

# IDENTIFICATION AND DETERMINATION OF HIGHLY CARCINOGENIC DIBENZOPYRENES IN STOCKHOLM AMBIENT AIR

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## INTRODUCTION

A group of organic compounds formed in incomplete combustion are Polycyclic Aromatic Hydrocarbons (PAH). Some PAH are found to be carcinogenic to animals and are thus potentially carcinogenic to humans. The most well-known PAH is benzo(a)pyrene (B(a)P), which is classified by International Agency for Research on Cancer (IARC, 1983; 1989) as 2A i.e. probably carcinogenic to humans. A way to compare individual PAH relative to each other with respect to cancer potency is to use Toxic Equivalence Factors (TEFs) of which the TEF for B(a)P is set to one by definition. Compounds with larger TEFs than one are more carcinogenic than B(a)P and vice versa. Some dibenzopyrenes reported in the scientific literature have TEF values in the range of 1 to 100 (Boström et al., 2002). A new developed analytical method for determination of B(a)P and highly carcinogenic dibenzopyrenes has been validated using Standard Reference Material (SRM) 1649a Urban dust, Washington air particles sampled 1976-1977, (Bergvall and Westerholm, 2005) and applied on Stockholm ambient air particulate material.

## METHODS

Ambient air particulate material samples were collected at the roof of the Arrhenius laboratory building located on the Stockholm University main campus at Frescati. The particulate material samples were collected on Teflon® coated glass fibre filters (149 mm, Pallflex T60A20, USA) at a flow of approximately 140 l/min during one week (4/10-11/10) in October 2005. Filters were changed around every 24 hours except for one filter, which was changed after 43 hours. The amount of particulate material collected on the filters (n=6) varied between 2,6-10,6 mg with an average of  $24 \pm 7,5$   $\mu\text{g}/\text{m}^3$ . After sampling the filters were folded, wrapped in aluminium foil and stored in a freezer at  $-20^\circ\text{C}$  until chemical analysis. Each filter was cut into two parts, which were analysed separately in order to produce a measurement of the uncertainty of the analytical method. In principal, the filters were placed in disposable 15 ml test tubes and internal surrogate standards (B(a)P-D12, coronene-D12 and dibenzo(a,i)pyrene-D14) and 5 ml acetone were added. The samples were ultrasonic extracted for 10 min and the extracts were then filtered through nylon syringe filters prior to pre-cleaning using silica Solid Phase Extraction (SPE) cartridges. The aliphatic/PAH enriched fractions were analysed using online hyphenated High Performance Liquid Chromatography (HPLC)- Gas Chromatography (GC) Mass Spectrometry (MS), which is described in detail elsewhere (Bergvall and Westerholm, 2005; Christensen et al., 2005). Blank samples were cleaned up and analysed at the same time as the air particulate samples in order to check for contamination and memory effects from the analytical method.

## CONCLUSIONS

The compounds B(a)P, perylene and coronene are determined and dibenzo(a,l)pyrene, dibenzo(a,e)pyrene, dibenzo(a,i)pyrene and dibenzo(a,h)pyrene are identified and determined for the first time in Stockholm ambient air particulate material.

Determined concentrations are presented in Figure 1 and 2. Figure 3 displays GC/MS chromatograms (SIM, extracted ion m/z 302) of (A) Stockholm air particulate matter and (B) SRM 1649a Urban dust (Bergvall and Westerholm, 2005). The dibenzopyrene isomers determined in this study are identified (Table 1) on the basis of their retention times and standard addition using reference standards. Other PAH with molecular weight 302 are tentatively identified (Table 1) based on comparison with a chromatogram of SRM 1649a Urban dust (Schubert et al., 2003), which is very similar in terms of relative intensity to chromatograms of Stockholm ambient air particulate material. Carcinogenic potencies of the determined dibenzopyrene isomers and B(a)P in the samples were calculated by multiplying the concentration of each compound with their individual TEF value. The result is displayed in Figure 4 and reveals that dibenzo(a,l)pyrene, although not the most predominant compound, is the major carcinogenic contributor of the determined PAH. Figure 5 shows the carcinogenic potency of B(a)P compared to the sum of the determined dibenzopyrenes (DBP) in each sample collected. The mean ratio, of the six samples, of carcinogenic potency between the DBP and B(a)P is  $3,1 \pm 0,65$  indicating that the dibenzopyrenes determined have a greater carcinogenic potency in comparison to B(a)P in Stockholm ambient air. Corresponding ratio (dibenzo(a,e)pyrene excluded) when multiplying the mean concentrations (n=12) with the TEF values is 2,78 in Stockholm air particulate matter compared to 1,84 for SRM 1694a Urban dust (Data from Bergvall and Westerholm, 2005). This indicates that air particles from Stockholm possess 50% larger carcinogenic potency compared to Washington air particles sampled 1976-1977. This study implies a need to investigate the seasonal variations of dibenzopyrenes in different Stockholm locations such as suburbs, road tunnels and city central areas. Furthermore, there is also a need to identify significant sources to dibenzopyrenes in general.

## ACKNOWLEDGEMENTS

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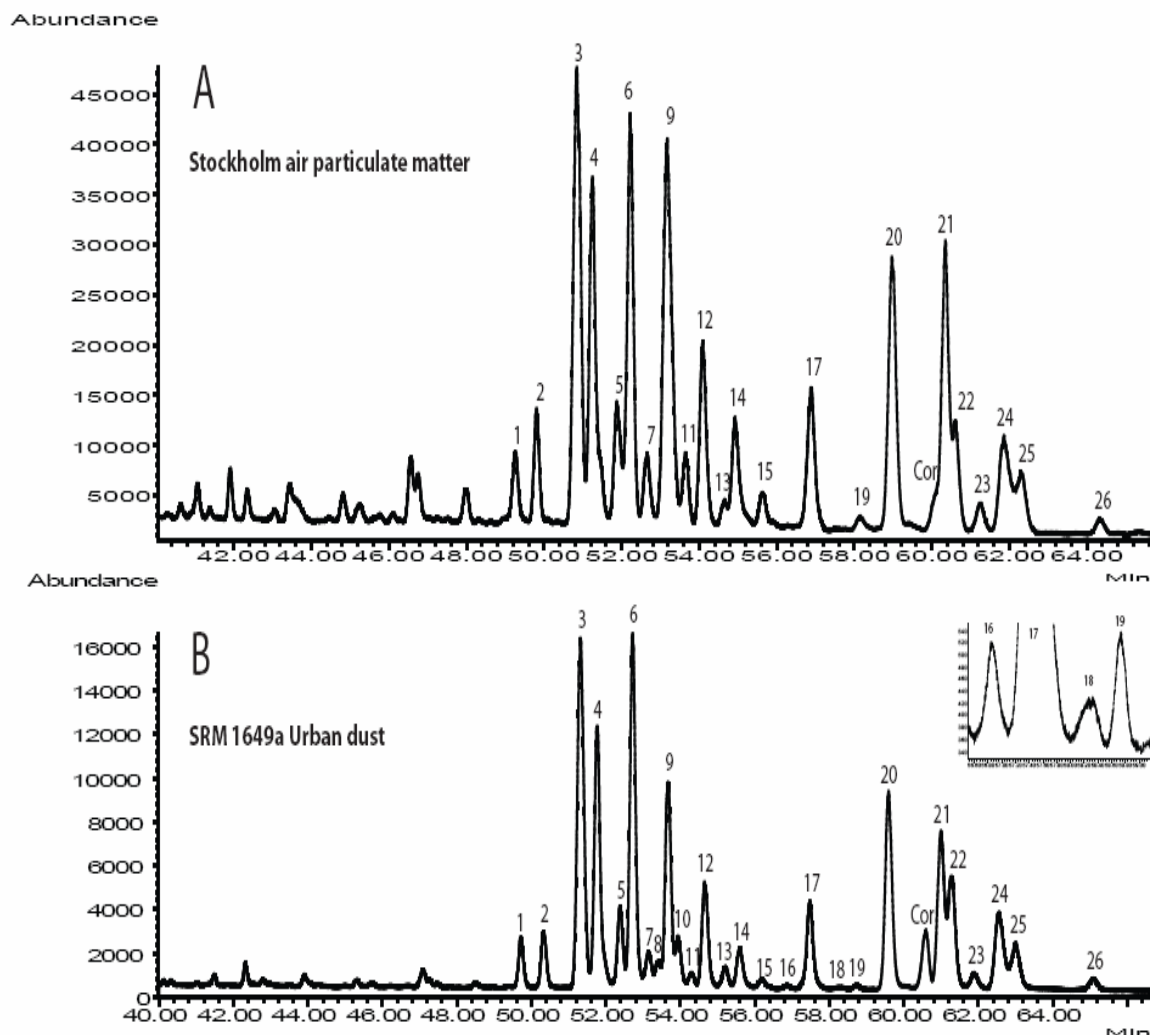


Figure 3. GC/MS selected ion monitoring (SIM) chromatogram (extracted ion  $m/z$  302) of (A) ambient Stockholm air particulate material and (B) Standard Reference Material (SRM) 1649a Urban Dust (enlarged picture showing peaks 16-19). See Table 1 for peak identifications. Cor, coronene.

**Table 1. Peak numbering for identified and tentatively identified PAH 302 isomers.**

Peak Nr	PAH 302 isomers	Abbreviations
1	Dibenzo( <i>b,e</i> )fluoranthenea	DB( <i>be</i> )F
2	Unknown	
3	Naphtho(1,2- <i>b</i> )fluoranthenea	N(12 <i>b</i> )F
4	Naphtho(1,2- <i>k</i> )fluoranthenea	N(12 <i>k</i> )F
5	Naphtho(2,3- <i>b</i> )fluoranthenea	N(23 <i>b</i> )F
6	Dibenzo( <i>b,k</i> )fluoranthenea	DB( <i>bk</i> )F
7	Dibenzo( <i>a,k</i> )fluoranthenea	DB( <i>ak</i> )F
8	Unknown	
9	Dibenzo( <i>j,l</i> )fluoranthenea	DB( <i>jl</i> )F
10	Naphtho(1,2- <i>e</i> )pyrenea	N(12 <i>e</i> )P
11	Dibenzo( <i>a,l</i> )pyreneb	DB( <i>al</i> )P
12	Unknown	
13	Naphtho(2,3- <i>k</i> )fluoranthenea	N(23 <i>k</i> )F
14	Naphtho(1,2- <i>a</i> )pyrenea	N(12 <i>a</i> )P
15	Unknown	
16	Unknown	
17	Naphtho(2,3- <i>e</i> )pyrenea	N(23 <i>e</i> )P
18	Unknown	
19	Unknown	
20	Dibenzo( <i>a,e</i> )pyreneb	DB( <i>ae</i> )P
21	Naphtho(2,1- <i>a</i> )pyrenea	N(21 <i>a</i> )P
22	Dibenzo( <i>e,l</i> )pyrenea	DB( <i>el</i> )P
23	Naphtho(2,3- <i>a</i> )pyrenea	N(23 <i>a</i> )P
24	Benzo( <i>b</i> )perylenea	B( <i>b</i> )Per
25	Dibenzo( <i>a,i</i> )pyreneb	DB( <i>ai</i> )P
26	Dibenzo( <i>a,h</i> )pyreneb	DB( <i>ah</i> )P

a tentatively identified by comparison to chromatogram from Schubert *et al.*, 2003.

b identified using reference standards.

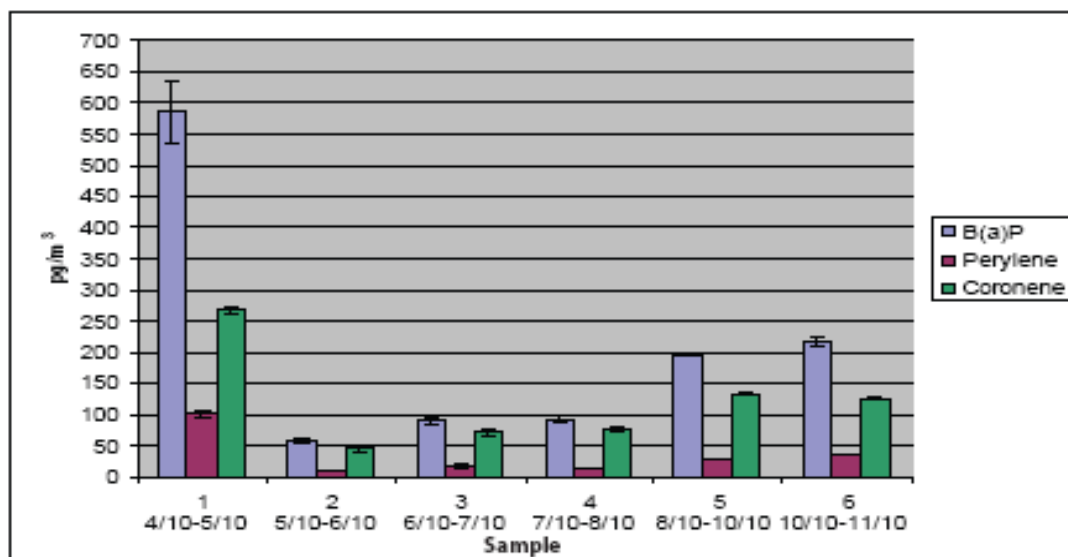


Figure 1. Determined concentrations ( $\text{pg}/\text{m}^3$ ) of B(a)P, perylene and coronene in Stockholm ambient air particulate matter.

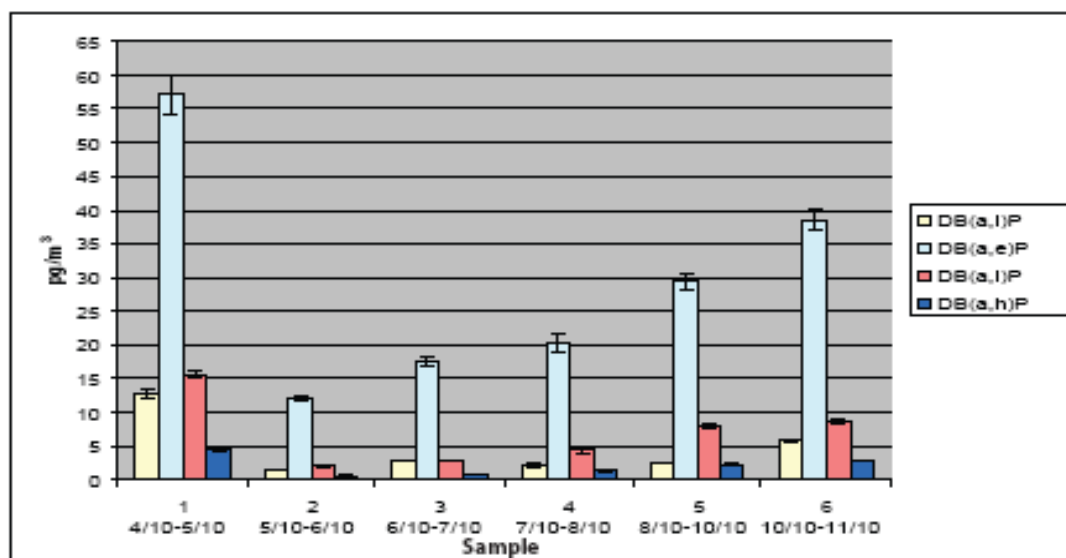


Figure 2. Determined concentrations ( $\text{pg}/\text{m}^3$ ) of the dibenzopyrene isomers in Stockholm ambient air particulate matter.

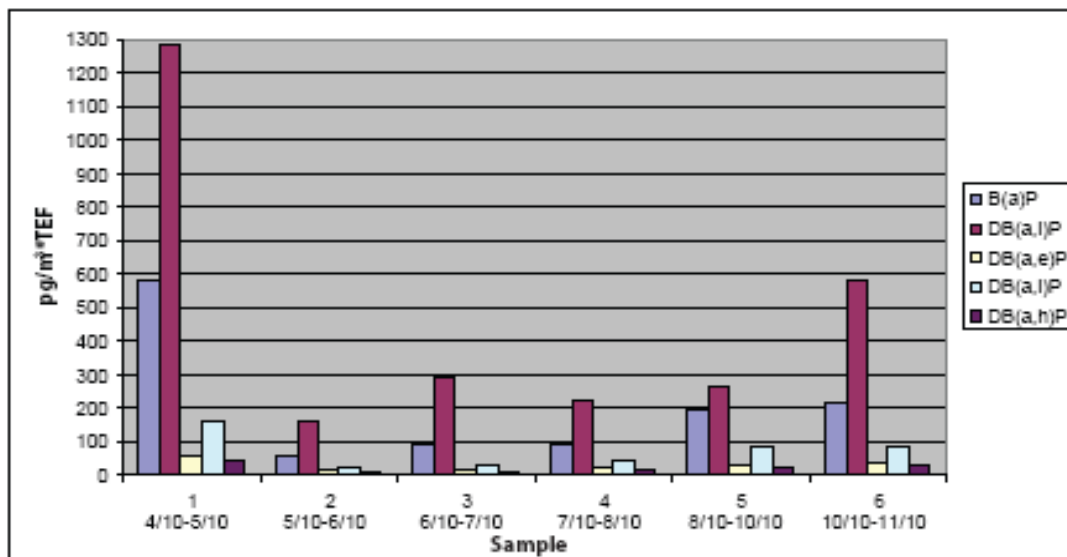


Figure 4. Determined carcinogenic potencies, expressed in  $\text{pg}/\text{m}^3 \cdot \text{TEF}$ , of the dibenzopyrenes and B(a)P in Stockholm ambient air particulate matter.

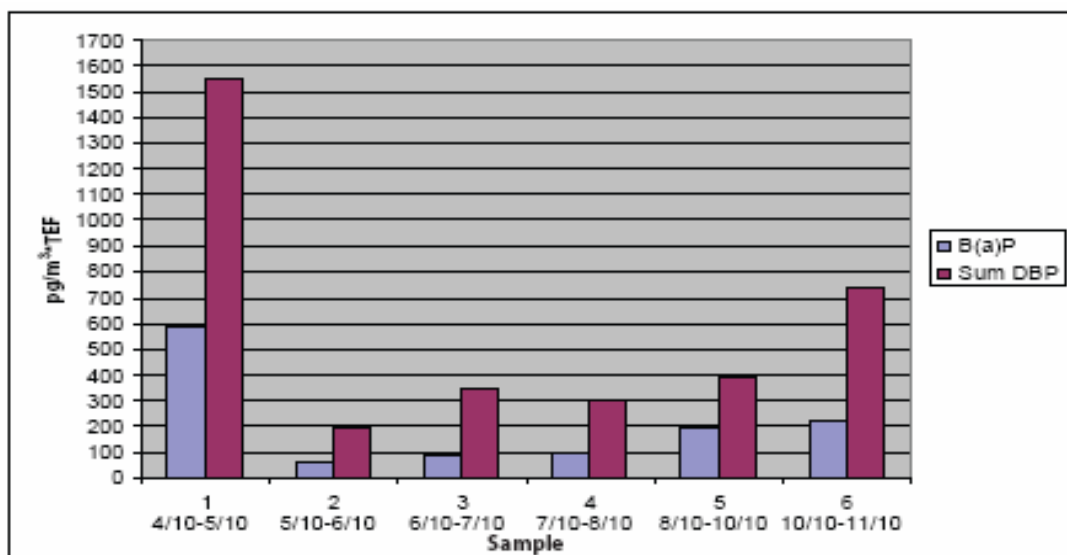


Figure 5. Comparison of the carcinogenic contribution between B(a)P and the sum of the determined dibenzopyrenes (DBP) in Stockholm ambient air particulate matter.