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Zunanji zrak - Poročilo za nitro- in oksi-PAH - Izvor, strupenost, koncentracije in merilne metode

Ambient air - Report on nitro- and oxy-PAH - Origin, toxicity concentrations and measurement methods

Außenluft - Nitro- und Oxy-PAHs - Herkunft, Toxizität, Konzentrationen und Messverfahren

Air ambiant - Rapport concernant les HAP nitrés et les HAP oxygénés - Origine, toxicité, concentrations et méthodes de mesure

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Ambient air - Report on nitro- and oxy-PAHs - Origin, toxicity, concentrations and measurement methods

Air ambiant - Rapport sur les nitro- et oxy-HAP - Origine, toxicité, concentrations et méthodes de mesure

Außenluft - Bericht über Nitro- und Oxy-PAHs - Herkunft, Toxizität, Konzentrationen und Messverfahren

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Contents

European foreword

This document (CEN/TR 16998:2016) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

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Introduction

Nitro-PAHs and oxy-PAHs are found in ambient air samples and there are strong indications that they are as harmful as PAHS. Several compounds are classified as probably carcinogenic for humans (see Table in Annex A) and nitro-PAHs are reported to be strongly mutagenic. Photooxidation of volatile PAHs gives rise to the formation of secondary aerosols (Chan et al. 2009, Kautzman et al. 2010, Shakya and Griffin, 2010).

1-Nitropyrene and 2-nitrofluorene are discussed as marker compounds for diesel exhaust and other combustion processes. 2-Nitropyrene and 2-nitrofluoranthene are good marker substances for the formation of nitro-PAHs by secondary reactions.

This Technical Report presents the state of the art of the oxy- and nitro-PAHS topics.

1 Scope

This Technical Report is focused on the presence of nitro- and oxy-PAHs in ambient air. It describes how nitro- and oxy-PAH are formed, what typical concentrations are found, what is known about their toxicity, and what sampling and measurement techniques are available.

The conclusions of this report are that nitro- and oxy-PAHs concentrations are present in the atmosphere in levels that are of concern regarding their high toxicity. Information on the presence of these compounds in ambient air is as relevant as information about PAHs. Validated techniques for the measurement of nitro- and oxy-PAHs are available.

2 Symbols and abbreviations

DNA	Deoxyribonucleic acid
EI	Electron ionization
CD	Chemiluminescence detection
FD	Fluorescence detection
GC-MS	Gas chromatography – mass spectrometry
GC-NICI-MS	Gas chromatography – negative ion chemical ionization – mass spectrometry
HPLC	High performance liquid chromatography
HPLC-FD	HPLC – fluorescence detection
HPLC-CD	HPLC – chemiluminescence detection
IARC	International Agency for Research on Cancer
LC	Liquid chromatography
MS	Mass spectrometry
NICI	Negative ion chemical ionization
Nitro-PAHs	Nitrated polycyclic aromatic hydrocarbons
Oxy-PAHs	Oxygenated polycyclic aromatic hydrocarbons
PAHs	Polycyclic aromatic hydrocarbons
SPE	Solid phase extraction
ToF-MS	Time of flight mass spectrometry

3 Literature overview

3.1 Nitro-PAHs

3.1.1 Sources

3.1.1.1 General

Nitro-PAHs in the atmosphere originate mainly from combustion sources and are produced from both gas and heterogeneous phase reactions of the parent PAHs with atmospheric oxidants such as NO_3, N_2O_5, O_3, OH and peroxide radicals (Arey et al., 1986; Atkinson et al., 1990; Keyte et al., 2013; Pitts et al., 1985; Pitts Jr et al., 1978) in the presence of nitrogen oxides.

3.1.1.2 Direct emissions

Nitro-PAHs from direct emissions are formed by high temperature electrophilic nitration of PAHs with NO_2 during combustion processes (Nielsen, 1984). Nitro-PAHs have been observed in vehicle exhaust (particularly diesel), industrial emissions, waste incinerator emissions (DeMarini et al., 1996) and emissions from domestic residential heating/cooking (Kinouchi et al., 1988; Van Houdt, 1990). Nitro-PAHs are also emitted by wood burning but in relative low amounts due to low emissions of NO_2 during this type of combustion process (Alfheim and Ramdahl, 1984, Orasche et al., 2012; Orasche et al., 2013; Shen et al., 2011; Shen et al., 2012a; Shen et al., 2012b), (Environmental Health Criteria (EHC) 229, 2003 and references therein).

Recently, nitro-PAHs have also been quantified in exhausts of modern biodiesel engines (Karavalakis et al., 2010a; Karavalakis et al., 2010b; Karavalakis et al., 2011). Additionally, several studies have shown the formation nitro-PAHs *in situ* on catalytic diesel particulate filters as they act as chemical reactors for the nitration of PAHs (Carrara et al., 2010; Carrara and Niessner, 2011; Heeb et al., 2008). In this case, nitro-PAHs would be considered as primarily emitted. Gasoline emissions have also been reported but at lower concentration levels (Alsberg et al., 1985; Hayakawa et al., 1994; IARC, 1989; Sera et al., 1994).

Overall, 1-nitropyrene, 2-nitrofluorene and 2-nitrofluoranthene are the most abundant nitro-PAHs in diesel and gasoline exhaust (gas and particulate phases) (Beije and Möller, 1988; Environmental Health Criteria (EHC) 229, 2003; Finlayson-Pitts and Pitts Jr, 2000; Paputa-Peck et al., 1983; Schuetzle and Perez, 1983).

3.1.1.3 Atmospheric formation

Gas-phase reactions of parent PAHs are initiated by OH radicals during the day and by NO_3 radicals at night in the presence of NO_x producing nitro-PAHs, with subsequent partitioning to or depositing on the particulate matter. (Arey et al., 1986; Atkinson et al., 1989a; Atkinson et al., 1989b; Atkinson et al., 1990; Atkinson and Arey, 1994; Environmental Health Criteria (EHC) 229, 2003; Helmig and Harger, 1994; Keyte et al., 2013; Sasaki et al., 1997; Vione et al., 2006).

Recently, research studies reported that heterogeneous reactions may be the dominant process for loss of atmospheric PAHs and a significant source for nitro-PAHs in the atmosphere (Keyte et al., 2013; Kwamena et al., 2007; Perraudin et al., 2007; Pöschl et al., 2001). These reactions may dramatically differ from the homogeneous reactions in their rates, mechanisms, and products. Numerous studies showed results obtained with model particles (soot, sea salt, organic aerosol, silica, graphite or azelaic acid particles) coated artificially with single or a mixture of PAHs and their reaction with various oxidants as OH, NO_3, O_3 or NO_2 (Cazaunau et al., 2010; Esteve et al., 2003; Kwamena et al., 2007; Miet et al., 2009; Perraudin et al., 2005; Zhang et al., 2011).

Few studies reported results obtained with natural soot particles laboratory generated (liquid carburant burners) (Bedjanian et al., 2010; Kwamena and Abbatt, 2008), with natural ambient air particles (Ringuet et al., 2012b; Zimmermann et al., 2013) or with diesel engine exhaust particles (Esteve et al., 2006; Kamens et al., 1990; Nguyen et al., 2009; Rattanavaraha et al., 2011).

Mechanistic reaction schemes for gas phase formation of nitro-derivatives of fluoranthene and heterogeneous formation of isomeric nitro-benzo[*a*]pyrenes are shown in Figure 1 and 2, respectively.

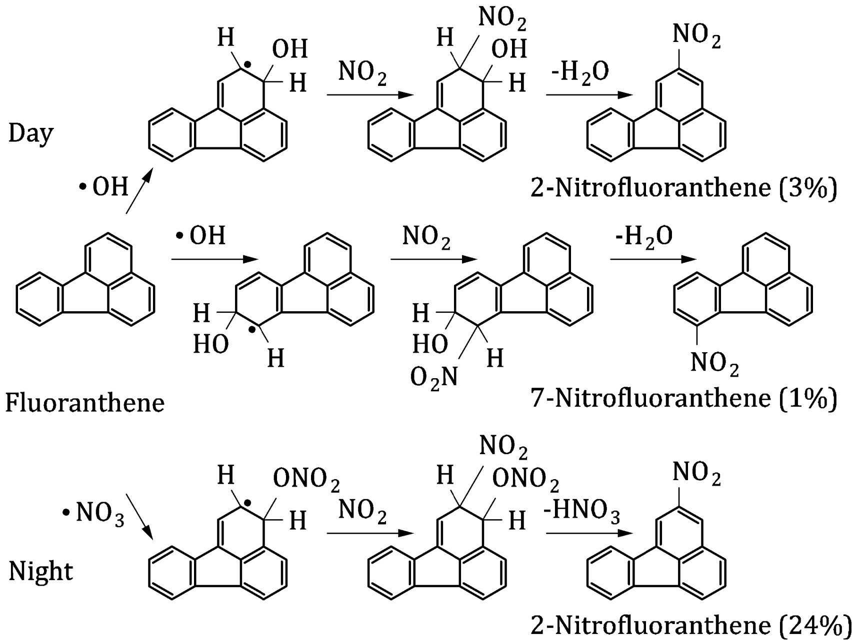


Figure 1 — Oxidation mechanisms of fluoranthene by OH during the day (Arey, 1998) and by NO_3 during the night (Atkinson and Arey, 1997)

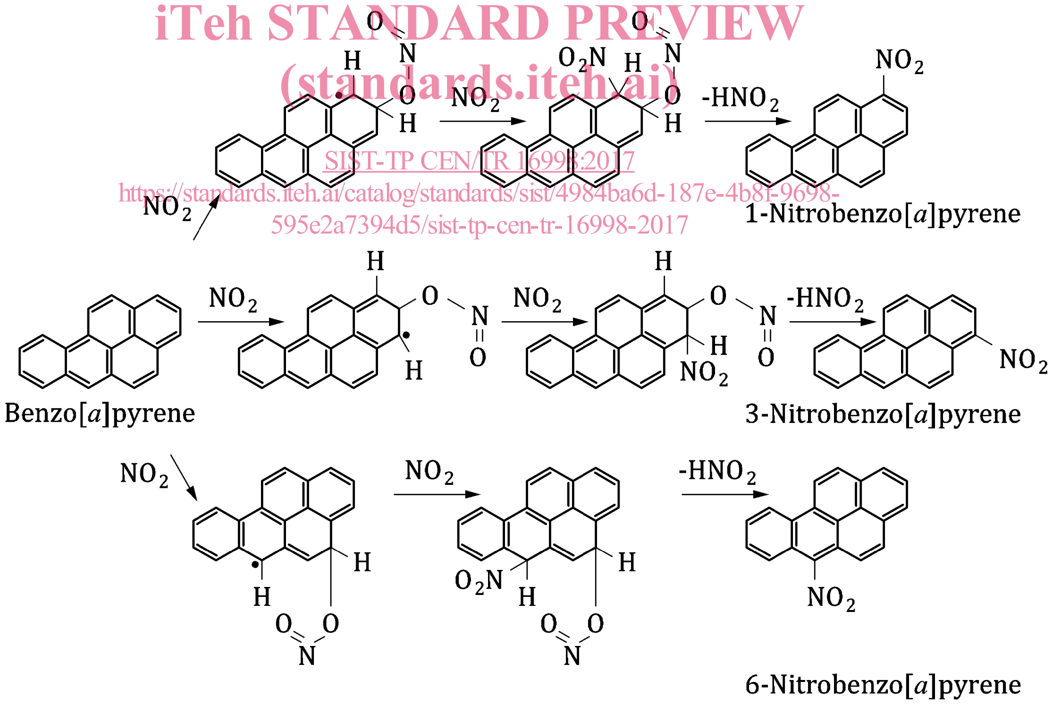


Figure 2 — Mechanism proposed for the nitration of benzo[a]pyrene (Cazaunau et al., 2010)

22-Nitrofluoranthene and 2-nitropyrene are the most abundant substances formed by gas phase reaction of PAHs with oxidants and oxides of nitrogen. A high 2-nitrofluoranthene/1-nitropyrene ratio is a good indicator for the secondary formation of nitro-PAHs (Albinet et al., 2007b; Albinet et al., 2008; Arey et al., 1989; Atkinson and Arey, 1994; Bamford and Baker, 2003; Reisen and Arey, 2005; Mariano et al., 2000; Ringuet et al., 2012a; Ringuet et al., 2012c; Zielinska et al., 1989; Zimmermann et al., 2012).

3.1.2 Concentrations, gas/particle partitioning and size distribution

Overall, in continental areas (urban, sub-urban and rural areas), nitro-PAHs atmospheric concentrations are one or two orders lower than PAHs atmospheric concentrations. Nitro-PAHs concentrations are in the range of 0,1 to 1000 pg·m^{-3} in both, gaseous and particulate phases (e.g. Albinet et al., 2007; Albinet et al., 2008a; Bamford and Baker, 2003; Ciccioli et al., 1995; Ciccioli et al., 1996; Feilberg et al., 2001; Feilberg and Nielsen, 2001; Hayakawa et al., 1995a; Hayakawa et al., 2002; Maria del Rosario Sienra, 2006; Valle-Hernandez et al., 2010; Wang et al., 2011). Nitronaphthalene isomers in gas phase and 2-nitrofluoranthene and 9-nitroanthracene in particulate phase are generally the most abundant nitro-PAHs and account for about 15 % to 50 % of the total nitro-PAHs concentrations.

Table 1 summarizes the reported concentration ranges of the most important nitro-PAHs.

Table 1 — List of concentration ranges of important nitro-PAHs in ambient air

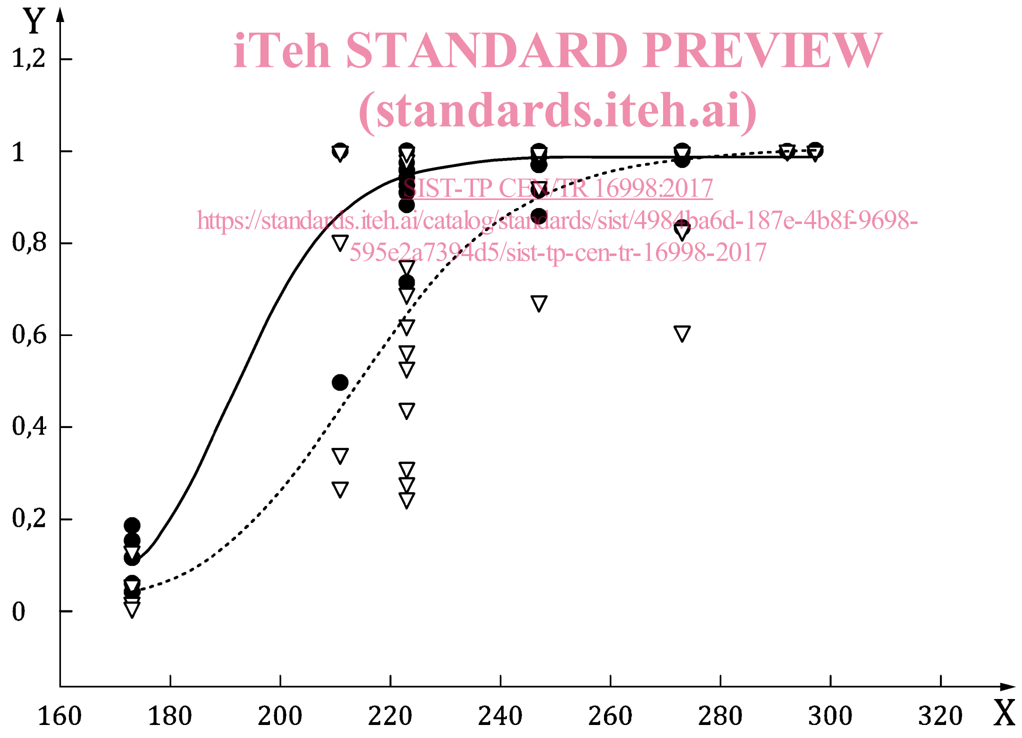
Substance	**Concentration range ng/m³**		
	Traffic	**Urban**	**Rural/remote**
1-Nitronaphthalene	0,07 – 0,2 (n, o)	0,2 (h, n)	0,01 – 0,2 (h, n)
2-Nitronaphthalene	0,03 – 0,06 (n, o)	0,12 (h, n)	0,01 – 0,1 (h, n)
2-Nitrofluorene	0,001 – 0,021 (l, n)	0,05 – 0,4 (d, g, h, n)	0,001 – 0,005 (h, n)
9-Nitroanthracene	0,002 – 0,01 (n, o)	0,03 – 0,2 (a, c, d, g, h, j, l, n)	0,002 – 0,03 (g, h, n)
3-Nitrophenanthrene	0,007 – 0,1 (n, o)	0,001 – 0,02 (l, o)	0,0007 – 0,001 (o)
9-Nitrophenanthrene	0,005 – 0,05 (l, n)	0,01 – 0,3 (h, i, n)	0,0002 – 0,03 (h, n)
2-Nitrofluoranthene	0,03 – 0,2 (l, o)	0,03 – 2 (a, e, f, g, j, l, m, n)	0,02 – 0,03 (e, k, n)
3-Nitrofluoranthene	0,018 (i)	0,003 – 0,1 (d, j, l)	0,01 (e)
1-Nitropyrene	0,02 – 0,2 (l, o)	0,01 – 2 (a, b, e, f, g, h, j, l, n)	0,0006 – 0,01 (e, h, n, o)
2-Nitropyrene	0,007 – 0,2 (n, o)	0,01 – 0,04 (a, h, j, n)	0,001 – 0,08 (e, h, k, n)
4-Nitropyrene	0,02 – 0,03 (o)	0,001 (h, n)	0,0006 (h, n)
1,3-Dinitropyrene	0,0009 – 0,02 (n, o)	0,01 – 0,03 (d, h, n)	0,004 (n)
1,6-Dinitropyrene	up to 0,0002 (o)	0,01 (d, h, n)	0,0001 – 0,004 (n)
7-Nitrobenzo[*a*]anthracene	0,005 – 0,01 (n, o)	0,004 – 0,3 (a, h, l, m)	0,002 (h, n)
6-Nitrochrysene	0,003 – 0,004 (n, o)	up to 1,5 (b, h, j, l, n)	0,0003 – 0,002 (e, h, n)
6-Nitrobenzo[*a*]pyrene	0,007 – 0,01 (l, n)	0,001 – 0,01 (h, n)	0,0002 – 0,005 (n, o)
3-Nitrobenzanthrone	0,001 – 0,01 (i)	–	–

a) Atkinson et al. (1988)	Glendora (USA)
b) Matsushita and Ida (1986)	Tokio (Japan)
c) Hunt and Meisel (1995)	Fresno (USA)
d) Tokiwa et al. (1990a)	Sapporo (Japan)
e) Vasconcellos et al. (1998)	Alta Floresta (Brazil)
f) Wilson et al. (1995)	Houston (USA)
g) Berlincioni et al. (1995)	Florence (Italy)
h) Albinet et al. (2007)	Marseille (France)
i) Mücke et al. (2009)	Munich (Germany)
j) Di Filippo et al. (2010)	Rome (Italy)
k) Tsapakis et al. (2007)	Finokalia (Greece)
l) Valle-Hernandez et al. (2010)	Mexico City (Mexico)
m) Wang et al. (2011)	Bejing (China)
n) Albinet et al. (2008a, 2008b)	Chamonix, Maurienne (France)
o) Ringuet et al. (2012)	Paris (France)

Nitro-PAHs gas/particle partitioning is poorly documented (Albinet et al., 2007; Albinet et al., 2008a; Araki et al., 2009; Atkinson and Arey, 1994; Bamford and Baker, 2003; Dimashki et al., 2000; Huang et al., 2014; Reisen and Arey, 2005; Wilson et al., 1995). 2-Rings nitro-PAHs (nitronaphthalenes) are mainly associated to the gaseous phase. Nitro-PAHs with 4 or more rings are mainly bound to particles. 3-ring nitro-PAHs are partitioned in both gaseous and particulate phase. Due to their relative low vapour pressures ($<10^{-4}$ Pa at 20 °C, Yaffe et al., 2001), nitro-PAHs resulting from gas phase reactions condense immediately to ambient particles (Fan et al., 1995). Gas/particle partition is depending on their vapour pressure and the ambient conditions as temperature but also on their origin (primary or secondary) (Albinet et al., 2007; Albinet et al., 2008a; Wilson et al., 1995).

Very few papers showed results about the particle size distribution of nitro-PAHs in ambient air (Albinet et al., 2008b; Cecinato et al., 1999; Di Filippo et al., 2010; Hayakawa et al., 1995a; Hayakawa et al., 1995b; Jinhui and Lee, 2000; Kawanaka et al., 2004; Kawanaka et al., 2008; Ringuet et al., 2012a; Teixeira et al., 2011). Overall, nitro-PAHs are mainly associated (>90 %) to the fine particle fraction ($D_p < 1$ µm) and about 20 % are associated to the ultrafine particle fraction ($D_p < 0,1$ µm). These results are important information regarding the risk assessment because nitro-PAHs can thus penetrate deeply into the lung.

Nitro-PAHs react with hydroxide and nitrate radicals, with ozone and they are decomposed by photolysis. As a result the atmospheric half life time of nitro-PAHs ranges from less than an hour to several days, depending on atmospheric conditions like temperature, sunlight intensity, on their structure and on the concentrations of reactive compounds in the air (Keyte et al. 2013).



Key

● Winter

▽ Summer

X Molecular weight in g/mol

Y Fraction in particulate phase

Figure 3 — Nitro-PAHs gas/particle partitioning according to their molecular weight (Albinet et al., 2008a)

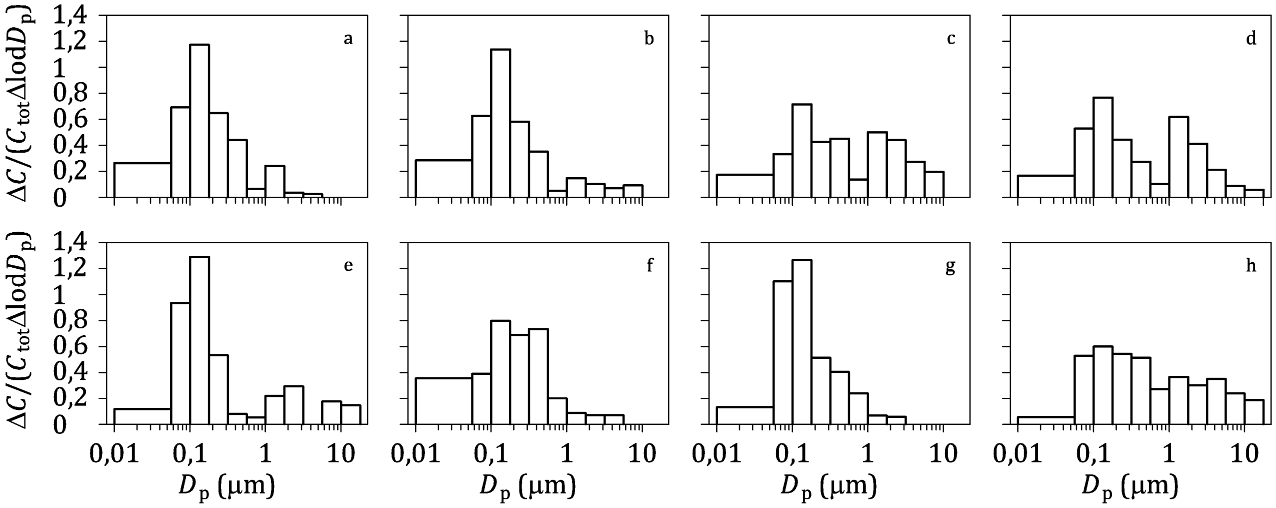


Figure 4 — Particle size distribution of 4 nitro-PAHs on a traffic (a – d) and suburban (e – h) site in the Paris region (France) (Ringuet et al., 2012c). a, e: 1-nitronaphthalene; b, f: 9-nitroanthracene; c, g: 2+3-nitrofluoranthene; d, h: 1-nitropyrene

3.1.3 Toxicity/mutagenicity

As they act as direct mutagens the mutagenic potential of nitro-PAHs can be 100 000 times greater than that of PAHs (Durant et al., 1996; Durant et al., 1998; Enya et al., 1997; Hannigan et al., 1998; Lewtas et al., 1990; Schuetzle, 1983; Landvik et al., 2007; Øvrevik et al., 2010). Four-ring nitro-PAHs seem to be the most toxic substances (Durant et al., 1996; Durant et al., 1998; Finlayson-Pitts and Pitts Jr, 1986). Overall, results from mutagenicity tests on bacteria (Ames test, *Salmonella typhimurium*) and on human cells (h1A1v2 cells) showed that 3,6-dinitrobenzo[*a*]pyrene, 3,7-dinitrofluoranthene, 3,9-dinitrofluoranthene, 6-nitrochrysene, 1- and 4-nitropyrene, 1,6-dinitropyrene and 1,8-dinitropyrene (the most powerful mutagens described in the literature) had the highest mutagenic activities (Environmental Health Criteria (EHC) 229, 2003; NTP, 2011; Enya et al., 1997; Pedersen et al., 2004; Pedersen et al., 2005).

Nitro-PAHs contributions to the mutagenic and/or carcinogenic activity of atmospheric inhalable particles were evaluated in the range 14 % to 50 % by different authors (Albinet et al., 2008a; Bandowe et al., 2014; Finlayson-Pitts and Pitts Jr, 2000; Kawanaka et al., 2008; Taga et al., 2005).

Substances with a coplanar nitro group are more carcinogenic than those with a perpendicular nitro-group. Dinitro-PAHs generally are more mutagenic than the mono-substituted compounds.

3.1.4 Carcinogenicity

Since the 1960s, evidence has increasingly supported the theory that chemical carcinogens (e.g. PAHs and nitro-PAHs) are metabolized via oxidative pathways to produce electrophilic reactive intermediates (e.g. nitrenium ions and epoxides) that react covalently with DNA and possibly with other cellular nucleophiles. Nitro-PAHs seem to be less carcinogenic than their parent PAHs (EHC 229, 2003; IARC, 2013; NTP, 2011; Benbrahim-Talaa et al., 2012). Different pathways seem to be possible for carcinogenic activity. If the nitro-PAHs contain a “bay region” similar to benzo[*a*]pyrene and benzo[*a*]anthracene their carcinogenicity is similar to the mechanisms described for the non-substituted substances: After formation of an dihydroepoxide in the “bay region” this reactive intermediate forms DNA adducts which are considered to be the first step causing carcinogenicity. If the nitro group of these substances is oriented parallel to the aromatic core of the substances, their carcinogenicity is not much lower than that of the non-substituted substances, but a perpendicular orientation of the nitro group largely attenuates the carcinogenicity of the compounds (Fu et al., 1994; Fu et al., 1998; Vogt et al., 2009; McDonald et al., 2004).

For some nitro-PAHs another pathway of carcinogenic action is postulated (Fu et al., 1994): The nitro group is partly reduced to a hydroxylamine derivative which after esterification (e.g. acetylation) forms a nitrenium ion, which reacts with DNA to form an adduct, which can cause carcinogenicity.

Additionally nitro-oxy-PAHs seem to be more toxic than oxy-PAHs or nitro-PAHs (Helmig et al., 1992a; Helmig et al., 1992b). For example, 3-nitrobenzanthrone is described as one of the the most potent mutagens and a potential carcinogen identified in diesel exhaust and ambient particulate matter (Arlt, 2005; Enya et al., 1997; Feilberg et al., 2002; Nagy et al., 2005; Phousongphouang and Arey, 2003). A list of the classification of the carcinogenicity of several nitro- and oxy-PAHs is given in Annex B.

3.1.5 Measurement

3.1.5.1 Sampling from ambient air

Nitro-PAHs with 4 rings or more are particle bound. For these substances sampling procedures for particulate matter (e.g. PM_{10} and $PM_{2,5}$, as described in EN 12341) are suitable. In order to collect more volatile compounds, a combination of a filter with, e.g. PUF as described in ISO 12884 is necessary.

Reaction of PAHs with oxidants in combination with nitrous oxides may lead to positive artefacts during sampling. Rearrangements of the nitro groups of the compounds during sampling are also possible.

The formation of nitro-PAHs via heterogeneous reactions with only nitrogen oxides has been shown to be unfounded in case of ambient air sampling (Arey et al., 1988; Dimashki et al., 2000). Only at elevated temperatures and extremely high concentrations of NO_2 direct nitration of PAHs is possible (Carrara et al., 2010; Carrara et al., 2011).

Studies delivered different results about the reactions of nitro-PAHs during sampling, possibly leading to artefacts, but until now no clear results about reactions of nitro-PAHs during sampling and about methods to inhibit these reactions have been published.

3.1.5.2 Analysis

A review paper on the analysis of nitro-PAHs in environmental samples was proposed by Zielinska and Samy (Zielinska and Samy, 2006). The analytical procedure of collected samples includes an extraction step prior to nitro-PAHs quantification. Several extraction procedures are reported (Soxhlet, microwaves, pressurized liquid extraction, sonication) using different solvents or solvent mixtures (dichloromethane, hexane, toluene, acetone). A purification step (e.g. SPE (solid phase extraction)) shall also be included. Alternatively to solvent extraction methods, SFE (supercritical fluid extraction) using pure CO_2 is also reported in numerous studies (Castells et al., 2003; Lewis et al., 1995). The use of solvent-free extraction techniques was also reported in different papers with thermal-desorption (TD) coupled with GC-ToF-MS or GC × GC-ToF-MS (Fushimi et al., 2012; Orasche et al., 2011) and laser desorption/ionization coupled to ToF-MS (LD-LI-ToF-MS) (Dotter et al., 1996). Finally, as an alternative to traditional procedures, recently Albinet et al. (2014) reported the use of QuEChERS-like (Quick Easy Cheap Effective Rugged and Safe) extraction approach for the analysis of nitrated and oxygenated PAHs.

Analysis of nitro-PAHs is generally achieved using GC-MS, GC-NICI-MS, HPLC-FD (fluorescence detection), HPLC-CD (chemiluminescence detection), LC-MS, LC-MS-MS.

Because of its great sensitivity and selectivity towards the nitro group, GC-NICI-MS using methane as the reactant gas minimizes the analytical interferences from co-eluted compounds by significantly improving signal-to-noise ratios (Bezabeh et al., 2003). Relative to GC-MS in EI ionization mode, a sensitivity improvement approaching two orders of magnitude could be obtained. Limits of detection in the lower picogram and femtogram ranges have been reported for this method (Albinet et al., 2006; Bezabeh et al., 2003). Actually, this analytical technique constitutes probably the best cost/performance compromise for the analysis of nitro-PAHs in ambient air samples. Maintenance requirement are mainly linked to the fouling of the MS source (due to the use of reagent gas for ionization) inducing a loss of sensitivity, but progress has been made enhancing the lifetime of the MS source.

HPLC-FD after reduction of the compounds to the corresponding amines or HPLC-CD is also widely used notably by Japanese research teams (e.g. Hayakawa et al., 1999; Hayakawa, 2000; Kawanaka et al., 2008; Nassar et al., 2011; Ohno et al., 2009; Tang et al., 2005, see also references in Zielinska and Samy, 2006). Greater precision and selectivity is obtained by increased automation of these kinds of analytical techniques. Limits of detection in the range of 1 pg to 10 pg injected have been reported for this method (Hayakawa et al., 1999; Hayakawa, 2000; Kawanaka et al., 2008; Ohno et al., 2009; Schauer et al., 2003; Tang et al., 2005; Zielinska and Samy, 2006 and references therein). The complexity and maintenance requirements of these kinds of systems (i.e. time automated switching valves, multiple plumbing components, and consumables), does implicate a need for highly specialized procedures with customized components and protocols.

The use of LC-MS and LC-MS-MS is also reported in several papers (e.g. Mirivel et al., 2010; Schauer et al., 2004; Zielinska and Samy, 2006 and references therein) but the sensitivity of this technique is still not optimal for nitro-PAHs analysis. Detection limits are 3 to 100 higher (5 pg to 100 pg injected) than those reported for GC-NICI-MS analytical systems. Only the possibilities of unknown species are a significant advantage of this method but the investment and working costs are really higher than for the other analytical techniques.

An example of an SOP dealing with sampling and analysis of nitro- and oxy-PAHs are given in Annex A.

3.2 Oxy-PAHs

3.2.1 Sources

3.2.1.1 General

Oxy-PAHs (ketones, aldehydes, hydroxy-PAHs) are both directly emitted from combustion processes and formed in the atmosphere as by-products of the photolysis of parent PAHs or photochemical reaction between parent PAHs and atmospheric oxidants (Vione et al., 2004; Yu, 2002).

3.2.1.2 Direct emissions

Major direct sources are diesel and gasoline combustions, biomass burning, waste combustion, coal and fuel burning, and production of charcoal (Abas et al., 1995; Akimoto et al., 1997; Cho et al., 2004; Choudhury, 1982; Leoz-Garziandia et al., 2000; Levsen, 1988; Orasche et al., 2012; Orasche et al. 2013; Ramdhal, 1983; Schauer et al., 1999, 2001, 2002; Schulze et al., 1984; Shen et al., 2011; Shen et al., 2012a; Shen et al., 2012b; Walgraeve et al., 2010 and references therein).

3.2.1.3 Atmospheric formation

Oxy-PAHs can be formed from PAHs via photochemical reactions and reactions with O_3, OH and NO_3 radicals Keyte et al., 2013). Given the partitioning of PAHs between the gaseous and particulate phases, transformation processes can take place in both phases. Reactions involving OH are considered to play a major role in gas phase reactions (Barbas et al., 1996; Bunce et al., 1997; Calvert et al., 2002; Vione et al., 2004; Wang et al., 2007). Additionally, several studies show the formation of Oxy-PAHs via heterogeneous reaction processes (Perraudin et al., 2007; Pöschl et al., 2001; Ringuet et al., 2012b). For example, major identified products of the reaction between ozone and anthracene adsorbed on silica particles were 1,1’-biphenyl-2,2’-dicarboxaldehyde, anthrone and 9,10-anthraquinone (Perraudin, 2004). Nevertheless, particle associated PAHs containing more than five rings are less susceptible to reaction with gaseous reactive radicals. Nevertheless, they can also undergo a wide variety of transformation processes, but often with slower kinetics than in the gas phase. Especially direct photolysis and photolysis in the presence of photosensitizers (e.g. ketones or aromatic carbonyls) play a significant role for these compounds (Yu, 2002). The wide electron delocalization of PAHs enables them to absorb sunlight, so that irradiation under atmospheric conditions may lead to photooxidation (Vione et al., 2004; Yu, 2002).