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Original Research

Chromatographic Determination of Polycyclic Aromatic Hydrocarbons (PAH) in Sewage Sludge, Soil, and Sewage Sludge-Amended Soils

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Abstract

An effective method for determining polycyclic aromatic hydrocarbons in soils fertilised with sewage sludge is presented in this paper. PAH extraction was carried out by ultrasound; dichloromethane was used as a solvent. Purification was done by means of solid phase extraction. Identification and determination was carried out by means of HPLC with a UV detector. The present analyses were carried out on the soil (control), sewage sludge, and soil fertilised with sewage sludge at a rate of 1, 2.5, 5, 10, and 20%.

Keywords: PAH, Polycyclic aromatic hydrocarbons, Sewage sludge, Sewage sludge-amended soil, HPLC-UV, Ultrasonic extraction

Introduction

Agricultural utilisation of sewage sludge is well justified from both agricultural and ecological points of view. On the one hand, it gets rid of the troublesome waste which is sewage sludge, while improving the chemical, physical and biological properties of the soil [1-4]. In some European countries about 50% of sewage sludge is utilised in this way [5].

Additionally, the application of sewage sludge into the soil allows for some organic and inorganic pollutants to enter the soil [5-7]. Their amount and type depends, to a large extent, on the origin of the sewage sludge and the method of its treatment. If the concentration of pollutants in the sewage sludge is high, its biological utilisation may be called into question.

Some of the most common pollutants in sewage sludge [8-10] coming from sewage treatment plants, are the polycyclic aromatic hydrocarbons and their derivatives [11].

A permissible concentration has already been established for heavy metals in sewage sludge for agricultural utilisation [12]. However, there is no such data on PAH. It is known that PAH [13] do undergo biodegradation processes in the soil. It would be useful to determine those conditions which would allow micro-organisms in the soil (capable of PAH degradation) to use up the hydrocarbons introduced to the soil with sewage sludge. This would allow for the safe neutralisation of polycylic aromatic hydrocarbons in the sewage sludge while utilising it.

The method presented in this study allows one to determine the content of polycyclic aromatic hydrocarbons in the soil samples analysed, and in particular the content of fluoranthene, benzo[b]fluroranthene and benzo[a]pyrene. The permissible level of the above hydrocarbons in the sewage sludge was established by the European Union for 5.55, 6.20, and 2.13 mg/kg dry mass, respectively [14, 15].

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Materials and Methods

A total of 16 PAH (naphthalene, acenaphthalene, acenaphtene, fluorene, phenanathrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, benzo[b] fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi] perylene, indenol[1,2,3-cd] pyrene (each in a concentration of 100 μg/ml) (Promochem, Warszawa, Poland) were used as standards. Dichloromethane was used for extraction, and acetonitrile, methanol, 2-propanol (Merck KGaA, Germany) (all "grade" HLPC) were used for the purification according to the solid phase extraction method.

An ultrasonic bath (Sonic-3, Polsonic, Poland) was used for the extraction. The extracts were purified on the C_{18} Octadecyl columns (500 mg, 3 ml) (J.T. Baker-Mallinckrodt). The elution was carried out at room temperature.

Quantitative and qualitative PAH determinations were carried out on a liquid chromatograph consisting of Spectra Series P100 pump (Thermo Separation Products) coupled with a Spectra Series UV100 detector (Thermo Separation Products). A Spherisorb PAH column (250 x 4.6mm) (Schambeck SFD GmbH, Germany) was used for 16 PAH separation. The column was installed in a thermostated oven at 31°C (LCO 101, ECOM, Czech Republic).

The elution was carried out with mobile phase flow rate of 1 ml/min. Acetonitrile-water mixtures applied for the elution was 80:20 (v/v). Quantitative determination was performed using the absolute calibration curve method. The correlation coefficients of calibration functions in the intervals of linearity were higher than 0.9982-0.9998.

The detection limits calculated with a signal to noise ratio of three (IUPAC criterion), for 20 μl loop injection, were less than than 0.5 μg/ml and 5 ng for the concentration and amount of the PAHs. A blank method did not show any influence of the individual elements of the set on an increase in PAH levels.

Recovery of PAHs was determined at two concentration levels: C1 and C2. The amounts of PAHs added to 1 g sample were always the same: C1 – 100 μl (16 PAHs standards), C2 – 200 μl (16 PAHs standards). Spiked quantities correspond to 10 and 20 mg/kg dry mass sewage sludge (concentrations are always reported per kg of dry mass) for each 16 PAHs.

Results and Discussion

PAH Extraction from sewage sludge and soil with added sewage sludge

Ultrasonic technique was applied for PAH extraction from the analysed soil samples. It is a simple and effective method which does not require huge amounts of solvent as is the case with the Soxhlet apparatus. The ultrasonic exposition time depends, to a considerable degree, on the

Table 1. Recoveries for ultrasonic extractions with DCM solvent.

PAHs	Recovery [%]					
	2,5 % sewage sludge			10 % sewage sludge		
	2x30 min	1x45min; 1x30 min	2x45 min	2x30 min	1x45 min; 1x30min	2x45 min
Naphthalene	45±11	62±8	62±9	40±16	61±9	59±10
Acenaphthalene	52±9	68±6	64±11	39±6	65±12	66±9
Acenaphtene	49±13	59±11	60±8	41±12	68±7	65±11
Fluorene	58±6	66±7	64±6	55±9	68±7	71±8
Phenanthrene	85±6	93±5	89±9	66±7	95±5	92±6
Anthracene	65±4	68±5	71±9	51±7	65±5	67±5
Fluoranthene	89±4	95±8	92±4	65±6	92±6	89±7
Pyrene	75±7	81±4	83±7	67±5	80±4	84±6
Benz[a]anthracene	68±6	85±7	82±11	60±8	77±7	73±4
Chrysene	60±2	86±9	86±8	46±6	85±6	85±11
Benzo[b]fluoranthene	79±3	90±8	91±6	58±6	88±5	90±3
Benzo[k]fluoranthene	82±4	92±8	90±4	65±6	89±9	84±6
Benzo[a]pyrene	70±4	89±5	91±7	57±5	90±6	88±5
Dibenz[a,h]anthracene	65±3	87±4	85±9	52±5	89±9	91±5
Benzo[ghi]perylene	60±3	79±4	76±9	52±5	83±4	85±8
Indeno[1,2,3-cd]pyrene	72±3	91±6	92±4	49±5	89±3	92±4

± - standard deviation for n=2

type of material extracted. The longest extraction time is required for fly ash or dust [16]. Extraction time for sediments and soils is varied and ranges from 5 min [17] to 120 min [18]. Sometimes certain modifications are applied such as a few minutes earlier / a later mixing of the extracted sample or the flooding of the extracted sample with solvent and extraction in an ultrasonic bath after 24 hours [19].

Our studies showed that the optimum time for PAH extraction from sewage sludge is 2 x 60 min [15], whereas from sewage sludge-amended soils it is 1 x 45 min with the first batch of solvent and then 1 x 30 min with the second batch (Table 1).

An extraction time of 2 x 30 min is not sufficient (Table 1), and the prolongation of the first extraction time to 45 min improves recovery by 10-15% on average, in particular the recovery of 4-6-ring PAHs, which are characterised by the highest degree of sorption on the soil particles [20].

The extraction time depends, to a high degree, on the properties of the soil fertilised with sewage sludge, as well as on the properties of the sewage sludge itself. It is well known that PAH in the soils are adsorbed mainly in the organic phase [21]. Hence, soils rich in organic matter would require more time, whereas in the case of "mineral soils", this time can be shorter. Composition is an important factor in the case of sewage sludge, since PAH in the sludge can be located inside microorganism cells (which are found in the sludge), as well as be adsorbed on the non-biological material.

Full recovery of hydrocarbons can be difficult due to strong adsorption on the substrate or due to the presence of trace amounts of water that can form a thin film, making full contact between the solvent and PAH adsorbed on the surface of the matrix particles. As suggested by Maliszewska-Kordybach [21], the presence of water can significantly decrease the efficiency of the extraction.

Another difficulty in PAH extraction from sewage sludge results from the fact that part of the PAH can undergo metabolic processes and possible attachment of PAH metabolites to the biological matrix [22].

The extracts obtained during release require centrifugation for the separation of the solid phase from the solution containing the extracted PAH. While analysing sewage sludge and soil with added sewage sludge (in the amount of 20%), problems with centrifugation of the light fraction were encountered. The removal of this fraction required very high rotations of the centrifuge or an additional filtration. In the case of soils with added sewage sludge in the amount of 10% (and lower), rotations at the level of 7,000 rpm were sufficient for the centrifugation.

Another important issue in the extraction phase is the selection of a suitable solvent. Dichloromethane and cyclohexan [16, 23] are most frequently used. In our own studies [15], the most effective solvent for the extraction of PAH from sewage sludge was dichloromethane, which is widely used in PAH extraction from sediments [24]. Hence, the above solvent was used in the present studies on PAH extraction from soil fertilised with sewage sludge. Fluoranthene recovery of above 100% most probably resulted from an accidental, one-off pollution of the system (Table 1). Due to the omnipresence of PAHs in the human environment it is difficult to obtain absolute purity even in sterile laboratory conditions.

Purification of Extracts

The solution obtained after extraction and centrifugation contains other pollutants besides the polycyclic aromatic hydrocarbons determined. The above pollutants can disturb the identification and quantitative determination of hydrocarbons. It is necessary to remove the substances when applying a UV detector.

Currently, the most frequently used technique for extract purification is solid phase extraction (SPE). Several sorbents have been used in the SPE of PAHs. The most frequently used are cartridges filled up with reversed phases (octadecyl, octyl) or adsorption phases (silica gel, florisil). Other sorbents are also used alongside the ones mentioned above [25]. However, they do not allow for such an efficient recovery. Combinations of cartridges with different types of sorbents are also used for the selective isolation of PAHs from complex environmental samples (joint, such as $NH_2 - C_{18}$) [26-28], together with immuno-sorbents (IS) based on antigen-antibody interactions [29].

The material used in the column should be characterised by a high retention of the concentrated or selected substances and be of sufficient volume [30].

Depending on the level of column filling and the solvent applied for the extraction, an appropriate analytical procedure is also required.

Our earlier studies [31] showed that the best effects can be obtained when the C_{18} (octadecyl) columns are applied. The above has also been confirmed by other authors [26, 32].

Application of non-polar (dichloromethane) and columns filled up with octadecyl sorbents for extraction require dichloromethane evaporation and the dissolving of the remains of acetonitrile before any addition to the column, which increases losses in the recovery of volatile PAH (2-3-ring) [33].

Solid phase extraction is accomplished mainly through the mutual reactions of the three components, i.e. solvent, substance and adsorbent. Proper selection of the eluent is also very important as the substance could be adsorbed weakly or not at all, which is unfavourable for elution. When there is complete adsorption, strong retention of the analysed substance can require high amounts of the eluent [30].

Application of a solvent with a weak elution strength can restrict elution of the PAH strongly bound to the adsorbent, as suggested by Fusheng Sun [34]. However, replacement of the solvent with a solvent of high elution strength will make elution of strongly bound hydrocarbons

possible but at the same time it could influence the release of other pollutants. Moreover, the application of a strongly non-polar solvent (THF, dichloromethane) and determination with the HPLC technique requires an increase in its polarity, for example by evaporation which, in consequence, influences a further decrease in the 2-3-ring PAH recovery. On the basis of literature data [14, 27, 32, 34] and earlier studies by the same authors [15, 31], tetrahydorfuran (THF) and acetonitrile were chosen for the elution.

Analysing the chromatograms obtained, no significant differences were observed. The level of pollution (interferences) is almost identical in the two chromatograms. As has already been suggested, no influence of a strong eluent on the increase of variability of the substance recovered from the column. When analysing data in Table 2, the differences in the recovery of individual PAHs are clear. Application of THF and its evaporation before it has been introduced into the chromatographic column results in considerable (up to 60%) loss in the recovery of low molecular PAHs (LPAHs) (2-3-rings). On the other hand, in the case of high molecular PAHs (HPAHs) (4-6-rings), application of THF increases their recovery by a few per cent. Application of a solvent with a higher elution power actually increases their recovery rate from the SPE column. HPAHs are characterised by low volatility, hence the process of their evaporation does not influence losses in their recovery.

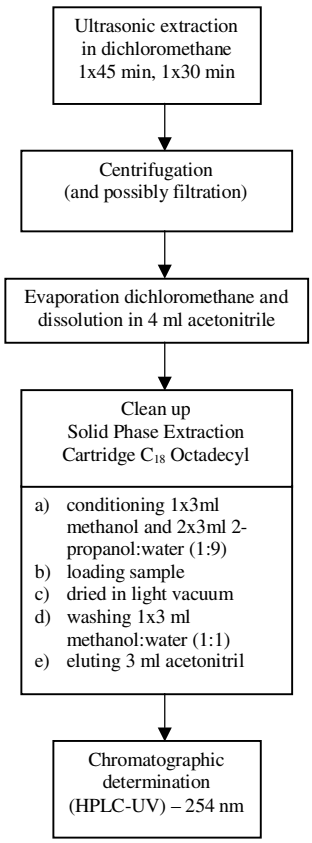

Fig.1. A schematic layout of the PAH determination process.

However, the application of solvents of varied elution strengths did not differentiate the profits from the recovery of 4-6-ring PAHs hydrocarbons as much as the losses of 2-3-ring PAHs resulting from evaporation. The highest losses were observed in the case of naphthalene and acenaphthalene (72%). Application of tetrahydorfuran resulted in about a 30% lower recovery of the PAH sum than when acetonitrile was applied. Hence, this last result was considered the most profitable. Fig. 1 presents a schematic layout of the PAH determination process described in the present paper.

Identification and Quantitative Determination of PAH

The determined PAH amounts in the soil, sewage sludge and sewage sludge-amended soil has been presented in Table 2. The influence of the sludge dose on the level of the fertilised soil pollution was clearly visible while analysing the data presented.

The highest concentration of PAH (1087 μg/kg) was determined in soils with a 20% addition of sewage sludge, and if the classification proposed by Maliszewska-Kordybach [35] is taken into consideration, these soils can be classed as polluted to a low degree. In the soils where the amount of sewage sludge is, respectively, 10, 5, 2.5, and 1%, a further gradual decrease in the PAH level was observed (Table 3).

In the control soil, small amounts of PAH were determined, since these soils were light soils with faulty sorption properties. The concentration levels of polycyclic aromatic hydrocarbons was 49.7 μg/kg and was comparable to their contents in soils from the unpolluted regions of Poland [36, 37]. Similar PAH concentrations and

Conclusions

The conditions applied in the present study, i.e. ultrasonic extraction, SPE purification, and HPLC analysis, allow for the effective determination of 16 PAHs in sewage sludge and soils with various additions of sewage sludge. The applied isocratic conditions (acetonitrile:water; 80:20, v/v) significantly lengthen the period of time required for the above analysis.

Loss of light PAHs due to solvent evaporation after extraction with dichloromethane is a disadvantage of this method.

However, this stage can be substituted by the technique of solvent evaporation in a nitrogen stream or, alternatively, by solvent evaporation up to a level of 2-3 ml by means of a vacuum evaporator, and then by removing the residue in a mild nitrogen stream.

The determined quantities show the necessity of monitoring the PAH level in the sewage sludge. It is not permissible to introduce sewage sludge which has not been examined for its PAH content since, from the results

Table 2. Effect of eluent on recovery PAHs from sewage sludge-amended soil [%].

PAH	2.5 % sewage sludge		10 % sewage sludge	
	ACET	THF	ACET	THF
Naphthalene	62±8	37±16	61±9	35±13
Acenaphthalene	68±6	44±13	65±12	41±11
Acenaphtene	59±11	49±14	68±7	39±11
Fluorene	66±7	59±11	68±7	61±9
Phenanthrene	93±5	82±9	95±5	80±9
Anthracene	68±5	65±7	65±5	67±10
Fluoranthene	95±8	85±9	92±6	84±7
Pyrene	81±4	73±5	80±4	77±6
Benz[a]anthracene	85±7	86±4	77±7	81±9
Chrysene	86±9	89±7	85±6	83±7
Benzo[b]fluoranthene	90±8	92±4	88±5	90±6
Benzo[k]fluoranthene	92±8	95±5	89±9	92±4
Benzo[a]pyrene	89±5	94±5	90±6	94±4
Dibenz[a,h]anthracene	87±4	91±8	89±9	96±3
Benzo[ghi]perylene	79±4	85±7	83±4	92±5
Indeno[1,2,3-cd]pyrene	91±6	96±3	89±3	93±5

ACET – acetonitrile, THF – tetrahydrofuran; time of extraction 1x45 and 1x30 min; ± - standard deviation for n=2

Table 3. Concentration of PAHs in sewage sludge-amended soil (horizon 0-20 cm) [µg/kg].

WWA	Participation of sewage sludge					
	0%	1%	2.5%	5%	10%	20%
Naphthalene	3.0±9	5.5±15	18.5±12	40.1±16	87.8±13	95.0±13
Acenaphthalene	13.0±11	16.0±17	41.1±15	59.4±12	115.0±17	143.8±15
Acenaphtene	10.6±17	11.2±9	19.0±12	46.0±15	96.0±13	96.0±13
Fluorene	3.6±6	1.1±11	2.6±8	14.9±9	40.6±9	21.5±10
Phenanthrene	0.8±9	1.9±9	5.1±11	16.1±12	32.3±8	31.5±11
Anthracene	0.1±9	0.2±7	1.1±11	4.6±13	14.4±10	11.9±10
Fluoranthene	2.4±11	5.6±19	21.0±13	50.6±18	40.2±12	107.9±14
Pyrene	1.8±8	3.3±16	2.5±12	41.1±9	109.6±8	111.3±7
Benz[a]anthracene	1.4±4	5.0±6	6.7±9	20.3±10	65.8±7	62.2±8
Chrysene	1.2±14	1.1±9	10.2±10	14.4±13	34.5±15	47.2±11
Benzo[b]fluoranthene	3.6±21	4.4±15	10.2±17	58.1±17	62.1±15	69.6±19
Benzo[k]fluoranthene	1.2±18	2.8±12	5.2±14	7.9±15	150.6±17	30.2±16
Benzo[a]pyrene	1.7±15	4. 8±16	11.1±15	17.5±17	53.7±13	45. 9±15
Dibenz[a.h]anthracene	2.2±6	3. 9±9	6.3±8	13.5±6	44.1±9	63.6±8
Benzo[ghi]perylene	0.7±10	2.7±8	8.4±9	10.9±8	28.4±9	31.2±10
Indeno[1,2,3-cd]pyrene	2.3±11	4.3±7	7.9±12	13.9±10	34.2±10	34.0±8

Time of extraction 1x45 and 1x30 min; acetonitryl as eluent in SPE, ± - relative standard deviation (%) (n=2)

obtained, as well as from studies by other authors [39, 40], it has been suggested that there may result an accumulation of hydrocarbons in the soil which may pose a danger to human health.

Doses of sewage sludge below 5% (i.e. 150 Mg sewage sludge/ha) with a PAH content of up to 6000 µg/kg, should not disturb the natural soil conditions, neither should they cause soil degradation, and when conditions are favourable, we can expect their partial biodegradation, which will form the subject of further studies to be carried out at our Institute.

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contribution of individual hydrocarbons in the sewage sludge were comparable to the results quoted by other authors [8, 38].

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