Research Articles: Soil Sciences

Determination of Polycyclic Aromatic Hydrocarbons and Substitutes (Nitro-, Oxy-PAHs) in Urban Soil and Airborne Particulate by GC-MS and NCI-MS/MS

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Abstract

A method involving high resolution gas chromatography combined with ion trap (HRGC-MS/MS) and negative chemical ionisation (NCI) was developed for the determination of nitrated or oxygenated polycyclic aromatic hydrocarbons (nitro-PAHs, oxy-PAHs) and other electrophilic substitutes in soil samples. Efficient clean-up was achieved by a combination of methods for the determination of PAHs in soil and nitro-PAHs in aerosol using solid phase extraction (SPE) and semipreparative high performance liquid chromatography (HPLC). In samples of surface soil from the city of Basle (Switzerland), nitro-PAHs (mainly 3-nitrofluoranthene and 1-nitropyrene) were found in concentrations between 30 and 800 ng/kg dry weight. Oxy-PAHs and parent PAHs revealed 10^2-10^4-fold higher levels. Nitro-PAHs which are up to 10^5 times more mutagenic seem to be less persistent in soil than the parent forms, although their entire mutagenic potential has to be estimated as being on the same order of magnitude. In urban air particulate matter, the amounts of nitro-PAHs (2-62 pg/m^3) were 10-100 times lower than oxy-PAHs and parent PAHs which were both found in a similar range. 3-nitrobenzanthrone, a recently described suspected human carcinogen has not yet been detected. Using multivariate statistical analysis, it was possible to elucidate similarities or special characteristics of substances in a given matrix reflecting their chemical properties or specific emission sources.

Keywords: 1-nitropyrene; 3-nitrobenzanthrone; 3-nitrofluoranthene; aerosol; airborne particulate matter; GC/MS/MS; nitro-PAH; oxy-PAH; PAH; soil, urban; substitutes, PAH

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are frequently found in various environmental samples as a result of anthropogenic contamination and/or natural processes [1]. In recent years, increasing attention has been focussed on nitrated substitutes because of the higher mutagenic (2 x 10^5 times) or carcinogenic (10 times) properties of certain congeners (e.g. 1-Nitropyrene) in comparison to underivatized PAH [2,3,4,5,6]. They are easily formed by atmospheric reactions of PAHs with nitrogen oxides and nitric acid in addition to combustion emissions [7]. Concentrations of nitro-PAH adhering to air particulate matter are generally 10 to 100 times lower than concentrations of PAH [1]. Even though many studies concerning nitro-PAHs or other derivatives (e.g. oxy-PAH) in aerosols have been carried out, as far as we know nothing has been published about their environmental aspects or levels in soil to date. Since earlier investigations of urban soil from the city of Basle (200,000 inhabitants) showed elevated PAH concentrations up to 60 mg/kg dry weight [8], it was essential to know if PAH derivatives could also play a significant role as priority pollutants for future soil monitoring programmes.

The aim of this work was to develop and validate techniques for the identification of nitro-PAHs and other substitutes in urban soil samples. Taking in account the extremely complex soil matrix an efficient clean-up procedure which was achieved by a combination of methods for the determination of PAHs in soil [8,9] and nitro-PAHs in aerosol is indispensable [10,11]. Current compound concentrations and their profiles in soils were compared with those found in air particulate samples. Using multivariate statistics, it was possible to describe similarities or special characteristics of substances or substance groups.

2 Experimental

Chemicals
All chemicals were of analytical grade or higher. Water was distilled and free of organic compounds.

Sample origin
Soil samples were taken at 26 sites lacking vegetation at a depth of 0-5 cm from 10 children playgrounds and 3 park areas as described in [8]. Air particulate matter from a square with heavy traffic was obtained by high-volume sampling (Digitel DHA-80) at a sampling rate of 40 m^3/h for 24 h with glass fibre filters (Ederol 227/1/60) over a period of

one month (Sept.-Oct. 1995). Additional Soxhlet-extracted airborne samples of the first quarter of 1997 from the air quality management office of Basle (LHA) were also included. All samples were stored at -18 °C until further preparation.

Extraction and clean up of organic compounds

An overview scheme of the clean up procedure is shown in Figure 1. Frozen soil (20 g fresh weight) or airborne samples filters (3 of them combined) were spiked with deuterated internal standards (→ Table 1) for quality control of the sample preparation steps and calibration. Soil samples were extracted with 40 ml methanol-acetone (1:1, v/v) by shaking for 2 hours at room temperature or, in the case of airborne samples, by microwave (MLS MEGA 240, 500 Watt, 17 min., 80°C). After prefiltering through a glass-microfibre filter (M&N GF4), the extract was diluted with water (1:7, v/v) of pH 2 (pH adjustment with 6 N HCl) and separated into two organic fractions differing in polarity by using a combination of reversed (C18, 500 mg, 6 ml, Varian) and normal (SiOH, 500 mg, 3 ml, M&N, overlayered with Na_2SO_4) solid phase extraction (SPE). The apolar fraction of PAHs was eluted with 8 ml of cyclohexane and the more polar fraction of nitro- and oxy-PAHs with 8 ml ethylacetate-cyclohexane (5:95, v/v) as eluant. These two fractions were collected separately, concentrated by rotary evaporator to a minimal volume and resuspended in toluene. Whereas the PAH-fraction could be used for subsequent analysis, the more polar fraction had to be cleaned up by semipreparative high-performance liquid chromatography (HPLC; Kontron 200,

2 pumps Kontron T-414, injector Rheodyne 7125, UV-VIS Lambda 1 Perkin Elmer) to obtain a nitro- and oxy-PAH-fraction [10] under the following conditions: 500 μl loop, 25 cm x 8 mm I.D. Lichrosorb Si-60 7μm column, solvents: cyclohexane (A) dichloromethane (B), solvent programme: linear 100% A to 40% A (0-20 min.), isocratic 100% B (20-35 min), isocratic 100% A (35-40 min), flow rate 3.0 ml/min, UV 254 nm.

Determination by GC-MS

Identification and determination of organic substances was performed by gas chromatography-mass spectrometry (Carlo Erba HRGC 5160, Fisons and GCQ, Finnigan MAT) under the following conditions: DB-5MS (J&W) fused silica column (30 m x 0.25 mm I.D., 0.25 μm film) with a retention gap (0.5 m x 0.32 mm I.D., deactivated) used with on column injection of 1.0 μl; temperature programme 90°C(1 min)-(30°C/min)-170°C-(10°C/min)-290°C(5-17 min); carrier gas (helium) 90 kPa; EI mode (trap offset 10) or NCI mode (methane, trap offset 5), mass range 50-500 amu, full scan mode or MSMS.

Quality control

The following substances (→ Table 1) were used for quality control, identification, calibration and quantitation:

- 5 deuterated compounds (Cambridge Isotope Laboratories) for identification and calibration in amounts of 5 ng (PAH) and 500 pg (nitro-PAH). Recovery rates of internal standards were between 80% and 90%.

- 16 PAHs (Supelco, US EPA SW-846) for calibration in amounts ranging from 40 ng to 2500 ng (correlation coefficients r > 0.995). Corrections of quantitation were based on the internal pyrene-d10 standard. Reproducibility of three soil sample replicates expressed as mean relative standard deviation of all PAHs was 11%. Accuracy was tested with certified PAH-contaminated soil reference material (CRM104-100, RTC, USA). The calculated limits of detection was approx. 3 μg/kg dwt for soil and 10 pg/m³ for air, respectively.

- 10 nitro-PAHs (Aldrich, amchro) for calibration in amounts ranging from 4 pg to 500 pg (correlation coefficients r > 0.993). Corrections of quantitation were based on the internal 1-nitropyrene-d9 standard. Recovery rates were about 80% and 90%, with the exception of DNfluo and DiNpyr (0%) which are lost during the clean-up. Reproducibility of two soil sample replicates expressed as relative standard deviation of 3 detectable nitro-PAHs (2Nfluo, 3Nfluant, 1Npyr) was 0-35%. The calculated limits of detection were approx. 30 ng/kg dwt for soil and 1 pg/m³ for air, respectively.

- 4 oxy-PAHs (Aldrich, Acros) for calibration in amounts ranging from 250 pg to 1000 pg (correlation coefficients r > 0.995). Corrections of quantitation were based on the internal 1-nitropyrene-d9 standard.
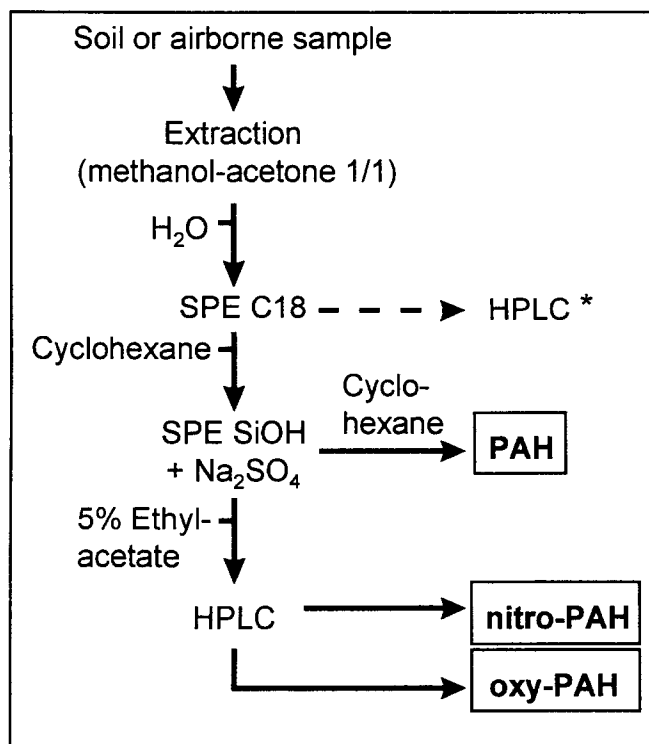

Fig. 1: Clean-up overview for soil and airborne samples with solid phase extraction (SPE) and High Performance Chromatography (HPLC). * Alternative variant exclusively for airborne samples

Table 1: Identification of PAHs and derivatives separated by gas chromatography-mass spectrometry (GCMS) on the basis of retention times and mass. Conditions see experimental section

Compounds and HPLC fraction	Abbr.	Retention time (min)	Mass	Remarks
PAH fraction	**PAH**			
Naphthalene-d8	Nap-d8	3:49	136	internal standard
Naphthalene	Nap	3:50	128	
Acenaphthylene	Acnyl	5:39	152	
Acenaphthene	Acna	5:53	154	
Fluorene	Fluo	6:43	166	
Phenanthrene	Phen	8:32	178	
Anthracene	Anth	8:38	178	
Fluoranthene	Fluant	11:11	202	
Pyrene-d10	Pyr-d10	11:42	212	internal standard
Pyrene	Pyr	11:43	202	
Benzo(b)naphtho(2,3)furane [c]	Bznap2,3fur	11:56	218	
Benzo(b)naphtho(2,1d)thiophene [c]	Bznap2,1thio	13:55	234	
Benzo(b)naphtho(1,2d)thiophene [c]	Bznap1,2thio	14:09	234	
Benzo(b)naphtho(2,3)thiophene [c]	Bznap2,3thio	14:23	234	
Benzo[a]anthracene [a, b]	Bzaan	14:41	228	
Chrysene-d12	Chry-d12	14:46	240	internal standard
Chrysene [a]	Chry	14:47	228	
Benzo[b]fluoranthene [a]	Bzbfl	17:26	252	
Benzo[k]fluoranthene [b]	Bzkfl	17:29	252	
Benzo[a]pyrene-d12	Bap-d12	18:25	264	internal standard
Benzo[a]pyrene [a]	Bap	18:26	252	
Indeno[123-cd]pyrene [a]	Ind	22:58	276	
Dibenzo[ah]anthracene [a]	Dibzan	23:08	278	
Benzo[ghi]perylene[b]	Bzper	24:16	276	
Dibenzo(a,i)pyrene [a, c]	Dbzpyr	37:01	302	
Nitro-PAH fraction	**NPAH**			
1-Nitronaphthalene	1Nnap	6:46	173	
2-Nitronaphthalene [a]	2Nnap	7:09	173	
9-Methylcarbazole [c]	Metcarb	8:50	181	
4-Nitrobiphenyl [a]	4Nbiph	9:00	199	
5-Nitroacenaphthene [a]	5Nacna	10:30	199	
2-Nitrofluorene [a]	2Nfluo	11:27	211	
3-Nitrofluoranthene [a, b]	3Nfluant	15:20	247	
1-Nitropyrene-d9	1Npyr-d9	15:47	256	internal standard
1-Nitropyrene [b]	1Npyr	15:48	247	
2,7-Dinitrofluorene [b]	DNfluo	16:11	256	lost by cleanup
6-Nitrochrysene [a]	6NChry	18:09	273	
1,6-Dinitropyrene [a, b]	DiNpyr	19:43	292	lost by cleanup
Oxy-PAH fraction	**OPAH**			
Anthraquinone	Anquin	10:44	208	
Benzanthrone [b]	Bzanon	15:27	230	
Benzo(a)anthracene-7,12-dione	Bzdion	16:18	258	
5,12-Naphthacenequinone	Napon	16:58	258	

[a] carcinogenic in animal experiments
[b] mutagenic in human cell test or in bacteria
[c] not quantified, used for identification

Multivariate statistical analysis

The Factor Analysis (STATISTICA for windows, StatSoft, Inc., Tulsa, OK) procedure extracts principal components of variables of interest and was used in this study to define groups of high correlated substances in soil and airborne matter by linear combination [12,13].

3 Results and Discussion

Analysis of individual nitro-PAH is difficult because of their potential chemical reactivity, their low abundance and their presence in a highly complex matrix [2]. High resolution gas chromatography combined with ion trap (GC-MS) and negative chemical ionisation (NCI) with methane was used for the selective detection of these electrophile substances, making the detection of picogram amounts possible [10]. Since artefacts may occur during any stage of the analytical process, the following provisions were carried out: All samples were spiked with deuterated 1-nitropyrene as an internal standard at the beginning of the clean-up for correction of losses e.g. by degradation of compounds. A mild extraction procedure involving shaking samples at room temperature was chosen. In preliminary tests with certified standard soil, the extraction efficiencies for PAHs were similar compared to Soxhlet or microwave extraction and in good agreement with other reports [14,15,16]. In order to prevent decomposition of nitro-PAHs during GC-MS analysis, cool on column injection and helium as a carrier gas were employed instead of hot splitless injection and hydrogen [2].

3.1 Effects of matrix on nitro-PAH determination

In initial experiments, extracts of soil and air particulate matter were purified by combined solid phase extraction (C18 and SiOH), either with or without subsequent semipreparative HPLC in order to test the clean-up efficiency. For both matrices, SPE treatment of the extracts was sufficient enough to produce undisturbed gas chromatograms of PAH and oxy-PAH. In the case of nitro-PAHs, however, subsequent HPLC is needed to eliminate compounds such as oxy-PAHs, e.g. benz(a)anthracene-7,12-dione (m/z 258), which strongly interfere with the determination of some nitro-PAHs, especially in soil samples ($\rightarrow$ Fig. 2A). Using semi-preparative HPLC, the peak of the internal standard 1-nitropyrene-d9 (m/z 256) as well as the expected native 1-nitropyrene and 3-nitrofluoranthene (m/z 247) are no longer distorted. Due to a better resolution of peaks, a typical shift of the retention time of 1Npyr-d9 some seconds prior to the undeuterated one can be seen ($\rightarrow$ Fig. 2B). Other benefits of HPLC clean-up are a prolonged resolving power of GC columns and the prevention of identification errors due to similar retention times of electrophile compounds when applying a less selective detector than MS (e.g. ECD).
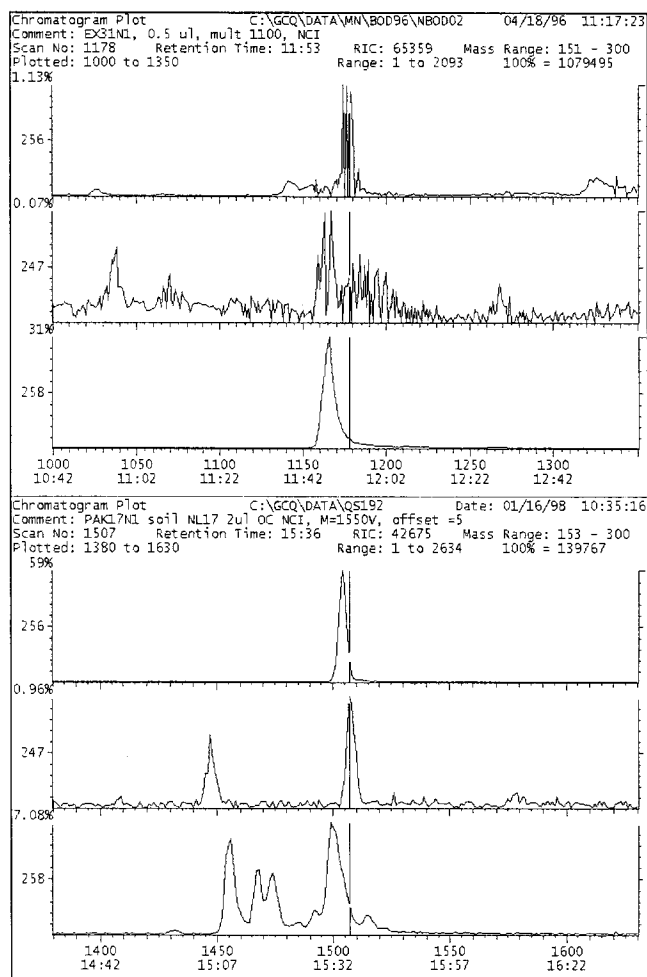

Fig. 2: Effects of matrix on nitro-PAH determination in soil. A: extract purified with SPE and without subsequent HPLC, B: extract purified with SPE and with subsequent HPLC

3.2 Identification of Nitro-PAH in soil with NCI-MS/MS

The applied GC-MS system allowed the identification of mainly 3-nitrofluoranthene and 1-nitropyrene in soil extracts by retention time and specific mass traces as shown in Figure 2. To verify, if the peak with mass 247 was in fact 1-nitropyrene and not an artefact deriving from decomposed deuterated standard (m/z 256), an unspiked soil sample was also analysed by NCI-MS/MS. In this technique, the molecular ion of 1-Npyr (m/z 247) was selectively isolated in the ion trap and dissociated to a daughter fragment (m/z 217). The resulting mass difference of 30 AMU (loss of NO-group) is very typical for this compound ($\rightarrow$ Fig. 3).

3.3 Nitro-, oxy-PAH and PAH concentrations of soil and aerosol

Since environmental aspects of PAH concentrations in urban soil have been discussed in detail earlier [8], this work is mainly focussed on the related derivatives. On the base of dry weight (dwt), very low concentrations of nitro-PAHs

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Chromatogram Plot          C:\GCQ\DATA\QS189          Date: 01/16/98  08:29:04
Comment: EX24N1 soil NL16 1ul OC NCI/MS/MS, M=1550V, offset =5
Scan No: 177      Retention Time: 15:31     RIC: 373     Mass Range: 216 - 248
Plotted: 120 to 240                Range: 1 to 474     100% = 373
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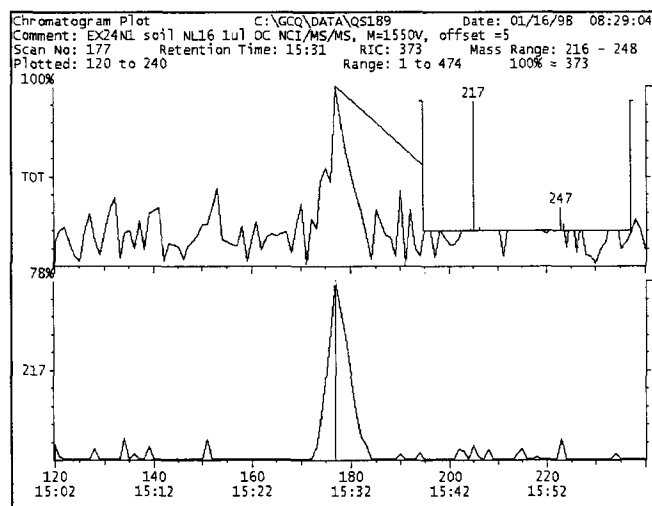
Fig. 3: Identification of 1-nitropyrene with NCI/MS/MS in an unspiked soil sample

between 30 (detection limit) and 800 ng/kg were found in soil samples from children playgrounds and park areas (→ *Table 2* and *Fig. 4A*). Oxy-PAHs showed significantly higher levels than the nitrated ones (100-400 times higher) and are similar to the lower range of PAHs (→ *Fig. 4B,C*). Additionally, it was also possible to identify benzo(b)naphtho(2,3)furane, some thiophenes as well as dibenzo(a,i)pyrene and 9-methylcarbazole (→ *Table 1*) in soil and airborne matter which were already mentioned for environmental samples elsewhere [17,18]. Concentrations of 1-nitropyrene were between 10^3-10^4 times lower than pyrene, with only a weak positive correlation existing between the two compounds (r = 0.48, p < 0.02). To this date, little or nothing has been published on oxy- or nitro-PAHs concentrations of soils. The only article we found deals with spiked samples [19]. Levels of the same order of magnitude as mentioned in our study are found in marine sediments for oxy-PAH and for nitrogen-containing aromatic compounds other than nitro-PAH (e.g. aza-pyrene) [18,20] as well as for nitro-PAHs in lettuce samples [21].
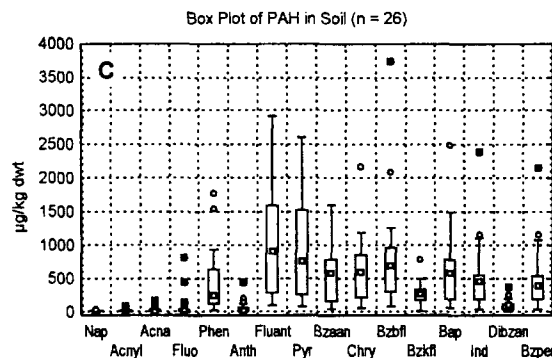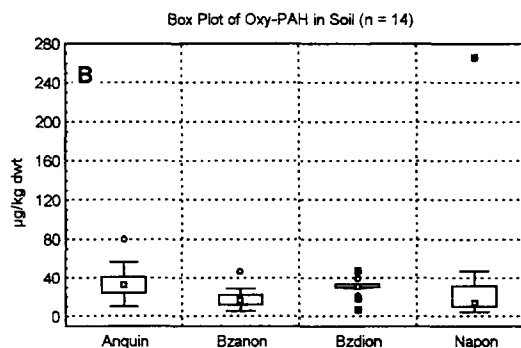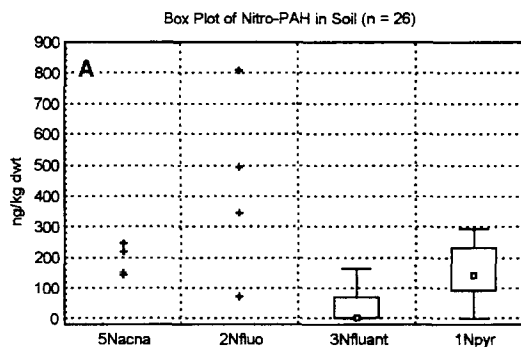
Fig. 4: Box and whisker-plot of PAH and derivative concentrations in soil samples (n = 26). Median (□), 25-75% percentile (box), non outlier minimum – maximum value (⊥), outlier (o), extreme (✳). Abbreviations see *Table 1*

Table 2: Compound specific concentrations of nitro and oxy-PAHs of soil and air particulate matter. Mean values and range of minima and maxima

Compounds	Soil μg/kg dwt	n	Air particulate matter pg/m³	mg/kg dwt	n
1-Nitronaphthalene	<0.03	26	0.7 (<1.0 - 4.9)	0.03 (<0.01 - 0.35)	23
2-Nitronaphthalene	<0.03	26	0.3 (<1.0 - 1.0)	0.01 (<0.01 - 0.04)	23
4-Nitrobiphenyl	0.01 (<0.03 - 0.33)	26	0.4 (<1.0 - 3.2)	0.01 (<0.01 - 0.16)	23
5-Nitroacenaphthene	0.03 (<0.03 - 0.25)	26	2.0 (<1.0 - 15.8)	0.02 (<0.01 - 0.30)	23
2-Nitrofluorene	0.07 (<0.03 - 0.81)	26	1.3 (<1.0 - 10.7)	0.05 (<0.01 - 0.78)	23
3-Nitrofluoranthene	0.03 (<0.03 - 0.16)	26	23.1 (4.5 - 61.9)	0.60 (0.01 - 1.72)	23
1-Nitropyrene	0.15 (<0.03 - 0.25)	26	10.3 (1.6 - 27.2)	0.24 (0.01 - 0.40)	23
6-Nitrochrysene	<0.03	26	<1.0	<0.01	23
Anthraquinone	35.6 (10.6 - 79.5)	14	528 (28 - 2676)	17.9 (0.6 - 91.0)	13
Benzanthrone	18.6 (5.9 - 46.4)	14	17 (<6 - 58)	0.3 (<0.2 - 0.8)	13
Benzo(a)anthracene-7,12-dione	30.3 (7.1 - 47.6)	14	165 (32 - 782)	5.2 (0.7 - 26.6)	13
5,12-Naphthacenequinone	35.9 (5.0 - 266.3)	14	66 (12 - 312)	2.0 (0.3 - 10.6)	13

3-nitrofluoranthene and 1-nitropyrene are predominant nitro-derivatives of PAH (2-62 pg/m³) found in high-volume sampled air particulate matter from a square with heavy traffic (Sept.-Oct. 1995) and in additional sample extracts from different urban sites (first quarter 1997) collected by the LHA (→ *Table 2* and *Fig. 5A*). The other investigated nitro-PAHs either occurred only occasionally or were below the detection limit of 1 pg/m³. It can not entirely be excluded that the artificial formation of nitro-PAHs contributes to the detected values as is especially known from the sampling of diesel exhaust [2, 25]. Considering the fact that filter reactions mainly occur on particles collected at NO_2 concentrations between 1 and 10 ppm and at temperatures over 50 °C, whereas urban air contains only approx. 40 ppb NO_2 and does not exceed 50 °C, such artefacts have to be estimated as minimal.

Box Plot of Nitro-PAH in Air Particulate Matter (n = 23)

Box Plot of Oxy-PAH in Air Particulate Matter (n = 13)

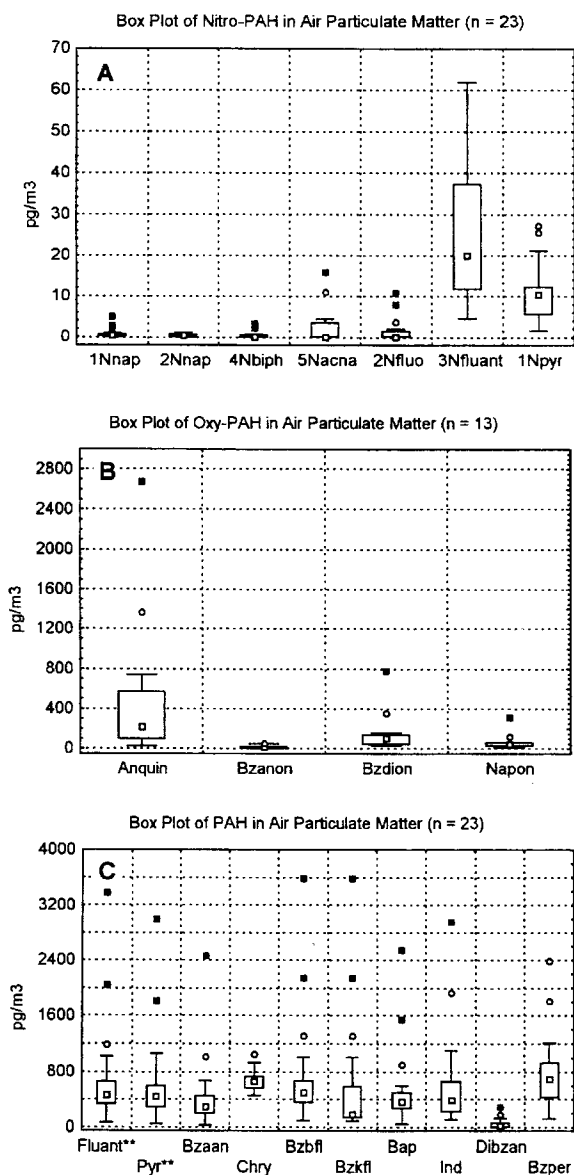Box Plot of PAH in Air Particulate Matter (n = 23)

Fig. 5: Box and whisker-Plot of PAH and derivative concentrations in air particulate matter (n = 23). Median (□), 25-75% percentile (box), non outlier minimum – maximum value (⊥), outlier (o), extreme (⋇). Abbreviations see *Table 1*. ** calculated values including blow-off effect

Compared to nitro-PAHs, significantly higher amounts of oxy-PAHs and PAHs were found (10-100 times higher) which were both in a similar range (→ *Fig. 5B,C*). PAH levels showed the largest variation reflecting seasonal dependency. Generally, the airborne concentrations of all compounds presented were of the same order of magnitude as those reported from other urban regions [3,4,7,22].

Some consideration should be made to the fact that only the particle phase has been examined and that the gas-phase, although not sampled here, may well contain a significant quantity of these compounds. Especially in the case of the more volatile components such as fluoranthene and pyrene as much as 90 % can be desorbed from the collected particulates (so called 'blow-off-effect') [23,24], whereas most of the nitrated PAHs are largely retained on the filter [11]. Interestingly, in spite of differing sampling efficiency, pyrene and 1-nitropyrene as well as fluoranthene and 3-nitrofluoranthene are highly correlated (r = 0.96, p < 0.001 and r = 0.85, p < 0.002) and may indicate that the blow off for pyrene and fluoranthene is constant and very reproducible. This knowledge combined with published blow-off values [23] allows the estimation of total levels of pyrene and fluoranthene in aerosol. Comparing estimated concentrations of pyrene and fluoranthene with originally measured levels of 1-nitropyrene and 3-nitrofluoranthene, 200-400-fold lower amounts of the nitrated congeners were established. Additionally, high correlations show that the nitrated compounds may be formed by atmospheric reactions of the gas-phase parent PAH [2,25].

At the time of writing this paper, we learned that 3-nitrobenzanthrone, a powerful bacterial mutagen and suspected human carcinogen, was detected in aerosol [26]. Therefore, compound specific mass traces (m/z 275, 245) of some Soxhlet extracts of air particulate matter were reanalysed by GC/MS, although it was not yet possible to detect this new mutagen.

3.4 Comparison of pollutant profiles of soil and aerosol

With the exception of predominant anthraquinone, which was used to norm profiles to 100%, the related average oxy- and nitro-PAH profiles of soil and air particulate matter are very different (→ *Fig. 6*). High relative levels of all oxy-PAHs and very low ones of nitro-PAHs are characteristic for soil samples, whereas relative quantities of oxygenated compounds in airborne samples are lower and levels of 3-nitrofluoranthene are enhanced. A link to possible emission sources due to characteristic profiles or compound ratios, e.g. of diesel exhaust [27], was not found for any matrices. Benzanthrone, for example, a main oxygenated component of diesel exhaust with a ratio compared to anthraquinone of 1.5 [27], showed extremely low ratios, especially in air (0.05) but also in soil samples (0.5). Perhaps the individual stability of components, as related to the photochemical or microbiological degradation, results in matrix profiles which
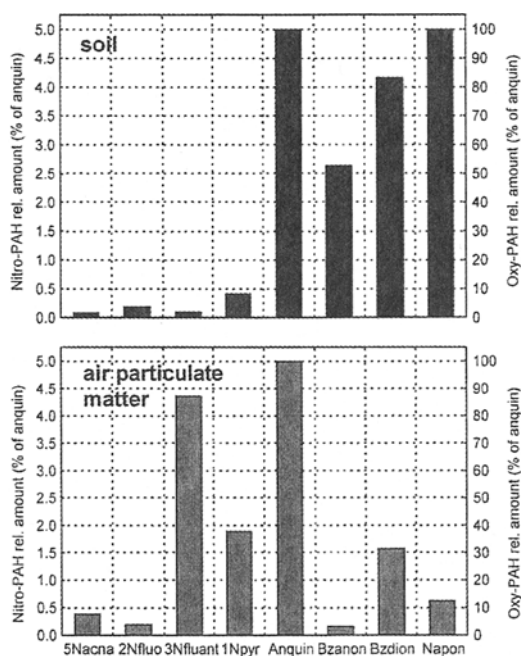
Fig. 6: Average profiles of nitro- and oxy-PAHs of soil (n = 26) and air particulate matter(n = 23). Mean value of anquin (= 100%): 36 µg/kg dwt soil, 528 pg/m³ air. Abbreviations see *Table 1*

no longer correspond to the originally emitted pattern as has also been demonstrated for PAHs [8].

3.5 Substances with similar characteristics

Factor Analysis (FA) was performed based on correlations between individual pollutant concentrations in soil and air particulate matrix in order to classify substances with similar characteristics (scores). Possibly similar characteristics, for example, can be the result of the same emission sources or emission patterns or the same chemical properties (e.g. volatility, solubility, photochemical stability).

For both soil and airborne samples, FA defined 3 scores (→ *Fig. 7*). In soil, the highly and positively correlated PAHs (score 1) are separated from the nitrated derivatives (score 3) whereas in aerosol they are grouped together in score 1.

The degree of correlation may also depend on the variable length of stay of pollutants in the respective matrix: Contaminants determined in soil may be the result of emissions of past decades, whereas those found in aerosol reflect immediate emissions. Therefore, high correlations of nitro-PAHs and PAHs possibly represent more undisturbed emission patterns indicating the same formation and/or emission source. On the other hand, the lower correlations found in soil may be the result of a longer degradation period and differences in decomposition rates of PAHs and nitrated derivatives.

Another point of interest is the behaviour of benzanthrone. In soil, it clearly showed the same characteristics as the other

oxygenated components of score 2 (→ *Fig. 7A*). In aerosol, however, no correlation with other compounds was found (→ *Fig. 7B*). Individual physicochemical properties of benzanthrone in the two matrices or different sources, as well as possible methodological artefacts due to differences in the analytical procedures (Soxhlet versus microwave extraction of airborne samples) or due to quantifying near the detection limits are possible explanations for this phenomenon.
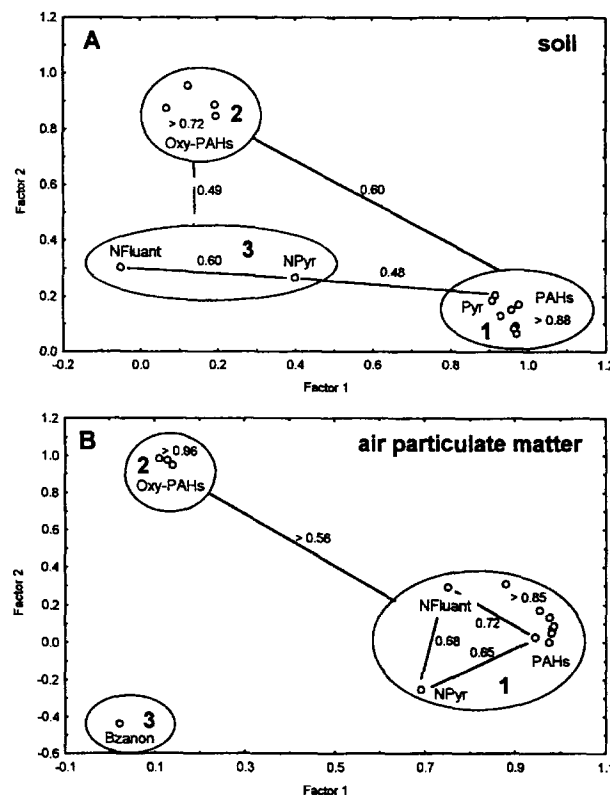

Fig. 7: Grouping of substances with similar characteristics (clusters 1-3) and correlations (r) of analysed substances in soil (A) and air particulate matter (B). P<0.05 (—), P<0.1 (--). Total variability accounted for by factors: 89 % (soil), 92 % (air). Abbreviations see *Table 1*

4 Conclusion

Nitro-derivatives of PAHs which are up to 10^5 times more mutagenic [2] seem to be less persistent in soil than the parent forms. This is indicated by a generally reduced number of individual nitro-PAHs and a higher ratio to the PAH-content compared to airborne samples. Since nitro-PAH concentrations of soil were approx. 10^3-10^4-fold lower than parent PAHs, their entire mutagenic potential has to be estimated as being the same order of magnitude. Especially in the case of children playgrounds, further investigation is recommended because of possible toxicological relevance for infants playing there. The estimation of nitro-PAH contents in soil based on the simpler measurement of highly correlated PAHs is not possible. For aerosol, however, first re-

sults indicate that blow-off resistant benzo(a)pyrene values could be used for a calculation of the 1-nitropyrene concentrations, although more data is required for verification. For soil samples, a clean-up procedure involving semi-preparative HPLC is highly recommended in order to eliminate compounds such as oxy-PAHs which can strongly interfere with the GC/MS determination of some nitro-PAHs. Oxy-PAHs, nitro-PAHs and parent PAHs should each be determined in separate fractions and separate GC runs. Multivariate statistic is a useful method to extract similarities or special characteristics of substances and study sites making an interpretation of environmental data much more easy.

Acknowledgements

4 References

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