Reactive Matrix clean-up of Polycyclic Aromatic Compounds in the Environment

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Abstract: Polycyclic aromatic compounds (PACs) are released into the environment in large quantities during incomplete combustion of fossil fuels. An efficient method of isolation from the environmental matrix is most important, since PACs normally occur at sub ppm levels in the environment. A new one step isolation method based on chemical similarity is being described in detail. All compounds having a polycyclic aromatic structure are being isolated together. The result of such a clean-up is a matrix of polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic ketones (PAKs) and nitro- and oxo- derivatives of PAHs. The chemically reactive nature of emissions of these compounds is demonstrated with samples from particulate emissions of gas turbines and gasoline driven automotive engines. Capillary gas chromatography is being applied to PACs. Indicator compounds and a degradation matrix are clearly visible in the gas chromatograms. The concentration of a degradation matrix and the concentration or absence of indicator compounds define the chemical state of environmentally occurring PACs as degraded, partially degraded or undegraded. Major and minor components of the degradation matrix are further characterised by capillary GC and GC/MS. GC/MS can identify compound classes. Isomers of PAHs have identical mass spectra and must be characterised by GC/FID using 4 stationary phases of different selectivity. Perylene occurs naturally in certain soils. The distinctive feature of naturally occurring perylene is the absence of other PACs. This is demonstrated with samples from various locations in Japan. The input of combustion related perylene into soil occurs along with other PACs. Thus, the source of perylene in soil can be identified. Final deposition of combustion related PACs occurs in surface soil. The major input results from precipitation of airparticulate matter and disposal of combustion residues. Biogenic and chemical degradation of PACs in soil are two different pathways of dissipation and decontamination, and details are being discussed.

Keywords: EcoTopia Science, Reactive matrix clean up, XAD-2, PACs, PAHs, Particulate matter

1. INTRODUCTION

Airparticulate matter is a dark fine powder like substance that carries organic compounds released during combustion processes. Polycyclic aromatic compounds (PACs) are of major concern because various substances belonging to this compound class possess carcinogenic properties. Residence times of particulate matter in air depend on the size of the particles. Finally, all particulate matter is precipitated on the surface of the earth and becomes a contaminant in surface soil.

Long residence times in the air facilitate the formation of secondary compounds. Such compounds can be formed by oxidation and nitration. Since all these reactions of chemical oxidation and nitration are simultaneously taking place with a great number of compounds being present in particulate matter, the number of such reaction products is enormous. The ring structure of polynuclear aromatic hydrocarbons can accommodate substituents in the various positions of the polyaromatic ring arrangement. Substituents can be hydroxy or nitro groups. Since atmospheric reactions are non-biogenic, characteristic metabolites cannot be expected to be formed at high concentrations. The degradation state of primarily released PACs can therefore not be characterised well by the formation of a distinctive metabolite at a high concentration. Instead, the sum of all secondary metabolites formed
can give an indication of the degradation state of PACs. In order to characterise the extent of dissipation reactions having taken place, an efficient new isolation procedure selectively separating PACs from non PACs is needed. The interaction between polymers and small molecules seems to be the method of choice for such a clean up. The reactive matrix of PACs being obtained this way provides two important informations on dissipation reactions having taken place. The first information is the disappearence of indicator compounds of degradation [1]. The second information is the amount of accumulation of secondary PACs. The nature of primary PACs in gas turbine emissions and gasoline combustion engine emissions will be compared with urban airparticulate matter and PACs in surface soil.

2. Experimental Part

Particulate matter is being sampled by the high volume method. The High volume method provides relatively large amounts of airparticulate matter and is therefore being preferred to low volume sampling. Filter materials used for a precipitation of particulate matter are membrane filters of cellulose acetate or glass fiber filters. Filters are placed on a stainless steel grid, and a sublayer of a large pore glass fiber filter is used for accommodating analytical filters. Sampling periods ranged from 1 hour to 100 hours, depending on the purpose of the sampling experiment.

Analytical handling of the precipitate on the filters begins with drying of filters in a desiccator over silica gel. Filters are then subdivided into small portions and transferred to glass fiber thimbles. Extraction is being done with toluene by the soxhlet method.

The crude extract is being concentrated to 0.5ml final volume with a rotary evaporator. The final solution is being transferred to a separation column of 1 cm internal diameter. The packing is a polymer based on XAD-2 with distinctive surface properties. Sequential elution is done with organic solvents.

The fraction containing PACs is further analyzed by GC/FID and GC/MS. EI ionization is done at 70ev. GC is done with glass capillary columns (30m x 0.22 mm) coated with OV1, SE-54, Dexsil 300 and OV-25. GC was done with a temperature program of 110-260 °C. Detector and injection port were kept at 300 °C. Injections were done in the splitless mode, and the split was kept closed for 60 sec using a stopwatch. The injector was a Grob type split/splitless injector with septum backflush fitted on a Carlo Erba 4130 High resolution GC.

Standard compounds were a gift of Professor Grimmer. Solvents were glass distilled through a vigreux column of 30 cm.

3. Results and Discussion

3.1. PACs in exhaust emissions

The most abundant PAH is cyclopenta(cd)pyrene (CYC). However, although being released in a 10-fold excess over benz(a)anthracene this compound is rapidly degraded in the air and is therefore less suitable for a source identification of PAHs originating from combustion engines. Benzo(ghi)fluoranthene (GHI) is released at a five-fold excess over benz(a)anthracene. This compound is not very persistent in the air. The overall pattern of PACs is being displayed in Figure 1. Benzo(ghi)perylene has a substantial excess over benzo(e)pyrene, and can be an indicator compound for gasoline combustion engine related PACs due to its persistence in airparticulate matter. The...
fingerprint of PACs was obtained by capillary GC, using a glass column of 30m length and 0.22 mm ID. The stationary phase was OV-1. Benzofluoranthenes (5) and Benzopyrenes (6,7) are released at concentrations comparable to benz(a)anthracene. All PACs with molecular weights up to 202 are mostly vaporised in the atmosphere. The excess of total emission of phenanthrene over benzo(e)pyrene may be 50 times or more. Over 90% of total phenanthrene is found in the gas phase. The same applies to fluoranthene and pyrene.

3.2. PACs in gas turbine emissions

The rapid increase in air traffic leads to substantial emissions of PACs into the environment. The amount of benzo(e)pyrene released during the combustion of 1t kerosene is in the range of 1-10 mg, depending on the type of gas turbine, fuel and operating conditions. Volatile PAHs like phenanthrene have a 50-fold excess over benzo(e)pyrene. Cyclopenta(cd)pyrene and benzo(ghi)fluoranthene occur at comparable concentrations, which is an important difference to combustion engines.

Benzanthrone is released in concentrations comparable to benz(a)anthracene. Another distinctive feature is the roughly comparable concentration of indeno 1,2,3(cd)pyrene and benzo(ghi)perylene. The fingerprint of PACs in Figure 4 was obtained by gas chromatography on the non-polar phase OV1 using a glass capillary column. GC conditions were the same as in figure 1. The sampling of particulate emissions was done during test runs of aircraft turbines. Sampling heads with membrane filters were placed 50 m behind the exhaust outlet of aircraft engines. Glass fiber filters were also used, but losses of volatile PACs were higher on such filter materials. Volatile PACs were aborbed from the gas phase by using several layers of membrane filters during short sampling periods (e.g. 10 min). The excess of volatile PAHs over benzo(e)pyrene was 20 to 50 fold. Total emission of benzo(e)pyrene was 0.3 or up to 4 mg/t kerosene for JT8D9 gas turbines. Total emission heavily depends on the type of fuel, engine and engine settings.

3.3 PACs in urban air particulate matter

Long term high volume sampling is most efficient in providing large amounts of urban air particulate matter. The black dust obtained this way contains PACs in concentrations of 10-1000 ppm. The aerial concentrations of total dust can vary widely. Average concentrations are between 30 -100 µg/m$^3$. Heavy road traffic should produce high levels of cyclopenta(cd)pyrene in urban air. However, this compound is not very stable. Actual values of cyclopenta(cd)pyrene are mostly below 20% of the concentration of benzo(e)pyrene, and always below 10 µg/m$^3$.

Figure 3 Benzo(ghi)fluoranthene

Figure 4 Fingerprint of PACs in aircraft turbine particulate emissions obtained by GC/FID

Figure 5 Fingerprint of PACs in urban air particulate matter obtained by GC/FID

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Figure 5 displays the pattern of PACs in urban particulate matter obtained by GC/FID. Peak numbers and GC conditions are the same as in Figure 4. Distinctive features are the relatively low concentrations of benzo(ghi)fluoranthene and cyclopenta(cd)pyrene. Benzanthrone is a polycyclic aromatic ketone that seems to be degraded in airparticulate matter more rapidly than most parent PAHs. It occurs at a rather low concentration. The concentration of benzo(ghi)perylene being equivalent to benzo(e)pyrene indicates substantial origination of PAHs from other sources than gasoline combustion engines.

The rapid degradation of cyclopenta(cd)pyrene is obvious from the low concentration of this compound in almost all samples of urban airparticulate matter. Secondary reaction products are not being present as distinctivly new GC-peaks, but there is an increased number of small peaks and multiple nonresolved small peaks. Nonresolved small peaks are the reason for a slightly elevated baseline in the later part of the chromatogram in Figure 5. The selective isolation of polynuclear compounds assures that the baseline rise is being related to the presence of polycyclic substances only.

The dissipation of PACs in airparticulate matter generates secondary metabolites by oxidation and nitration. Such metabolites cannot be identified due to the large number of isomers, and the resulting coelution of multiple peaks. The state of degradation of PACs, therefore, must be defined by the disappearance of certain compounds, which can act as indicator compounds for degradation [1]. The absence of high concentrations of benzo(ghi)fluoranthene and cyclopenta(cd)pyrene defines the fingerprint of PACs in Figure 5 as a rather degraded profile that has probably resided in the atmosphere for some time.

The ratio of benzo(a)pyrene to benzo(e)pyrene is almost 1, and this means that on the other hand degradation reactions have not been in a very advanced stage. Heavily degraded patterns of urban airparticulate matter mostly show a low ratio of benzo(a)pyrene to benzo(e)pyrene of 0.5 or less, although the ratio of these two compounds is close to 1 in emissions from almost all sources. Obviously, a source identification of PACs in urban airparticulate matter faces the difficulty of original ratios of PACs having been altered by reactions of degradation.

### 3.4 PACs in urban surface soil

The abundance of PACs in urban surface soil is almost exclusively a result of precipitation of airparticulate matter. Thus, those PACs that are stable in the atmospheric environment can be expected to be found in surface soil.

Figure 7 is a fingerprint of PACs near Nagoya airport, Japan. GC conditions: Stationary phase SE 54, fused silica capillary column [2].

The concentration of benzo(e)pyrene was 220 µg/kg. These results show that there is a drop in concentration by 3 orders of magnitude compared to the concentration of benzo(e)pyrene in pure airparticulate matter, where values of 1-100 ppm benzo(e)pyrene are being found. The ratio of benzo(ghi)pyrenes is distorted in this sample. 6-H-benzo(cd)pyrene-6-one is coeluted with benzo(a)pyrene on the stationary phase SE-54. This can be confirmed by mass spectrometry. Another method of confirmation of peak purity is the application of multiple stationary phases having a different selectivity towards PACs [3]. Benzanthrone (4) is present at a concentration suggesting that its dissipation proceeds at a speed com-
parable to benz(a)anthracene. Surprisingly, relatively low concentrations of PACs with molecular weights of 202 or less are being found. These compounds are vaporised in the air and have a 10 to 100-fold excess over heavier PACs absorbed on particulate matter. These compounds are probably not absorbed at all in substantial amounts from the atmosphere by surface soil.

### 3.5 Composition of the reactive matrix of PACs

Polycyclic aromatic compounds include parent PAHs along with nitroderivatives and polycyclic aromatic ketones. Species of all three compound classes occur together in the environment. Their common feature is the polycyclic aromatic base structure, and some of these substances are carcinogenic. They have been the target of environmental chemical analysis for some time.

All methods of isolation and clean-up that are based on a polarity of analytes can never keep these compounds together during the different stages of analysis, since their polarity is largely different depending on which functional groups have been introduced. Unlike analytical methods that are based on the polarity of chemical substances, the reactive matrix clean-up aims at isolating nitro- and oxo-derivatives along with parent PAHs in one final fraction. The obvious advantage of such a procedure is the clear result on the quantitative ratio of parent compounds to nitro- and oxo-derivatives.

![Figure 8](image)

**Figure 8** Fingerprint of PACs in urban airparticulate matter by GC/FID. Glass capillary 30m x 0.22mm, stationary phase OV-25 X: PAHs ● polynuclear aromatic ketones (PAKs)

The reactive matrix clean-up provides comprehensive information on the occurrence of PACs in airparticulate matter. This information can be derived directly from this FID trace without employing further methods of clean-up or GC/MS. PAHs (X) and PAKs (●) are present within the same order of magnitude in concentration. Nitroderivatives of PAHs, however, are present at much lower concentrations. These substances disappear in the baseline rise that is due to various coeluting polycyclic aromatic compounds. These unresolved PACs are fragments and derivatives of parent PAHs and cannot be resolved due to their excessive number. Their total amount is proportional to the area between the dark, thick bottom line and the FID-trace.

Reaction products of PAC dissipation being responsible for the baseline rise are supposed to be chemically less stable than parent compounds. Once derivatisation of these compounds has started, it can be supposed to proceed at an increasing reaction speed. The result is an enormous number of derivatives, that can no longer be separated from each other by capillary GC. All these compounds still have a polycyclic aromatic base structure and can still be isolated as one compound class, PACs. The extent of derivatisation cannot be appreciated well by the generation of new signal compounds. Molecules having no longer a polycyclic aromatic structure stand at the end of the degradation pathway. However, the disappearance of certain signal compounds can give an indication of the advance of degradation.

It has been proposed that cyclopenta(cd)pyrene, benzo(ghi)fluoranthene and benzo(a)pyrene are suitable to act as indicator compounds of PAH degradation in particulate emissions [1]. Dissipation of PACs by chemical degradation is indicated by the disappearance of these compounds from profiles of PACs. Chemical degradation reactions are an important first step in the environmental dissipation of this carcinogenic class of compounds. Once chemical degradation has started, PACs become more polar and water soluble, which facilitates additional degradation by biogenic reactions.

The reactive matrix clean-up provides comprehensive information on the very large number of substances belonging to this carcinogenic compound class. Polarity based methods of clean-up alone, however, can never give this comprehensive information. The polymer based group clean-up seems to work surprisingly well. The clean-up can also handle very high column loads of interfering compounds like phthalates or hydrocarbons. Chlorinated polycyclic compounds (e.g. PCBs) are also target compounds of this clean-up and can be quantitatively recov-
Table 1 PACs in the gas chromatograms

<table>
<thead>
<tr>
<th>Substance</th>
<th>Peak</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>1</td>
<td>178</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>2</td>
<td>202</td>
</tr>
<tr>
<td>Pyrene</td>
<td>3</td>
<td>202</td>
</tr>
<tr>
<td>Benzanthrone</td>
<td>4</td>
<td>230</td>
</tr>
<tr>
<td>Benzo(b,j,k)fluoranthenes</td>
<td>5</td>
<td>252</td>
</tr>
<tr>
<td>Benzo(e)pyrene</td>
<td>6</td>
<td>252</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>7</td>
<td>252</td>
</tr>
<tr>
<td>Coronene</td>
<td>8</td>
<td>300</td>
</tr>
<tr>
<td>Benzo(ghi)fluoranthene</td>
<td>GHI</td>
<td>226</td>
</tr>
<tr>
<td>Cyclopenta(cd)pyrene</td>
<td>CYC</td>
<td>226</td>
</tr>
<tr>
<td>Benzo(ghi)perylene</td>
<td>B(ghi)per</td>
<td>276</td>
</tr>
</tbody>
</table>

Table 2 PACs in atmospheric particulate matter

<table>
<thead>
<tr>
<th>Substance</th>
<th>Sample 1 ppm</th>
<th>Sample 2 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoranthene</td>
<td>340</td>
<td>50</td>
</tr>
<tr>
<td>Pyrene</td>
<td>340</td>
<td>30</td>
</tr>
<tr>
<td>Benzo(ghi)fluoranthene</td>
<td>132</td>
<td>15</td>
</tr>
<tr>
<td>Cyclopenta(cd)pyrene</td>
<td>228</td>
<td>0</td>
</tr>
<tr>
<td>Benzo(b,j,k)fluoranthenes</td>
<td>293</td>
<td>90</td>
</tr>
<tr>
<td>Benzo(e)pyrene</td>
<td>139</td>
<td>47</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>135</td>
<td>22</td>
</tr>
<tr>
<td>Benzo(ghi)perylene</td>
<td>126</td>
<td>37</td>
</tr>
</tbody>
</table>

Table 1 lists the peak numbers in the figures with the corresponding compound names and their molecular weights. The concentrations of PACs in urban air particulate matter are listed in Table 2. Sample one results from short high volume sampling overnight in winter time. A high concentration of total dust (221 µg/m³) indicates the accumulation of smoke and exhaust gases in the atmosphere. Sample 2 results from high volume sampling at the low total dust concentration of 40 µg/m³. The absence or decreased concentration of benzo(ghi)fluoranthene and cyclopenta(cd)pyrene indicate the advance of PAC degradation, and concentrations of all PACs are lower.

Compound class selective methods of chemical analysis can be supplemented well by methods based on polarity or molecular weight, and modern instrumental methods like HPLC/MS or GC/MS. In many cases compound class selective clean-up is fully sufficient for a characterisation of analytes, if GC/MS is applied in detection of compounds.

3.6 Discussion

Fresh emissions of combustion processes contain reactive PACs. Degradation reactions result in the introduction of nitro-, oxo- and hydroxy- functions into the polynuclear aromatic environment. Such reactions result in more polar compounds of increased water solubility [4,5]. PACs need to be activated before their carcinogenic potential is fully developed [6]. The increased water solubility of metabolites formed by chemical reactions seems to facilitate additional biogenic degradation. Thus, the analytical investigations of PACs must deal with the complete group of compounds and must find a measure for a definition of their degradation state in order to appreciate their carcinogenic potential.

Clean-up of PACs with the help of an organic absorbent [7,8] will provide selectively purified compound mixtures of PAHs, PAKs and nitro derivatives of PAHs [9]. It is demonstrated that reactive compounds are not altered by this clean-up. The reactive matrix obtained this way can be further analyzed by GC/FID in order to obtain a fingerprint of PACs along with comprehensive information on the advance of degradation of reactive compounds.

Primary and secondary reaction products of PACs can develop some carcinogenic potential [10]. The carcinogenic potential is not limited on primary emissions and parent compounds. The group selective clean up provides a first information on the carcinogenic potential of environmentally occurring mixtures of PAC, since all polynuclear aromatic compound classes and their primary metabolites are covered by this method. Fingerprints of PACs obtained this way are a simple visual database for a comparison of different samples.

The reactive matrix clean-up provides samples that can

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be further characterized by polarity selective LC, HPLC or GC/MS. The additional data obtained by such methods supplement well the basic “fingerprint” information received by GC/FID. Reactive matrix clean up becomes an important stage in characterising the exceedingly complex mixture of polynuclear aromatic substances abundant in the environment.

4. Conclusion
The characteristic fingerprint of PACs in the environment reveals comprehensive information about the origin of PACs and their reactivity and degradation state. The reactive matrix clean-up provides this fingerprint most easily. Hydrocarbons, ketones and nitroderivatives are being isolated together without a distortion of their quantitative ratios. The method is compatible with additional analytical steps like GC/MS or polarity selective liquid chromatography in order to identify minor components of environmentally occurring PACs. The simultaneous display of PAHs along with their keto- and nitro-derivatives in one fingerprint like profile cannot be achieved by other methods of clean up. Such a unique information of the abundance of all carcinogenic PACs in the environment is most important in ecotopia science.

REFERENCES

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