Bull. Environ. Contam. Toxicol. (1987) 38:1020–1028

Bulletin of Environmental Contamination and Toxicology

Characterization of the PAC Profile in Settling Particulates from the Urban Waters of Stockholm

Dag Broman,[1] Anders Colmsjö,[2] and Carina Näf[2]

Departments of [1]Zoology and [2]Analytical Chemistry, University of Stockholm,
S-106 91 Stockholm, Sweden

Polynuclear aromatic compounds (PAC) in urban areas emanate primarily from incomplete combustion of fossil fuels and fossil fuel products. A vast number of "nonpoint sources" are accountable for the contribution to the aquatic environment such as house heating, power plants and municipal incinerators, automobile exhaust emissions and rub-off substances from the traffic such as asphalts and rubber tires. These PACs reach the water through municipal sewage effluents, urban runoff and direct deposition of airborne particulates. Direct spills of different kinds e.g. fuel oils, bunker oils, crankcase oils and greases, also contribute to the PAC pollution in water (Björseth 1983; Hoffman 1985; Neff 1979).

PACs that enter the aquatic environment either are, or quickly become, adsorbed to particulate matter of anthropogenic and natural origin, and a useful technique for sampling these settling particulates is the use of sediment traps. These vertically-transported particulates which are collected, correspond to the bulk material of the surface bottom sediments (Prahl and Carpenter 1979).

The sampling area in this investigation is located in the waters of central Stockholm. This area is affected by one of the most densely populated urban districts in the Baltic region, inhabited by more than one and a half million people. The total import of petroleum products for consumption to the area in 1985 was 2.5 x $10^6 m^3$. Several power plants and municipal incinerators are situated in the region and several ports and oil terminals are located in the immediate vicinity of the sampling site. The entire population of Stockholm and most industries and are connected to municipal waste water treatment plants which also affect these waters. The runoff from a fresh water lake* passes by the sampling site.

---

* Lake Mälaren 1140 km^2.

Send reprint requests to Dag Broman at the above address.

MATERIALS AND METHODS

The moored sediment trap (Larsson et al. 1986) with cylindrical sedimentation vessels of glass, was positioned under the thermocline 15 m above the bottom in a water area in central Stockholm, Sweden. Seston was collected from the beginning of January to the middle of May 1985. During the sedimentation process, chloroform was used as preservative.

The workup procedure started with sedimentation of the particulate matter in an Imhoff funnel for 24 h followed by centrifugation. The pellet was homogenized and spiked with internal PAC-standards (2-methylanthracene, D_{12}-perylene, picene and dibenzo(a,i)pyrene), the resulting mixture being then transferred to a prewashed cellulose thimble and extracted with acetone for 24 h in a Soxhlet apparatus. Prolonged extraction for 24 h with dichloromethane was also carried out in order to check the efficiency of the first extraction. After evaporation of the solvent the residue was extracted with water and dichloromethane. The solvent was again evaporated and the extract treated by a DMF (dimethylformamide) clean-up procedure. The cyclohexane solution finally obtained was concentrated and further purified by elution through a 10 % deactivated silica gel column. All solvents used were of HPLC quality. After drying the samples at 105° C for 24 h, the dry weight was determined.

Identification and quantification of the PACs were made by using gas chromatography-mass spectrometry (GC-MS). The compounds were identified by means of GC retention time, obtained from twentyfive standard PAC, retention indices (Lee et al. 1979), and electron impact mass spectra. The PACs were quantified from the molecular peaks of the mass spectra and the response factors for the alkylated PACs were approximated to be the same as for the nearest parent compound. The GC-MS system consisted of a Hewlett-Packard A1680 gas chromatograph with a SE-54 capillary column connected to a JEOL JMS-D300 mass spectrometer. Control of the spectrometer and processing of the data were made with a Finnigan Incos computor.

RESULTS AND DISCUSSION

The sampling water-area in the study is surrounded by the city of Stockholm and is therefore, like other urban areas, heavily exposed to runoff from hard surfaces and direct atmospheric deposition of anthropogenic particulates, e.g., different types of black carbon (Goldberg 1985). Particulate matter sedimented in the vessels during a winter to early spring situation. During this season, the consumption of petroleum products reaches its annual peak, which can be explained by extensive house heating and a constantly high automobile traffic intensity. The anthropogenic particulates that deponate on the snow in the drainage areas reach the sampling site via urban runoff and sewage effluents during the melting months of this period. At this time, the runoff is extensive and the scavenging of particulates is probably very efficient. During the whole period traffic-snow dumping activities also occur in the proximate water-area. An example of the pathways of high molecular weight aromatics (>3 rings) to the aquatic environment from an urban area has been estimated by Hoffman (1985) to be 45 % from urban runoff, 20 % sewage effluents, 20 % atmospheric deposition and 15 % from other sources.

During the winter to early spring, the water mass in the investigated area is very unstable, with no developed thermocline. The outflowing water from Lake Mälaren, which passes the sampling area, reaches its annual peak during the period. This suggests that a proportion of the particulate matter collected in the sediment vessels is aged, resuspended bottom material.

Lee and Ryan (1983) have shown that the rate of microbial degradation of higher molecular weight polyaromatics is very low in both sediments and water, during the winter with cold water temperatures. The photo-oxidation of the same compounds is correlated to the light (of short wavelengths which penetrate water less easily than air) and the total light intensity is low during the winter in this region. Therefore, high concentrations of PACs were to be expected in the particulate matter collected during the winter. This is also shown in table 1, where the concentrations of 200 PACs are presented.

Table 1. Abundance of PAC in waterborne particulate matter collected in sediment trap near the city of Stockholm. Abbreviations: Compound (number of isomers):cumultative index

Compound	Conc. ng/g	Retention Index	MW
fluorene	26	264.94	166
methylfluorenes	25	-	180
phenanthrene	563	300.00	178
anthracene	152	301.66	178
3-methylphenanthrene	121	319.19	192
2-methylphenanthrene	156	320.22	192
9+4-methylphenanthrene	106	323.25	192
1-methylphenanthrene	145	324.17	192
dimethylphenanthrene:1	9	334.69	206
dimethylphenanthrene:2	46	337.64	206

Table 1. continued

dimethylphenanthrene:3	51	339.11	206
dimethylphenanthrene:4	45	339.85	206
dimethylphenanthrene:5	12	340.77	206
dimethylphenanthrene:6	227	341.51	206
dimethylphenanthrene:7	102	342.25	206
dimethylphenanthrene:8	173	343.17	206
dimethylphenanthrene:9	33	344.28	206
dimethylphenanthrene:10	48	345.02	206
dimethylphenanthrene:11	6	346.68	206
dimethylphenanthrene:12	5	347.05	206
dimethylphenanthrene:13	10	349.26	206
trimethylphenanthrene:1	4	352.77	220
trimethylphenanthrene:2	31	354.98	220
trimethylphenanthrene:3	22	355.72	220
trimethylphenanthrene:4	52	357.56	220
trimethylphenanthrene:5	85	357.93	220
trimethylphenanthrene:6	237	359.04	200
trimethylphenanthrene:7	4	360.70	220
trimethylphenanthrene:8	12	361.62	220
trimethylphenanthrene:9	24	362.73	220
trimethylphenanthrene:10	16	363.28	220
trimethylphenanthrene:11	18	364.58	220
trimethylphenanthrene:12	26	365.50	220
trimethylphenanthrene:13	20	366.79	220
trimethylphenanthrene:14	82	368.08	220
trimethylphenanthrene:15	60	370.30	220
trimethylphenanthrene:16	2	371.22	220
trimethylphenanthrene:17	3	372.14	220
fluoranthene	1013	345.20	202
pyrene	940	352.77	202
methyl-202:1	64	362.92	216
methyl-202:2	61	366.05	216
methyl-202:3	188	366.97	216
methyl-202:4	125	369.37	216
2-methylpyrene	120	370.11	216
methyl-202:5	3	371.59	216
4-methylpyrene	91	373.43	216
1-methylpyrene	60	374.35	216
dimethyl-202 (10)	498	-	230
benzo(ghi)fluoranthene	253	390.77	226
cyclopenta(cd)pyrene	15	397.79	226
benzo(a)anthracene	541	398.71	228
chrysene	904	400.00	228
methyl-228 (12)	615	-	242
dimethyl-228 (12)	556	-	242
trimethyl-228 (20)	363	-	242
benzo(j)fluoranthene	749	443.26	252
benzo(k)fluoranthene	608	443.91	252
benzo(e)pyrene	596	453.26	252
benzo(a)pyrene	570	455.00	252
methyl-252 (13)	729	-	266
dimethyl-252 (14)	395	-	266

Table 1. continued

trimethyl-252 (14)	320	-	280
indeno(1,2,3-cd)pyrene	486	494.13	276
benzo(ghi)perylene	353	502.39	276
methyl-276 (4)	193	-	290
coronene	284	-	300
Mw302	834	-	302
S-PAC			
dibenzothiophene	34	295.38	184
4-methyldibenzothiophene	26	312.36	198
2+3-methyldibenzothiophene	15	315.87	198
1-methyldibenzothiophene	7	319.58	198
dimethyldibenzothiophene (10)	188	-	212
s-phenanthrene	23	350.18	208
benzo(b)naphtho(2,1-d)thiophene	151	389.48	234
benzo(b)naphtho(1,2-d)thiophene	25	392.80	234
benzo(b)naphtho(2,3-d)thiophene	45	395.76	234
epithiabenzo(a)anthracene	21	444.35	258
epithiatriphenylene	57	449.34	258
epithiachrysene	36	451.52	258

The compounds studied are in the weight range from three- up to six fused benzene rings. This includes a large number of compounds with known strong mutagenic and/or carcinogenic properties, such as methylated chrysenes and phenanthrenes etc, as well as strongly active parent (unsubstituted) compounds such as benzo(a)pyrene, or heterocyclic compounds such as 1,12-thiabenzo(a)anthracene (Mix 1986; Neff 1979).

The collected particulates are not affected by bioturbation and by use of preservative in the sediment vessels, microbial degradation is reduced. This implies that the material from sediment traps is representative of the gross deposition of PAC, in contrast to bottom sediments, analyses of which only show the net deposition. The presence of more physically and biologically affected material, with lower levels of PAC, would therefore be expected to occur in bottom sediments.

Isomer specific analysis has not been possible to perform consistently, due to the very large number of possible isomers and lack of reference compounds. Nevertheless, by the use of retention indices according to Vassilaros et al. (1982) it is possible to characterize and quantify separate unidentified isomers. These indices usually show very little variation when applied to different non-polar temperature programmed capillary columns for gas chromatography. Thus, they can be used by other analysts when comparing the relative distribution of compounds.

The sum of compounds with a molecular weight of 302, given at the end of the PAC section in table 1, originates from 31 possible isomers of dibenzopyrenes and dibenzofluoranthenes, 2 isomers of benzoperylenes and one dibenzonaphthacene. These compounds are usually difficult to separate unambigously by gas chromatography and have therefore been quantified as one group.

Apart from the pure hydrocarbons detected, a number of sulfur heterocyclic aromatic compounds (S-PAC) can be distinguished. These consist of dibenzothiophene, all three possible isomers of benzonaphthothiophene and bay-region sulfur substituted PACs with a molecular weight of 228 (giving a total molecular weight of 258). These have been reported to originate from both combusted fossil fuels and unburned fuels e.g. crude-, bunker- and fuel oils. Together with epithio-benzo(a)anthracene, epithio-triphenylene and epithio-chrysene they have also previously been detected in cultivated fossil products, for example carbon blacks (Colmsjö et al. 1982).

It has been verified that the S-PACs are easily bioconcentrated in aquatic organisms and the alkylated dibenzothiophenes are described to be the most persistent fossil fuel derived compounds in the aquatic environment (Cooke et al. 1982).

In order to discuss the origin of emission sources, the PAC profile, i.e. the relative concentrations of the PACs, was compared with profiles from other studies (Björseth 1983; Masclet et al. 1986). However, the profile shows a complex composition and it is difficult to distinguish similarities with any other specific PAC source of urban character e.g. samples from highways, underground car parks, diesel vehicles or municipal incinerators. The largest described emission source of PAC in the ambient air of Stockholm originates from automobile exhaust emissions. Because of the contribution from many other sources in an urban area, however, the PAC profile from the sediment trapped material does not correlate perfectly to the profile from automobile emissions.

In Figure 1 are shown the relative concentrations of methylated PAC versus their parent compounds. This comparison can also be used when discussing different PAC sources. A traffic PAC profile is usually heavily predominated by parent compounds with only small contributions from alkylated PACs, such as the compounds 2 to 5 in Figure 1.

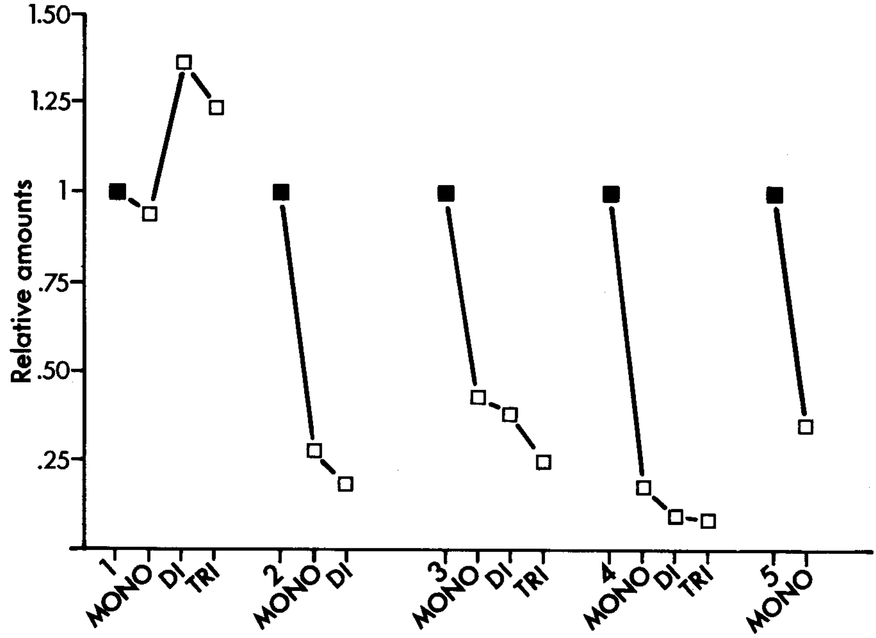

Figure 1. Relative amounts of methylated PAC versus parent compounds. 1= phenanthrene, 2= pyrene + fluoranthene, 3= benzo(a)anthracene + chrysene, 4= benzo(j+k)fluoranthene + benzo(e+a)pyrene + perylene, 5= indeno(1,2,3-cd) pyrene + benzo(ghi)perylene.

Automobile exhausts emissions can be distinguished by typical markers such as high levels of coronene, also found in the sediment trap sample. The high relative concentrations of methylated compounds strongly indicate that other types of sources also give a significant contribution to the particulate sample.

PAC mixtures with a high degree of methylated polynuclear aromatic compounds have recently been demonstrated to be present in, for example, crude oil and asphalts, but high levels may also be generated by inefficient combustion conditions, as in the case of smouldering of organic fuels. According to Sporstöl et al. (1983) the distribution of dibenzothiophenes, parent compounds versus the methylated, found in the particulate material points to an impact which originates from unburned fossil fuel products, in contrast to this the distribution (parent versus the methylated) of the fluoranthenes/ pyrenes and relative amounts of the sums of phenanthrenes/ anthracenes, dibenzothiophenes, fluoranthenes/ pyrenes indicates a combustion origin. Furthermore, a predominance of unsubstituted three-, four-, and fiveringed PAC indicates a combustion origin, whereas a relative high abundance of alkylated phenanthrene compounds indicates a noncombusted fossil fuel origin for the PACs. Finally, the fossil fuel pollution index (FFPI) points to a petroleum impact of approximately 14 percent (naphthalenes were not quantified and are therefore not included in the formula) (Boehm and Farrington 1984). All this illustrates the difficulty in attempting to evaluate the importance of different PAC sources in a "nonpoint source" pollution impacted water-area such as this.

Acknowledgments. Support for this project was provided by Stockholm Water and Wastewater Works, Port of Stockholm, Swedish Petroleum Institute, Nynäs Petroleum, the Environmental Control Fund of Stockholm County Council and the National Swedish Environmental Protection Board. We thank Beryl Holm for reviewing the manuscript.

REFERENCES

Björseth A (ed)(1983) Handbook of polycyclic aromatic hydrocarbons. Marcel Dekker Inc. New York

Boehm PD, Farrington JW (1984) Aspects of the polycyclic aromatic hydrocarbon geochemistry of recent sediments in the Georges Bank Region. Environ Sci Technol 18:840-845

Colmsjö A, Zebühr Y, Östman C (1982) Shpol'skii effect in the analysis of sulfur-containing heterocyclic aromatic compounds. Anal Chem 54:1673-1677

Cooke M, Dennis AJ, Fisher GL (1982) Polynuclear aromatic hydrocarbons: physical and biological chemistry. Proceedings from the sixth international symposium. Battelle Press Columbus, Ohio, p947

Goldberg DE (1985) Black carbon in the environment properties and distribution. John Wiley & Sons, New York

Hoffman EJ (1985) Urban runoff pollutans inputs to Narragansett Bay: comparison to point sources. Perspective on nonpoint source pollution. Environmental Protection Agency. Proceedings of a national conference, Kansas City, Missouri 159-164

Larsson U, Blomqvist S, Abrahamsson B (1986) A new sediment trap system. Mar Ecol Prog Ser 31:205-207

Lee RF, Ryan C (1983) Microbial and photochemical degradation of polycyclic aromatic hydrocarbons in estaurine waters and sediments. Can J Fish Aquat Sci 40(Suppl 2):86-94

Lee M, Vassilaros BL, White CM, Novotny M (1979) Retention indices for programmed-temperature capillary-column gas chromatography of polycyclic hydrocarbons. Anal Chem 51(6):768-773

Masclet P, Mouvier G, Nikolaou K (1986) Relative decay index and sources of polycyclic aromatic hydrocarbons. Atmos Environ 20:439-446

Mix MM (1986) Cancerous diseases in aquatic animals and their association with environmental pollutants: A critical literature review. Mar Environ Res 20(1/2): 1-141

Neff JM (1979) Polycyclic aromatic hydrocarbons in the aquatic environment. Sources, fates and biological effects. Applied Science Publishers Ltd, London

Prahl FG, Carpenter R (1979) The role of zooplankton fecal pellets in the sedimentation of polycyclic aromatic hydrocarbons in Dabob Bay, Washington. Geochim Cosmochim Acta 43:1959-1972

Sporstöl S, Gjös N, Lichtenthaler RG, Gustavsen KO, Urdal K, Oreld F (1983) Source identification of aromatic hydrocarbons in sediments using GC/MS. Environ Sci Technol 17:282-286

Vassilaros DL, Kong RC, Later DW, Lee ML (1982) Linear retention index system for polycyclic aromatic compounds. J Chromatogr 252:1-20

Received November 17, 1986; accepted January 20, 1987