

Determination of Polynuclear Aromatic Compounds in Composted Municipal Refuse and Compost-amended Soils by a Simple Clean-up Procedure

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A rapid and reproducible procedure suitable for the analysis of polycyclic aromatic compounds (PACs) in sludges and soil samples has been developed. The PACs are isolated by ultrasonic extraction with methyl chloride, redissolution of the crude extract in isooctane and clean-up of the PAC-containing fraction by chromatography on alumina micro-columns. After separation and quantitative determination of the various PACs by capillary gas chromatography/mass spectrometry, more than 50 PAC compounds which cover a wide range of concentrations were detected in the sludge samples. The most abundant compounds were mono-, di- and trimethyl derivatives of naphthalene, phenanthrene, fluorene, dibenzothiophene and naphthothiphenene. No accumulation of PAC in an agricultural soil after an experiment of compost application over three years was observed.

INTRODUCTION

Application of recycled municipal wastes to agricultural land as a means of maintaining or increasing soil fertility has become a topic of major interest for soil scientists, agronomists and environmentalists throughout the world. Although these organic additives can exert a beneficial influence on the physical and biochemical properties of soils,^{1,2} major concern arises owing to the presence in the wastes of hazardously high levels of heavy metals and organic pollutants, derived largely from industrial effluents that reach the treatment plants.

While a considerable amount of literature has been published about the negative effects caused by toxic metals in plant-soil systems, more work must be done on the presence and fate of undesirable organic compounds, in order to know whether agricultural soils could become contaminated by such chemicals and could enter the food chain through this route. The discovery of elevated levels of polynuclear aromatic compounds (PACs) in composts^{3,4} and sewage sludges⁵⁻⁷ that were being applied to home gardens and agricultural soils has given considerable impetus to this concern, owing to the recognized carcinogenic activity of many of these compounds.

A prerequisite for the control of possible contamination by PACs is to develop sensitive and cost-effective analytical methods to measure their concentrations in complex sample matrices, such as sludges and soils. For separation, identification and quantification of PACs, gas chromatography/mass spectrometry (GC/MS) is the most widely used method.⁸ However, their extraction and isolation from complex samples, where the PACs are only a minor fraction of

the organics present, require time-consuming enrichment protocols, which tend to increase the chances of loss of compounds of interest and reduce the reproducibility of the analysis. In fact, the fewer steps used in any given protocol, the simpler, more convenient and less tedious it is.

Following the trend to avoid extensive manipulations, several simpler methods for the analysis of PACs in a variety of sample matrices have been developed in the last few years.^{7,9-12} In this work we present our preliminary evaluation of an alternative simple sample preparation technique to perform complete quantitative analysis of PACs in municipal wastes and soils by capillary GC/MS.

EXPERIMENTAL

Characteristics of a raw refuse, collected from the metropolitan area of Seville (southern Spain), as also chemical analyses of the derived compost (sample R, 15.2% C), were previously reported.¹³ The soil sample (1.5% C) used in this study was taken after a field experiment¹⁴ of application of this compost over three years. Two representative anaerobic sewage sludge samples were taken at different seasons (spring 1985, sample SS-1, 34.5% C; fall 1986, sample SS-2, 36.4% C) from a residual water treatment plant of Seville. They were lyophilized and then ground to obtain homogeneous, powdered (<2 mm) samples. The samples (10-20 g for SS-1, SS-2 and R; 50-100 g for soil) were extracted with methylene chloride (MeCl) (3 × 20 ml) in an ultrasonic bath and the combined crude extracts evaporated to dryness with a rotary evaporator at 35 °C under reduced pressure. The residues were partially redissolved in isooctane (5 ml), and aliquots (2 ml) were

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actionated using neutral alumina Sep-Pak cartridges. Sequential elution with each 15 ml of *n*-hexane and MeCl gave fractions enriched in *n*-alkanes and PACs, respectively, which can be submitted to GC/MS directly. A simplified schematic representation of the PAC isolation procedure is shown in Fig. 1.

A Hewlett Packard 5730A gas chromatograph equipped with FID and a Hewlett Packard 5988A GC/MS computer system were used for separation, identification and quantification of individual components. Separation of compounds was achieved using a 12 m (0.32 mm i.d.) SE-52 fused silica capillary column, with the oven temperature programmed from 50 (1 min) to 100 °C at a rate of 30 °C min⁻¹, and then from 100 to 280 °C at 6 °C min⁻¹, with 15 min final hold. Helium at a flow rate of 1.5 ml min⁻¹ was used as carrier gas. Mass spectra were measured at 70 eV ionizing energy. The recognition of each compound was achieved using GC (on the basis of retention times and co-injection with standards), mass fragmentography (by key ion monitoring of the mass of molecular ion or typical base peak for isomeric mixtures) and low-resolution mass spectra.

Recoveries of several PACs spiked in sample SS-1 at varying concentrations by the procedure described were compared with those obtained using classic methods

proposed by Giger and Schaffner¹⁵ and Vassilaros *et al.*¹⁶ for the analysis of PAC in environmental and biological samples, respectively.

RESULTS AND DISCUSSION

From 10 to 12% of the total weight of the sludges and 7% of the compost sample were extracted by MeCl. These values represent approximately 4% and 1% of the total organic carbon present in the whole material.

As shown in Table 1, the recoveries of hydrocarbons with two to four rings obtained after the sample preparation technique used in this work are close to 100%, which clearly improve on those obtained by the more extensive procedures.

With the exception of fatty acids almost all interfering substances could be removed from crude extracts of compost and sludge samples by the proposed clean-up procedure, and thus different polynuclear hydrocarbons, sulphur-containing PAC and mixtures of their methyl-, dimethyl- and trimethyl-substituted derivatives could be separated by direct capillary GC/MS analysis from the resultant PAC-enriched fractions. No peaks resulting from PCB, which usually interfere with PAC, were observed.

The identities of the PACs in the samples are tabulated in Table 2. The different isomer mixtures are not separated into single components, so the values in Table 2 show their total concentrations. The most abundant compounds are alkylated derivatives of naphthalene, phenanthrene, fluorene, dibenzothiophene and naphthothiophene, while more condensed PAC (pyrene, benzfluoranthene, chrysene) are present in minor amounts. PACs of these types have been reported in engine exhausts, fuel products and in air samples from urban and industrialized areas.¹⁷⁻¹⁹ Non-detectable amounts of benzo(a)pyrene, used in many investigations⁷ as an indicator for the extent of contamination with carcinogenic PAC, were found.

The concentrations of PACs present in the residues seem to be at sufficiently high levels to give concern. However, long-term application of the compost has not led to an increase of PAC in the soil. Only slight increases (5–10 ng g⁻¹) in some PACs present in the added residue (acenaphthene, acenaphthylene, phenanthrene, methylidibenzothiophene and dimethylphenanthrene) were detected. Even considering the various detoxification mechanisms (absorption, leaching, biodegradation, etc.) that occur in soils^{3,20,21} this result

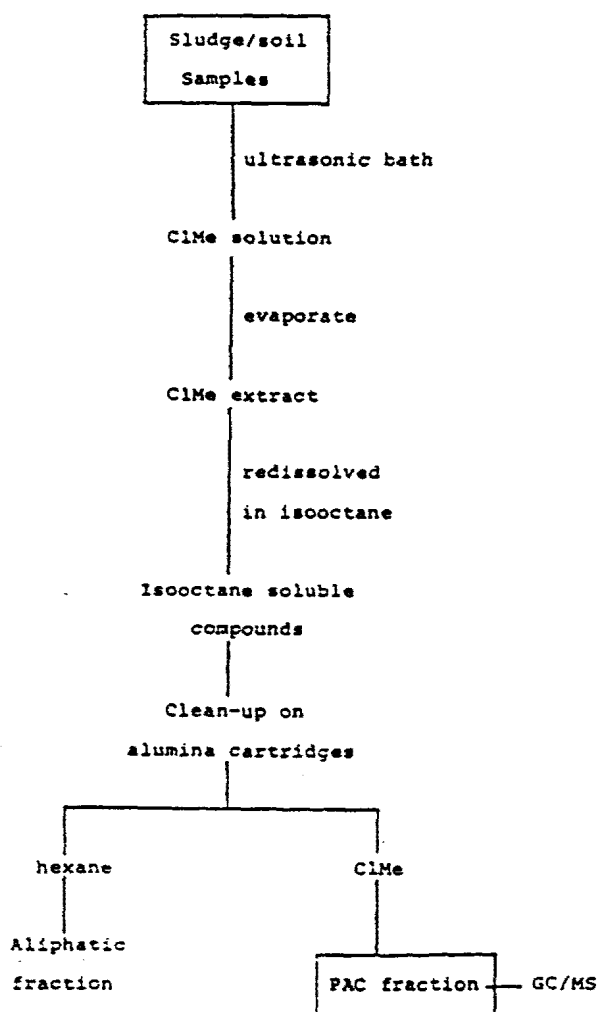


Figure 1. Analytical procedure for determining PACs in sludges and soils.

Table 1. Recoveries (%) of PAHs from sample SS-1 by different procedures

	Conc. (ppm)	Ref. 15	Ref. 16	This work
Naphthalene	100	70	56	78
2-Methylnaphthalene	200	74	61	96
Acenaphthene	150	83	70	95
Fluorene	100	86	78	94
Anthracene	70	85	77	91
2-Methylanthracene	150	82	73	93
Pyrene	250	87	79	100

Table 2. Average values (ppm) of PACs in the residue samples

Compound	SS-I	SS-II	R
Naphthalene*	4.5	8.6	—
Acenaphthylene*	—	—	0.5
C ₂ -Naphthalenes	14.7	15.2	13.4
Acenaphthene*	—	—	9.1
Fluorene*	3.5	5.8	4.2
C ₃ -Naphthalenes	15.3	10.1	27.6
C ₁ -Fluorenes	19.7	13.6	—
Dibenzothiophene	11.3	11.7	6.6
Anthracene/phenanthrene*	18.6	15.2	6.7
C ₁ -Naphthothiophenes	—	—	4.5
C ₂ -Fluorenes	13.2	5.3	13.2
C ₃ -Fluorenes	4.4	8.6	—
C ₁ -Dibenzothiophenes	83.7	51.7	36.2
C ₁ -Phenanthrenes	25.2	18.5	13.1
C ₂ -Naphthothiophenes	21.4	8.1	38.7
C ₃ -Dibenzothiophenes	32.2	13.1	—
C ₂ -Phenanthrenes	0.5	15.3	14.8
Methoxyphenanthrene	4.7	4.2	—
Fluoranthene/pyrene*	5.6	5.2	3.2
C ₃ -Dibenzothiophenes	32.9	19.8	—
C ₃ -Phenanthrenes	13.0	0.5	11.3
C ₃ -Naphthothiophenes	0.2	1.3	6.1
Benzfluoranthene*	—	5.1	18.3
Dibuthyl-naphthalene	12.5	3.4	—
C ₁ -Pyrene	6.8	0.1	6.2
C ₂ -Phenanthrenes	4.3	0.5	—
C ₁ -Benzfluoranthene	—	—	9.3
Chrysene*	—	—	0.5

* Included in the EPA priority pollutants list.

suggests that the triennial experiment achieved is too short to draw definite conclusions regarding the fate of PACs in the soil, and more studies on compost- and sludge-amended soils are needed.

In any case, the proposed method can be used for rapid and accurate analysis of PACs present in very low concentrations (ppb) in complex matrices.

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