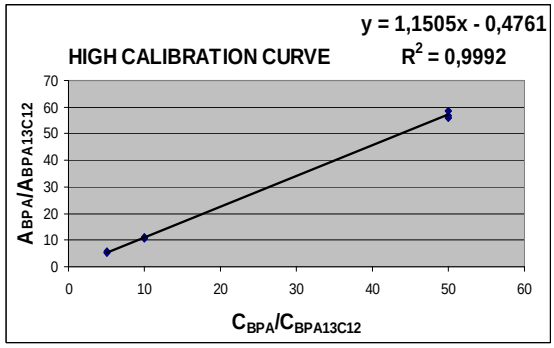



Fig.55 - Trend of absolute mount injected of bisphenol A for Indoor and Outdoor PM2,5 samples, compared with the LOD and LOQ amounts.

An external standard calibration was used to study the linearity range of analytical method. The external standard calibration method was performed using calibration curves obtained by adding different amounts of bisphenol A standard spikes to LC-MS methanol. Each diluted standard was injected 3 times and the correlated Area was considered as a single point. A parent standard solution of BPA in LC-MS methanol (100 µg/ml) was prepared from the BPA reagent and diluted to 1 µg/ml. From this solution, stock standard solutions of BPA in methanol were prepared with concentration of 0,1-0,5-1,0-5,0 ng/ml and 10-50-100-500 ng/ml. Each stock solution was 0,1 µg/ml (from the parent 100 ng/ml) $^{13}$C12 BPA concentrated. Each range of standard concentration was well correlated as the equations showed, but with a different linearity (Figure 56).

An estimation of the LC-MS/MS instrumental method repeatability was obtained from six measurements of a Response Factor, analyzed three times each, at the concentration of 10 ng/ml both of bisphenol A and $^{13}$C12 bisphenol A.

The relative standard deviation was 4,5%. While the relative standard deviation for the entire analytical method, was estimated processing five blank filter additioned of 10 ng (final concentration of 50 ng/ml) of bisphenol A, treated and extracted as samples and additioned of 10 ng of the labelled standard (final concentration of 50 ng/ml), before the injection. The average of recovery of bisphenol A on four spiked blank samples was 86% and the relative standard deviation associated is 6,5%. To estimate the accuracy of the method, a recovery test was carried out on five blank filters by adding standard spikes of a 10 ng bisphenol A and 10 ng $^{13}$C12 bisphenol A and then treated and extracted as samples. In this case the associate error was the 4,3%. Both, the method repeatability and accuracy were evaluated after the subtraction of the blank signal (five filters added only of native standard and processed as the samples).



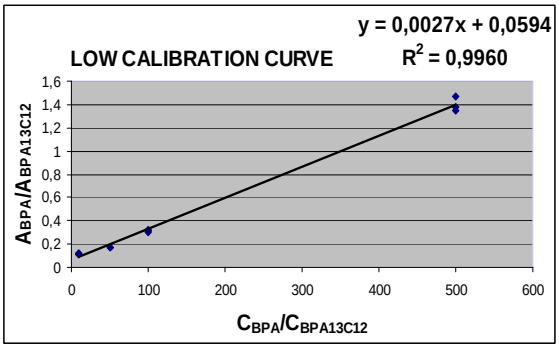




Fig.56 - The two different ranges of linearity for the quantitation of bisphenol A in the particulate matter, by LC-MS/MS. The lowest calibration curve ranged from 0,1 to 5 ng/ml and the highest calibration curve ranged from 10 to 500 ng/ml.

### 3.2 Analysis Results

The presence of organic micropollutants in the Particulate Matter has been investigated and the results were interpreted from an environmental point of view. A deeper insight into the interpretation of the results was achieved by the extension of this analysis of the same samples including general PM quality analytical parameters such as Polyciclic Aromatic Hydrocarbons, Ozone, Temperature, Solar Radiation and Rain. The PMx samples Indoor/Outdoor, Nightly and Daily, Winter and Summer, Remote, Urban and Rural allowed the exploration of the main pollution sources as well as the characterization of their geographical and temporal distribution.

#### 3.2.1 Oxy-PAHS in the PM10 samples.

The Appendix 1 – tab.2-5 presented the obtained data of PAHs and Oxy-PAHs for some summer night and day time analyzed PM10 samples. The concentration values in ng/m$^3$ are indicated and their correlation with the particulate matter total mass expressed in ng/mg. As an example, in fig.57 a chromatogram of an analyzed PM10 sample is presented.

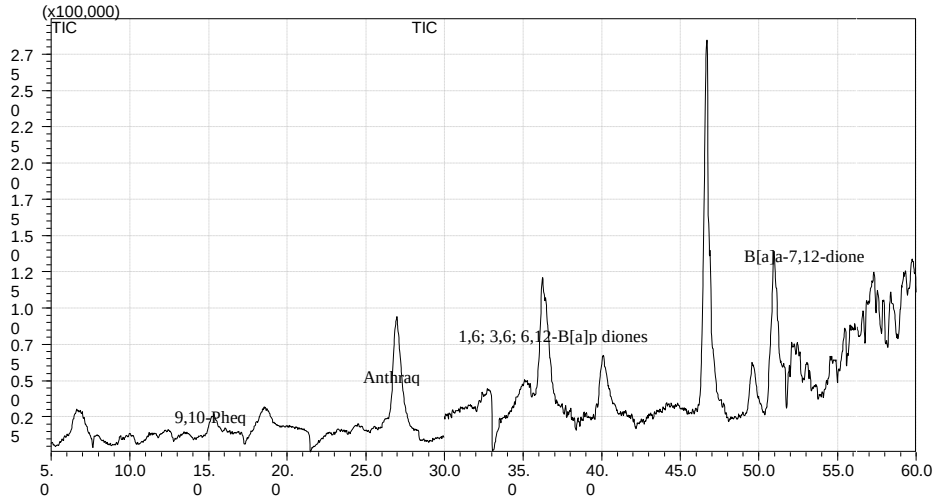


Fig. 57- A total ion current of a sample chromatogram.

From the obtained data of PAHs a graph can be drawn (fig.58) for the correlation of night and day concentration as sum of each single compound. The punctual correlation doesn't have a pronounced trend, but the relative's sum of day and night samples shows a major concentration of these compounds in the daily hours as it could be expected as a consequence of the photoxidation process.

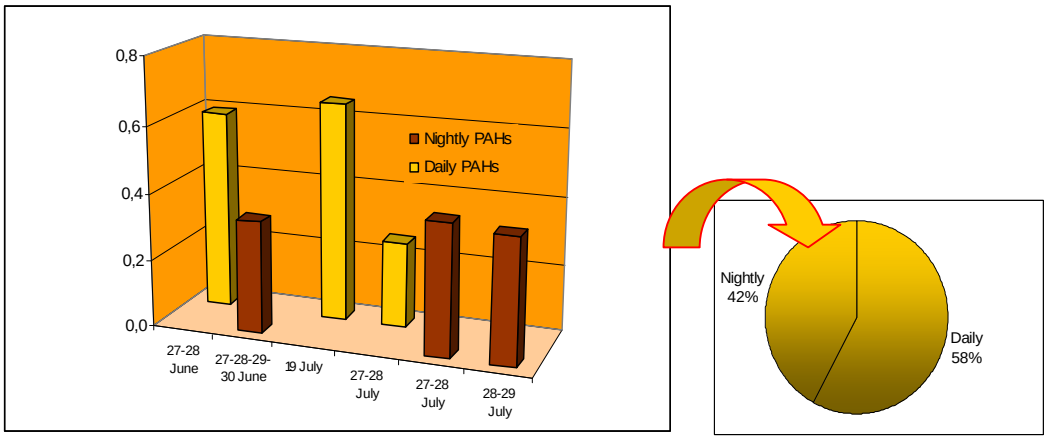



Fig.58 - Daily and Nightly concentration of ΣPAHs, differed for dates, expressed in ng/m$^3$, and the pie chart of the sum of daily and nightly analyzed samples for PAHs.

For a better understanding of the general trend the average results of each analyzed PAH compound it could be correlated. In fig.59 the trends of each compound are presented and differed by daily and nightly results. A good correlation above all can be shown for the compounds with an higher Molecular Weigh, together with their Boiling Point: the Indeno[1,2,3-c,d]perylene; Benzo[a]pyrene and Benzo[k]fluoranthene is directly emitted like Particulate Matter.

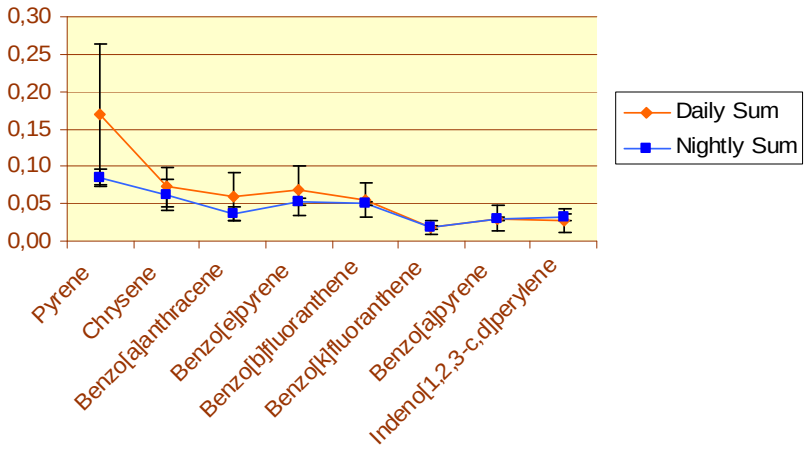



Fig. 59 - PAHs' sum concentration trend differed by compound and daily and nightly samples.

Considering the data elaborations of Oxy-PAHs partial sum (fig.60) parted by low Molecular Weigh Oxy-PAHs and high Molecular Weigh Oxy-PAHs: the Oxy-PAHs' compounds, 9,10-Phenanthraquinone and Anthraquinone, are more concentrated in the PM compared to the Benzo(A)pyrene-Diones and Benzo(a)Anthracene-7,12-Dione. These results will be rethought after the presentation of radiation and ozone data.

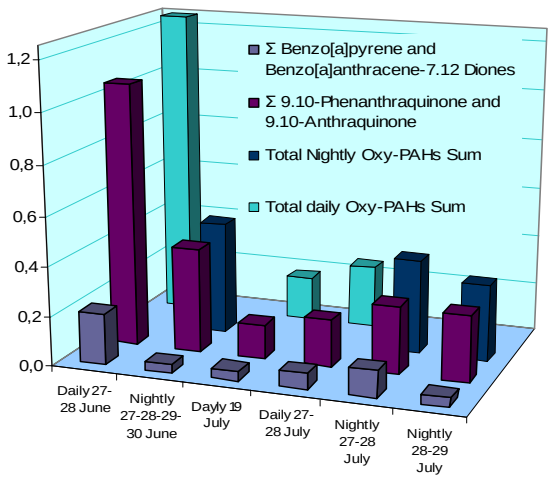



Fig.60 - Correlation of Oxy-PAHs partial sum.

The sum for the total samples of Benzo[a]pyrene-Diones and Benzo[a]pyrene, fig.61, shows a presence of about 60% of Diones versus 40% of PAHs. This result leaded to the hypothesis of a photochemical activity in the atmosphere in the summer time.

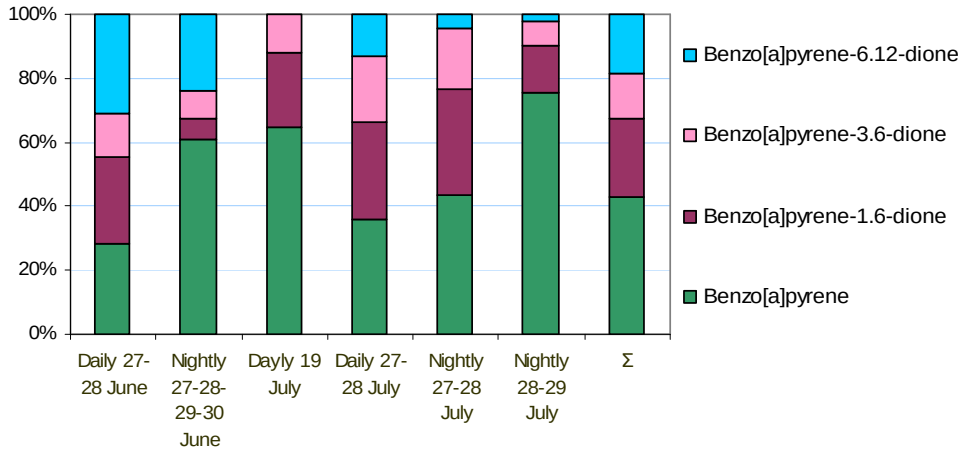



Fig.61 - Percentage comparison of Benzo[a]pyrene-Diones and Benzo[a]pyrene for each extracted and analyzed sample and final result percentage for the indicated compound.

For the evaluation of the photoxidation of PAHs by ozone, in Appendix 1 – tab.6, the ozone data for the considered days of sampling are reported. The ozone is expressed in $\mu g/m^3$, and it could be compared with the net radiation (expressed in $W/m^2$) for the same days. In order to present a reliable correlation, , the particulate matter masses are reported on the same table, expressed in $\mu g/m^3$, for the same days. The Italian D.Lvo 183/04 explains how the Attention Level for Ozone is set at 180 $\mu g/m^3$, and the Alarm Level at 240 $\mu g/m^3$. For the considered days the $O_3$ concentration is quite low and was under the Attention Level, [106].

The obtained results for the net radiation, ozone and particulate matter, are fitted with the data of Oxy-PAHs, like a single compound and partial or total sums (fig.62).

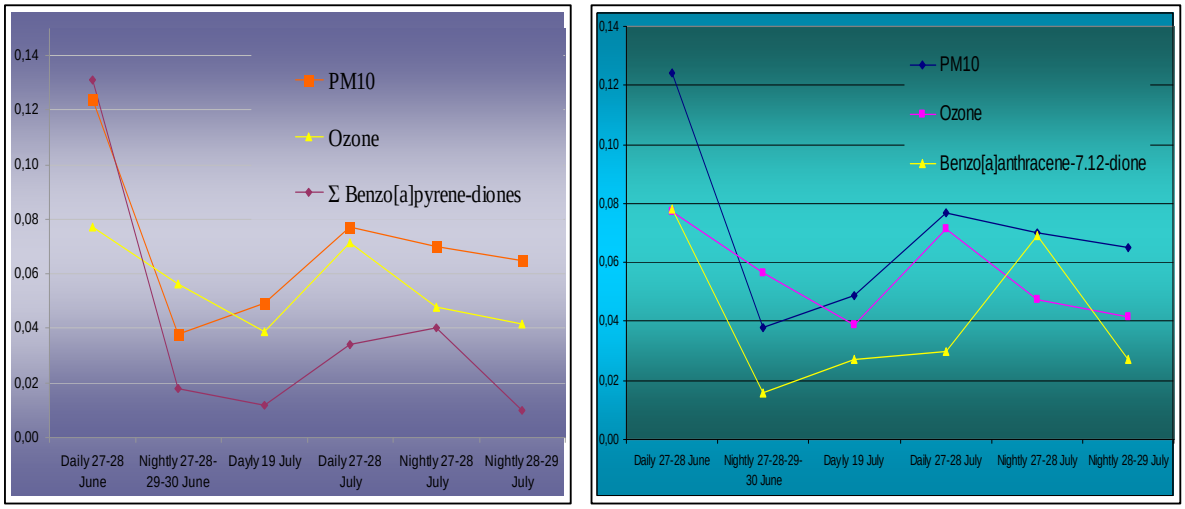



Fig.62 - Compared data of Oxy-PAHs, PM10 and Ozone concentration.

The Diones' concentrations were affected by the high presence of Ozone (photochemical activity marker) of the previous daily hours.

As it could be seen from the tab.33, the concentration of benzo[a]pyrene has a good fit with particulate matter, with Benzo[a]pyrene Diones, like could be expected. The benzo[a]anthracene-7.12-dione doesn't have a linear correlation with the benzo[a]anthracene and with the presence of ozone, but the formation of this compound occurs: it is an important constituent of particulate matter for the analyzed samples, probably for a more complex kinetic of reaction as could be expected from the fig.27. All Benzo[a]pyrene Diones have a linear good correlation with ozone ($r^2$ = 0.58 as sum) and for the Benzo[a]pyrene-6.12-dione there is also an interesting $r^2$ with the net radiation.

Tab.33 – Correlation data ($r^2$) for PM10, Net Radiation and Ozone with PAHs and Oxy-PAHs.

| $r^2$ | ΣPAHs | B[a]p | B[a]a | B[a]a7.12d | ΣB[a]pd | B[a]p1.6d | B[a]p3.6d | B[a]p6.12d | Aq | 9.10-Pheq |
|---|---|---|---|---|---|---|---|---|---|---|
| Radiation | 0,05 | 0,00 | 0,08 | 0,04 | 0,19 | 0,20 | 0,18 | **0,44** | 0,05 | 0,01 |
| O3 | 0,33 | 0,20 | 0,33 | 0,16 | **0,58** | **0,47** | **0,58** | **0,56** | 0,39 | 0,02 |
| PM10 | 0,30 | **0,59** | 0,25 | **0,65** | **0,85** | **0,90** | 0,86 | 0,67 | 0,53 | 0,02 |
| 9.10-Pheq | **0,52** | 0,12 | 0,48 | 0,01 | 0,04 | 0,01 | 0,00 | 0,30 | 0,22 | |
| Aq | 0,04 | **0,88** | 0,05 | 0,39 | **0,82** | **0,64** | 0,61 | 0,93 | | |
| B[a]p-6.12d | 0,00 | **0,76** | 0,00 | 0,38 | **0,92** | **0,74** | 0,72 | | | |
| B[a]p-3.6d | 0,21 | **0,57** | 0,17 | **0,79** | **0,94** | **0,98** | | | | |
| B[a]p-1.6d | 0,16 | **0,65** | 0,12 | **0,83** | **0,95** | | | | | |
| Σ B[a]pd | 0,14 | **0,74** | 0,12 | **0,67** | | | | | | |
| B[a]a7.12d | 0,14 | 0,53 | **0,09** | | | | | | | |
| B[a]a | **0,98** | 0,09 | | | | | | | | |
| B[a]p | 0,08 | | | | | | | | | |

### 3.2.2 Oxy-PAHs, Nitro-PAHs in Outdoor/Indoor PM1 and PM2.5 samples for Urban, Rural and Remote Sites.

In the Appendix 1 – tab.7, 8 the obtained results are presented and expressed respectively in pg/m$^3$ PM2.5 and PM1. In the same tables are presented the sum of ten PAHs, the less volatile ones (from the Benzo[a]Anthracene to the Benzo[g,h,i]Perylene) and the total 14 PAHs analyzed. At last the 17 compounds sum represents the concentration of all Polycyclic Hydrocarbons analyzed (both PAHs; Oxy-PAHs and Nitro-PAHs). In fig.63 is shown a chromatogram of an analyzed PM10 sample and a white sample: it could be seen that the white has a negligible signal if compared with a sample one (fig.64).

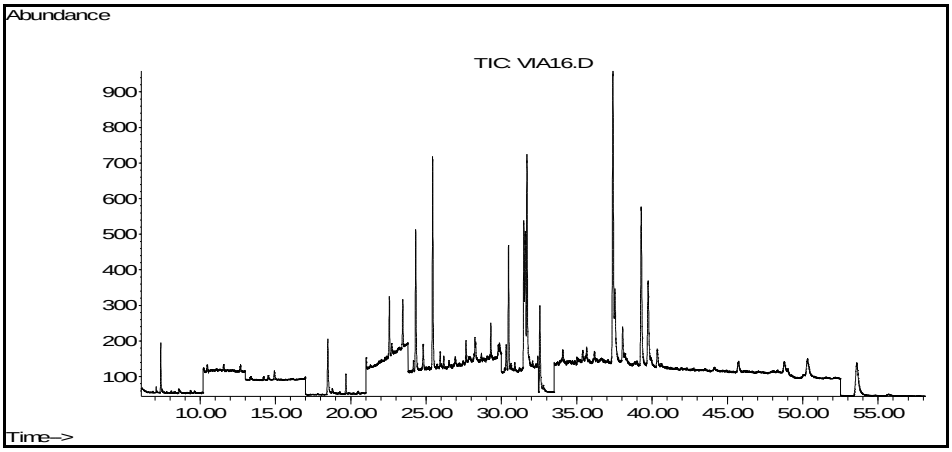



Fig.63 - Total Ion Current of a sample of PM1 Indoor containing PAHs, Oxy-PAHs and Nitro-PAHs.

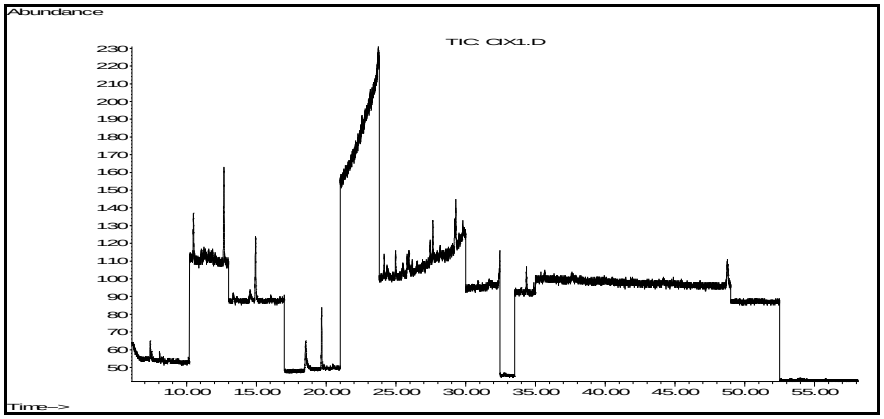



Fig.64 - Total Ion Current of a White Sample.

The elaboration presented for all data reported account of the different compounds analyzed; the different types of samples: PM1 indoor; PM2.5 indoor and PM1 outdoor and PM2.5 outdoor.

The following graph (fig.65) allows to focus the mass results expressed in µg/m$^3$ for indoor-outdoor and PM1-PM2.5 summer samples. It has to be specified each single sample: the 1-2-3-4-7-8 indoor-outdoor PM1 samples and indoor-outdoor PM2.5 samples were made in the same day; while 5-6 were sampled in close days of the same week but for both indoor-outdoor PM1 and indoor-outdoor PM2.5. Theoretically the PM1 had to be lower than outdoors, but sample

7 shows a different trend for the PM1 and PM2.5 indoor sampling. The reason is necessary correlated with the mode of sampling or weighing.

Moreover it could be expected that the indoor mass is lower than the outdoor one. This is not always respected and could be correlated with environment factors like the behaviour of people or structural features of the building construction (presence of conditioned air; smoking; closeness of traffic density; the opening of windows) could be combined to bring about concentration of particulate matter.

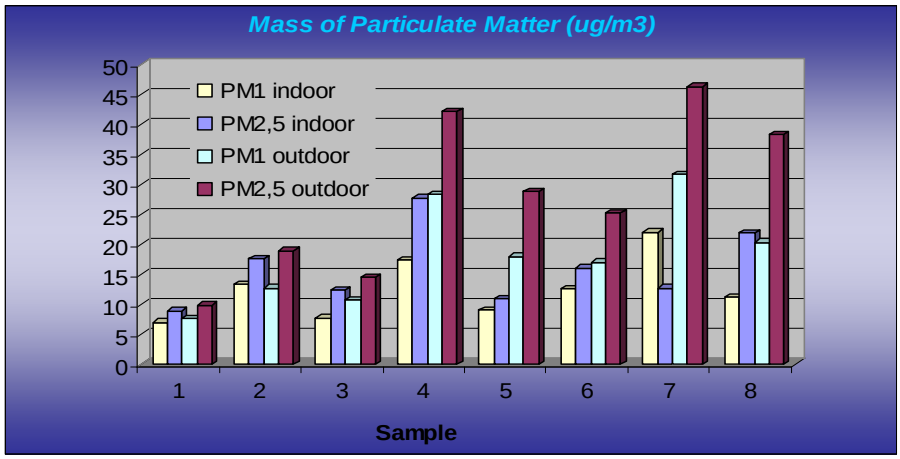



Fig.65 - Mass results expressed in μg/m$^3$ for indoor-outdoor and PM1-PM2.5 samples.

Considering the composition of PM2.5 of all compounds analyzed in fig.66, the high concentration of Benzanthrone (BZAT) is evident.

For a better definition of each correlation, table 34 and 35 were made, separated from PM1 and PM2.5: the interesting cells are highlighted. The Oxy-PAHs sum (Σopah, in the first column) correlates with some PAHs compound and with PAHs sum: the Benzanthrone has a good correlation with the 14 PAHs' sum ($r^2$=0.93 and 0.83 respectively), (second column).

At last the Anthraquinone (Aq) fits with the Anthracene (Ant), its rising compound ($r^2$ = 0.82 and $r^2$ = 0.44). In general the PM2.5 data has a better correlation than PM1, even the trend is the same.

For example the difference in the correlation of Anthracene and Anthraquinone could be originated from the different environmental conditions of reaction or transport from outdoor to indoor space.

Tab.34 – Correlation data of PM2.5 ng/m$^3$ indoor and outdoor samples.

| PM2.5 | Σopah | Σ14pah | Σ10pah | BP | dBA | IP | BaP | BeP | BkF | BbF | BaAd | Bzat | Chr | Cpp | BaA | Pyr | Flnt | Aq | Ant |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Phe** | 0,01 | 0,03 | 0,00 | 0,02 | 0,54 | 0,06 | 0,01 | 0,00 | 0,01 | 0,00 | 0,03 | 0,00 | 0,03 | 0,01 | 0,00 | 0,23 | 0,74 | 0,00 | 0,37 |
| **Ant** | 0,37 | 0,19 | 0,14 | 0,05 | 0,29 | 0,09 | 0,12 | 0,14 | 0,06 | 0,10 | 0,39 | 0,17 | 0,23 | 0,15 | 0,19 | 0,37 | 0,46 | 0,82 | |
| **Aq** | 0,51 | 0,20 | 0,17 | 0,13 | 0,38 | 0,22 | 0,17 | 0,16 | 0,06 | 0,13 | 0,73 | 0,21 | 0,21 | 0,16 | 0,19 | 0,25 | 0,09 | | |
| **Flnt** | 0,24 | 0,33 | 0,15 | 0,03 | 0,59 | 0,00 | 0,09 | 0,11 | 0,04 | 0,12 | 0,01 | 0,22 | 0,34 | 0,29 | 0,25 | 0,68 | | | |
| **Pyr** | 0,67 | 0,71 | 0,53 | 0,28 | 0,54 | 0,15 | 0,40 | 0,43 | 0,26 | 0,45 | 0,13 | 0,68 | 0,79 | 0,72 | 0,72 | | | | |
| **BaA** | 0,77 | 0,89 | 0,87 | 0,58 | 0,45 | 0,48 | 0,77 | 0,76 | 0,59 | 0,78 | 0,24 | 0,87 | 0,97 | 0,96 | | | | | |
| **Cpp** | 0,69 | 0,80 | 0,75 | 0,45 | 0,37 | 0,34 | 0,63 | 0,62 | 0,42 | 0,65 | 0,20 | 0,78 | 0,91 | | | | | | |
| **Chr** | 0,80 | 0,94 | 0,88 | 0,59 | 0,55 | 0,46 | 0,77 | 0,79 | 0,63 | 0,80 | 0,25 | 0,89 | | | | | | | |
| **Bzat** | 0,88 | 0,93 | 0,92 | 0,78 | 0,71 | 0,58 | 0,83 | 0,86 | 0,64 | 0,90 | 0,33 | | | | | | | | |
| **BaAd** | 0,59 | 0,29 | 0,33 | 0,35 | 0,50 | 0,56 | 0,33 | 0,32 | 0,15 | 0,30 | | | | | | | | | |
| **BbF** | 0,75 | 0,92 | 0,98 | 0,93 | 0,71 | 0,78 | 0,97 | 0,99 | 0,85 | | | | | | | | | | |
| **BkF** | 0,48 | 0,73 | 0,83 | 0,77 | 0,38 | 0,68 | 0,89 | 0,88 | | | | | | | | | | | |
| **BeP** | 0,75 | 0,91 | 0,98 | 0,91 | 0,73 | 0,79 | 0,98 | | | | | | | | | | | | |
| **BaP** | 0,80 | 0,89 | 0,97 | 0,89 | 0,69 | 0,83 | | | | | | | | | | | | | |
| **IP** | 0,58 | 0,63 | 0,76 | 0,76 | 0,75 | | | | | | | | | | | | | | |
| **dBA** | 0,88 | 0,71 | 0,70 | 0,74 | | | | | | | | | | | | | | | |
| **BP** | 0,65 | 0,78 | 0,88 | | | | | | | | | | | | | | | | |
| **Σ10pah** | 0,79 | 0,95 | | | | | | | | | | | | | | | | | |
| **Σ14pah** | 0,83 | | | | | | | | | | | | | | | | | | |

Tab.35 – Correlation data of PM1 ng/m$^3$ indoor and outdoor samples.

| PM1 | Σopah | Σ14pah | Σ10pah | BP | dBA | IP | BaP | BeP | BkF | BbF | BaAd | Bzat | Chr | Cpp | BaA | Pyr | Flnt | Aq | Ant |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Phe** | 0,10 | 0,49 | 0,13 | 0,01 | 0,02 | 0,00 | 0,04 | 0,09 | 0,01 | 0,07 | 0,04 | 0,18 | 0,33 | 0,29 | 0,38 | 0,51 | 0,91 | 0,02 | 0,28 |
| **Ant** | 0,42 | 0,36 | 0,20 | 0,01 | 0,26 | 0,08 | 0,05 | 0,20 | 0,11 | 0,11 | 0,09 | 0,24 | 0,43 | 0,31 | 0,40 | 0,61 | 0,61 | 0,44 | |
| **Aq** | 0,34 | 0,03 | 0,05 | 0,00 | 0,77 | 0,05 | 0,01 | 0,07 | 0,09 | 0,02 | 0,10 | 0,07 | 0,13 | 0,09 | 0,06 | 0,13 | 0,13 | | |
| **Flnt** | 0,25 | 0,62 | 0,22 | 0,02 | 0,00 | 0,00 | 0,08 | 0,16 | 0,05 | 0,14 | 0,15 | 0,32 | 0,49 | 0,44 | 0,45 | 0,76 | | | |
| **Pyr** | 0,61 | 0,72 | 0,43 | 0,06 | 0,10 | 0,04 | 0,21 | 0,37 | 0,23 | 0,31 | 0,19 | 0,58 | 0,75 | 0,69 | 0,64 | | | | |
| **BaA** | 0,60 | 0,85 | 0,74 | 0,23 | 0,11 | 0,15 | 0,52 | 0,64 | 0,44 | 0,58 | 0,00 | 0,71 | 0,91 | 0,88 | | | | | |
| **Cpp** | 0,67 | 0,80 | 0,71 | 0,20 | 0,17 | 0,13 | 0,51 | 0,60 | 0,41 | 0,54 | 0,01 | 0,74 | 0,90 | | | | | | |
| **Chr** | 0,73 | 0,87 | 0,77 | 0,22 | 0,27 | 0,15 | 0,53 | 0,69 | 0,57 | 0,62 | 0,02 | 0,79 | | | | | | | |
| **Bzat** | 0,85 | 0,83 | 0,90 | 0,52 | 0,32 | 0,39 | 0,75 | 0,86 | 0,67 | 0,85 | 0,11 | | | | | | | | |
| **BaAd** | 0,18 | 0,08 | 0,03 | 0,04 | 0,10 | 0,08 | 0,01 | 0,05 | 0,03 | 0,04 | | | | | | | | | |
| **BbF** | 0,66 | 0,73 | 0,96 | 0,79 | 0,27 | 0,67 | 0,96 | 0,97 | 0,85 | | | | | | | | | | |
| **BkF** | 0,58 | 0,53 | 0,81 | 0,62 | 0,45 | 0,54 | 0,81 | 0,85 | | | | | | | | | | | |
| **BeP** | 0,73 | 0,77 | 0,98 | 0,75 | 0,39 | 0,68 | 0,92 | | | | | | | | | | | | |
| **BaP** | 0,58 | 0,64 | 0,92 | 0,81 | 0,19 | 0,71 | | | | | | | | | | | | | |
| **IP** | 0,36 | 0,28 | 0,58 | 0,90 | 0,35 | | | | | | | | | | | | | | |
| **dBA** | 0,64 | 0,13 | 0,31 | 0,21 | | | | | | | | | | | | | | | |
| **BP** | 0,36 | 0,40 | 0,69 | | | | | | | | | | | | | | | | |
| **Σ10pah** | 0,74 | 0,84 | | | | | | | | | | | | | | | | | |
| **Σ14pah** | 0,67 | | | | | | | | | | | | | | | | | | |

A graph that represents each compound for the PM2.5 is presented in fig.66 and in fig.67. Only for the 14 PAHs analyzed; from the graph the percentage of the considered pollutants can be read.

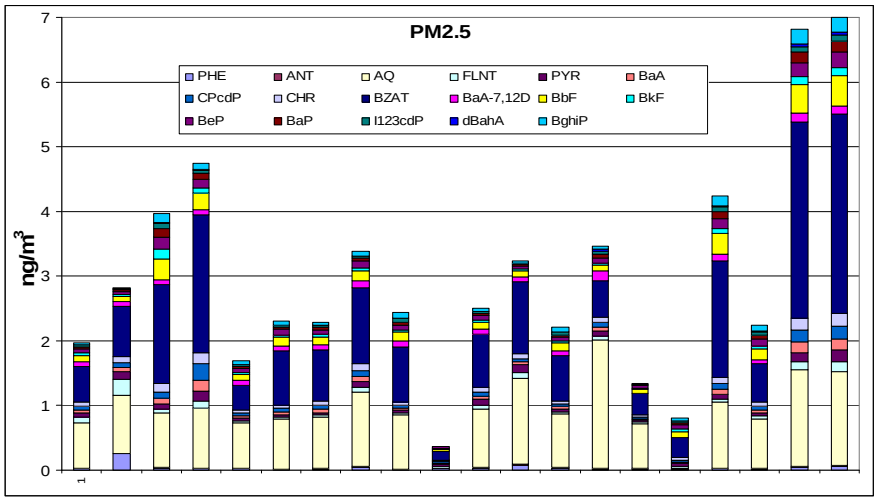



Fig.66 - The PM2.5 composition for the Polycyclic Aromatic Hydrocarbons and Oxygenated Polycyclic Hydrocarbons (the 17 compound analyzed).

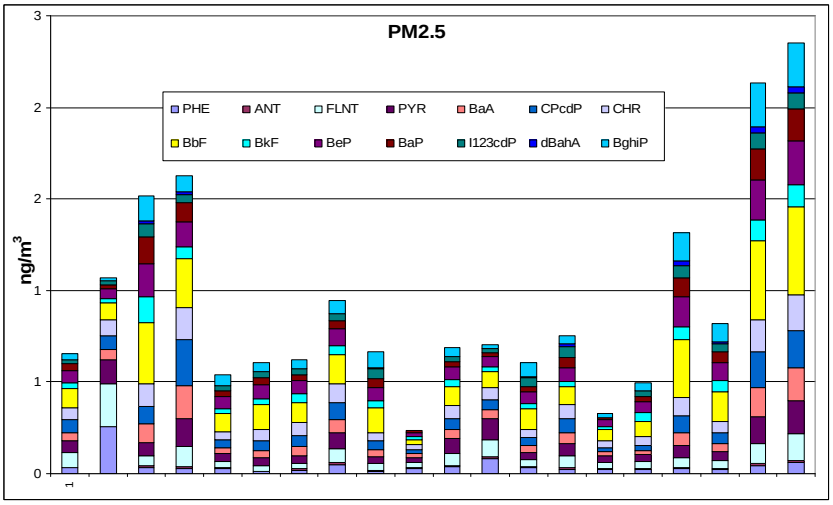



Fig.67 - The PM2.5 composition for the 14 Polycyclic Aromatic Hydrocarbons analyzed.

In the previous chapters two different types of analysis as preliminary study of feasibility were considered: an HPLC-FLD analysis of PAHs coupled with an LC-MS analysis of Oxy-PAHs compounds. For this kind of analysis the time of work is high: each sample had to be processed tewice with different eluent and detector configuration even the extract is the same. So it another kind of system can be found (GC-MS) that could be supported the identification and quantification in a single run of PAHs, Oxy-PAHs and Nitro-PAHs. In this case the much polar and higher molecular weight compounds, the Benzo[a]pyrenediones could not be analysed, but as it could be seen in the chapter 3.2.1, they are present in very low concentrations, in the PM10 fraction, so by necessity the opportunity of the analysis of these compounds by LC-MS [47] will be considered.

The method set by GC-MS allows to consider a very large batch of samples as support to important environmental considerations and conclusions. Following the results obtained from all processed samples.

Firstly the winter samples of the urban sites of Milan in January, February and March 2008 directly of the summer and autumn 2007, in both cases in order to estimate the behaviour of PM1-PM2.5 indoor and outdoor environmental compartment. In Appendix 1 – tab.9 the concentrations of the samples collected for the summer and wintertime.

Fig.68 and 69 show the concentrations of PAHs; Oxy-PAHs and Nitro-PAHs monitored as percentage of μg/m$^3$ respectively in the PM1 and PM2,5 winter samples. At last in fig.70, the results were monitored as sum in order to compare directly Indoor and Outdoor Data of both campaigns.

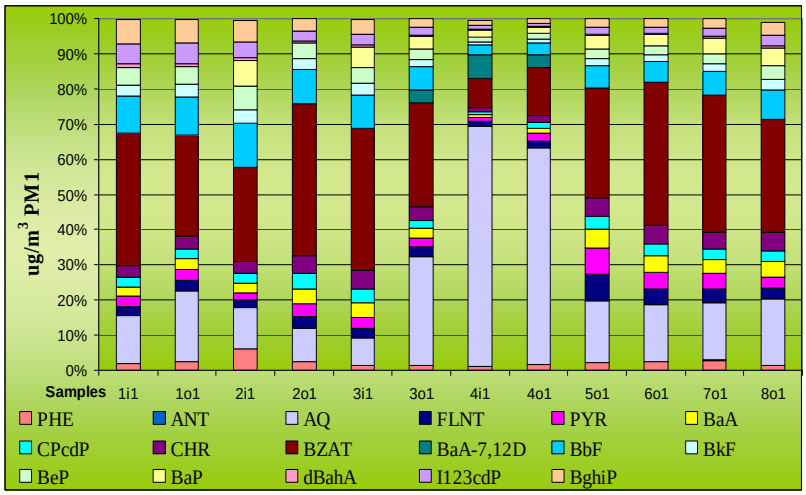



Fig.68 – PM1 Winter samples processed by GC-MS for PAHs, Oxy-PAHs and Nitro-PAHs, both indoor and outdoor sampling type: the abbreviation "i" mean Indoor while the abbreviation "o" mean Outdoor samples.

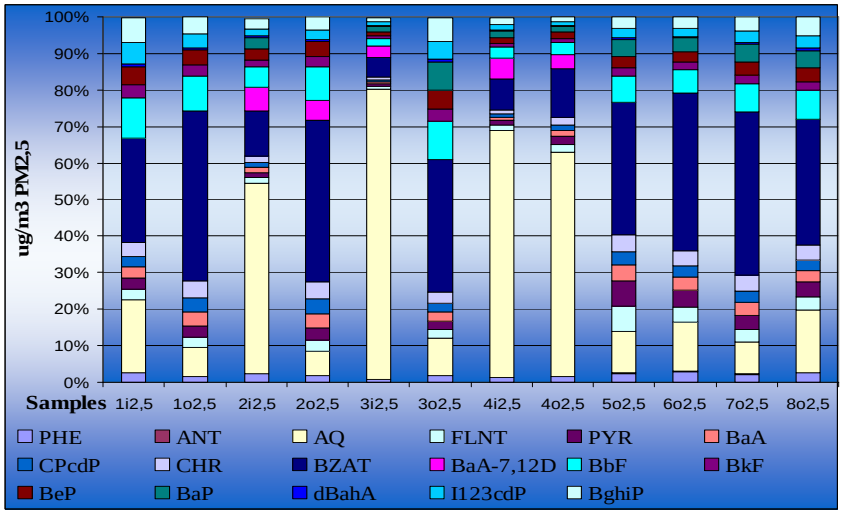



Fig.69 – PM2,5 Winter samples processed by GC-MS for PAHs, Oxy-PAHs and Nitro-PAHs, both indoor and outdoor sampling type: the abbreviation "i" means Indoor while the abbreviation "o" means Outdoor samples.

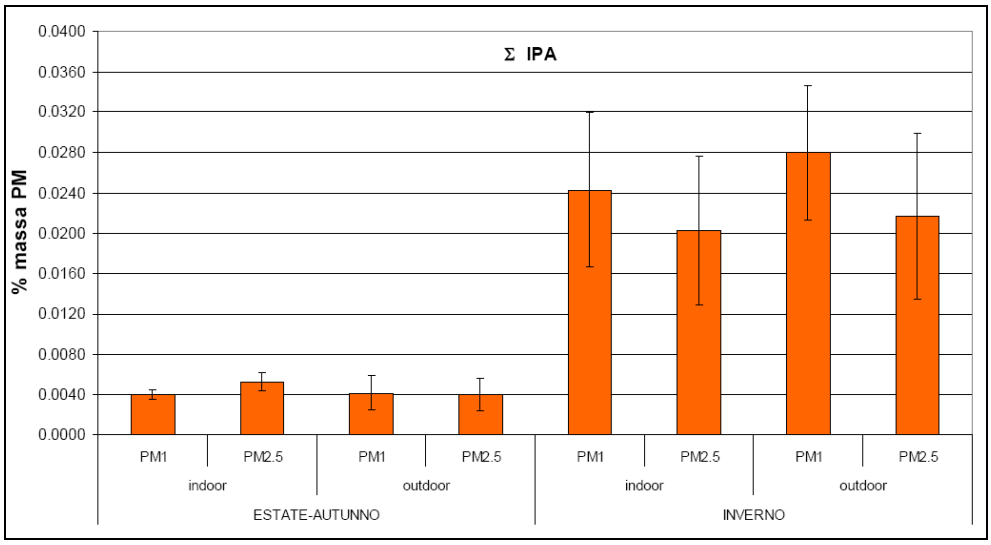



Fig.70 - Sample processed by GC-MS for PAHs analysis, partitioned by summer and winter and PM1 and PM2.5 indoor and outdoor sampling.

Summarizing the obtained results: the IPA/OPA ratio is lower in wintertime, when the photochemical activity is lower; the IPA/OPA ratio is higher in the PM Indoor rather than the Outdoor, where the photochemical activity is lower, (fig.71).

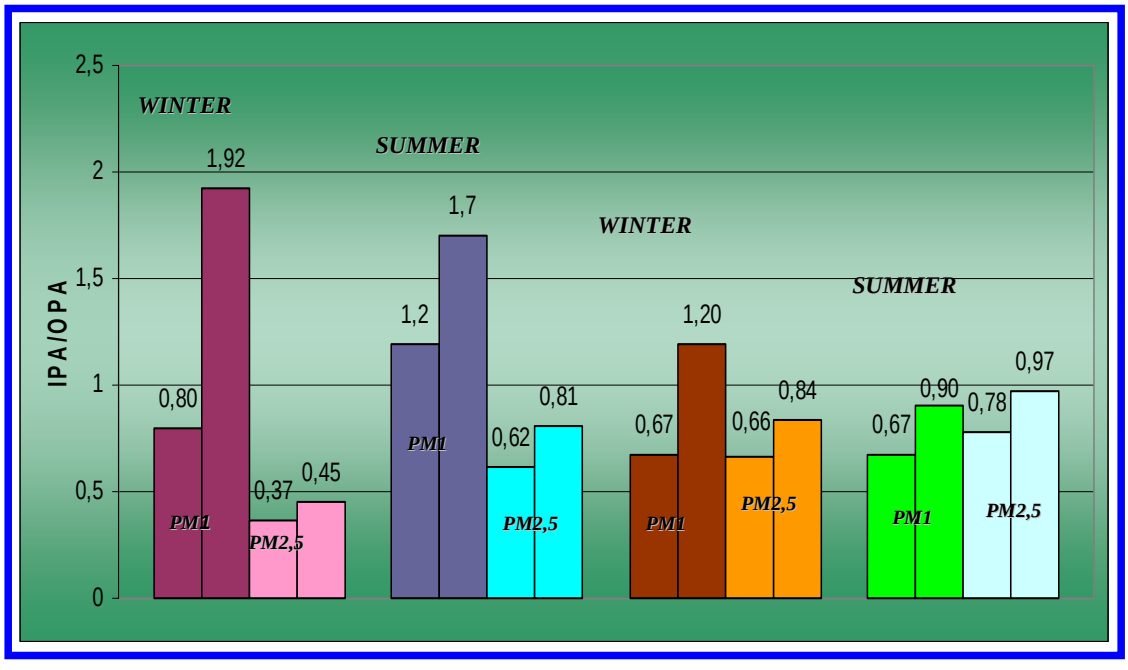



Fig.71 – IPA /OPA ratio for both PM1; PM2,5 Indoor; Outdoor; summer and winter samples.

Also three different sites in spring time (2007-2008) were monitored: an urban site of Milan, a rural site and a remote alpine site. The collected samples are presented in the Appendix 1 – tab.10. In this case the traffic source of emission as could be seen in fig.72 could be focused.

The results regarding the Nitro-PAHs and Oxy-PAHs show the presence of 1-Nitro-pyrene only in Milan as primary pollutant of traffic emission and the Oxy-PAHs as predominant primary but also secondary pollutant, derived from atmospheric reactions. The Benzo[a]anthracene-7,12-dione allows seeing the presence of the direct traffic source: as we move away from the city the percentage concentration of this compound increase**.** The reason is the absence, in the rural and alpine sites, of the direct source of emission that decreases the concentration of the primary pollutants (dilution factor), if compared with the secondary ones.

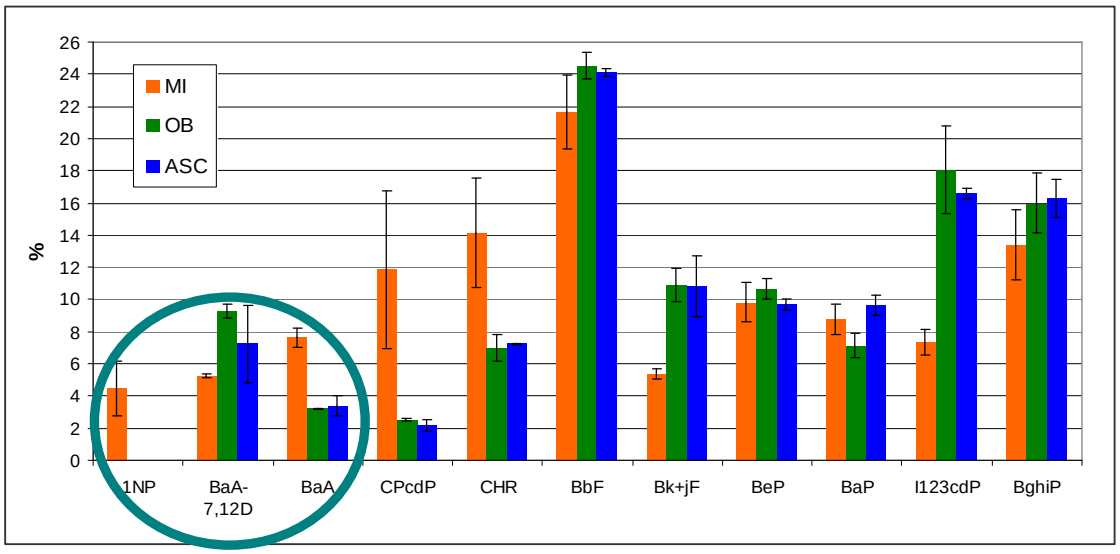



Fig.72 - Correlation between three different sites of sampling for the analysis of PAHs; Oxy-PAHs and Nitro-PAHs.

Not all the primary pollutants react in atmosphere. An example are the Benzo(e)pyrene and the Benzo(a)pyrene. In fig.73 the ratio B(e)P/(B(a)P+B(e)P) decreases from summer to winter: in fact the Benzo(e)pyrene doesn't have photochemical reaction products as Benzo(a)pyrene.

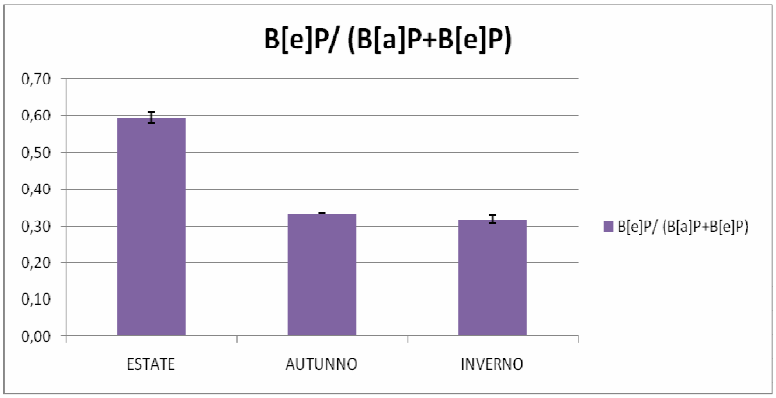



Fig.73 – Photochemical behaviour of Benzo(e)pyrene and Benzo(a)pyrene.

At the same manner the rate from Benzo(a)anthracene and Benzo(a)anthracene-7,12-dione, its photochemical reaction product could be compared. Their ratio increases from the summer to wintertime, fig.74.

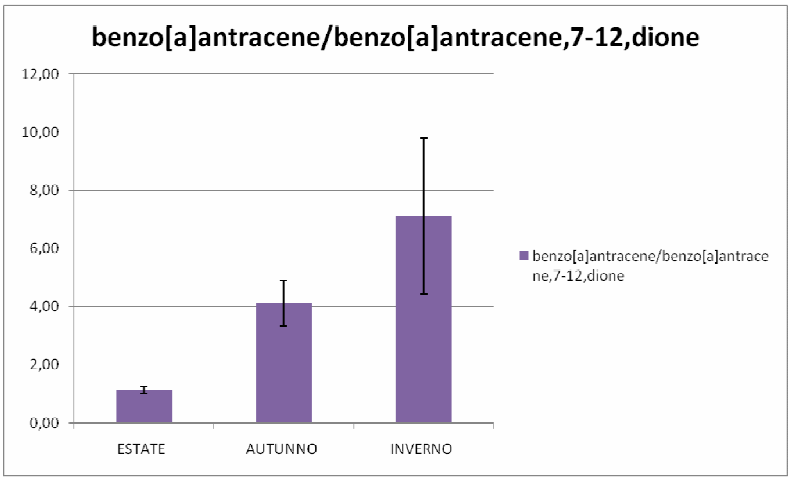



Fig.74 - Photochemical behaviour of Benzo(a)anthracene.

So for each primary pollutant it had to be defined its own reactivity and behaviour in atmosphere.

### 3.2.3 Bisphenol A in summer and winter; Indoor and Outdoor PM2,5.

Four sampling indoor and outdoor sites were set up in the urban city of Milan. For the study were chosen 34 samples and 6 blank fields. The obtained results showed the ranges reported (punctual data in Appendix 1 – tab.11):

Indoor 1,70-118,31 ng/mg; 27,59-786,07 pg/$m^3$
Outdoor 0,70-45,90 ng/mg; 51,58-733,46 pg/$m^3$

The concentration is summed in fig.75: it's clear how the presence of Bisphenol A increases in confined environments and in the wintertime.

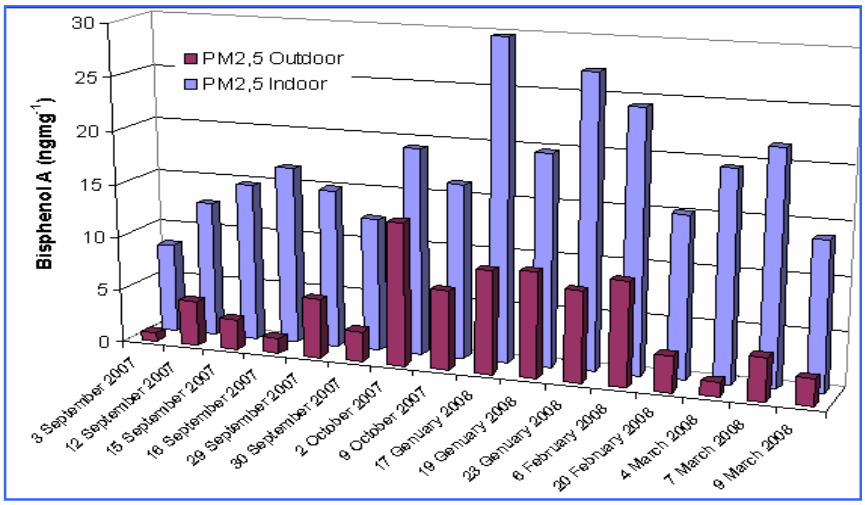



Fig.75 - Seasonal Trend and Indoor/Outdoor correlated concentration of Bisphenol A in PM2,5 samples.

In order to estimate the indoor contribution from Indoor source three statistical methods were used:

1) Linear Regression [Indoor]/[Outdoor];
2) Quartiles;
3) Minimum Outdoor Amount.

In the first case, the Indoor and Outdoor concentration results (expressed in ng/m$^3$) were plotted, ordered for the same data of sampling, with the least square approach, the obtained curve is following reported:

Y = 0,817X+0,152 with a Coefficient of Determination $R^2$=0,876

The relationship between the two variables is shown in fig.76. The positive intercept represents the indoor contribution from indoor source, equal to **0,152 ng/m$^3$**. The Indoor feels the effect of outdoor/indoor exchange: the 82% (pendence) of outdoor concentration of BPA moved to the Indoor Environment.

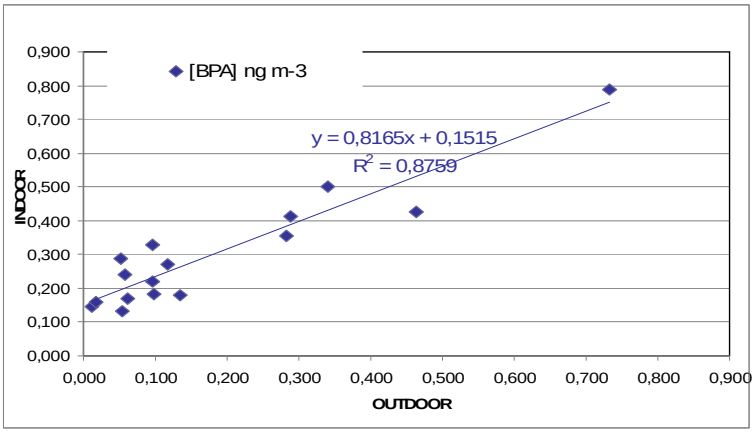


Fig.76 - Liner Regression from Outdoor and Indoor Sample Data for the BPA analysed.
In the second case, the data set had to be ordered as follow:

**Outdoor** BPA ng/m$^3$: **Q1**(0,0118; 0,0175; 0,0516; 0,0544); Q2 (0,0580; 0,0621; 0,0959; 0,0970); Q3 (0,0986; 0,1182; 0,1351; 0,2836); Q4 (0,2880; 0,3396; 0,4637; 0,7335).
**Indoor** BPA ng/m$^3$: **Q1** (0,1441; 0,1600; 0,2879; 0,1322); Q2 (0,2414; 0,1687; 0,2194; 0,3295); Q3 (0,1828; 0,2704; 0,1806; o,3565); Q4 (0,4116; 0,5004; 0,4251; 0,7883).

To each Outdoor data, in increasing order, the correspondent Indoor value is set. The first quartile (designed Q1) is the lower quartile corresponding to the 25th percentile. The mean value of **Q1 Indoor ng/m$^3$** is equal to **0,1811.**
At last, for the third method, at the minimum Outdoor amount, the minimum Indoor amount is equal to **0,1441 ng/m$^3$**.
As it could be seen, the three data essentially agree (0,1515; 0,1811; 0,1441 ng/m$^3$). The average value is equal to 0,1589 ng/m$^3$.
Then the Indoor and Outdoor data (ng/m3) is correlated, with the linear regression, with the PM2,5 and PM1 concentration in the atmosphere (μg/m3), (fig.77): the $R^2$ results better for the PM1 concentration of BPA. It could mean that the pollutant is concentrated in the finest fraction.

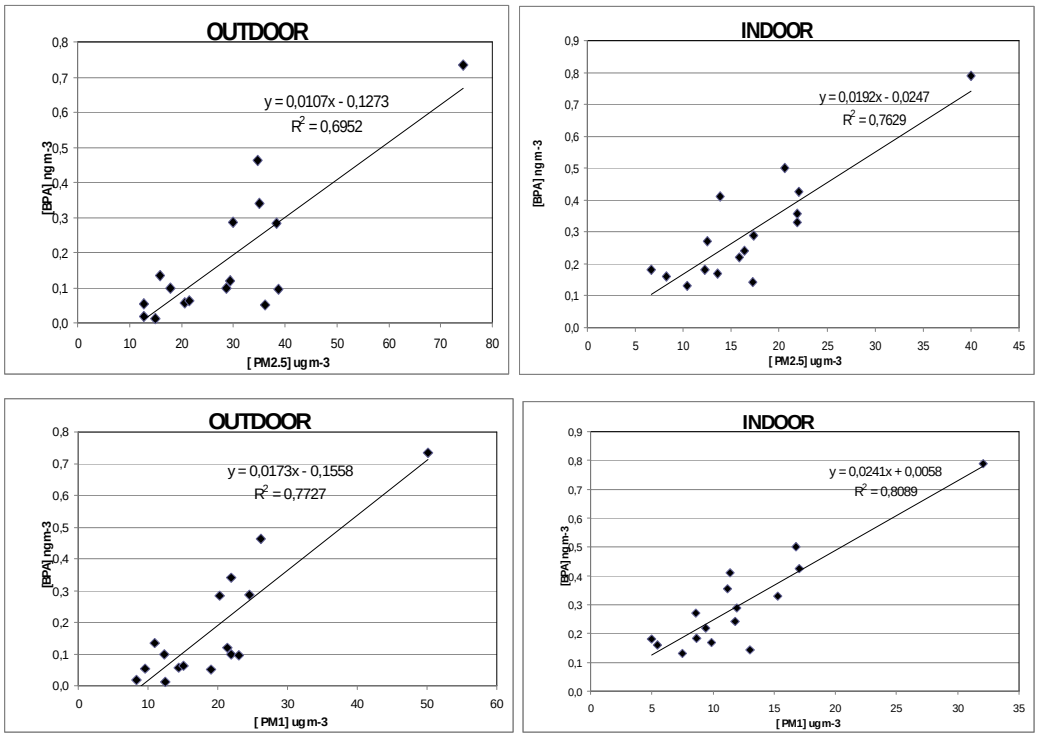



Fig.77 - Correlation between BPA concentration and obtained PM1 and PM2,5 data.

The assumption of BPA by inhalation was estimated at about 0,5% in comparison to the assumption by ingestion [77].
In wintertime, in the city of Milan, the assumption by inhalation in the Indoor Environment represented 1,24%, (considering the average of 20 $m^3$/day of inhalated air for the adults, and 10 $m^3$/day for children; 70 kg of weight for adults and 35 kg for children). More than double if compared with the data reported in Bibliography.
The data was important because of the continuous all day long exposure; an exposure that had to be added to the data is ingestion during meal; aside from habits and culture.