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## Evidence for the adsorption of nitrated polycyclic aromatic hydrocarbons by tree bark

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### Abstract

It has been previously demonstrated that polycyclic aromatic hydrocarbons (PAH) are adsorbed onto tree bark and that bark may in fact be used as a passive sampler for these compounds. It is now demonstrated that by suitable modification of this methodology nitrated polycyclic aromatic hydrocarbons (nitro-PAH) may also be detected in bark. Bark samples were taken from urban locations in Sheffield, South Yorkshire, UK. After soxhlet extraction using dichloromethane, the nitro-PAH fraction was isolated by solid-phase extraction using amino and alumina cartridges in series. Nitro-PAH were detected by gas chromatography with electron capture detection and gas chromatography–mass spectrometry in the negative chemical ionisation mode. A comparison is made with nitro-PAH found in diesel particulate extracts. © 1997 Elsevier Science B.V.

**Keywords:** Tree bark; Polynuclear aromatic hydrocarbons; Nitrated polynuclear aromatic hydrocarbons

### 1. Introduction

Nitrated polycyclic aromatic hydrocarbons (nitro-PAH) are one of the many families of organic compounds known to be produced as micropollutants from the combustion of organic materials including diesel [1–12], gasoline [2,3], and wood [2,3]. The release of these substituted polycyclic aromatic hydrocarbons (PAH) is however relatively small in comparison to other more common groups of compounds such as aliphatic hydrocarbons and PAH. However, their toxicity has been found to be far greater than that of unsubstituted PAH; they have been identified as direct acting mutagens and carcinogens to mammalian systems [13–15].

Nitro-PAH produced from combustion processes are predominantly formed by electrophilic aromatic substitution reactions. These yield isomers corresponding to the cationic (Wheland) intermediates that have the greatest resonance stabilisation. It has also been shown that nitro-PAH can be formed, alternatively, by the reaction of PAH with reactive species found in ambient air, i.e. dinitrogen pentoxide ( $N_2O_5$ ) and oxygen radicals in the presence of  $NO_x$ . These gas-phase reactions have different mechanisms and produce different isomers to those formed in combustion processes. It can therefore be assumed that nitrated PAH isomers corresponding to the most stabilised cationic intermediates are formed almost entirely from the combustion of anthropogenic materials, and should therefore be a guide to the quantity of nitro-PAH released into the atmosphere

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from combustion sources. Examination of the literature on measured nitro-PAH confirms this and shows that the isomers expected from conventional electrophilic substitution (e.g. 1-nitropyrene, 1-nitronaphthalene, 3-nitrofluoranthene and 2-nitrofluorene) are detected in emissions from combustion sources (e.g. [1–12]) while the isomers due to gaseous reactions (e.g. 2-nitropyrene and 2-nitrofluoranthene) have only been found in ambient air [16] and emissions from an electrode factory [12].

The low levels of nitro-PAH released directly into the atmosphere dictates that a large sample of ambient air needs to be taken when conventional active sampling systems are employed in analyses. If a passive sampling system could be found readily available in the environment, costly sampling systems and sampling media would not be necessary. Many types of vegetation have been used as passive samplers for atmospheric pollutants. Reported systems have included pine needles for polychlorinated biphenyls (PCBs [17,18]) and pesticides, [18,19] and tree bark used for PCBs [20,21] and PAH [20,22,23] amongst others. As tree bark is ubiquitous throughout the environment, it was decided to examine this material for the presence of nitro-PAH. For comparison purposes diesel particulates were collected from the exhaust of a diesel engine running under controlled conditions.

The soluble organic extracts obtained from tree bark and diesel particulate exhaust filters are very complex mixtures. The extract may contain; aliphatics, simple aromatics, polycyclic aromatic hydrocarbons (PAH), nitrogen- and sulphur-containing derivatives of PAH along with polycyclic ketones, quinones, anhydrides, heterocyclic compounds and organometallics. Hence fractionation of this highly complex mixture is necessary prior to analysis. A variety of fractionation methods have been reported including; liquid–liquid partition [24,25], semi-preparative chromatography [4,26], low- and high-resolution chromatography [5–7,27] and chromatographic separation following a derivatisation step [8]. All these chromatographic fractionation methods have been applied to the pre-concentration of nitrated PAH from diesel exhaust particulates or air samples. More recently solid-phase extraction cartridges have been used as a possible method of pre-concentrating and fractionating nitrated PAH from complex ma-

trices [28,29]. However, no methods were found in the literature which describe a comprehensive fractionation of complex samples obtained from tree bark. Therefore, as part of this work, a solid-phase extraction method for the fractionation of bark extracts was developed.

Many methods also exist for the analytical determination of nitro-PAH. These include; capillary gas chromatography using flame ionisation (FID) [4,8,26,30], electron capture (ECD) [8,30], nitrogen phosphorous (NPD) [1,8,11,26], chemiluminescent nitrogen detector (CLND) [5,7,31] and mass spectrometric detection [1,6,8–11,31,32].

High-performance liquid chromatography (HPLC) has also been used for the final determination of nitrated PAH. Ultra violet absorbance detection at 254 nm has been used [33], however better sensitivity has been obtained from fluorescence detection after reduction to their corresponding amine [34], and in a recent paper this was carried out on-line using a zinc dust column [35].

In the work reported here we have employed gas chromatography with electron capture detection for qualitative and semi-quantitative determination of nitro-PAH in tree bark and diesel particulate extracts. The qualitative data have been confirmed and levels of nitro-PAH quantified by using gas chromatography–mass spectrometry with negative chemical ionisation and selected ion monitoring.

## 2. Experimental

### 2.1. Sampling

#### 2.1.1. Tree bark

Tree bark was sampled from two different locations around the city of Sheffield. Maple trees (which have a smooth bark) were identified in each location and used for these experiments. The two locations were: (A) a tree situated in the central bus terminus of the city; (B) a tree situated in a park on the outskirts of Sheffield away from major roads and bus routes.

Samples of 1–3 g of bark were removed from the surface of each tree, 1–2 m above the ground. A surface area of approximately 15 cm<sup>2</sup> of bark was removed, with the depth of bark removed not

exceeding 2 mm. Samples were stored in amber screw-top vials at 0°C until they were extracted. Samples were taken on the following dates; 1/95, 7/95, 1/96.

### 2.1.2. Diesel samples

Diesel particulate exhaust samples from a four-cylinder, 4-1, non-inter-cooled direct-injection diesel engine with turbo charger in a controlled test environment were collected on glass fibre filter papers. The engine was run at 1600 rpm at full rated power. Samples were taken after the emissions were diluted and cooled to below 52°C using a dilution tunnel. This was carried out in order to reduce chemical reactions occurring on the filter surface. Sampling times of between 1 and 2 h were required to yield sufficient organic material to quantify the nitro-PAH of interest.

## 2.2. Solvents and standards

All solvents used in the following procedures were HPLC grade or better. All standards and solvents were purchased from Sigma-Aldrich Co. (Poole, Dorset, UK).

### 2.3. Extractions

A relevant quantity of the sample in question was finely chopped and placed into a cellulose extraction thimble in a Soxhlet apparatus. The samples were then extracted with 80 ml of dichloromethane for 96 h. The Soxhlet apparatus was wrapped in aluminium foil to minimize photochemical degradation of the desired analytes. This length of time was found to be necessary from earlier work [36] on the extraction of nitrated PAH spiked onto tree bark. In order to identify any contamination from the extraction process, clean thimbles were extracted and subjected to the same procedures as all other samples to produce reagent blanks.

## 2.4. Fractionation

### 2.4.1. Solid-phase extraction

Solid-phase extraction (SPE) was performed using a polypropylene cartridge containing amino-bonded phase (200 mg of sorbent with a 10-ml reservoir,

obtained from International Sorbent Technology, Jones Chromatography, Mid Glamorgan, Wales, England) and alumina (500 mg of sorbent with a 6-ml reservoir obtained from J.T. Baker, UK, Milton Keynes, Bucks, UK) cartridges in series. The cartridges were initially cleaned with 30 ml of acetone to remove all adsorbed water. Fifteen ml of each eluting solvent were then passed through the cartridges, starting with methanol and continuing back through the solvents with reducing polarity to hexane, leaving a layer of 10 ml of hexane in the top cartridge reservoir. The sample extract was then loaded onto the cartridge using the smallest quantity of dichloromethane (often 50–100 µl) introduced directly into the 10 ml of hexane. Fractionation was achieved by elution of compounds with 10 ml of the following solvents of increasing polarity:

Solvent	Eluting compounds
Hexane	Aliphatics
Cyclohexane	2–4 ringed PAH (up to pyrene)
20% Dichloromethane in cyclohexane	Larger PAH and nitrated derivatives
Dichloromethane	Polar species
Acetonitrile	Polar species
Methanol	Polar species

The fractions were reduced to approximately 500 µl with a dry stream of nitrogen and transferred to pre-weighed amber vials. These were reduced to dryness once again by nitrogen to produce a residual weight. An internal standard (8-nitroquinoline; obtained from Sigma-Aldrich Co., Poole, Dorset, UK, at 98% purity) and 100 µl of dichloromethane were added prior to analysis by GC–ECD and GC–NICIMS–SIM.

## 2.5. Instrumentation

### 2.5.1. Gas chromatography with electron capture detector (GC–ECD)

The instrument used in all cases was a Hewlett-Packard 5880 gas chromatograph using a 5% diphenyl wall-coated open tubular capillary column (Rtx-5, Restek, Thames Chromatography UK) (20 m×0.32 mm) with a film thickness of 0.25 µm. The carrier gas used was nitrogen, at a flow-rate of 1

ml/min, with nitrogen as the makeup gas yielding a total flow of 30 ml/min; 1  $\mu$ l of each sample was injected splitless using a Hewlett-Packard 7673A autosampler. The injector temperature was set at 275°C with the detector at 300°C. The oven program temperature used was 40°C for 4 min, ramp 1; 25°C/min to 145°C hold for 1 min, ramp 2; 5°C/min to 280°C with a final hold time of 15 min.

### 2.5.2. Gas chromatography with negative-ion chemical-ionisation mass spectrometry working in selective ion-monitoring mode (GC–NICIMS–SIM)

This work was performed on two instruments due to the purchase of a more sensitive VG Trio III midway through the study. Initial work was completed on a Hewlett-Packard 5890 (Series II) gas chromatograph coupled to a VG Trio 1 mass spectrometer (VG MassLab, Manchester, UK) with the MS working in the selective ion monitoring (SIM) mode.

The column used was a 30 m  $\times$  0.32 mm I.D. 5% diphenyl wall-coated open tubular capillary column (Rtx-5 Thames Chromatography UK), with a film thickness of 0.25  $\mu$ m. Helium was used as the carrier gas at a flow-rate of 1 ml/min. The injector temperature was set at 275°C with the oven temperature program being 40°C, held for 4 min then increased at 25°C/min to 175°C, held for 1 min; the temperature was then increased at 5°C/min to the final temperature of 280°C for 15 min. All samples (1  $\mu$ l) were injected manually in splitless mode.

Later work was undertaken using a Hewlett-Packard 5890 (Series II) gas chromatograph coupled to a VG Trio 3 mass spectrometer working in SIM mode. In both cases the reagent gas used for chemical ionisation was methane with an ion source temperature of 125°C. The NICI conditions were optimised by injecting a small quantity of methyl iodide via the septum inlet and tuning the instrument via the peak at  $m/z$  127. A SIM experiment was set up monitoring each of the  $M^-$  ions for the nitrated PAH studied (Fig. 1). The column used was a 60 m  $\times$  0.32 mm I.D. 5% diphenyl wall-coated open tubular capillary column (Rtx-5 Thames Chromatography UK) with a film thickness of 0.25  $\mu$ m. The injector temperature was set at 275°C and the oven temperature program was as described earlier. The

carrier gas was helium at a flow-rate of 1 ml/min; 1  $\mu$ l of each sample was injected splitless.

## 3. Results and discussion

After soxhlet extraction, the residues obtained from the tree bark extracts were green/brown in colour. The diesel particulate extract was black in colour due to carbon particles extracted over the siphoning mechanism of the soxhlet.

### 3.1. Fractionation procedure

An amino cartridge was used as the initial sorbent of the SPE system. The bonded amino group strongly interacts with its nitrogen lone pair producing adsorption of nitrated compounds. The nitrated PAH can then be removed from the cartridge by a moderately polar eluent (i.e. 20% dichloromethane/80% cyclohexane). They then pass through the alumina cartridge with little retention whilst any other polar compounds that have been removed from the amino cartridge by the moderately polar eluent are retained by the alumina cartridge.

Table 1 shows the percent recoveries obtained from the tandem SPE fractionation of a standard containing seven nitro-PAH studied (Fig. 1). Complete separation into one fraction was achieved with four of the seven nitrated PAH having a percent recovery of greater than 94%. 9-Nitroanthracene and 1-nitropyrene have recoveries of 53 and 72%, respectively, with 1-nitronaphthalene having the lowest recovery at approximately 30%. This could possibly be due to irreversible adsorption to the alumina sorbent which occurred when alumina was used solely as the sorbent. A more likely reason for the losses of especially the volatile compounds could be attributed to the sample drying stage.

### 3.2. Tree bark

The quantitative results obtained from GC–NICI–SIM (Table 2, Fig. 2A (standards) and Fig. 2B (bark A)) indicate that the bus station sample, tree bark A, contained a larger quantity of nitrated PAH than tree bark B throughout the year. The exceptions to this were 5-nitroacenaphthene (Jan./96) and 1-nitronaph-

Table 1  
Average percentage recovery and standard deviation data of amino/alumina fractionation method used to selectively pre-concentrate nitrated PAH

Compound	Hexane		Cyclohexane		20% Dichloromethane		Dichloromethane		Acetonitrile	
	% recovery	S.D.	% recovery	S.D.	% recovery	S.D.	% recovery	S.D.	% recovery	S.D.
1-Nitronaphthalene	0	0	0	0	28.27	1.92	0	0	0	0
4-Nitrobiphenyl	0	0	0	0	105.25	6.78	0	0	0	0
5-Nitroacenaphthene	0	0	0	0	94.97	7.37	0	0	0	0
2-Nitrofluorene	0	0	0	0	106.15	1.02	0	0	0	0
9-Nitroanthracene	0	0	0	0	53.25	1.17	0	0	0	0
3-Nitrofluoranthene	0	0	0	0	72.15	2.24	0	0	0	0
1-Nitropyrene	0	0	0	0	108.31	10.2	0	0	0	0

thalene (July/95 and Jan./96) which were found to be higher in bark B than in bark A at these sampling times.

The semi-quantitative values obtained by GC–ECD (Table 3, Fig. 3A (standards), Fig. 3B (bark A)) show a similar trend to that in Table 2, with tree bark A consistently containing a larger amount of in-

dividual nitrated PAH compared to tree bark B. Here, the only exception is 4-nitrobiphenyl which is seen to have a greater amount in bark B than in the bark A (Jan./96).

Over the three sampling dates both the GC–NICI–SIM data (Table 2) and the GC–ECD data (Table 3), show higher levels of nitrated PAH in bark samples taken during January compared to July. The only compounds quantified in both trees during the summer sampling period were 1-nitronaphthalene and 4-nitrobiphenyl, with a further two nitrated PAH, 5-nitroacenaphthene and 2-nitrofluorene, being detected in the bus station bark (July/95). With the exception of 1-nitronaphthalene in bark B (Jan./95), all nitrated PAH were detected at higher concentrations in the January samples compared to the July 1995 sample. The reasons for this may be a combination of the following. (1) All nitrated PAH investigated in this study are found to some extent in the vapour phase at ambient temperatures. Average temperature and pressure will therefore have a great effect on the condensation of pollutants onto surfaces. For example, compounds will condense out during times of cold ambient temperatures (i.e. November–February in Britain) this is called the ‘cold condensation effect’. (2) During warmer ambient temperatures, photodegradation of these vapour phase organic molecules is likely due to the higher levels of UV radiation and the presence of radicals capable of causing degradation i.e. OH [16]. (3) The cold winter months always induce an increase in the emissions of organic combustion material due to the extra use of vehicular transport by commuters and travellers. More organic fuel is also burnt due to the increased use of electricity for heating and lighting.

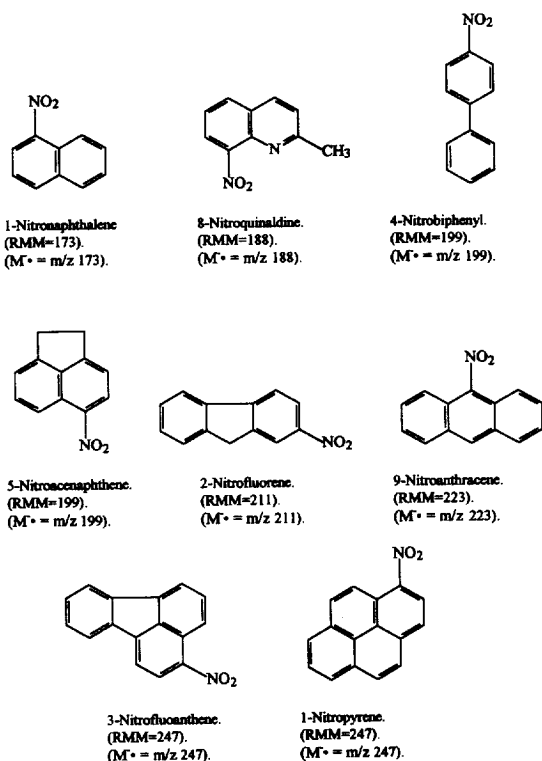


Fig. 1. Structures and molecular ions of all seven nitrated PAH and the internal standard.

Table 2

GC–NICI–SIM quantitative results of specific nitrated PAH in tree bark A and B (three samples over a 1-year period) along with diesel particulate extracts: quantitative results are ng of compound in 1 g of bark or diesel particulates as appropriate

Compound	SIM molecular ion	Tree A Jan./95	Tree A July/95	Tree A Jan./96	Tree B Jan./95	Tree B July/95	Tree B Jan./96	Diesel particulates
1-Nitronaphthalene	173	70.48	2.48	22.11	0.71	8.07	26.53	1.64
Internal standard	188							
4-Nitrobiphenyl	199	37.99	16.42	37.26	8.19	6.23	16.59	6.14
5-Nitroacenaphthene	199	20.67	0.71	32.3	15.38	Trace	38.4	2.48
2-Nitrofluorene	211	11.79	1.79	45.62	1.28	N.D.	30.59	N.D.
9-Nitroanthracene	223	76.19	Trace	23.77	D.S.	N.D.	7.69	4.13
3-Nitrofluoranthene	247		Trace	45.3	—	N.D.	26.69	Trace
1-Nitropyrene	247		N.D.	52.91	—	N.D.	25.4	21.73

N.D., none determined. Trace, peak present but below limit of detection. D.S., nitrated PAH had degraded in sample.

(4) In winter, deciduous trees are without any foliage so any gaseous or particulate associated pollutants condensing out onto vegetation can only condense upon the bark. (5) Preferential adsorption of certain nitrated PAH could be a reason for the increased quantities of some compounds observed. The ambient temperature and the individual vapour pressures will determine whether the compound is predominantly in the gaseous phase or adsorbed onto a particulate surface. A variation in the degradation rate of certain compounds (e.g. 9-nitroanthracene, which is known to rapidly degrade to anthraquinone [37]), may also play a part.

However the small number of samples taken in this present study only allow us to present these ideas 'for discussion' rather than make any definitive conclusions.

### 3.3. Diesel particulates

The particulate extracts were fractionated using the previously described tandem amino/alumina SPE method. Nitrated PAH were only identified in the 20% dichloromethane/80% cyclohexane fraction. Samples were analysed by both the GC–NICI–SIM (Fig. 2C) and GC–ECD methods with the GC–NICI–SIM performed on the VG Trio III instrument.

These GC–NICI–SIM results (Fig. 2C, Table 2) show that, except for 2-nitrofluorene, all the nitrated PAH studied were present in the GC–NICI–SIM chromatogram (Fig. 2C). This is surprising as 2-nitrofluorene has previously been detected in diesel

particulates [1]. 3-Nitrofluoranthene is present in the diesel particulates but only at a relatively low concentration. The tree bark sample (Fig. 2B), however, contains a large amount of 3-nitrofluoranthene. This could be due to preferential adsorption of 3-nitrofluoranthene on the surface of the bark or it could be due to co-elution with 2-nitrofluoranthene, which is known to be produced by atmospheric reactions [38]. The problem of separating these closely eluting isomers has been described in the literature [12]. The results obtained from the mass spectrometer using the SIM mode often contained several peaks in each mass chromatogram. These additional peaks could be isomers of the same nitrated PAH or compounds with the same empirical formula but a different structure, i.e., nitrofluoranthene and nitropyrene, produced from either polluting sources or atmospheric processes.

The semi-quantitative GC–ECD results (Table 3) also allowed identification and semi-quantification of five of the seven nitrated PAH. (3-Nitrofluoranthene was not quantifiable due to an impurity identified from the solvent or thimble in the blank experiments which obliterated the area of the chromatogram where 3-nitrofluoranthene would appear.) The quantities identified by the two methods are similar, however, with all the values being in the tens of ng per gram of diesel particulates. The GC–ECD results for the diesel particulates are consistently higher than the GC–NICI–SIM results (excluding 1-nitropyrene). This is probably due to the integration data from the GC–ECD being high due to incomplete baseline

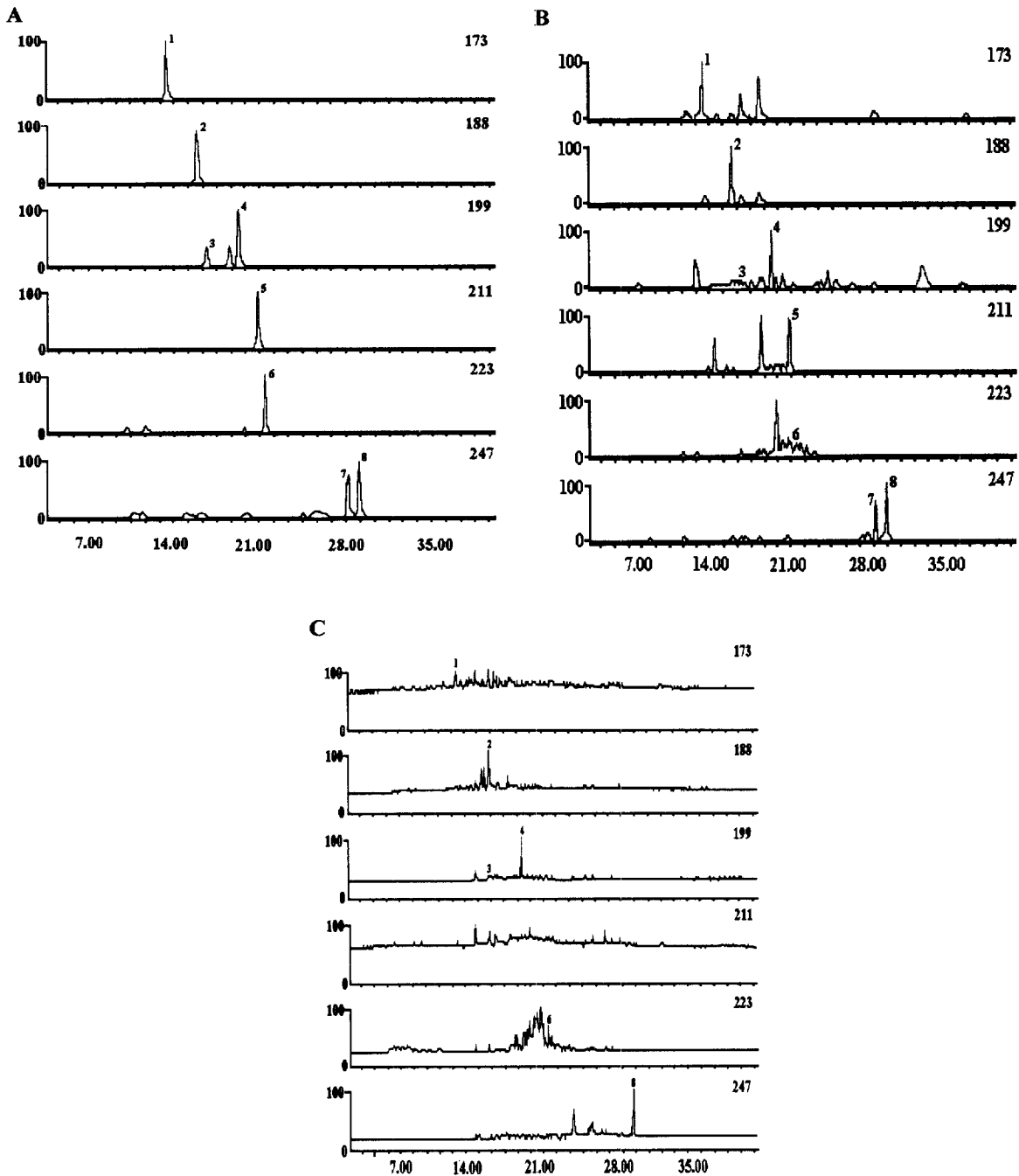


Fig. 2. (A) GC-NICI-SIM chromatograms of a standard containing seven nitrated PAH and an internal standard: (1) 1-nitronaphthalene, (2) internal standard, (3) 4-nitrobiphenyl, (4) 5-nitroacenaphthalene, (5) 2-nitrofluorene, (6) 9-nitroanthracene, (7) 3-nitrofluoranthene, (8) 1-nitropyrene. (B) GC-NICI-SIM chromatograms of tree bark A (2/96) after fractionation, identifying: (1) 1-nitronaphthalene, (2) internal standard, (3) 4-nitrobiphenyl, (4) 5-nitroacenaphthalene, (5) 2-nitrofluorene, (6) 9-nitroanthracene, (7) 3-nitrofluoranthene. (C) GC-NICI-SIM chromatograms of diesel particulates (11/95) after fractionation, identifying: (1) 1-nitronaphthalene, (2) internal standard, (3) 4-nitrobiphenyl, (4) 5-nitroacenaphthalene, (6) 9-nitroanthracene, (8) 1-nitropyrene.

Table 3

GC-ECD semi-quantitative results of specific nitrated PAH in tree bark A and B (three samples over a 1-year period) along with diesel particulate extracts: quantitative results are ng of compound in 1 g of bark or diesel particulates as appropriate

Compound	Tree A Jan./95	Tree A July/95	Tree A Jan./96	Tree B Jan./95	Tree B July/95	Tree B Jan./96	Diesel particulates
1-Nitronaphthalene	48.52	6.33	39.37	3.43	4.17	28.9	2.5
Internal standard							
4-Nitrobiphenyl	38.99	Trace	26.33	3.3	Trace	35.4	13.19
5-Nitroacenaphthene	20.67	N.D.	103.39	7.49	N.D.	71.09	12.43
2-Nitrofluorene	11.79	Trace	91.49	3.4	N.D.	43.94	N.D.
9-Nitroanthracene	N.D.	N.D.	57.49	Degraded	N.D.	11.09	9.79
3-Nitrofluoranthene		Obscured	Obscured		Obscured	Obscured	Obscured
1-Nitropyrene		N.D.	89.98		N.D.	73.63	18.39

N.D., none determined. Trace, peak present but below limit of detection. D.S., nitrated PAH had degraded in sample. Obscured, the relevant peak was obscured beneath a large contamination peak.

resolution of some of the relevant peaks. 1-Nitropyrene is often identified as being the major nitrated PAH present in diesel exhaust fumes, [1], and the data presented here supports this.

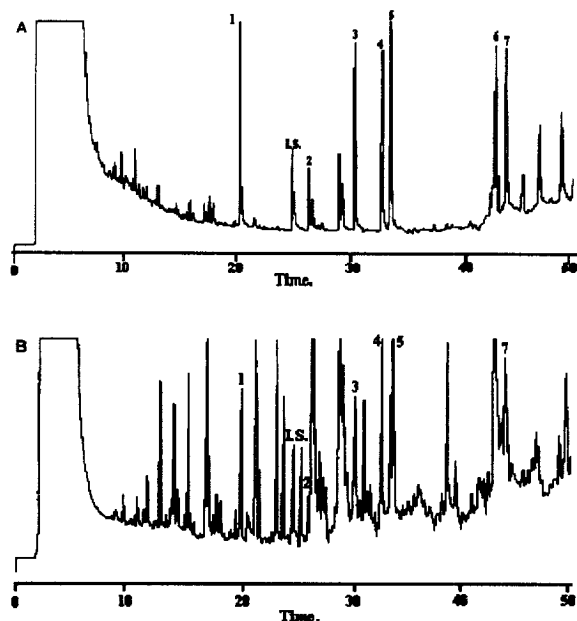


Fig. 3. (A) GC-ECD chromatogram of seven nitrated PAH with internal standard: (1) 1-nitronaphthalene, (2) internal standard, (3) 4-nitrobiphenyl, (4) 5-nitroacenaphthalene, (5) 2-nitrofluorene, (6) 9-nitroanthracene, (7) 3-nitrofluoranthene, (8) 1-nitropyrene. (B) GC-ECD chromatogram of tree bark (1/96): (1) 1-nitronaphthalene, (2) internal standard, (3) 4-nitrobiphenyl, (4) 5-nitroacenaphthalene, (5) 2-nitrofluorene, (6) 9-nitroanthracene, (7) 3-nitrofluoranthene, (8) 1-nitropyrene.

#### 4. Conclusions

The literature has shown that tree bark can act as a passive sampler for certain atmospheric pollutants. Here we have demonstrated the adsorption of nitrated PAH from the atmosphere by tree bark. The seven nitro-PAH studied (Fig. 1) were all from the most stable intermediate in electrophilic aromatic substitution and are, therefore, formed in combustion processes. Their major source in the centre of Sheffield is likely to be vehicular emissions. The presence of six out of the seven studied compounds was confirmed in separate experiments using a diesel engine under controlled test conditions. All nitrated PAH studied were found by GC-NICI-SIM in the January 1996 bark samples (Table 2) while four were found in both of the January 95 tree bark samples. (Note: 1-nitropyrene and 3-nitrofluoranthene were not analysed for in the Jan./95 samples.)

Nitrated PAH are produced in relatively large quantities with one route of removal from the environment being adsorption onto tree bark and/or other vegetation, especially during colder climatic periods. The extent to which this occurs, appears to be seasonally dependent since concentrations in the bark are lower in the summer than during the winter. This has also been observed by Librando and Fazzino [5] who analysed air samples over a period of 1 year. Identification of the mechanism by which these pollutants are adsorbed onto vegetation (i.e. either from the gas phase or directly from particulates) is required as the sampling method could be expanded to the analysis of nitrated PAH pro-



duced in ambient air [16,39]. Then possible sources and routes to removal could be investigated with the result being a mass-balance model of nitrated PAH and their ultimate removal from the environment. The necessity for quick, robust methods for the determination of these compounds is important along with the identification of any other major sources. If the other sources of nitrated PAH are of little consequence, nitrated PAH could be used as markers to identify areas which are heavily polluted from diesel emissions.

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