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Quantitative analysis of polycyclic aromatic hydrocarbons in sewage sludge from wastewater treatment plants

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are an important group of organic contaminants present in sewage sludge. Due to their persistence and toxic potential, information about their presence in sewage sludge is needed in order to assess applicability on agricultural land. A method for the gas chromatographic–mass spectrometric (GC–MS) determination was developed and applied to the trace determination of PAHs present in sewage sludge samples from six wastewater treatment plants (WWTPs) differing in the type of treatment and the origin of wastewater. PAHs were extracted from freeze-dried samples by a dichloromethane–methanol (2:1) mixture in a sonication bath. The sludge extracts were cleaned-up by an alumina column. The method showed recovery values varying from 60 to 98%. Four surrogate standards ($[^2\text{H}_8]$ naphthalene, $[^2\text{H}_{10}]$ anthracene, $[^2\text{H}_{12}]$ benzo[*a*]anthracene, and $[^2\text{H}_{12}]$ benzo[*ghi*]perylene) were used for quantitation by GC–MS. A reference sludge sample was analysed in order to validate the method. The sum of the 16 US Environmental Protection Agency PAHs analysed in the sewage sludge samples varied from 1.13 to 5.52 mg/kg. No significant difference between the different WWTPs was found. © 2001 Published by Elsevier Science B.V.

Keywords: Sewage sludge; Polycyclic aromatic hydrocarbons

1. Introduction

Sewage sludge is what is left behind after water is cleaned in wastewater treatment plants (WWTPs), generally after primary and secondary treatment processes. Wastewater catchments receive organic pollutants from different sources: human excretion products, household disposals, fossil fuel spillages, and urban runoff inputs that flush the organics deposited on the ground surface from vehicles or heating systems [1]. A wide range of different processes during the wastewater treatment that have a different dynamic nature can remove these organic

pollutants. These processes can be volatilisation, sorption onto solid surfaces or association with fats and oils, biodegradation and chemical degradation. The final product, the sewage sludge, is a mixture of organic (over 300 organic compounds have been identified [2]), inorganic, microbiological pollutants and pathogens.

Sewage sludge can be disposed of in different ways. The most commonly used procedures are: (1) incineration, (2) deposition in landfills and (3) application to agricultural land. The latter form benefits from the high content of organic matter (40–80%) and plant nutrients [3]. The application of sewage sludge as fertiliser to agricultural lands since the late 1980s, when the international clean water regulations prohibited the ocean dumping of sludge, represents an economic but environmentally doubtful

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method for the high amounts of sludge produced by the WWTPs. In many industrialised countries, the application of sewage sludge to agricultural land is a major route for disposal, e.g. in many of the European Union member states over 30% of the total sludge is disposed of by this route [4]. Spain produces every year ca. $280 \cdot 10^9$ kg dry mass of sewage sludge and 10% of which is used for agricultural purposes [5]. However, most member states regulate its use because it contains a multitude of heavy metals (Pb, Cd, Cr, Cu, Ni, Hg, Zn), organic pollutants [e.g. polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins]. These compounds can damage soil organisms and adversely affect the growth of crops [6]. The regulations restrict the total amount of sludge applied to arable land in view of the content of heavy metals, and only for a few organic pollutants. In Germany, Switzerland, and the Netherlands the maximum concentrations of halogenated pollutants in sewage sludge are restricted to 500 mg/kg adsorbable halogenated organics (AOXs), 200 $\mu\text{g}/\text{kg}$ individual PCB congeners and 100 ng/kg toxic equivalents for polychlorinated dibenzodioxins/furans (PCDDs/Fs) [7]. In 1986, the US Environmental Protection Agency (EPA) proposed a regulation to minimize risks of agricultural land pollution by sludge application, and included concentration limits for organic pollutants such as trichloroethylene, benzo[a]pyrene, aldrin, dieldrin, chlordane, DDT, DDE, DDD, heptachlor, hexachlorobenzene, hexachlorobutadiene, lindane, toxaphene, PCBs and dimethylnitrosamine. However, only metallic compounds were taken into account in the final regulation edited in 1993, because of the lack of knowledge concerning the toxicity and analysis of the organic compounds [8]. A new draft directive of the Council of the European Community has been released regulating, nonylphenol ethoxylates, AOXs, linear alkylbenzene sulfonates (LASs), di(2-ethylhexyl)phthalate, PCDDs/Fs, PCBs, and PAHs allowed in sewage sludge used in agriculture [9]. The cut-off value for PAHs will be set at 6 mg/kg. The interest for PAHs in sewage sludge is because of their persistence in the soil, their low biodegradability, high lipophilicity, their ultimate fate in agricultural systems, food chain biomagnification and possible harmful effects on biota and

carcinogenicity on humans [10]. This paper examines the contamination of different WWTPs investigating specifically PAHs. These compounds belong to the most important and ubiquitous environmental pollutants. PAHs originate from industrial waste as well as from domestic sludge, atmospheric rainfall, airborne pollutants and runoff of road surfaces. They are also produced in smaller amounts naturally by forest fires and possibly microbiological synthesis [11]. A number of PAHs have been identified to be potent mammalian carcinogens and they are designated as priority pollutants with respect to the public health risk [12].

PAHs originate to a large extent (up to 90%) from sewage during their treatment in WWTPs [13] and concentrated in sludges yielding concentrations several orders of magnitude higher than in raw water [14]. The subsequent fate of these organic compounds following sewage sludge disposal is a topic of current concern and there is a requirement for such basic information as concentrations of PAHs in sludge in order to assess the environmental impact of specific compounds in sludge [15].

The objective of the present work was to determine the concentrations of the 16 EPA PAHs in sewage sludge from six Spanish and Portuguese WWTPs, differing in the type of wastewater and the applied treatment technology, by utilising a methodology based on gas chromatography–mass spectrometry (GC–MS). This methodology has been validated by analysing PAHs in reference sewage sludge. To our knowledge, similar work like this has not been performed in Spain since most of PAHs methods are applied to one or two types of sewage sludges. This paper will give information about PAHs content on different WWTPs and to which extent variations in PAHs content can be expected.

2. Materials and methods

2.1. Reagents and standards

HPLC-grade acetonitrile, dichloromethane, hexane, isooctane, water were purchased from Merck (Darmstadt, Germany). Analytical-grade anhydrous sodium sulphate was from Merck and was treated at 400°C for 12 h before the analysis. Neutral

aluminum oxide 90 active (63–200 μm) was supplied by Merck. PAHs standards were obtained from Dr. Ehrendorfer (Augsburg, Germany) and deuterated PAHs standards from Cambridge Isotopes (Cambridge, UK).

2.2. Reference materials

Aquacheck sludges (WRC, Medmenham, UK): the Aquacheck scheme provides proficiency testing samples for the analysis of organic and inorganic chemicals and bacteria in saline, fresh and wastewater, sludges, sediments and soils as well as in biota. Samples and determinants that are closely similar to those that are part of normal laboratory operation. Laboratories should look carefully at the determinants offered, the concentration range, and the matrix composition. These services help laboratories to optimize their quality control and analytical performance for the benefit of their customers. The sludge samples provided by Aquacheck containing known amounts of the spiked target analytes were determined.

2.3. Sampling

Glass containers were used for the collection of sludge samples from six WWTPs located in Catalonia, Spain (Manresa, Igualada, Ripoll, Montornès and Abrera) and Porto, Portugal. The samples were frozen upon arrival in the laboratory and stored at -20°C until analysis. The WWTPs Montornès and Abrera apply only physico-chemical treatment, while the facilities at Manresa, Igualada, Ripoll and Porto also include a secondary treatment. Sludge samples from the Manresa WWTP (WWTP-1) treating only domestic wastewater were taken in May, June and July 1998. The WWTP at Ripoll (WWTP-2), receives domestic effluents and was sampled in June. The WWTP of Igualada (WWTP-3) receiving mainly industrial effluents of the tannery sector was sampled in May, June, July and September 1998. The three other WWTPs were sampled in June 1998, Porto WWTP (WWTP-4) receiving more than 65% of industrial waters principally of textile industrial waters and 35% of urban wastewater. Montornès (WWTP-5) and Abrera WWTP (WWTP-6) treated

industrial effluents (around 60%) from various types of industries.

The different plants have a similar flow capacity, except WWTP-2, that has lower flow. With exception of WWTP-2 that receives only 9000 m^3/day , the other WWTPs receive between 20 000 and 30 000 m^3/day . The average flow per hour can vary between 900 and 1500 m^3/h , except in WWTP-2 that has a much lower value (approximately 350 m^3/h). The treated water is discharged by a population varying between 180 000 and 200 000 inhabitants, except for WWTP-3 that treats the water of a population of 40 000 inhabitants [16]. The total organic carbon (TOC) of the sludges ranged between 50 and 60 g C/kg and the content of chromium Cr(V) was 14 g/kg in the samples of WWTP-3 whereas its content was below 0.5 g/kg at the other WWTPs. Cr content is very important in the case of WWTPs receiving tannery effluents.

2.4. Sample preparation

A 2 g sample of lyophilised sludge were extracted in triplicate by sonication (20 min each) with 20 ml dichloromethane-methanol (2:1). The organic phase was separated from solid sludge particles by centrifugation. The combined organic phases were evaporated to dryness and redissolved in 0.5 ml hexane-dichloromethane (19:1). Then, the extracts were purified on 2 g of aluminum oxide (120°C , 12 h) column and on the top a thin layer of anhydrous sodium sulphate (1 g). In order to remove hydrophobic impurities the column was washed with 10 ml hexane-dichloromethane (19:1) and subsequently eluted with 15 ml hexane-dichloromethane (1:2). The analyte fraction was preconcentrated in a rotary evaporator to 0.5 ml, further carefully evaporated to dryness under a gentle stream of nitrogen and finally brought up to 200 μl with isooctane.

2.5. GC-MS analysis

GC-MS analyses were performed with a Carlo Erba GC8000 Series system coupled to a mass spectrometer (Fisons MD800). A 30 m HP-5 column (5% phenylmethylsilicone; 0.25 mm I.D., 0.25 μm film thickness) was used. The oven temperature was

increased from 60 to 175°C at 6°C/min, further increased at a rate of 3°C/min until 240°C and finally held at 300°C for 7 min. Injector and transfer line temperatures were 280 and 300°C, respectively. Data acquisition was carried out in the selected ion monitoring (SIM) mode (see Table 1). Each PAH was separately quantified using a five-point calibration of mixed standard solutions in the range from 50 to 1000 µg/l. The recoveries obtained for the reference samples spiked with deuterated PAHs were 70–95% (Table 1), therefore we considered the procedure completely reliable for real sewage sludge. Recoveries of the PAHs obtained by this method using the four surrogate standards for the real samples, [²H₈]naphthalene, [²H₁₀]anthracene, [²H₁₂]-benzo[*a*]anthracene, and [²H₁₂]benzo[*ghi*]perylene, varied between 60 and 98% primarily depending on the volatility of the compounds. The two deuterated PAHs [²H₁₀]pyrene and [²H₁₂]perylene served as internal standards.

3. Results and discussion

3.1. Calibration curves and limits of detection

Calibration curves were constructed for all target compounds analysed in the sewage sludge samples. The calibration was performed under the previously described optimised conditions in SIM recording M⁺ ions [17]. The curves were linear in the range studied from 0.05 to 1.0 µg/ml and the correlation coefficients were ≥0.998 for all PAHs studied. The limits of detection (LOD) in the low range (1 to 10 µg/kg) were obtained due to the sensitivity of GC–MS in SIM mode allowing quantifying PAHs at the low levels present in the sewage sludge samples.

3.2. Determination of the reference material

Quality control of analytical procedures aims at

Table 1

Molecular masses of PAHs and average recoveries of extraction (%) obtained after extraction, clean-up and evaporation processes of the reference and real sewage sludge samples with the mixture of deuterated PAHs

Compound	Molecular ions (<i>m/z</i>)	Recoveries of reference samples (%)	Recoveries of real samples (%)
Naphthalene	128		
[² H ₈]Naphthalene	136	70	66
Acenaphthylene	152		
Acenaphthene	154		
Fluorene	166		
Phenanthrene	178		
Anthracene	178		
[² H ₁₀]Anthracene	188	95	98
Fluoranthene	202		
Pyrene	202		
[² H ₁₀]Pyrene	212		
Benzo[<i>a</i>]anthracene	228		
Chrysene	228		
[² H ₁₂]Benzo[<i>a</i>]anthracene	240	78	74
Benzo[<i>b</i>]fluoranthene	252		
Benzo[<i>k</i>]fluoranthene	252		
Benzo[<i>a</i>]pyrene	252		
[² H ₁₂]Perylene	264		
Indeno[1,2,3- <i>cd</i>]pyrene	276		
Dibenz[<i>a,h</i>]anthracene	278		
Benzo[<i>ghi</i>]perylene	276		
[² H ₁₂]Benzo[<i>ghi</i>]perylene	288	75	60

determining PAHs in environmental samples requires not only the availability of PAHs calibration standards of high purity but also of matrix materials in order to verify all steps of the analytical procedure. Analysing a certified standard reference material like Aquacheck samples, it is possible to test the accuracy of the experimental procedure. Analytical blanks (one for each of the six environmental samples) were analysed using the same procedure, comprising sonication, clean-up on alumina and quantification by GC–MS.

Table 2 compares the concentrations of PAHs in the reference sludge determined by GC–MS and the target values provided by the Aquacheck organisation showing that findings obtained by GC–MS are in good agreement with the target values from the organisation. The PAHs concentrations in the reference sludge are in a range similar to the levels found in the real samples (see below).

3.3. PAH concentrations in the real sewage sludges

The GC–MS chromatogram obtained from the sludge extract of WWTP-1 illustrates that all target compounds present in the extracts can be clearly identified (Fig. 1) and the quantification with the method presented in this paper is feasible.

In Tables 3 and 4 the PAHs concentrations in all

sewage sludge from the six WWTPs are shown. The standard deviations of the volatile compounds (naphthalene, acenaphthylene, acenaphthene) are high due to losses of these compounds during the evaporation of the solvent in the nitrogen stream. Moreover, high standard deviations of the closely eluting isomeric compounds benzo[*b*]fluoranthene and benzo[*k*]fluoranthene were noticed due to difficulties in separating these compounds under the applied chromatographic conditions.

The results obtained from two WWTPs (Tables 3 and 4) show that the sum concentration of PAHs (Σ PAHs) is in the range between 1.13 to 5.52 mg/kg. However, we observe that there are no significant differences between the studied WWTPs. There is a tendency: WWTP-1 and WWTP-2 treating domestic effluents, exhibit higher total concentrations compared to those receiving industrial discharge. Only WWTP-4 and -5 present a high Σ PAHs like domestic WWTPs. The interpretation of these results is problematic without information on PAH value influent concentrations, point emission sources, atmospheric inputs and catchment area characteristics.

In WWTP-1, the concentrations of PAHs vary strongly between the samples from 3 months analysed (Table 3). However, phenanthrene is the most abundant compound in all samples. Its percentage is 35% in May, 37% in June and 25% in July. In WWTP-2 pyrene, phenanthrene and the high-molecular mass compounds (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene and benzo[*ghi*]perylene) are the most prominent compounds with a lower proportion of phenanthrene amounting only to 13%.

In Table 4, mean concentrations of the PAHs are listed for the four WWTPs that treat industrial wastes but with two different treatments: biological (WWTP-3 and WWTP-4) and physico-chemical (WWTP-5 and WWTP-6). The most concentrated compound is phenanthrene. In WWTP-3, the percentages of phenanthrene are between 22 and 24% whereas in WWTP-5 and WWTP-6 42 and 46% are detected. The percentages obtained and the Σ PAHs from WWTP-3 showed that there are no significant differences between the analysed months. Comparison of WWTP-3 and -4 to WWTP-5 and -6 does not

Table 2

Concentrations of PAHs determined in reference sewage sludge sample from Aquacheck Organization (error corresponds to absolute standard deviation of quintuple determination), target values of the analytes in the reference sludge and recoveries

Compound	Determined concentration ($\mu\text{g}/\text{kg}$)	Target value ($\mu\text{g}/\text{kg}$)	Recovery (%)
Fluoranthene	911 \pm 6	810	113
Benzo[<i>b</i>]fluoranthene	749 \pm 13	820	91.3
Benzo[<i>k</i>]fluoranthene	580 \pm 10	630	92.1
Benzo[<i>a</i>]pyrene	233 \pm 10	260	89.6
Indeno[1,2,3- <i>cd</i>]pyrene	610 \pm 13	710	85.9
Benzo[<i>ghi</i>]perylene	266 \pm 36	340	78.3
Σ PAHs	3350		

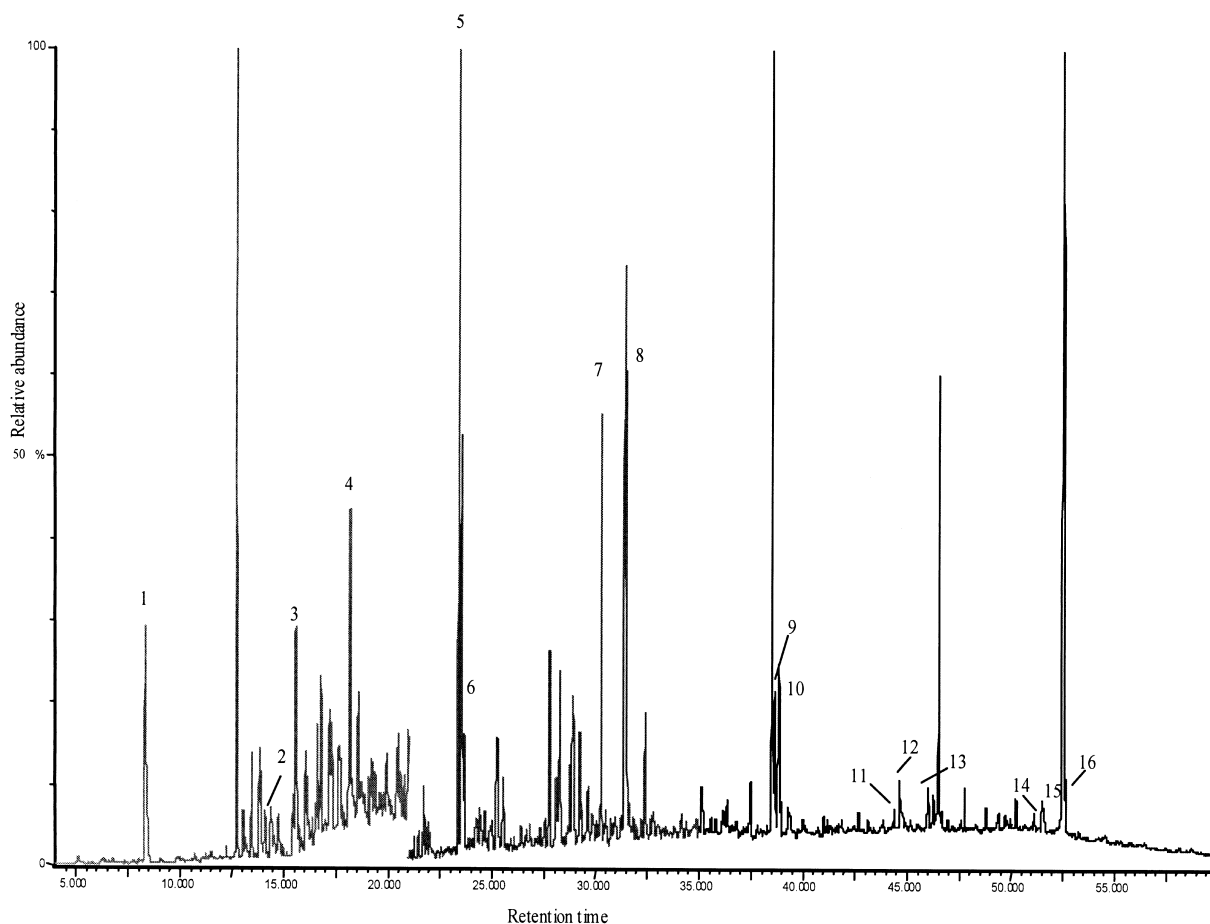


Fig. 1. GC-MS chromatogram (SIM mode) corresponding to the analysis of WWTP-1 July extract; Peaks: 1=naphthalene, 2=acenaphthylene, 3=acenaphthene, 4=fluorene, 5=phenanthrene, 6=anthracene, 7=fluoranthene, 8=pyrene, 9=benzo[*a*]anthracene, 10=chrysene, 11=benzo[*b*]fluoranthene, 12=benzo[*k*]fluoranthene, 13=benzo[*a*]pyrene, 14=indeno[1,2,3-*cd*]pyrene, 15=dibenz[*a,h*]anthracene, 16=benzo[*ghi*]perylene.

allow inferring conclusions on the effect of different treatment technologies.

Fig. 2 shows the concentration of individual PAHs in ten samples from the six WWTPs classified in three groups: (1) biologically treated domestic sewage (●), (2) biologically treated mainly industrial sewage (⊕), and (3) physico-chemically treated mainly industrial sewage (∇). Two tendencies can be extracted from the graph, first the concentrations naphthalene to phenanthrene are generally higher in (●) than in (⊕). Second, the levels of benzo[*a*]anthracene to benzo[*k*]fluoranthene are always lowest in sludges from primary treatment of industrial wastes.

In comparison to monitoring data of PAHs found

in the literature, the values were commonly between 0.1 and 100 mg/kg. In 12 German WWTPs, Σ PAHs concentrations were determined in sewage sludge between 2 and 15 mg/kg in a sampling period from 1995 to 1998 [18]. In 1997, another German study also reported the total amounts of PAHs in 25 WWTPs ranging from 2 to 80 mg/kg [19]. Different sludges were analyzed in Germany in the 1970s showing that the concentration of all PAHs determined were as high as 10 mg/kg and in one sample the concentration was found to be 200 mg/kg [20]. A Polish study in 1997 stated that PAHs contents in sewage sludges from Upper Silesia were lower than PAHs concentrations in domestic and industrial

Table 3

Concentrations of PAHs determined in sewage sludge samples from two WWTPs applying secondary treatment; error corresponds to absolute standard deviation of triplicate determination; concentrations are given in $\mu\text{g}/\text{kg}$

Compound	Concentration ($\mu\text{g}/\text{kg}$)			WWTP-2
	WWTP-1			
	May	June	July	
Naphthalene	108±49	198±22	287±3	27±10
Acenaphthylene	32±21	31±8	118±13	n.d.
Acenaphthene	315±12	492±15	149±11	n.d.
Fluorene	464±7	704±4	249±6	28±9
Phenanthrene	1370±8	2030±6	637±6	540±2
Anthracene	172±3	234±4	91±5	34±5
Fluoranthene	458±0.2	629±5	258±14	100±9
Pyrene	596±6	702±4	277±16	600±17
Benzo[<i>a</i>]anthracene	157±6	184±12	80±9	125±13
Chrysene	147±4	177±9	79±16	312±7
Benzo[<i>b</i>]fluoranthene	41±20	52±18	35±12	479±6
Benzo[<i>k</i>]fluoranthene	39±17	49±10	11±36	289±9
Benzo[<i>a</i>]pyrene	45±17	35±13	23±26	522±2
Indeno[1,2,3- <i>cd</i>]pyrene	n.d.	n.d.	189±10	461±2
Dibenz[<i>a,h</i>]anthracene	n.d.	n.d.	2±26	66±17
Benzo[<i>ghi</i>]perylene	n.d.	n.d.	21±13	589±3
Σ PAHs	3940	5520	2510	4270

n.d.: not detected.

Table 4

Concentrations of PAHs determined in sewage sludge samples from four industrial WWTPs applying either primary or secondary treatment; error corresponds to absolute standard deviation of triplicate determination; concentrations are given in $\mu\text{g}/\text{kg}$

Compound	Concentration ($\mu\text{g}/\text{kg}$)					
	WWTP-3 (secondary treatment)			WWTP-4 (secondary treatment)	WWTP-5 (primary treatment)	WWTP-6 (primary treatment)
	May	June	July			
Naphthalene	n.d.	73±24	93±54	n.d.	309±6	n.d.
Acenaphthylene	n.d.	30±9	18±4	n.d.	n.d.	n.d.
Acenaphthene	n.d.	50±11	56±16	72±5	44±22	n.d.
Fluorene	196±9	77±7	108±4	102±24	909±1	349±13
Phenanthrene	405±16	250±2	357±8	898±9	1760±4	820±18
Anthracene	92±11	71±3	61±4	52±15	292±2	n.d.
Fluoranthene	83±7	82±3	56±5	685±16	244±12	108±7
Pyrene	273±7	112±33	187±3	706±11	158±14	124±6
Benzo[<i>a</i>]anthracene	101±5	96±2	64±9	155±1	29±30	30±15
Chrysene	283±19	113±13	67±14	212±10	50±6	13±22
Benzo[<i>b</i>]fluoranthene	70±10	33±15	45±5	234±15	19±18	n.d.
Benzo[<i>k</i>]fluoranthene	n.d.	19±5	17±24	95±11	6±19	n.d.
Benzo[<i>a</i>]pyrene	79±8	32±10	32±11	144±23	17±8	275±7
Indeno[1,2,3- <i>cd</i>]pyrene	52±9	46±11	295±12	156±13	129±12	27±36
Dibenz[<i>a,h</i>]anthracene	7±11	n.d.	n.d.	42±17	125±13	n.d.
Benzo[<i>ghi</i>]perylene	74±5	43±17	n.d.	160±1	29±42	n.d.
Σ PAHs	1720	1130	1460	3710	4120	1750

n.d.: not detected.

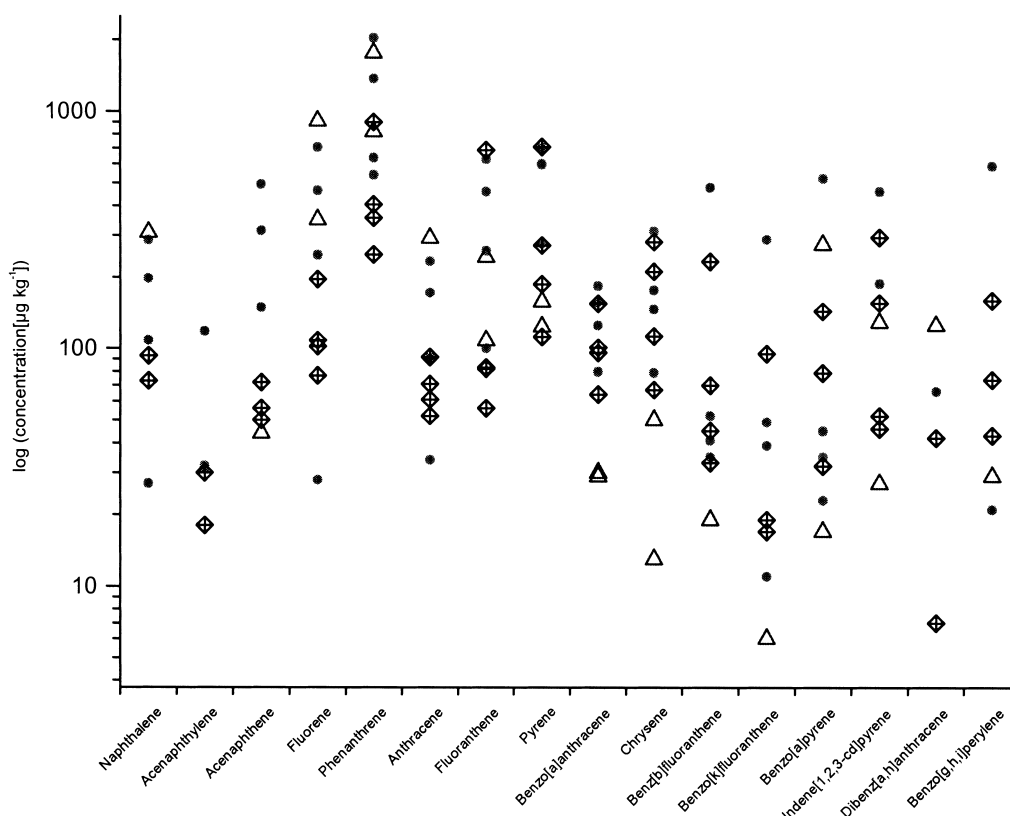


Fig. 2. Concentrations of PAHs in ten sewage sludge samples from six WWTPs. (●) Biologically treated domestic sewage (four samples), (⊠) biologically treated main industrial sewage (four samples) and (▽) physico-chemically treated main industrial sewage (two samples).

sludges in the USA and Canada, but higher than concentrations in other European countries. The total content was 330 mg/kg, the maximum value from 1990 sludges. In sewage sludges from industrial and municipal WWTPs in Switzerland in 1999, Σ PAH values were found in the range from 1 to 10 mg/kg [11]. Earlier the same laboratory reported levels of PAHs in digested sewage sludge between 1.7 and 15 mg/kg [21].

As for our own data presented, the values are in the range of the concentrations found in European countries. They do not exceed the cut-off limits that the Draft Directive of the European Community permits (6 mg/kg) for the sludge to farm land. The level might be exceeded after anaerobic digestion, which is likely to lead to an increase in PAHs level due to the degradation of other organic materials. An early investigation of German WWTPs (1976–1978) showed that the Σ PAHs from anaerobically digested

sludge was higher than the activated: 28.8 compared to 10.4 mg/kg [20].

4. Conclusions

An analytical methodology for the determination of PAHs, was validated for its reliability by analyzing reference sludge material and enabled the accurate analysis of these xenobiotics in sewage sludges. The total amounts of PAHs were in the low mg/kg range and therewith in the range reported by other studies. No significant differences in overall values between the sampled WWTPs were recognizable, but certain tendencies within the pattern of individual PAHs were found correlating with the origin of sewage and the applied type of treatment.

Although the concentrations detected did not exceed the projected European Union cut-off limits

in sludge to be considered for agricultural application, the values being close to the limit (6 mg/kg) were likely to be higher in anaerobically digested sludge. Hence, it will be necessary in forthcoming studies to monitor both activated sludge and digested sludge in order to assess the impact of digestion on the fate of PAHs.

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References

- [1] H.R. Rogers, *Sci. Total Environ.* 185 (1996) 3.
- [2] R. Duarte-Davidson, K.C. Jones, *Sci. Total Environ.* 185 (1996) 59.
- [3] J.M. Moreda, A. Arranz, S. Fdez de Betoño, A. Cid, J.F. Arranz, *Sci. Total Environ.* 220 (1998) 33.
- [4] S.R. Wild, K.S. Waterhouse, S.P. McGrath, K.C. Jones, *Environ. Sci. Technol.* 24 (1990) 1706.
- [5] R. Renner, *Environ. Sci. Technol.* 34 (2000) 430A.
- [6] H.H. Harms, *Sci. Total Environ* 185 (1996) 83.
- [7] Klärschlammverordnung-AbfklärV (1989)
- [8] C. Miège, J. Dugay, M.-C. Hennion, *J. Chromatogr. A* 823 (1998) 219.
- [9] Council of the European Community, Working Document on Sludge, 3rd Draft, Brussels, 27 April, 2000.
- [10] E.R. Alcock, K.C. Jones, *Chemosphere* 26 (1993) 2199.
- [11] J.D. Berset, R. Holzer, *J. Chromatogr. A* 852 (1999) 545.
- [12] M. Casellas, P. Fernández, J.M. Bayona, A.M. Solanas, *Chemosphere* 30 (1995) 725.
- [13] L. Lazzari, L. Sperti, M. Salizzato, B. Pavoni, *Chemosphere* 38 (1999) 1925.
- [14] D. Bodzek, B. Janoszka, C. Dobosz, L. Warzecha, M. Bodzek, *J. Chromatogr. A* 774 (1997) 177.
- [15] W. Klöpffer, *Chemosphere* 33 (1996) 1067.
- [16] M. Farré, A. Oubiña, M.P. Marco, A. Ginebreda, L. Tirapu, D. Barceló, *Environ. Sci. Technol.* 33 (1999) 3898.
- [17] S. Pérez, M. Farré, M.-J. García, D. Barceló, *Chemosphere* 45 (2001) 705.
- [18] C. Fooker, R. Gühr, M. Häckl, P. Seel, *Orientierende Messungen gefährlicher Stoffe – Landesweite Untersuchungen auf organische Spurenverunreinigungen in hessischen Fließgewässern, Abwässern und Klärschlämmen, Hessische Landesanstalt für Umwelt, Germany, 1998.*
- [19] W. Schnaak, Th. Küchler, M. Kujawa, K.-P. Henschel, D. Süssenbach, R. Donau, *Chemosphere* 35 (1997) 5.
- [20] G. Grimmer, G. Hilge, W. Niemitz, *Vom Wasser* 54 (1980) 255.
- [21] J.D. Berset, R. Holzer, *Int. J. Environ. Anal. Chem.* 59 (1995) 145.