



DETERMINATION OF HIGHLY CARCINOGENIC DIBENZOPYRENES IN STOCKHOLM AMBIENT AIR USING A VALIDATED HYPHENATED LC-GC-MS METHOD

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INTRODUCTION

A group of organic compounds formed during 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. The dibenzopyrene isomers dibenzo(a,h)pyrene, dibenzo(a,e)pyrene, dibenzo(a,i)pyrene and dibenzo(a,j)pyrene determined in this study have reported TEF values in the range of 1 to 100 (Boström *et al.*, 2002). Dibenzo(a,l)pyrene is considered to be the most carcinogenic isomer with a TEF value of 100 (Muller *et al.*, 1997) and claimed to be probably the strongest chemical carcinogen ever tested (Platt *et al.*, 2004). 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 (Bergvall and Westerholm, 2006) 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. The particulate material samples were collected on Teflon® coated glass fibre filters (149 mm) at a flow of approximately 140 l/min during two weeks (4/10-18/10) in October 2005 and one week (27/4-3/5) in 2006. During the first week the 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±7.5 µg/m³. The second week in October 2005 (37 mg, 27 µg/m³) and the week in 2006 (77 mg, 53 µg/m³) air particulate material were collected on the same filter during the entire week. After sampling the filters were folded, wrapped in aluminium foil and stored in a freezer at -20°C until chemical analysis. Each filter was cut into smaller 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 and dibenzo(a,l)pyrene-D14) and 5 ml acetone were added. The samples were ultrasonically 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, 2006; 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.

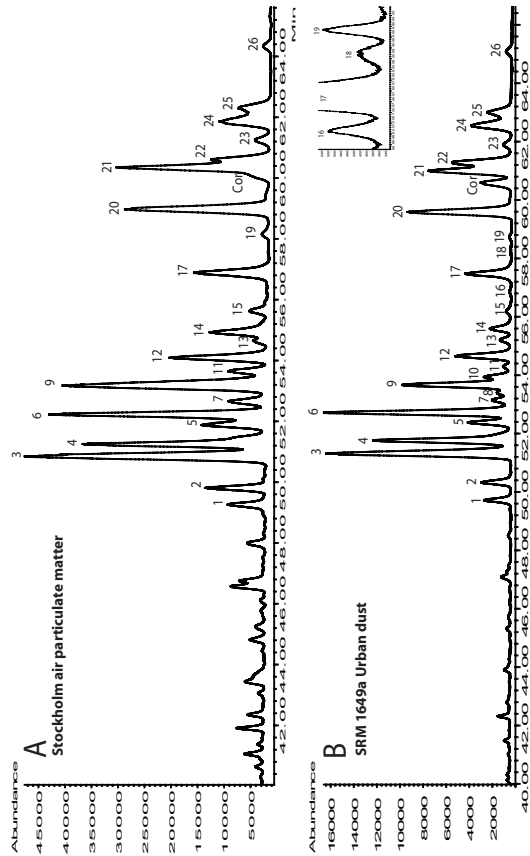


Figure 3. GC/MS selected ion monitoring (SIM) chromatogram (extracted ion m/z 302) of Stockholm air particulate material and SRM 1649a Urban dust. The retention times (RT) and the peak identifications, Cor, coronene.

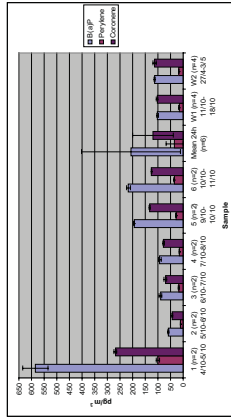


Figure 1. Determined concentrations (pg/m³) of B(a)P, perylene and coronene in Stockholm ambient air particulate material for samples 1-6. W1 and W2 are week samples.

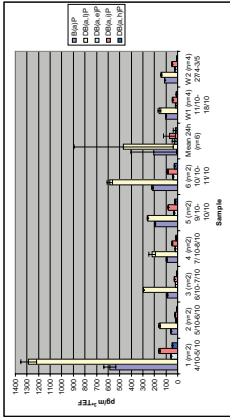


Figure 4. Determined carcinogenic potencies, expressed in pg/m³*TEF, of the dibenzopyrenes and B(a)P in Stockholm ambient air particulate material for samples 1-6. W1 and W2 are week samples.

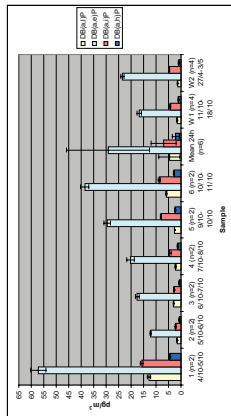


Figure 2. Determined concentrations (pg/m³) of the dibenzopyrene isomers in Stockholm ambient air particulate material for samples 1-6. W1 and W2 are week samples.

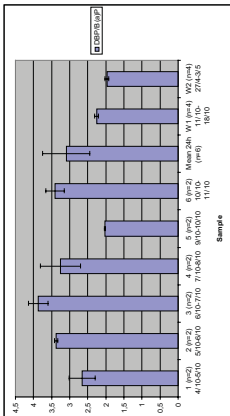


Figure 5. Comparison of the carcinogenic contribution (pg/m³*TEF) between the sum of the determined dibenzopyrenes (DBP) and B(a)P in Stockholm ambient air particulate material for samples 1-6. W1 and W2 are week samples.

CONCLUSIONS

For the first time the highly carcinogenic compounds dibenzo(a,l)pyrene, dibenzo(a,e)pyrene, dibenzo(a,i)pyrene and dibenzo(a,h)pyrene are determined in Stockholm ambient air particulate material. The compounds B(a)P, perylene and coronene are also determined in this study. Determined concentrations are presented in Figure 1 and 2. The mean concentrations of the 24-hour samples collected during the first sampling week are up to three times higher than the concentrations determined in the two week samples (W1 and W2). There is also a large day-to-day variation between the different 24-hour samples. One possible explanation could be biomass burning at nearby allotment plots during the first sampling week. This raises the question if biomass burning is a significant source of dibenzopyrene emissions. The determined concentrations in the two week samples are very similar indicating no major differences in concentrations between fall and spring. 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, 2006). The dibenzopyrene isomers determined in this study are identified (Table 1) on the basis of their retention times and standard addition using reference standards. 15 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 (Boström *et al.*, 2002). 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 in all samples. Figure 5 shows the ratio of the carcinogenic potency between the sum of the determined dibenzopyrenes and B(a)P in each sample collected. The ratio of carcinogenic potency is between two and four indicating that the dibenzopyrenes determined have a greater carcinogenic potency in comparison to B(a)P in Stockholm ambient air. This study implies a need to further investigate the seasonal variations of dibenzopyrenes in different Stockholm locations such as suburbs, road tunnels, city central areas and the underground. Furthermore, there is also a need to identify significant sources to dibenzopyrene emissions.

ACKNOWLEDGEMENTS

The research project is partly financed by the Swedish Emission Research Program (EMIS) and partly by Stockholm University.

REFERENCES

Bergvall C and Westerholm R. (2006). Determination of dibenzopyrene in standard reference material (SRM) 1649a, 1639, and 2975 using ultrasonically assisted extraction and LC-GC-MS. Environmental Health & Safety Research, 12, 1-10.
 Bergvall C, E. Gede F, Bergvall C, W. Lundström, M. Westberg, R. Westerholm, K. Christensen, J. Andersson, and guidelines for polycyclic aromatic hydrocarbons (PAH) in urban dust and diesel particulate matter. Environmental Health & Safety Research, 12, 1-10, Supplement 3, 451-488.
 Boström M, O. Hansson, B. Strandberg, and S. Strandberg. (2002). Determination of polycyclic aromatic hydrocarbons (PAH) in urban dust and diesel particulate matter. Analytical and Bioanalytical Chemistry, 382, 1601-1616.
 Muller J. (1983). Polycyclic aromatic compounds. Part 1. Chemical, environmental and experimental data. International agency for research on cancer (IARC), Lyon, France.
 Muller J. (1997). Scientific Criteria Document for Multimedia Standard Development Polycyclic Aromatic Hydrocarbons (PAH). Part 1. Hazard Identification and Dose-Response Assessment. Ontario, ON: Standard Development Branch, Ontario Ministry of Environment and Energy.
 Schubert J, Schwan M, Sauer L, and W. S. (2003). Determination of Polycyclic Aromatic Hydrocarbons with Molecular Weight 300 and 302 in Environmental Matrix. Standard Development Branch, Ontario Analytical Chemistry, 7, 234-246.
 Westerholm R, Bergvall C, and W. S. (2003). Determination of dibenzopyrene in standard reference material (SRM) 1649a, 1639, and 2975 using ultrasonically assisted extraction and LC-GC-MS. Environmental Health & Safety Research, 12, 1-10, Supplement 3, 451-488.
 Westerholm R, Bergvall C, W. Lundström, M. Westberg, R. Westerholm, K. Christensen, J. Andersson, and guidelines for polycyclic aromatic hydrocarbons (PAH) in urban dust and diesel particulate matter. Environmental Health & Safety Research, 12, 1-10, Supplement 3, 451-488.
 W. Lundström, M. Westberg, R. Westerholm, K. Christensen, J. Andersson, and guidelines for polycyclic aromatic hydrocarbons (PAH) in urban dust and diesel particulate matter. Environmental Health & Safety Research, 12, 1-10, Supplement 3, 451-488.
 W. Lundström, M. Westberg, R. Westerholm, K. Christensen, J. Andersson, and guidelines for polycyclic aromatic hydrocarbons (PAH) in urban dust and diesel particulate matter. Environmental Health & Safety Research, 12, 1-10, Supplement 3, 451-488.