ATMOSPHERIC PAHs DETERMINATION: INFLUENCE OF THE AIR SAMPLING TIME PROGRAM IN THE OCCURRENCE OF ARTIFACTS

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One of the greatest challenges in air pollution research, especially which is focuses on the study of PAHs, is the development of systems and sampling procedures to obtain more accurate, reliable and representative information about concentrations of these compounds and their variation in time.
SAMPLING ARTIFACTS

• REACTIONS OF PAH’s WITH COMPOUNDS PRESENT IN THE AIR

PAH’s +

• NOx
• O3
• ACID GASES AND O3

NITRO-PAH’s
OXY-PAH’s
HIGHLY POLAR COMPOUNDS

Atmospheric Environment, 33, 4977-4986 (1999)


• Exchange of PAHs between gaseous and particulate phases

- Artifact negative: some of the particulate organic compounds is volatilized
- Artifact positive: a portion of the organic vapor phase is adsorbed onto the filter surface or onto the deposited particulate matter

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Atmospheric Environment, 33, 4977-4986 (1999)
THE OBJECTIVE OF THIS WORK WAS: TO DETERMINE A SAMPLING TIME PROGRAM THAT SATISFIES THE FOLLOWING CONDITIONS:

✓ Collect enough PAHs amount to be measurable by GC-FID and GC-MS

✓ Minimize the occurrence of sampling artifacts, and generate a representative sample for a 24 hour period
Sampling site: Santiago de Chile, Metropolitan Region
Parque O’Higgins monitoring station is located in downtown Santiago. It is placed in a large park about 2 km south of the city downtown and 1 km west of a major highway with traffic of about 60,000 vehicles per day.
Sampling System Outline
Speciation Sampler Partisol 2300 (R&P)

PAHs in Gaseous phase
PUF

PAHs absorbed/adsorbed on particulate matter
FILTER

Outlet Air

Inlet Air

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Dr. Francisco Cereceda
### Sampling Times Program (STP)

<table>
<thead>
<tr>
<th>Program 1</th>
<th>Program 2</th>
<th>Program 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min / 1 hour = 10min/1hr</td>
<td>1 hour / 6 hour = 1hr/6hr</td>
<td>24 continuous hours = 24chr</td>
</tr>
<tr>
<td>Effective sampling time = 4hr</td>
<td>Effective sampling time = 4hr</td>
<td>Effective sampling time = 24hr</td>
</tr>
</tbody>
</table>
Qualitative and quantitative determination of PAHs (PM + gas phase)

PM phase → Gaseous phase → Sampling → Extraction → Evaporation/concentration → Purification (clean-up) → Identification → Quantification

Multi-step Environmental Analytical Process
Real Samples Chromatograms of PAHs, (Filter and PUF)

Filter (escale 20 a 200 mV)

PUF (escale 20 a 200 mV)
### Results

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Concentration Mean (TF+PUF) (ng/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 min/1hr</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>27.17 ± 6.59</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>27.21 ± 9.13</td>
</tr>
<tr>
<td>Fluorene</td>
<td>23.87 ± 6.42</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>39.66 ± 4.22</td>
</tr>
<tr>
<td>Anthracene</td>
<td>46.89 ± 31.96</td>
</tr>
<tr>
<td>Fluoranthenhe</td>
<td>14.91 ± 6.94</td>
</tr>
<tr>
<td>Pyrene</td>
<td>26.99 ± 8.51</td>
</tr>
<tr>
<td>Retene</td>
<td>11.23 ± 3.43</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>23.38 ± 15.99</td>
</tr>
<tr>
<td>Chrysene</td>
<td>10.21 ± 1.57</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>8.40 ± 2.45</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>3.22 ± 0.63</td>
</tr>
<tr>
<td>Benzo(g,h,i)perylenne</td>
<td>3.25 ± 0.56</td>
</tr>
<tr>
<td>Indene(1,2,3-cd)pyrene</td>
<td>0.71 ± 0.61</td>
</tr>
</tbody>
</table>

*udl: under detection limit*
Total PAH concentration obtained at different Sampling Times Program

- Sampling Program:
  - 10 min/1hr
  - 1hr/6hr
  - 24 hr

Comparison:
- Equivalent Sampling Programs
- Sampling Programs with More Artifacts

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Regression analysis

Hypothetical equivalence case $a = 1$

\[
\frac{1.2538}{0.3129} = 4.0
\]
Conclusions

- Were made a concentration analysis of atmospherics samples of HAPs, obtained in a urban sampling station and performed with three different STP.

- A significant sampling artifact was found when sampler works continuously for 24 hours.

- Statistical analysis showed that concentrations of PAHs obtained with longer time sampling (24 chr) are 4 times lower than those found at 1hr/6hr or 10min/1hr.

- 1hr/6hr or 10min/1hr are equivalents; nevertheless to get a wider picture of the variation of pollutants through the day (eg PAHs) it is proposed that the program of 10min/1hr is the most appropriate.
ACKNOWLEDGEMENTS

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PUF Cleaning comparison between AutoExtract-PUF® and Soxhlet extraction (EPA-TO13A) with GC-FID

AutoExtract-PUF Blank
(escale 0 a 150 mV)

Soxhlet Blank
(escale 0 a 150 mV)

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Comparison between before and after PUF cleaning procedure with AutoExtract-PUF® (GC-FID)

PUF Before cleaning
(escale -15 a 700 mV)

PUF After cleaning
(escale -15 a 700 mV)
Chromatogram of 1 µl standard of 16-EPA HAPs (8 ng/µl)
Samples processing of PAHs in gas phase and particulate matter (MP$_{2,5}$)

- PAHs ab/adsorbed on particulate matter
  - FILTER
teflon membrane 0,45 µm Ø pore
  - Filter extraction with Toluene during 1h using reflux system
  - Extract filtration on specially designed vacuum system

- PAHs in gas phase
  - PUF
Polyurethane foam filter
  - PUF extraction in a automatic pneumatic extraction system
AutoExtract PUF®

- Similar samples treatment is made, but separately

© Patent pendent
Samples processing of PAHs in gas phase and particulate matter (MP\(_{2,5}\))

- Extract Concentration with rotary evaporator
- Evaporation under controlled nitrogen stream
- Redisolution with 50 ul of Toluene
- Sample Clean Up on Silica Gel Column
- PAHs Fraction
  - chromatographic Identification - Quantification
  - GC-MS
  - GC-FID
Regression analysis: comparison results of PAHs concentrations obtained with different STP

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Regression Analysis (y vs x; y = ax)</th>
<th>$r^2$ (fitted)</th>
<th>Probability error for $a \neq 0$ (%)</th>
<th>Coeff. $a$</th>
<th>Confidence Interval $a$ (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (27th Jun 2007)</td>
<td>1hr/6hr vs 10min/1hr</td>
<td>0.81</td>
<td>1.7 x 10^{-5}</td>
<td>1.06</td>
<td>(0.84 – 1.29)</td>
</tr>
<tr>
<td></td>
<td>24chr vs 10min/1hr</td>
<td>0.60</td>
<td>1.6 x 10^{-2}</td>
<td>0.30</td>
<td>(0.18 – 0.42)</td>
</tr>
<tr>
<td></td>
<td>24chr vs 1hr/6hr</td>
<td>0.54</td>
<td>5.1 x 10^{-2}</td>
<td>0.25</td>
<td>(0.13 – 0.37)</td>
</tr>
<tr>
<td>2 (28th Jun 2007)</td>
<td>1hr/6hr vs 10min/1hr</td>
<td>0.64</td>
<td>1.2 x 10^{-2}</td>
<td>1.28</td>
<td>(0.78 – 1.78)</td>
</tr>
<tr>
<td></td>
<td>24chr vs 10min/1hr</td>
<td>0.42</td>
<td>4.2 x 10^{-1}</td>
<td>0.31</td>
<td>(0.12 – 0.50)</td>
</tr>
<tr>
<td></td>
<td>24chr vs 1hr/6hr</td>
<td>0.62</td>
<td>3.1 x 10^{-2}</td>
<td>0.19</td>
<td>(0.11 – 0.27)</td>
</tr>
</tbody>
</table>