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DETECTION OF NITRO-SUBSTITUTED POLYCYCLIC AROMATIC HYDROCARBONS IN THE ANTARCTIC AIRBORNE PARTICULATE

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Nitro-PAH have been determined in the Antarctic air particulate for the first time. This achievement was made possible by the use of an extremely sensitive and specific analytical procedure, which allowed us to investigate the composition of size-fractionated airborne particulates, collected in the Terra Nova Bay area (Antarctica) during two-days high-volume sampling periods. Eleven air-particulate samples and three blanks were extracted and analyzed by gas chromatography – electron capture negative ion – tandem mass spectrometry. The high specificity of the procedure relies on both the ionization method and the fixed setting of the second mass-analyzer, selectively filtering the NO_2^- ions (m/z 46). Only the most volatile nitro-PAHs (nitro- and dinitronaphthalenes) were detected in the Antarctic air particulate, unlike in temperate areas. Single nitro-PAH concentrations varied in the 1–200 fg/m^3 range. Principal component analysis allowed to cluster the blanks, clearly distinguishing them from the samples, and to classify the samples, as a function of their composition. Nitro-PAH distribution proved to depend on the sampling day but not on the particle size-fraction within the same sampling period. For two air particulate samples the analytical data proved to be biased by sea-triggering the sampling device.

The origin of Antarctic nitro-PAHs remains uncertain: while the abundance ratio of the two nitronaphthalene isomers supports the hypothesis of local direct emission, the high abundance of dinitro- with respect to mononitro-derivatives suggests that an efficient gas-phase nitration may take place on a substrate possibly transported from other continents.

Keywords: Nitro-PAH; Nitroarenes; Antarctica; Airborne Particulate; Electron Capture MS; Tandem Mass Spectrometry

INTRODUCTION

The analytical and toxicological interest for the nitro-substituted polycyclic aromatic hydrocarbons (nitro-PAHs) bursted out at the beginning of the '80s, when

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their presence was revealed in the exhaust emissions of diesel engines.^[1,2] At the Ames test, several nitro-PAHs proved to be direct mutagens (i.e. mutagens even without metabolic activation) and suspected strong carcinogens.^[3-8] Subsequent studies showed that the most abundant nitro-PAH isomers found in several airborne particulates were different from those found in diesel engine emissions and other direct emission sources. It was concluded that these isomers should not originate from combustion processes.^[9-11]

At present, it is clear that nitro-PAHs adsorbed on the airborne particulate can originate from at least three distinct processes, including (i) direct electrophilic nitration at high temperatures (i.e. in combustion of hydrocarbons); (ii) nitration of PAHs in the atmosphere during daylight hours, mediated by OH[•] radicals and (iii) nitration of PAHs in the atmosphere during the night, mediated by NO₃[•] radicals. Processes (ii) and (iii) occur in the gas phase, but other atmospheric mechanisms are likely to contribute to the overall nitro-PAH production.^[12,13]

The multiplicity of nitro-PAH generation mechanisms, as well as the key-role played by the solar light in formation process (ii), make the genesis of these pollutants feasible also in remote regions of the globe. For example, positive detection of nitro-PAHs in the air particulates collected in amazonic and scandinavian forests does not imply that these pollutants had been transported from industrialized areas, but rather they were generated locally by atmospheric processes from ubiquitous PAHs.^[14-16] The forests themselves are likely to provide the PAH reserve (possibly also from fires) from which nitro-derivatives can be generated. Different conditions apply to the Antarctic, where primary PAH sources are limited. Nevertheless, the most volatile PAHs typically remain in the gas phase (i.e. are not associated to atmospheric particles) and can be transported over quite large distances. This raises a question on the possible formation of nitro-PAHs also in the Antarctic, during the summer season, as a consequence of the OH[•] radicals activation, generated by the solar radiation.

The purpose of the present study was to answer the foregoing question, namely to verify whether an extremely sensitive analytical technique was able to detect the presence of ultra-trace nitro-PAHs in the antarctic airborne particulate, considering that the primary pollutants are extremely scarce, but the atmospheric conditions may be favourable for radical-initiated gas-phase reactions to occur.

We developed in the past an extremely sensitive analytical method for the selective determination of nitro-PAHs in complex environmental samples, such as air particulate and soil samples.^[17] We adopted the approach proposed by Schilhabel and Levsen,^[18] and improved it considerably, resulting in a reliable analytical procedure for ultra-trace nitro-PAH quantitative determination in crude environmental sample extracts. Other laboratories have used similar approaches more recently.^[19] The unique specificity of this GC/MS/MS detec-

tion method is provided by the electron capture negative ionization, which is selective for the molecules with high electron affinity, together with a selected reaction monitoring transition, that links the nitro-PAHs molecular ion with the nitrite fragment ion (m/z 46).^[17]

EXPERIMENTAL

Sample preparation

Airborne particulate samples were collected on fiberglass filters mounted on a Graseby-Andersen (United Kingdom) PM10 volumetric-flow controller high-volume sampling system model SAUV-15HBL, equipped with a six-stages cascade impactor model SA-236. The flow rate was $34 \text{ m}^3\text{h}^{-1}$ ($20 \text{ f}^3 \text{ min}^{-1}$). The sampling area was the Terra Nova Bay in the Antarctica. The sampling time was 48 hours for all samples (approximately 1600 m^3). The six stages cascade impactor separated air particulates fractions as a function of their size. These fractions were collected on four different fiberglass filters. Thus, each sampling experiment provided four particulate samples with particle sizes of, respectively (a) $3.0 \mu\text{m} < x < 10.0 \mu\text{m}$; (b) $1.5 \mu\text{m} < x < 3.0 \mu\text{m}$; (c) $0.95 \mu\text{m} < x < 1.5 \mu\text{m}$; (d) $0.49 \mu\text{m} < x < 0.95 \mu\text{m}$. At the end of the sampling period one quarter of each fiberglass filter was cut in pieces and inserted into a $100 \times 15 \text{ mm}$ screw-capped vial. The vials were capped and maintained at $-20 \text{ }^\circ\text{C}$ for all the time during the transportation and storage. These vials had been preventively washed with a dicromate-sulfuric acid mixture, then several times with ultrapure water ($\text{TOC} < 50 \text{ ppb}$) and lastly with aliquots of redistilled dichloromethane (Merck Suprasolv for organic trace analysis, Darmstadt, Germany). On the forth aliquot, the presence of residual nitro-PAHs was determined, resulting absent ($< 10 \text{ pg}$, total nitro-PAH). All the glassware used for sample manipulation was cleaned in the same way.

Before opening, each vial was kept at room temperature until the thermal equilibrium was reached. Then, the vial was opened and the pieces of fiberglass filter were transferred into a cellulose extraction thimble, previously cleaned. The vial was washed with aliquots of dichloromethane and this solvent was transferred into the extraction device. The extraction was carried out in a Prolabo, model Soxwave 2000, microwave-assisted extraction soxhlet, equipped with a solvent evaporation device. The extraction program included (i) reflux solvent (50 mL) heating for 30 minutes with the thimble introduced into the solvent; (ii) reflux solvent heating for 30 minutes with the thimble lifted above the solvent; (iii) par-

tial solvent evaporation by distillation, leaving 15 mL solution. This solution was concentrated further to 1 mL under a flow of nitrogen using a Zymark Turbovap apparatus. The exact final volume of the extract was determined by weighing. All sample manipulations were carried out under a laminar-flow hood.

Before extracting the fiberglass filter samples, two blanks were extracted using the same procedure described above. The first was a "glassware blank", i.e. an empty vial which underwent the same manipulations as the ones used for sampling, including the transfer back and forth from Antarctic, opening and closure at the sampling site. The second was a "filter blank", i.e. a vial filled with a fiberglass filter cut in pieces in the Antarctic and closed, without being exposed to air pumping.

Extract analysis

The extracts were equilibrated at room temperature and then concentrated to approximately 100 μL under a gentle stream of nitrogen. The final volume was determined again by weighing. 1 μL was injected into the GC/MS/MS instrument. The analysis of each sample was repeated three times.

A Finnigan-MAT 95 Q (Bremen, Germany) hybrid tandem mass spectrometer was utilized for the analyses. In this instrument the magnetic, electrostatic and quadrupole analyzers are mounted sequentially (BEQ geometry). An octapole collision cell is located between the electrostatic and the quadrupole sector for activating the parent ion dissociation in MS/MS experiments at low kinetic energy. A Varian 3400 (Palo Alto, CA) gas chromatograph is interfaced to mass spectrometer.

Sample injection was carried out in the splitless mode (splitless for 60 s), with the injector at 300 °C. The GC column was a bonded-phase DB-5-MS capillary column (J&W Scientific, Folsom, CA), 30 m long, 0.25 mm internal diameter, and 0.25 μm film thickness. The oven temperature was programmed with a linear ramp from 40 to 300 °C at 12 °C/min, isothermal at 300 °C for 10 min. The column end was introduced directly into the ion source of the mass spectrometer, through a transfer line heated to 270 °C.

The analytes were ionized by electron capture negative ionization (ECNI). Methane was flowed into the ion source at a pressure of 50 Pa (0.5 mBar). The electron emitting filament was kept at 220 V and the electron current at 0.2 mA. The ion source temperature was 230 °C. Negative ions generated in the ion source were accelerated to 5000 eV, analyzed by the magnetic sector, then driven through the electrostatic analyzer and decelerated to 80 eV by means of a series of cylindrical lenses. At this kinetic energy the ions underwent multiple collisions with 0.12 Pa of argon within the octapole collision cell, resulting in moder-

ate fragmentation. Among the fragments generated by collision induced dissociation, only the ions of m/z 46 (the NO_2^- ion) were filtered through the quadrupole mass-analyzer and allowed to reach the detector. The first mass analyzer was programmed so as to perform cyclic mass-hopping among the molecular ions of target nitro-PAH. This multiple reaction monitoring (MRM) experiment is the tandem mass spectrometric equivalent of selected ion monitoring (SIM). Different time windows in the chromatographic run were organized in order to match the molecular ions of the eluted nitro-PAHs.

RESULTS AND DISCUSSION

Airborne particulate analysis

Air particulate and primary air pollutants are extremely scarce in the Antarctic. Consequently, very low abundances of secondary pollutants adsorbed on air particulate were expected as well. Under such circumstances, it would not be safe to quantify the nitro-PAH analytes using internal standardization. In fact, the specificity of the mass spectrometric method implies that only a nitro-PAH could be used as an internal standard, because any other substance would not provide any signal. However, most nitro-PAH standards have isomeric and other nitro-substituted impurities which cannot be eliminated easily. Thus, introducing a nitro-PAH internal standard into the particulate extracts would possibly contaminate the samples.

We preferred to determine the analytes by external standardization, using a standard mixture of eleven nitro-PAHs at a concentration ($1 \mu\text{g/L}$) approximately ten-times higher than the detection limits. The analysis of this standard mixture was repeated four times, three times before starting the analysis of blanks and samples, and the last time at the end of all determinations. The corresponding results are shown in Table I. The chromatographic profiles of two consecutive analysis are depicted in Figure 1. From Table I, the repeatability of GC/ECNI-MS/MS determination method can be evaluated. For 10 analytes, the standard deviation ranges from 7% to 21%, while for 2-nitrofluorene the standard deviation is considerably higher (36%), due to the polar character of this compound, which produces large and tailed chromatographic peaks. Given the uncertainty factors associated with the present determinations, the repeatability of this method was considered satisfactory.

The last column of Table I indicates the response factors for eleven nitro-PAHs as calculated from averaging the area counts for the four standard mixture analyses. It should be noted, however, that the range of analytes that could be deter-

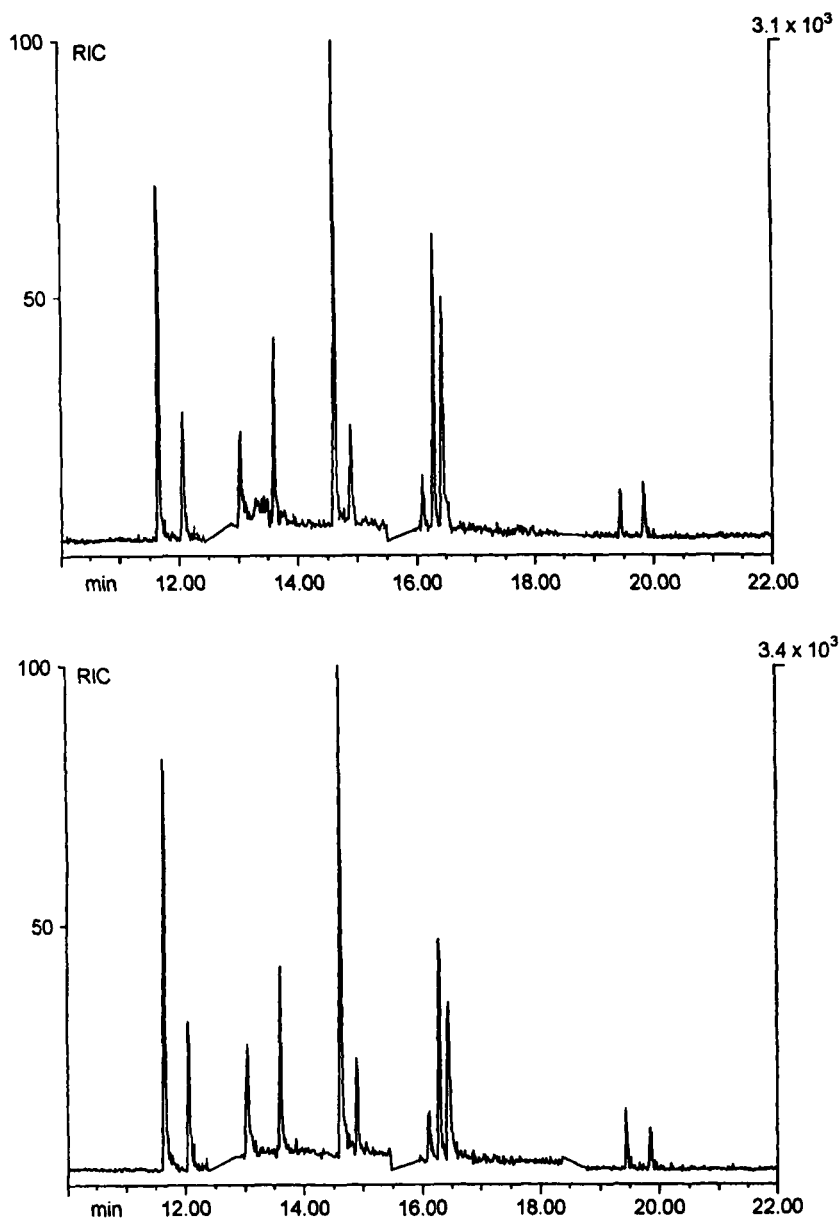


FIGURE 1 Reconstructed ion chromatograms from two consecutive GC-ECNI-MS-MS analysis of a $1 \mu\text{g/L}$ eleven-standards nitro-PAH mixture. The signal represents the current generated by the m/z 46 negative ion, selected by the second mass analyzer after collision induced dissociation of the negative molecular ions of the standards. Breaks on the baseline correspond to switches among time-windows, when different precursor ions were selected by the first mass analyzer

mined by the present method is not restricted to the eleven standards, as all the nitro-PAH isomers with retention times falling within the same time window of the standard (the chromatographic run was split into four time windows) would produce a signal. These isomers could either be relative to the position of the nitro-group or to the bridging of the aromatic rings. For example, the three isomers of nitroanthracene and the five isomers of nitrophenanthrene could all provide an analytical signal, were they present, even if only the 9-nitroanthracene standard was available.^[20] Obviously, the response factor for all the compounds unavailable as pure standards cannot be determined and should be approximated.

Table II reports the quantitative determinations of nitro-PAHs in the antarctic air particulate samples. The results are averaged values (from three repeated analyses) expressed as femtograms per cubic meter of air pumped through the fiberglass filter. Standard deviations were similar to those found for the standards and below 30% in all cases. The analytes listed in Table II include only the compounds that have been detected in at least two samples. Thus, several standards listed in Table I proved not to be present in the environmental samples, while two new dinitronaphthalene isomers (possibly, 1,4- and 1,2-dinitronaphthalene) were detected in almost all samples. Their response factor (5000) was calculated from averaging the response factors of the two dinitronaphthalene standards, also detected in the particulate extracts. Figure 2 shows the chromatographic profile of sample 4/04 and, for comparison, the profile of blank 1. In these profiles, the four time windows are evident, which separate the retention times of (1) nitronaphthalenes, (2) dinitronaphthalenes and nitroanthracenes, and (3) nitrofluorantenes and nitropyrenes, respectively. All the peaks present in sample 4/04 have been positively classified as nitro-PAH, and no major interferences are evident.

From Table II, it is evident that only seven nitro-PAHs are systematically present in most samples, including the two isomers of nitronaphthalene, four isomers of dinitronaphthalene and 9-nitroanthracene. Occasional presence of other analytes is scarcely informative. For easier comparison, the concentrations of these seven compounds has been added together and the result is reported in the last row of Table II. The absence of nitro-PAHs with four and five aromatic rings, which are very common at temperate latitudes, is not surprising. In fact, volatile nitro-PAHs are by far the ones formed most abundantly also in the industrialized countries, but they basically remain in the gas phase, i.e. are not adsorbed on the particulate. In a continental climate, the concentrations of the volatile nitro-PAHs in the air particulate is minimal during the day hours of the summer, but increases dramatically during the coldest winter nights. In the Antarctic, low atmospheric temperatures are likely to favour the condensation of volatile nitro-PAHs onto the particulate.

TABLE I Repeatability of data obtained by GC-ECCI-MS-MS (MIRM) and calculation of response factors. Analysis of a nitro-PAH standard mixture at 1 µg/L concentration

Nitro-PAH	1 µg/L standard mixture				Injection 1		Injection 2		Injection 3		Injection 4	
	Mol. W.	Ret. T.	Counts	Counts	Counts	Counts	Counts	Counts	Counts	Counts	St. Dev. %	Resp. Fact.
1-Nitronaphthalene	173	11,38	4578	6000	6976	5036	18,9	5647,50				
2-Nitronaphthalene	173	12,02	2005	2292	2174	1521	17,0	1998,00				
8-Nitroquinoline	174	13,01	1800	2653	2362	1884	18,6	2174,75				
3-Nitrobiphenyl	199	13,35	2166	2557	2271	1890	12,4	2221,00				
1,5-Dinitronaphthalene	218	14,36	6217	6956	6766	5880	7,7	6454,75				
1,3-Dinitronaphthalene	218	14,52	1619	1451	1345	1430	7,9	1461,25				
2-Nitrofluorene	211	16,05	700	1080	580	504	35,7	716,00				
9-Nitroanthracene	223	16,16	3660	3380	3634	3067	8,0	3435,25				
1,8-Dinitronaphthalene	218	16,25	3939	3142	3417	3300	10,0	3449,50				
3-Nitrofluoranthene	247	19,26	646	675	457	496	19,0	568,50				
1-Nitropyrene	247	19,50	807	686	724	481	20,5	674,50				

TABLE II Nitro-PAHs determined in antarctic air particulates. The results are expressed as fg per cubic meter of air filtered

Sample Name	2/00	4/20	4/15	4/07	4/04	8/20	8/15	8/07	8/04	10/07	10/04	Solvent	Blank 1	Blank 2
Particulate Fraction (μm)	Integrated	>3.0	1.5<x<3.0	0.95<x<1.5	0.49<x<0.95	>3.0	1.5<x<3.0	0.95<x<1.5	0.49<x<0.95	0.95<x<1.5	0.49<x<0.95		Vial	Filter
Triggering	No	No	No	No	No	No	No	No	No	Sea	Sea			
	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ³	fg/m ^{3a}	fg/m ^{3a}	fg/m ^{3a}
1-Nitronaphthalene	205,6	113,6	93,2	13,7	53,1	57,5	18,3	49,9	9,8	3,4	89,3	2,0	6,3	4,6
2-Nitronaphthalene	118,8	59,8	47,0	10,0	27,0	23,6	14,6	31,1	10,2	3,1	43,8	2,7	3,7	5,9
x,y-Dinitronaphthalene	10,6	23,0	27,7	14,3	15,7	5,9	2,6	0,0	0,0	5,9	17,6	1,7	1,9	4,5
3-Nitrobiphenyl	0,0	22,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	19,7	0,0	0,0	0,0	0,0
w,z-Dinitronaphthalene	50,8	56,0	56,6	17,7	17,7	18,1	15,1	11,2	18,9	8,3	24,0	1,5	3,4	1,8
1,5-Dinitronaphthalene	10,1	10,9	5,5	7,5	15,7	10,5	8,4	3,4	6,0	4,7	14,9	1,8	3,1	4,9
9-Nitroanthracene	27,0	11,9	16,5	20,9	14,9	12,1	13,6	16,7	11,6	18,0	27,5	6,1	7,3	14,8
1,8-Dinitronaphthalene	2,8	0,0	6,4	6,7	6,0	10,6	7,7	0,0	2,1	3,3	130,3	8,9	10,9	9,4
2-Nitrofluoranthene	0,0	0,0	0,0	10,5	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	27,0
1-Nitropyrene	0,0	0,0	0,0	14,4	0,0	0,0	0,0	0,0	0,0	0,0	31,7	0,0	0,0	0,0
Total Nitro-PAHs	425,7	297,1	252,8	115,6	150,0	138,2	80,5	112,4	58,7	66,4	379,2	24,5	36,6	72,9
Naphthalenes+Anthracene	425,7	275,2	252,8	90,7	150,0	138,2	80,5	112,4	58,7	46,7	347,4	24,5	36,6	45,9

a. For solvent and blanks the results are expressed in the same unit, using the same air volume.

The relative abundance of 1- and 2-nitronaphtalene is close to 2 in all samples. This finding suggests that the major source of nitro-PAH is local direct emissions from combustion processes. In fact, •OH radical-initiated gas-phase nitration processes produce the two isomers in approximately equal amounts, while 1-nitronaphtalene is photolyzed more rapidly than 2-nitronaphtalene.^[21,22] The consequence is that in remote areas the concentration of 1-nitronaphtalene is expected to be equal or slightly lower than that of 2-nitronaphtalene. In contrast, emissions from combustion processes contain the 1-nitronaphtalene isomer exclusively.^[11] Our data represent an intermediate (2:1) situation, where both isomers are present, but 1-nitronaphtalene is prevalent.

On the other hand, it should be noted that laboratory experiments may not entirely apply to the Antarctic environment. A peculiar result that we found is the high concentration of three dinitronaphtalenes. The abundance ratio between dinitro- and nitronaphtalenes in the Antarctic air particulate samples is considerably higher than that usually found in air particulate samples collected at lower latitudes. This finding suggests a different interpretation than that expressed above. An efficient nitration reaction should exist to convert nitro- to dinitro-derivatives in the atmospheric conditions found during the antarctic summer. A •NO₃ radical-initiated mechanism would be consistent with the concentration ratio found for 1- and 2-nitronaphtalene, but it must be excluded as it is active only in the absence of the daylight, a circumstance never occurring during the Antarctic summer. The existence of further nitro-PAH formation processes taking place at the particulate surface have recently been advanced to explain unexpected congener distributions, but have still to be fully clarified.^[23] Thus, a process involving the transport of naphtalene from other continents and the local transformation into the nitro-derivatives should not be excluded. The mechanism by which relatively volatile pollutants tend to migrate to the poles, where they condense, resulting in a global enrichment at the low latitudes, is well-documented, and it is called global distillation effect.^[24] Transportation of heavier PAHs than naphtalene to the poles has been demonstrated.^[25] Moreover, the absence of four- and five-rings nitro-PAH, and the low concentration of precursor PAHs in the same air particulate^[26] constitute strong evidence that local contamination of the filters from human activity should have not occurred.

Principal component analysis

The principal component analysis (PCA) has been applied to the data of Table II. From the first screening, it appears that samples 10/07 and 10/04 are outliers. They correspond to the only filters whose sampling was triggered to the sea. The analysis of sample 10/07 provides very low concentrations (comparable to the

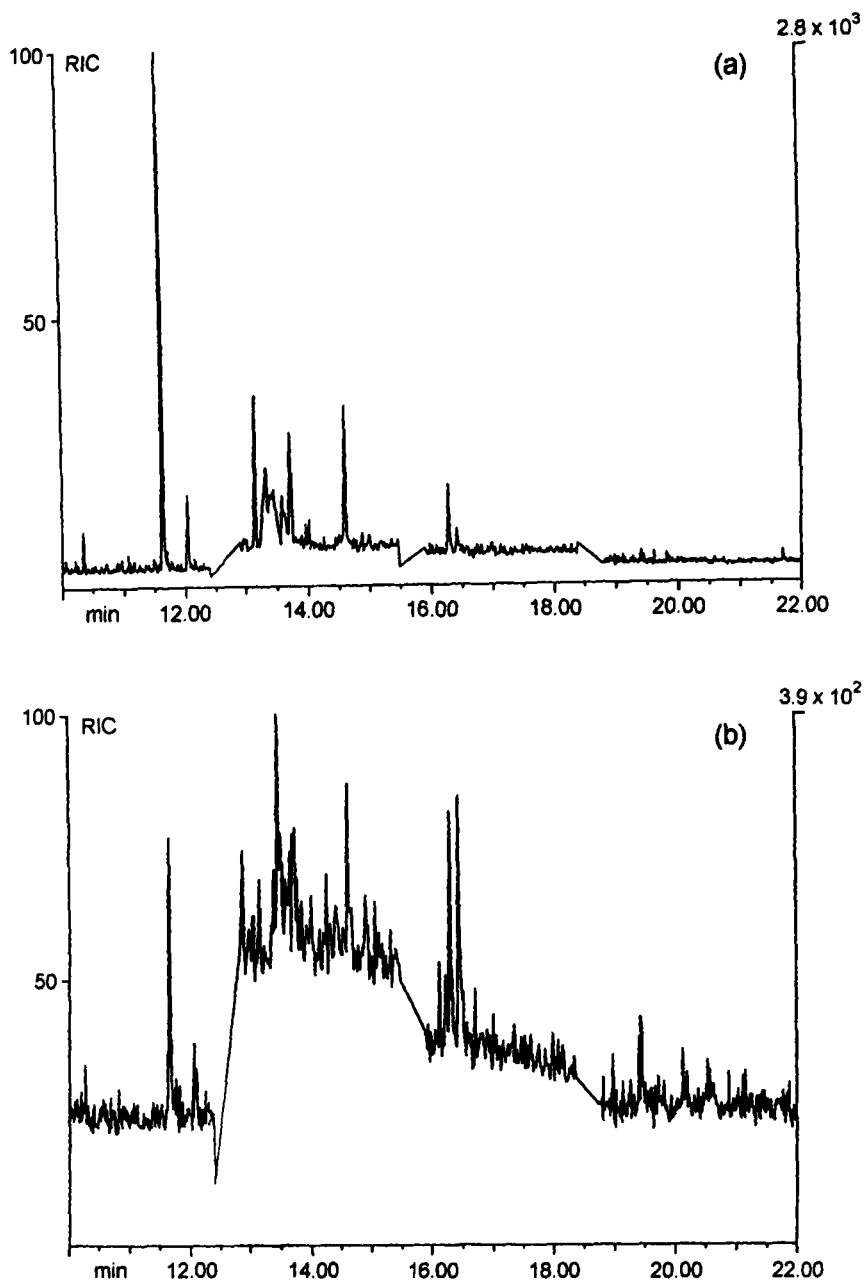


FIGURE 2 Reconstructed ion chromatograms from GC-ECNI-MS-MS analysis of (a) sample 4/04 and (b) blank 1. Conditions as for Figure 1

blanks) of almost all nitro-PAHs, particularly of 1- and 2-nitronaphthalene. Also the results of sample 10/04 are anomalous, since exceptionally high concentration levels for 1,8-dinitronaphthalene, 9-nitroanthracene and 1-nitropyrene are observed. Taking into account that 10/07 and 10/04 arise from the same sampling, with a different cut in their particle size, the remarkable difference in their analytical results confirms that some bias had occurred from sea-triggering. Thus, the results from these samples were taken out from the subsequent elaborations of PCA.

PCA was also restricted to the seven components constantly observed in the samples, together with the total nitro-PAH concentration. From PCA, X-loadings and scores for the first two components are depicted in Figures 3 and 4. Two principal components explain 77% of the total variance. The first component is basically associated with the total concentration of nitro-PAHs. In fact, all but one nitro-PAHs have positive X-loading values on PC1 (Figure 3) and all samples are ordered by decreasing score values on the first component, accordingly with their total nitro-PAH concentration (Figure 4 and Table II). It is also interesting that the three blanks (1, 2 and solvent) form a cluster located in the most negative side of PC1, with almost no score on the second component (Figure 4). This clustering provides graphical representation of their inherent difference from real particulate samples. The anomalous position of 1,8-dinitronaphthalene (Figure 3) highlights its nature of interfering contaminant, as is easily recognized also from Table II.

The second component cannot be attributed univocally, but mononitro-derivatives have negative loadings, while all dinitronaphthalenes have positive loadings (Figure 3). Although more samples would have been necessary to draw any definite conclusion, it appears that nitronaphthalenes and dinitronaphthalenes belong to different groups and this may be related to the occurrence of conditions favouring the nitration process during specific sampling periods. For example, the integrated sample 2/00 have high concentration of nitronaphthalenes, and is consequently located in the field of negative PC2 values, while all particulates arising from sampling n° 4 have positive PC2 values, with relatively high concentration of dinitronaphthalenes (Figure 4). Particulates arising from sampling n° 8 are scattered along the PC2 axis. No correlation is observed for particulate fractions having the same size (i.e. 4/04 does not correlate with 8/04), suggesting that the nitro-PAH congeners do not distribute preferentially on particulates of definite size. A much larger set of data will be necessary to confirm these suggestions in forthcoming studies.

The distribution of nitro-PAHs on the different particulate fractions for the same sampling is rather uniform, with total nitro-PAH concentrations ranging by a factor of 3, from the highest to lowest value, for both series 4 and series 8 sam-

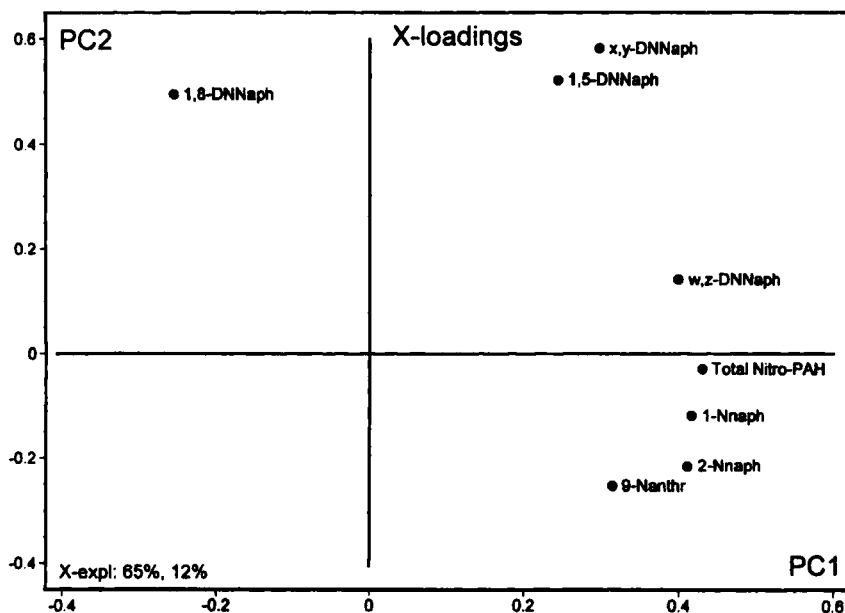


FIGURE 3 X-loadings from principal components analysis of Table II data. The first and second components are represented

ples. In both samplings, the highest concentration values were found for the particulates of the largest size, i.e. comprised between 3.0 and 10.0 μm . This observation does not necessarily mean that nitro-PAHs are preferentially adsorbed on large-size particles, because the total and relative amount of particles collected on each filter is not known. Thus, nitro-PAH distributions can only be read in absolute terms, not as relative to surface particle concentrations.

Although sample 2/00 exhibits the highest nitro-PAH concentrations, it should be reminded that this is an integrated sample, collecting together all particles with dynamic diameter lower than 10 μm . Nitro-PAH concentrations for sample 2/00 should be compared with the data obtained by adding the four values relative to sampling 4 (or sampling 8). From this calculation, it arises that total nitro-PAH concentrations are approximately 400 fg/m^3 for sampling 2 and 8, and 800 fg/m^3 for sampling 4. By comparing these approximate concentrations with those found in urban and rural sites of Northern Italy during the cold season,^[27] it is deduced that nitro-PAH concentrations in the Antarctic are roughly three orders-of-magnitude lower than in rural areas and four orders-of-magnitude lower than in urban areas. Taken into account that nitronaphtalenes are the most abundant nitro-PAHs, but that they are generally sampled in minimal amount at

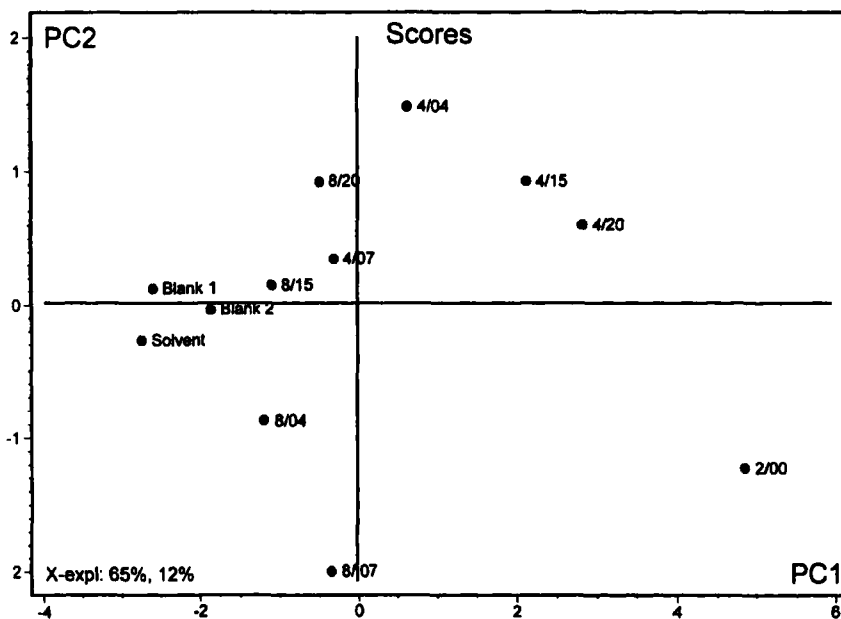


FIGURE 4 Scores from principal components analysis of Table II data. The first and second components are represented

temperate climates, the nitro-PAH concentration difference between Italy and the Antarctic may possibly be even larger than three and four orders-of-magnitude, respectively. More precise comparison is not possible, due to the different nitro-PAH species determined in the two sites.

CONCLUSIONS

The number of air particulate samples that can be collected in the Antarctic during each expedition is limited, as long sampling times are necessary to collect enough material for the analytical determinations. Despite this limitation, a restricted number of data were sufficient to draw some conclusions and formulate a few hypothesis on the genesis of nitro-PAHs, which need to be confirmed with more extensive activity. The first important achievement is that the analytical procedure developed proved effective for the determination of at least the most abundant nitro-PAH congeners, at extremely low concentration levels. This achievement was also made possible by the favourable circumstance that under

the climatic conditions found in the Antarctic the most volatile (and abundant) nitro-PAHs tended to partition on the solid phase and did not remain in the vapor phase. The lack of heavier nitro-PAH detection has not been attributed to instrumental bias, but rather to the substantial absence of the corresponding precursors, which evidently were not transported from other continents nor were produced locally. The high abundance of three dinitronaphtalene isomers suggests that the atmospheric conditions found in the Antarctic summer can promote the nitration of aromatic substrates, although (i) no conclusion can be drawn on the reaction mechanism and (ii) the abundance ratio between 1- and 2-naphtalene would rather be consistent with the prevalence of direct emission sources.

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References

- [1] J.N. Pitts, Jr., K.A. Cauwenberghe, D. Grosjean, J.T. Schmid, D.R. Fitz, W.L. Belser, Jr., G.B. Knudson and P.M. Hynds, *Science*, **202**, 515–519 (1978).
- [2] H.S. Rosenkranz, E.C. McCoy, D.R. Sanders, M. Butler, D.K. Kiriazides and R. Mermelstein, *Science*, **209**, 1039–1043 (1980).
- [3] I. Salmeen, A.M. Durisin, T.J. Prater, T. Riley and D. Schützle, *Mutat. Res.*, **104**, 17–23 (1982).
- [4] H.S. Rosenkranz, *Mutat. Res.*, **101**, 1–10 (1982).
- [5] E.T. Wei and H.P. Shu, *Am. J. Public Health*, **79**, 1085–1088 (1983).
- [6] H.S. Rosenkranz, *Mutat. Res.*, **140**, 1–6 (1984).
- [7] H. Tokiwa and Y. Ohnishi, *CRC Crit. Rev. Toxicol.*, **17**, 23–60 (1986).
- [8] IARC. *Diesel and Gasoline Engine Exhausts and Some Nitroarenes*. In: Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 46, (Lyon, International Agency for Research on Cancer, 1989).
- [9] T. Ramdahl, B. Zielinska, J. Arey, R. Atkinson, A.M. Winer and J.N. Pitts, Jr., *Nature*, **321**, 425–427 (1986).
- [10] J. Lewtas and M.G. Nishioka, *Nitroarenes: their Detection, Mutagenicity and Occurrence in the Environment*, In: Nitroarenes, (P.C. Howard, S.S. Hecht, F.A. Beland (eds.), Plenum Press, New York, 1990, pp. 61–72).
- [11] B. Zielinska, J. Arey and R. Atkinson, *The Atmospheric Formation of Nitroarenes and their Occurrence in Ambient Air*, In: Nitroarenes, (P.C. Howard, S.S. Hecht, F.A. Beland (eds.), Plenum Press, New York, 1990, pp. 73–84).
- [12] R. Atkinson and J. Arey, *Environ. Health Perspectives*, **102**, 117–126 (1994).
- [13] J. Arey, *Atmospheric Reactions of PAHs Including Formation of Nitroarenes*, In: The Handbook of Environmental Chemistry, Vol. 3 Part 1, (A.H. Neilson, O. Hutzinger (eds.), Springer-Verlag, Berlin, Germany, 1998).
- [14] P. Ciccioli, A. Cecinato, E. Brancaleoni, M. Frattoni, P. Zacchei and P. de Castro Vasconcellos, *Ann. Chim. (Rome)*, **85**, 455–469 (1995).
- [15] P. Ciccioli, A. Cecinato, E. Brancaleoni, M. Frattoni, P. Zacchei, A.H. Miguel and P. de Castro Vasconcellos, *J. Geophys. Res.*, **101**, 19567–19581 (1996).
- [16] T. Nielsen, B. Seitz and T. Ramdahl, *Atmos. Environ.*, **18**, 2159–2165 (1984).

- [17] M. Vincenti, C. Minero, E. Pelizzetti, M. Fontana and R. De Maria, *J. Am Soc. Mass Spectrom.*, **7**, 1255–1265 (1996).
- [18] J. Schilhabel and K. Levsen, *Fres. Z. Anal. Chem.*, **333**, 800–805 (1989).
- [19] M. Niederer, *Environ. Sci. & Pollut. Res.*, **5**, 209–216 (1998).
- [20] M.C. Paputa-Peck, R.S. Marano, D. Schütze, T.L. Riley, C.V. Hampton, T.J. Prater, L.M. Skewes and T.E. Jensen, *Anal. Chem.*, **55**, 1946–1954 (1983).
- [21] R. Atkinson, J. Arey, B. Zielinska and S.M. Aschmann, *Environ. Sci. Technol.*, **21**, 1014–1022 (1987).
- [22] J. Sasaki, S.M. Aschmann, E.S.C. Kwok, R. Atkinson and J. Arey, *Environ. Sci. Technol.*, **31**, 3173–3179 (1997).
- [23] A. Feilberg, R.M. Kamens, M.R. Strommen and T. Nielsen, *Atmos. Environ.*, **33**, 1231–1243 (1999).
- [24] S.L. Simonich and R.A. Hites, *Science*, **269**, 1851–1854 (1995).
- [25] C.J. Halsall, L.A. Barrie, P. Fellin, D.C.G. Muir, B.N. Billeck, L. Lockhart, F. YA. Rovinsky, E. YA. Kononov and B. Pastukhov, *Environ. Sci. Technol.*, **31**, 3593–3599 (1997).
- [26] R. Fuoco, personal communication.
- [27] V. Maurino, C. Minero, E. Pelizzetti, M. Vincenti, 2nd Annual Report to the Provincia di Torino Government, Program “Investigation on the Space and Temporal Distribution of Toxic and Carcinogenic Substances in Areas with Heavy Traffic Loading”, Technical Report, 1999, University of Torino, Italy.