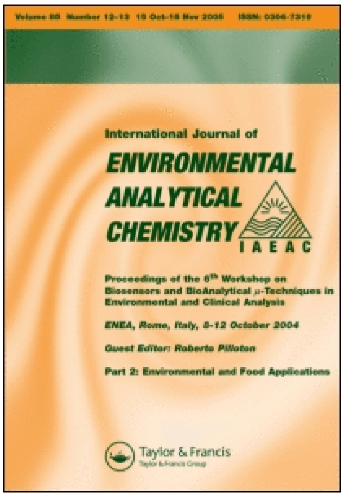

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Analysis of Polycyclic Aromatic Hydrocarbons in Sediments, Sewage Sludges and Composts from Municipal Refuse by HPLC

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The extraction of 6 selected PAHs, Fluoranthene, Benzo(b)fluoranthene, Benzo(k)-fluoranthene, Benzo(a)pyrene, Benzo(ghi)perylene and Indeno(1, 2, 3-cd)perylene has been improved by hot soxhlet extraction with hexane/acetone. Overall concentrations for sediments (Neckar) lie between 4.6 and 21.8 mg/kg (mean value 8.6 mg/kg). The corresponding values for the other substrates are waste water 129–2504 (791) ng/kg; sewage sludge 2.2–20.4 (9.7) mg/kg; municipal refuse 0.06–187 (6.9) mg/kg and waste compost 10.7–173.4 (14.7) mg/kg. It can therefore be concluded, that in all sinks of PAHs (sediments, sewage sludge and municipal refuse) the content is roughly the same. The PAH pattern of sediments and sewage sludges is very constant for different sampling sites. In contrast organic municipal waste shows marked pattern variations. For waste water treatment plants a positive correlation between daily water input and PAH content could be shown. PAH pattern comparison shows decreasing in-homogeneity from municipal refuse over sewage sludge to river sediments.

KEY WORDS: Polycyclic aromatic hydrocarbons, sediments, sewage sludge, waste compost.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are known to be ubiquitous.[1,2] Therefore it has not been very surprising, finding them in normal sinks like sediments, sewage sludges and municipal wastes too. We therefore analyzed hundreds of samples of these sites from the southwestern part of Germany to allow an estimation of the accumulation or the fate and the potential hazard eventually resulting from this group of compounds.

There are several theories concerning the origin(s) of PAHs. Pyrolytic, geochemical as well as biological processes have been discussed.[3-5] The sinks we investigated are "nourishing" themselves from different sources. Main sources for sediments and sludges could be the automotive or stationary burning processes the products being dislocated by water. The fouling process of sewage sludge could lead to additional biogenic production. We hoped to get more information on the importance of some of these processes for the overall concentration of PAHs.

As indicators for PAH concentration we selected the 6 polycyclic compounds for which tolerance values in the German legislation of drinking water are existing: Fluoranthene (Fl), Benzo(b)fluoranthene (B(b)Fl), Benzo(k)fluoranthene (B(k)Fl), Benzo(a)pyrene (B(a)P), Benzo(ghi)perylene (BPer) and Indeno(1, 2, 3-cd)pyrene (IP).

EXPERIMENTAL

Samples

Sediments The samples have been taken from the upper 2–3 cm of the sediment layer of the river Neckar, a confluent of the Rhine, by the Institut für Sedimentforschung, Heidelberg.[6] Forty-seven points along this river have been chosen in distances of approximately 5 kilometers; rural as well as industrial areas being crossed.

Sewage sludges In 33 waste water treatment plants of Southern Germany, samples of primary sludge and of fouled sludge have been taken.[7] In the Tübingen plant samples of the water influent have been taken too.

Municipal refuse (*organic fraction*) During a 13 months period, municipal refuse from a small town in Southern Germany (Baienfurt) was separated in intervals of two months into fractions (paper, plastics, glass, metal and organic material),[8] the original sample size being in the order of one metric ton. The organic fraction was further separated by sieving into <8 mm, 8–40 mm and >40 mm material.

Refuse from quarters with big apartment buildings have been collected and analyzed separately.

Sample preparation

There are various methods described in the literature to extract PAHs from environmental samples. Extraction of the wet material followed by liquid/liquid distribution, soxhlet extraction of dried material with different solvents and ultrasonic extraction of dried material are some of the most used methods.[9]

We compared six different approaches to optimize the extraction conditions for sewage sludge, sediments and organic fractions of municipal refuse. The results for sediment extraction are shown in Figure 1.

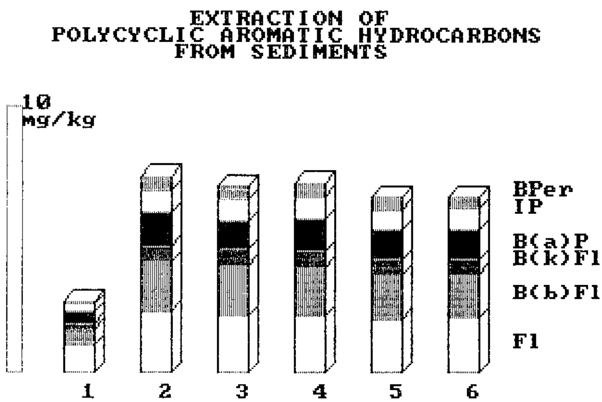

FIGURE 1 Extraction of PAHs from sediments by various methods 1: wet extraction with acetone/liquid-liquid distribution with petrol ether-water; 2: lyophilized material/hot soxhlet extraction with acetone-hexane (1:1); 3: wet sediment + sodium sulfate (1:4)/hot soxhlet extraction with hexane; 4: wet sediment + sodium sulfate (1:4)/hot soxhlet extraction with hexane acetone (1:1); 5: lyophilized material/hot soxhlet extraction with hexane; 6: lyophilized material/ultrasonic extraction (2 × acetone, 1 × hexane).

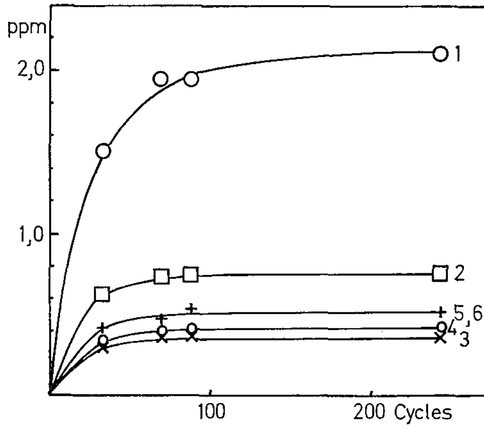

FIGURE 2 Extraction of PAHs from sewage sludge by hot soxhlet extraction with acetone/hexane as solvent. 1: Fluoranthene; 2: Benzo(b)fluoranthene; 3: Benzo(k)-fluoranthene; 4: Benzo(a)pyrene; 5: Benzo(ghi)perylene; 6: Indeno(1, 2, 3-cd)pyrene.

Best results have been obtained using hot soxhlet extraction with an acetone–hexane 1:1 (v/v) mixture (examples 2 and 4) with an additional advantage for the extraction of lyophilized material.

In the next step, we tried to optimize the number of extraction cycles for hot soxhlet extraction. A typical example is shown in Figure 2.

In this experiment lyophilized sewage sludge (4 grams) was used as a sample. The hot soxhlet extractor had an extraction volume of 50 ml. After 120 cycles corresponding to 4 hours, extraction was $>98\%$ complete. We therefore did all our extractions with 4 hour hot solvent soxhlet extraction with acetone–hexane (1:1).

Waste water samples (970 ml) have been extracted three times with cyclohexane (50 ml each) in a volumetric flask by vigorous stirring.

All extracts have been concentrated by evaporation to dryness followed by subsequent redissolution in benzene–methanol (1:1).

Further cleanup of the extracts was not necessary in most cases.

Separation and identification of PAHs

Separation was done by high performance liquid chromatography using LiChrosorb RP-18 (5 μ) of different distributors. A mixture of methanol/water (9:1) was used as solvent. Problems resulting from

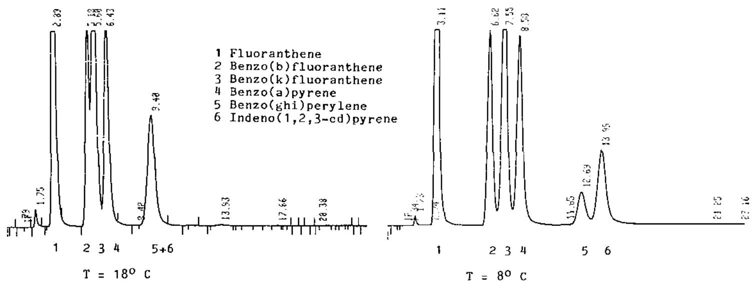

FIGURE 3 Influence of column temperature on the separation of Benzo(ghi)perylene and indeno(1, 2, 3-cd)pyrene.

working with RP-18 material of various sources and charges could be counteracted by changing the column temperature (see Figure 3). Especially benzo(ghi)perylene and indeno(1, 2, 3-cd)pyrene are often not fully separated. Lowering the temperature from room temperature to 7°C leads to better separation. If necessary, the methanol content was varied up to a ratio of 13:1 (methanol/water).

Full separation of all six PAHs under investigation was then possible.

The peaks were detected fluorimetrically with wavelengths of 365 nm for excitation and 408 nm for emission. Correction for perylene, normally occurring at the same retention time as Benzo(b)fluoranthene, was done by additional registration of the 435/470 nm wavelengths, typical for perylene.

RESULTS AND DISCUSSION

Concentration ranges

Table I shows, that depending on the substrate, different concentration ranges have been found.

The organic fractions of *municipal refuse* are characterized by the greatest differences in minimal and maximal values. The two extrema are both from samples of the >40 mm sieving fraction. For the >40 mm fraction the extremely high values were found during one sampling period only. This is clearly shown in the bar graph of Figure 4 where the mean values for all three sieving fractions are compared, the lowest values being found in bulk material (>40 mm),

TABLE I

Concentration range of PAHs in waste water, sewage sludge, sediments and municipal refuse

Substrate	Range	Max/Min	Mean value	*n*
Waste water	129–2,504 ng/kg	19	791 ng/kg	16
River water	219–552 ng/kg	2	403 ng/kg	3
Sewage sludge (primary sludge)	2.2–20.4 mg/kg	9	9.7 mg/kg	68
Sediments	4.6–21.8 mg/kg	5	8.6 mg/kg	47
Municipal refuse	0.06–187 mg/kg	3,117	6.9 mg/kg	101
Compost from municipal refuse	10.7–173.4 mg/kg	16	14.7 mg/kg	24

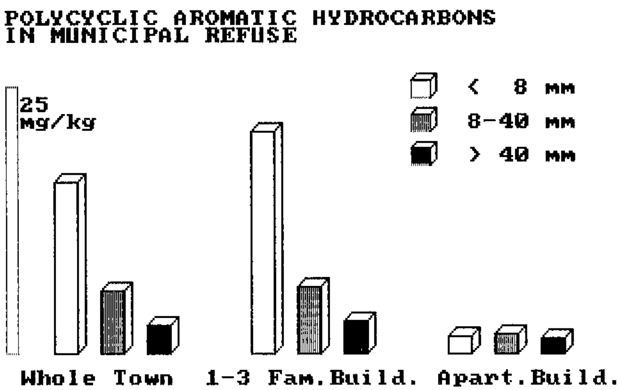

FIGURE 4 Polycyclic aromatic hydrocarbons in municipal refuse. The organic fraction of municipal refuse has been separated in 3 fractions (<8 mm, 8–40 mm, >40 mm) for two different types of social surroundings. PAH content means the sum of 6 selected PAHs.

followed by a middle fraction (8–40 mm) and with highest values for the fine fraction (<8 mm). The effect is even more pronounced in a refuse-collection area dominated by houses with one to three families. In contrast it is nearly absent in collection areas with big apartment buildings. Extreme maxima are closely related to the fact that the chimney sweeper has worked in the collecting area just before our sampling was carried out. Soot, which is known to contain large amounts of PAHs, was obviously added to the normal household garbage.

On composting municipal refuse (or at least the organic part of it), which is a well known and often used process especially in the Netherlands, France, Italy, Sweden and Germany, the range of PAH expressed as the maximum/minimum ratio diminishes, because of intense mixing during the composting process. The fact that the amount of PAHs increases during composting from 6.9 to 14.7 mg/kg is due to the fact that losses of organic material take place (mainly as water and carbon dioxide) by the action of aerobic bacteria. An inverse effect has been observed in composting plants with composting periods of more than half a year.[10] This would mean that under prolonged aerobic conditions degradation of PAH can occur.

Waste water has a wide range of PAH content too. Values from some hundred to several thousand nanograms/litre have been observed. Figure 5 shows that high PAH contents in municipal waste water are closely correlated to the daily waste water input to a purification plant. Hence days with rainfall, leading to high waste water yields are at the same time days with high PAH content. There is not a dilution effect by the additional water which one might expect, but a strong increase in polycyclic aromatics. When both the water quantity and the PAH content increase, an immense freight rate will be the consequence. One of the sources is street dust,

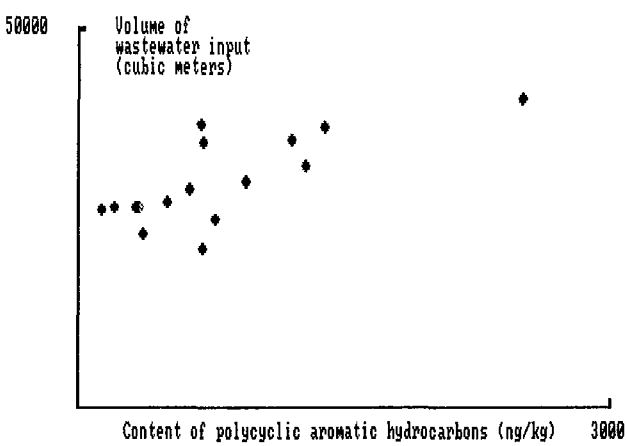

FIGURE 5 Correlation of waste water input and PAH content of a municipal waste water treatment plant.

polluted mainly by automobile exhaust[11,12] and mobilized by such events as rainfall. The other, probably even more important source, is particulate matter from fossil solid fuel burning, mobilized by the same events.

Sewage sludge and *sediments* of the Neckar river are varying only by factors of about ten and five, respectively, in their PAH content, the mean values being in the same order as for organic municipal refuse.

The PAH content of *fouled sewage sludge* lies approximately twice as high as for primary sludge yet there is no evidence for biosynthesis or biotransformation of PAHs because carbon losses as methane can account for the relative increase. Figure 6 shows the

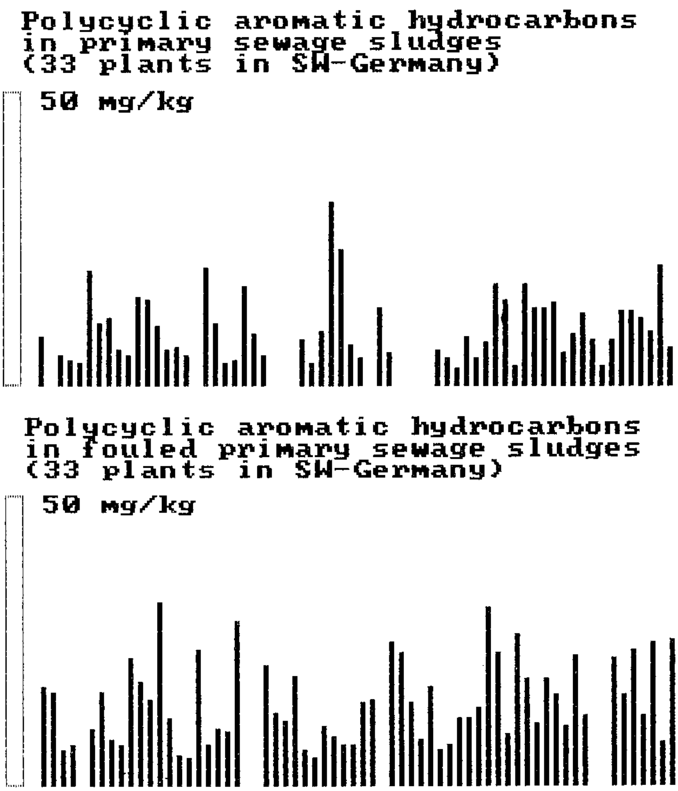

FIGURE 6 Comparison of the PAH content in primary (left) and fouled primary (right) sewage sludge of 33 waste water treatment plants in Southern Germany.

absolute content of primary and fouled primary sludges over a period of several months in SW-German waste water treatment plants.

Pattern distribution

It has been shown by Grimmer,[13] that pattern analysis can be a useful tool for the assessment of the origin of polycyclic aromatic hydrocarbons. In Figures 7–10 the patterns for the 6 PAHs under investigation are shown.

The most striking fact is the heterogeneity of the municipal refuse pattern, the fluoranthene content ranging between 13.4 and 79.1 percent. The samples have been taken from January 1982 to January 1983. In the same order (from left to right) the corresponding PAH values are noted in the bar graph of Figure 7. No seasonal variation is observed. This is equally true for the absolute concentration of polycyclic aromatics.

From Table II it becomes clear that the fluoranthene content is dominating in all substrates we have been looking at. This is

TABLE II

PAH pattern of water, wastes and sediments (values in percent of total 6 PAHs)

Substrate	Fl	B(b)Fl	B(k)Fl	B(a)P	BPer	IP	*n*
Waste water	59	13	6	10	6	6	16
Sewage sludge (primary sludge)	29	20	8	15	15	13	68
Fouled sludge	31	20	8	14	14	13	68
Sediments	35	20	8	15	13	9	47
Municipal refuse	43	21	8	9	9	10	101
Compost from municipal refuse	27	24	10	14	12	13	24
Aerosol from anthracite[a]	41	23	8	7	11	11	—
Aerosol from brown coal[a]	53	11	2	4	15	15	—
Automotive sources[b]	58	4	2	7	22	7	—
Air (Duisburg)[c]	48	20	8	5	10	9	—
Air (Los Angeles)[d]	5	9	3	8	53	22	—
Dust polluted vegetables (Duisburg)[e]	72	9	4	4	5	6	—

Recalculated after [a]lit. 14; [b]lit. 15; [c]lit. 16; [d]lit. 11; [e]lit. 16.

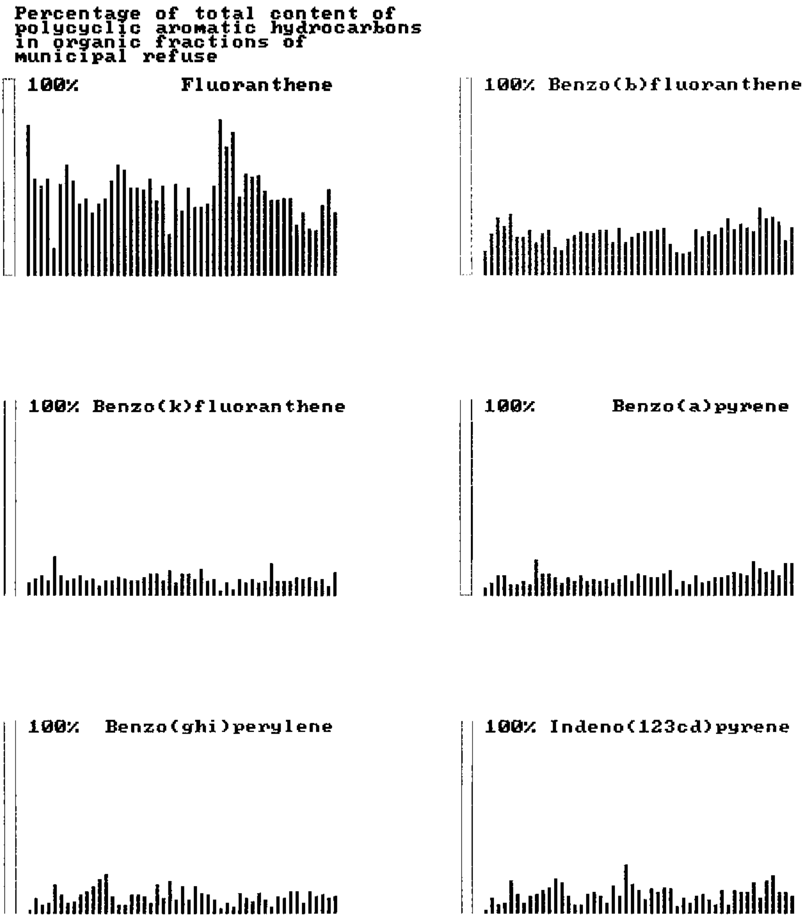

FIGURE 7 Percentage of total content of PAHs in organic fractions of municipal refuse.

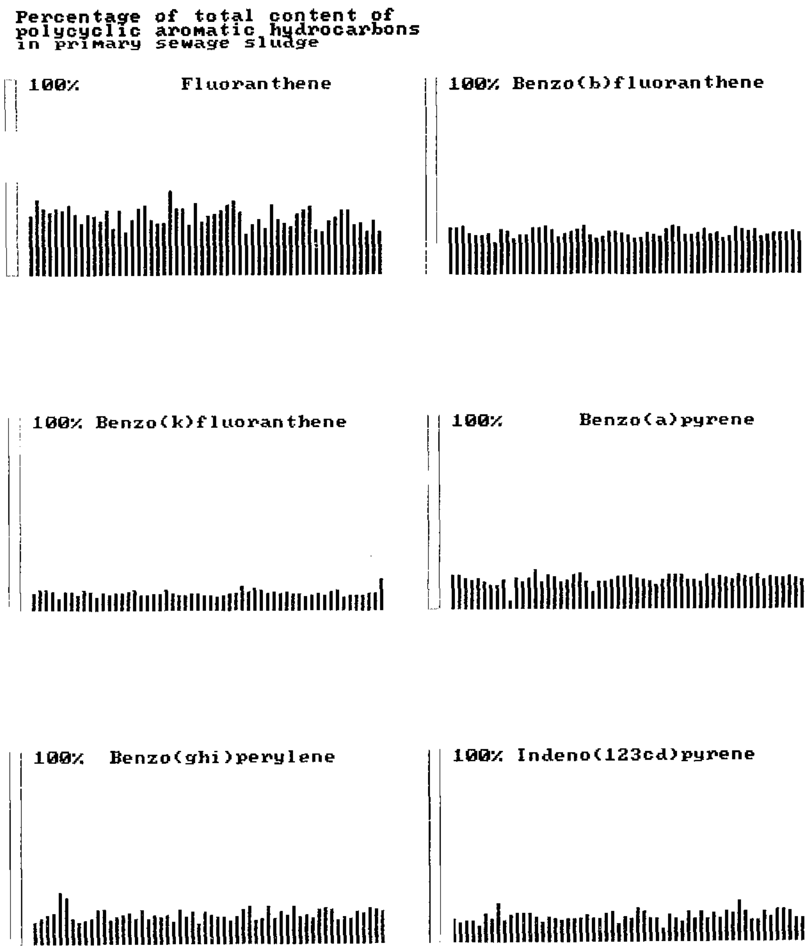

FIGURE 8 Percentage of total content of PAHs in primary sewage sludge.

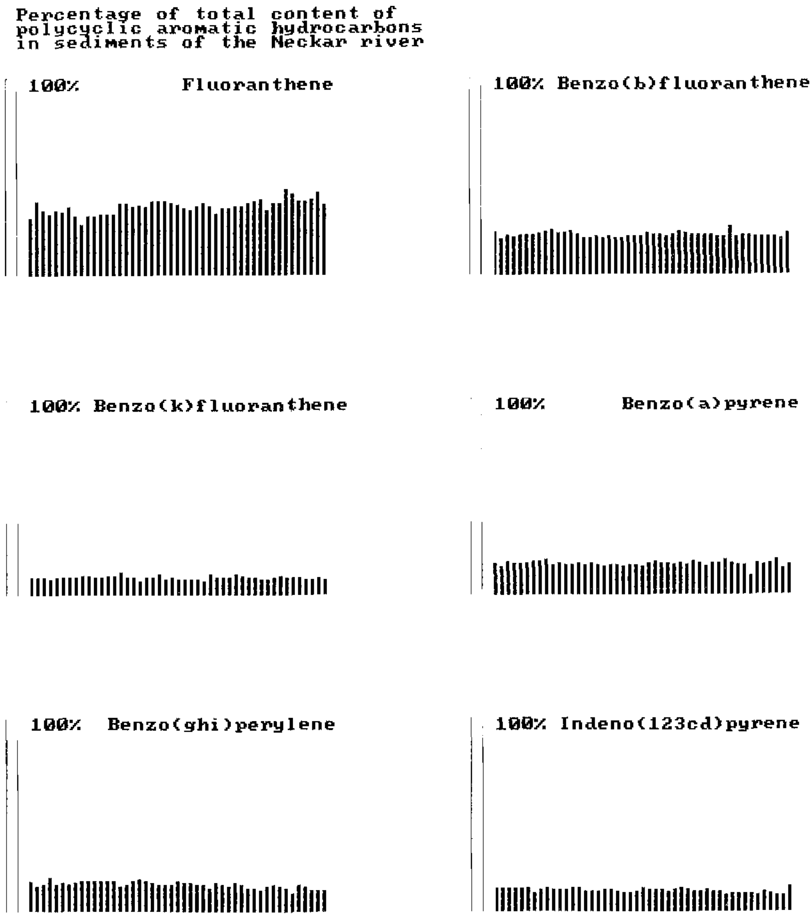

FIGURE 9 Percentage of total content of PAHs in sediments of the Neckar river.

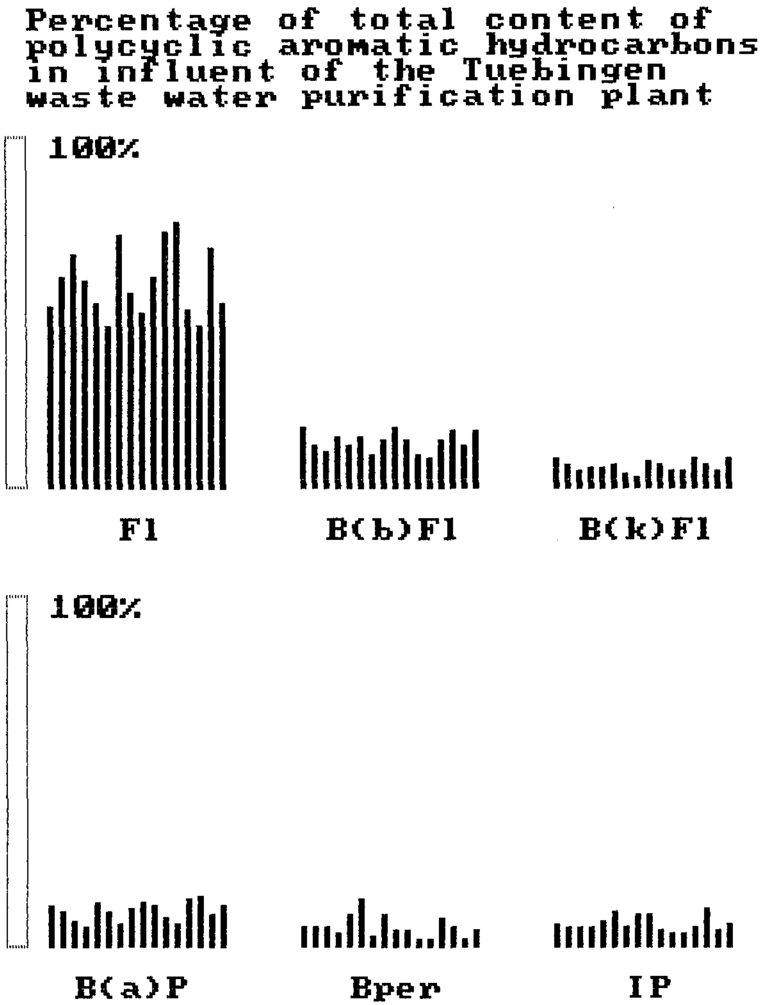

FIGURE 10 Percentage of total content of PAHs in the influent of the Tübingen waste water treatment plant.

especially true for municipal waste water and municipal refuse, the percentage of the other five PAHs being more or less constant. The only notable exception are the relatively low B(a)P and BPer values for municipal refuse. Regarding the high variation in PAH content of different refuse samples, this should not be overvalued.

The pattern of primary sludge does not change during the fouling process. This can be an additional proof that biological degradation or synthesis of PAHs related to fouling is not significant.

There is a great stability in the PAH pattern of sewage sludge from different waste water treatment plants and an even more marked stability for sediments. Despite the fact that the absolute PAH concentrations may vary by a factor of five to nine respectively (see Table I), the relative concentrations are constant.

Compost from municipal refuse has a decreased fluoranthene content compared with refuse itself, the PAH pattern now closely resembling that of sewage sludges and sediments. The pattern variation of compost (not shown in a figure) is much smaller than for its precursor, the organic waste.

Some of the possible anthropogenic sources of PAHs are also listed in Table II. Automotive sources are characterized by a BPer/IP factor of about 3. It is therefore reasonable that Gordon[11] suggests Los Angeles dust to be of mainly automotive origin. In contrast burning of solid fossil fuel leads to particulates with an even BPer/IP ratio, characteristic for sewage sludge, municipal refuse and compost from municipal refuse too.

CONCLUSIONS

In a region like Southern Germany with high population density, the 6 PAHs for which tolerance values in the German legislation exist are found in sediments, sewage sludges and municipal refuse at a mean concentration of 10 mg/kg. Traffic yields only a minor amount of the total PAH content in solid and liquid municipal wastes. The PBer/IP ratio for sediments being >1 gives evidence that traffic as one of the origins for polycyclic aromatic hydrocarbons is slightly more important there. The transport to sediments and sludges as sinks for PAHs occurs mainly via heavy rainfalls, washing down particulate matter in the surroundings of burning sites.

There has been found no evidence for biosynthesis or biotransformation of PAHs during the fouling process of sewage sludge, giving a further proof that biological processes do not play any role in PAH production.

In municipal refuse, soot is a major source. Therefore refuse from big apartment buildings having no residential wood-fired stoves and fireplaces has by far the lowest PAH content.

In regions with residential fireplaces (normally 1–3 family buildings) particulates <8 mm like household dust very often contain 100 mg/kg PAH and more.

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