A thermal desorption method for determining atmospheric Semivolatile Organic Compound concentrations

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Abstract

It is now recognised that indoor environments contribute significantly to human exposure to airborne pollutants. People spend a large amount of time in indoor environments and there are many indoor sources that are not present outdoors. Among the chemicals released in indoor environments, some of them have been identified as hormonally active or carcinogens. Indoor air pollution problems are likely to become more as stricter controls limit outdoor pollution levels. Reduction of air exchange rate and the use of new insulating materials are likely to contribute to the build-up of pollutants in indoor air.

The objective of this thesis has been to develop an analytical method based on thermal desorption for the measurement of semivolatile organic compounds (SVOCs) to be use for indoor and personal measurements. The sampler consists of a small $PM_{2.5}$ impactor upstream of a sample tube filled with the adsorbent Tenax TA to collect the particulate and gaseous phases respectively. The analytical technique was based on thermal desorption to compensate for the low sampling volumes available with the personal sampling pump so that the entire sample can be injected on the analytical system. In addition, the current technique reduces the analytical time and cost because little sample handling is required and it is more environmental friendly because no solvents are used.

The experimental work focused on the development of a vapour generation system to determine breakthrough volumes of the least volatile target compounds on the adsorbent Tenax TA, the development of the analytical method for the analysis of both the gaseous and particulate phases and the evaluation of the performance of the developed method. Finally, the applicability of the method was verified by performing a short study involving indoor and personal samplings.

The developed vapour generation system (Fagault *et al.*, 2003) permitted vapours to be generated at concentrations that are representative of indoor air concentrations **(appendix 1)**. The apparatus has been evaluated for a number of SVOCs including PAHs, phthalates, organophosphate esters and alkylphenol with a broad range of volatility (from naphthalene to pyrene).

The breakthrough measurement study performed in the worst conditions (30°C and 70% relative humidity) demonstrated that the adsorbent Tenax TA was appropriate to quantitatively collect even the least volatile compound naphthalene over a 24 hours sampling period.

The analytical method was developed for 16 PAHs, 6 OPAHs, 5 phthalates, 2 organophosphate esters, 3 alkylphenols and 5 pesticides (2 organophosphorous, 1 carbamate, 1 pyrethroïd and 1 organochlorine). Its applicability for PAHs measurements was verified with a standard reference material (SRM1649a, NIST) and by comparison of indoor air filter strips analysed by the thermal desorption method and a conventional solvent extraction method. The thermal desorption method was shown to be quantifiable for PAHs up to benzo(a)pyrene but less effective for less volatile PAHs due to their incomplete desorption.

A side by side comparison between the developed sampler and a low volume Filter/PUF sampler clearly demonstrate that the developed method was much more efficient than the low volume PUF sampler for the measurement of gaseous low molecular weight compounds (MW$\leq$178 g.mol^{-1}).

Regarding the particulate phase, measured concentrations from both samplers were highly correlated with the exceptions of the heavy PAHs (IP, DahA and BghiP). These results suggest that sampling artifact were limited or similar to those of the low volume sampler. The precision of the method was evaluated by the relative standard deviation from co-located measurements in an indoor environment (n=6). A number of target compounds were detected including PAHs, OPAHs, phthalates, organophosphate esters and phenol. The relative standard deviation was generally less than 10% indicating good reproducibility.

A small demonstration study consisting of twenty four hours indoor and personal measurements was carried during six days. The results obtained in this demonstration study were in agreement with most previous studies reporting indoor heavy PAHs concentrations lower or similar than outdoor PAHs concentrations and light PAHs concentrations higher indoors than in outdoor environments. This demonstration study also confirmed that phthalates and organophosphate esters are ubiquitous in indoor environment.

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List of abbreviations

Chemical abbreviations

1-Nap	1-naphthaldehyde
2-PP	2-phenylphenol
4-t-BP	4-tertbutylphenol
4-t-NP	4-nonylphenol
4-t-OP	4-octylphenol
9-FlO	9-fluorenone
9-PheC	9-phenanthrenecarboxaldehyde
9,10-AQ	9,10-anthraquinone
AcN	Acenaphthene
AcNP	Acenaphthylene
Ant	Anthracene
BaA	Benzo(a)anthracene
BaA-7,12-O	Benz(a)anthracene-7,12-dione
BAO	Benzanthrone
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthene
BBP	Butylbenzylphthalate phthalate
BghiP	Benzo(g,h,i)perylene
BjF	Benzo(j)fluoranthene
BkF	Benzo(k)fluoranthene
Chr	Chrysene
cis-Perm	Cis-permethrin
DahA	Dibenzo(a,h)anthracene
DBP	Dibutylphthalate
DEHP	Bis(2-ethylhexyl)phthalate
DEP	Diethylphthalate
DMP	Dimethylphthalate
End II	Endosulfan I
Fl	Fluorene
Flu	Fluoranthene
IP	Indeno(1,2,3-cd)pyrene
Nap	Naphthalene
Phe	Phenanthrene
ProP	Propoxur
Pyr	Pyrene
TBP	Tributylphosphate
Trans-Perm	Trans-permethrin
TriP	Triphenylene

Various abbreviations

ASE	Accelerated solvent extraction
BaP_{equ}	Benzo(a)pyrene equivalent
bp	Boiling point
EI	Electron impact
FID	Flame ionisation detector
FRM	Federal reference method
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectrometry
HAA	Hormonally active agents
HPLC	High performance liquid chromatography
HPLC	High performance liquid chromatography
I.d	internal diameter
IARC	International agency for research on cancer
MSD	Mass selective detector
MSSV	Micro-scale sealed vessel
MW	Molecular weight
ND	Not detected
NICI	Negative ion chemical ionisation
NIST	National Institute of Standards and Technology
NQ	Not quantify
OP	Organophosphate esters
OPAH	Oxygenated polycyclic aromatic hydrocarbons
PAH	Polycyclic aromatic hydrocarbons
PM	Particulate matter
PTFE	Polytetrafluoroethylene (Teflon)
PUF	Polyurethane foam
QFF	Quartz fibre filter
RH	Relative humidity
SIM	Single ion monitoring
SVOC	Semivolatile organic compounds
TD	Thermal desorption
TEF	Toxic equivalent factor
USEPA	United states environmental protection agency
VOC	Volatile organic compounds

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Introduction and scope of the thesis

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Air contains many gaseous and particulate pollutants apart from its natural constituents. These contaminants originate from various sources. Common sources of outdoor air pollution are burning of fuel fossils, road vehicles, forest burning, chemical industries, fertiliser, paper manufacture or waste incineration. Indoor air pollutants include for example, combustion sources such as oil, gas, coal, wood, and tobacco smoking; building materials, asbestos-containing insulation, carpet, and cabinetry or furniture made of certain pressed wood products; products for household cleaning and maintenance, personal care, central heating, cooling systems; humidification devices; and outdoor sources.

Depending on the sources, various categories of organic pollutants are released into the atmosphere. These pollutants can be divided in four distinct groups:

- ✔ Very volatile organic compounds (VVOC)
- ✔ Volatile organic compounds (VOC)
- ✔ Semivolatile organic compounds (SVOCs)
- ✔ Organic compounds associated with particulate matter (POM)

This study focuses on the measurements of SVOCs. This group of compounds have been classified as compounds with vapour pressures at ambient temperature from approximately 10^{-2} to 10^{-8} kPa (10^{-1} to 10^{-7} mm Hg) or with a boiling point ranging from 240°C to 400°C (WHO, 1989). Owing to their low vapour pressure, SVOCs may be found in the atmosphere either in the gas phase or adsorbed onto particulate matter (particulate phase). Many pollutants from this group have shown to have adverse health effects to human. For instance, some PAHs are mutagens and humans carcinogens and other SVOCs including phthalates, pesticides have been identified as endocrine-disrupting agents. Accurate measurement of human exposure for use with epidemiological studies and risk assessment studies is therefore necessary to understand health effect associated with air pollutants.

The assessment of exposure to pollutants has often been based on ambient air measurements from fixed-site monitors. However, this approach has been found inadequate since human populations in occidental countries spend 80% to 95% of their time in indoor environments (NRC, 1981) and because indoor concentrations for non ambient pollutants are vastly different from those typically encountered outdoor. Pollutants with indoor sources tend to concentrate indoor due to the limited ventilation and slow degradation processes, thus resulting in a concentration build-up. It should be pointed out that environmental policies that focus solely on reducing harmful chemical emissions from stationary measurement in outdoor may be misleading or not be effective in reducing human exposures and risks when the indoor environment is a significant contributor to exposures. A different measurement method should be used for accurate assessment of human exposure for many pollutants.

An alternative approach is to estimate the exposure to pollutants by placing fixed samplers in microenvironments that people pass through and to combine concentrations with time activity patterns. This method can also lead to an underestimation of the exposure because the human activity is not taken into account.

The only way to take into account both the diversity of the microenvironments and the human activity is by means of a personal sampler as these samplers measure the concentrations within the persons breathing zone. Personal monitoring integrates exposure across multiple times and locations through which an individual passes in the course of daily activities.

Personal samplers are available for many VOCs and particulate matter measurements but up to now, very few samplers have been developed and evaluated for sampling semivolatile organic compounds. The aim of this research project is, therefore, the development and evaluation of a personal sampling method for semivolatile organic compounds.

There are two different sampling methods that can be used for personal sampling measurement (i) Active methods and (ii) passive methods. Active methods directly pump air through collection devices to collect air pollutants. They can be equipped with both filter and an adsorbent cartridge to collect the particulate and gaseous phases respectively. A passive (or diffusive) sampler is a device, which is capable of taking samples of gas, or vapour pollutants from the atmosphere at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane. Since SVOC are partitioned between both the particulate and gaseous phase, passive samplers are inadequate for SVOCs measurements. The aim of this research project is, therefore, the development and evaluation of a personal active (dynamic) sampling method for semivolatile organic compounds. Available personal samplers for SVOCs measurements are only compatible with a solvent extraction procedure. One of the problems when conducting risk assessment studies is the need of a high number of measurements. The number of measurements is often limited because of the time and cost of conventional solvent extraction techniques. In addition the detection limits achievable with solvent extraction methods combined with the low sampling volume obtained with personal sampling are not sufficiently low for many SVOCs which are found in the atmosphere at concentrations levels of few ng/m^3 or less (i.e. only a fraction of the enriched sample is injected in the analytical system). Thermal desorption on the contrary is a very sensitive method because the entire sample can be injected into the analytical system and time and cost are greatly reduced because this technique requires little sample handling. The overall time spent for thermal desorption procedure (desorption and analyses) generally do not exceed 2 hours. The aim of this study is therefore the development and evaluation of a personal active sampler for SVOCs measurements compatible with a thermal desorption procedure for both the particulate and gaseous phase. High sensitivity and safe identification is obtained by coupling the thermal desorption (TD) to a gas chromatograph interface with a mass spectrometer (GC/MS).

Thermal desorption of SVOCs trapped on solid sorbents has been used at very few occasions. Most of the studies have been carried out on specific compounds such as pesticides in contaminated atmospheres. Analysis of a wider range of compounds is even more rare. The applicability of thermal desorption procedure to remove SVOCs from filter media has been demonstrated at few occasions . In the state of the art, none of the adsorbents commercially available has been characterised for sampling SVOCs during 24 hours. A better characterisation of the adsorbents is clearly needed to make thermal desorption procedure attractive for sampling SVOCs.

Desorption efficiency and safe sample volumes are two key parameters to define the suitability of an adsorbent. The safe sample volume is defined as the volume of air that can be drawn through a sampler without appreciable loss in the effluent. Safe volume sample is estimated from breakthrough volume measurements. Breakthrough volume can be estimated either from a direct or indirect method. The direct method was used in this study because measurements are more representative of field sampling conditions. In the direct method, a gas containing the target compound is led continuously through an adsorbent bed at a defined temperature. Breakthrough is said to occur once a fraction of the gas contained in the incoming flow is detected at the outlet of the tube.

Breakthrough measurements require the development of a vapour generation system. This system was developed to generate vapours under conditions representative of field sampling (concentrations, humidity and temperature). Contrary to VOC, generation of SVOCs has been carried out at very few occasions. Among the generation techniques available, the diffusion method was preferred in this study because diffusion cells can be laboratory made and diffusion rate can be estimated from an empirical formula.

After the selection of the appropriate adsorbent to collect a broad range of SVOCs, the breakthrough volume was studied for selected compounds and a thermal desorption method was developed for both the measurements of the gaseous and particulate phases.

The performance of thermal desorption procedure for the measurement of particulate phase was compared with a conventional solvent extraction method and the performance of the sampler was compared with low volume sampler compatible with a solvent extraction procedure. Finally a demonstration study was performed to validate this sampler for field measurements.

To summarise, the main aim of this project is, therefore, the development and evaluation of a personal sampler compatible with a thermal desorption technique for both the analysis of the gaseous and particulate phases. Experimental work has focused on the following objectives:

- ✔ Selection of an adequate adsorbent
- ✔ Development of a vapour generation system
- ✔ Development and validation of the analytical method (thermal desorption GC based techniques for both filter and adsorbent)
- ✔ Comparison of the performance of the analytical method for the measurement of the particulate phase with a conventional extraction procedure
- ✔ Comparison of the performance of the sampler with other sampling devices
- ✔ Demonstration study

Part I: Theory and literature review

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Chapter 1: Semivolatile organic compounds

Since most of the general population spends more than 80% of their time indoors , this study focuses on target compounds commonly present in indoor environments. This study aims to demonstrate the feasibility of the method for a broad range of organic chemicals that may be harmful to human health. Based on the literature focusing on SVOCs in indoor air, it was decided to select compounds from 6 chemical families including polycyclic aromatic hydrocarbons (PAHs), oxygenated polycyclic aromatic hydrocarbons (OPAHs), organophosphate esters (OPs), phthalate esters, alkylphenols and pesticides.

1.1. Polycyclic Aromatic Hydrocarbons (PAHs)

1.1.1. Health effects

Adverse heath effects of PAHs have been recognised for more than 60 years. Because of the toxicological effect, the carcinogenic and mutagenic properties of some PAHs, and their widespread presence in the environment, PAHs have been thoroughly studied for several decades.

Because of their toxicity and stability in the environment, 16 of them have been classified as priory pollutants by the United States Environmental Protection Agency (USEPA). One reason for which the USEPA has classified PAHs as a priory pollutant is due to the carcinogenic properties of some of them. Benzo(a)pyrene and Benzo(a)anthracene have been classified by the International Agency for research on cancer (IARC) as agents which are probably carcinogenic to humans (group 2A), and others may be carcinogenic to humans (group 2B). BaP is one of the most incriminated PAHs in terms of toxicity. Several studies have shown that the carcinogenic properties of this compound were some of the most elevated among its congeners. Its toxicity is directly linked to the strong carcinogenic properties of benzo(a)pyrene-7,8-dihydriol-9,10-epoxide, which is one of its metabolites. The working group on polycyclic aromatic hydrocarbons of the European Union (European Commission, 2001) has estimated that BaP represents at least 50% of all PAHs carcinogenic activity for an ambient air sample. This estimate was based on the concentrations measured in different locations and weighed using toxic equivalent factors (TEF). Toxic equivalent factors represents the relative carcinogenic potency of a given compound by reference to the specific compound BaP. Examples of toxic equivalent factors can be found in the information provided in **Table 1.**

In addition to their carcinogenic properties, some PAHs are suspected of being mutagenic and hormonally active agent (Lintelmann *et al.*, 2003, Pait *et al.*, 2004).

Table 1: Compiled Toxic equivalent factors (TEF) for PAHs

Compounds	Nisbet et LaGoy (1992)[1]	INERIS (2003)[2]	USEPA[3]	Larsen (1998)[4]
Naphthalene	0.001	0.001	-	-
Acenaphthene	0.001	0.001	-	-
Acenaphthylene	0.001	0.001	-	-
Fluorene	0.001	0.001	-	-
Phenanthrene	0.001	0.001	-	0.0005
Anthracene	0.01	0.01	-	0.0005
Fluoranthene	0.001	0.001	-	0.05
Pyrene	0.001	0.001	-	0.001
Benzo(a)anthracene	0.1	0.1	0.1	0.05
Chrysene	0.1	0.1	0.001	0.03
Benzo(b)fluoranthene	0.1	0.1	0.1	0.1
Benzo(k)Fluoranthene	0.1	0.1	0.01	0.05
Benzo(a)pyrene	1	1	1	1
Indeno(1,2,3-cd)pyrene	0.1	0.1	0.1	0.1
Dibenzo(a,h)anthracene	5	1	1	1
Benzo(g,h,i)pyrene	0.01	0.01	-	0.02

[1] (Nisbet et al., 1992), [2] (Doonaert et al., 2003), [3] (Schoeny et al., 1993), [4] (Larsen et al., 1998)

1.1.2. Sources and indoor air concentration levels

(i) Sources

Since most people spend the majority of their time in indoor environments, human exposure to PAHs in indoor environments has received increasing attention in recent years (Adgate *et al.*, 2003, Bornehag *et al.*, 2005, Chuang *et al.*, 1991, Chuang *et al.*, 1999, Fromme *et al.*, 2004b, Levy *et al.*, 2002, Mitra *et al.*, 1992, Mitra *et al.*, 1995, Naumova *et al.*, 2002, Naumova *et al.*, 2003, Ohura *et al.*, 2002, Ohura *et al.*, 2004a, Ohura *et al.*, 2005, Wilson *et al.*, 1995, Wilson *et al.*, 2000, Zhu *et al.*, 2003). The California environmental protection agency has conducted a large field study in northern California in the late eighties (CARB, 1993). They measured 13 PAHs inside and outside 280 homes during the winter. The homes were selected based upon the occupants use of tobacco, fireplaces, wood stoves, gas heat and no sources. They concluded that the concentrations of all 13 PAHs were substantially higher inside homes where smoking occurred. In addition, burning wood in fireplaces and wood stoves appeared to cause slight to moderate increases in concentrations of benzo(a)anthracene, chrysene, benzofluoranthenes, and Benz(a)pyrene indoors. Investigators estimated that infiltration of polluted outdoor air was also a major contributor to concentrations of PAHs indoors. In a different study with different indoor PAH sources, namely tobacco smoking, gas cooking/heating and electrical cooking stoves. Mitra *et al* (1995) also confirmed that tobacco smoking had the greatest impact on total PAH concentrations. They estimated that in smokers homes, 87% of the total PAH was due to smoking. The results of this study also indicated that in the absence of tobacco smoking, gas use contributed significantly to total PAHs in indoor air. A previous study by Mitra *et al* (1992) also identified gas use as a potential source of PAH in indoor air.

Cooking activities may also contribute significantly to PAH concentrations in indoor air (Dubowsky *et al.*, 1999, Levy *et al.*, 2002, Zhu *et al.*, 2003). Dubowsky *et al* (1999) have demonstrated that cooking, and especially frying/sautéing, may be a significant source of indoor PAH concentrations. The influence of the cooking method (Chinese, western, fast food, Japanese) on the emission of PAHs was investigated by Li *et al* (2003). Their results indicate that the emission intensity for both the total PAH emission and total PAH emission in BaP_{equ} shared the same trends in all of the restaurants investigated (n=10): Chinese>western>fast food>Japanese. These results are consistent with the study by Dubowsky *et al* (1999), since the Chinese cooking method uses frying/sautéing heavily.

Burning candles and incense has also been identified as a potential contributor to PAHs in indoor air (Dubowsky *et al.*, 1999).

Contrary to many PAHs which are exclusively emitted by combustion sources, Naphthalene is used as a pure product or a mixture in homes as a moth repellent. Very high naphthalene concentrations in indoor air are generally associated with mothball usage (Van Winkle *et al.*, 2001).

Finally, as previously mentioned, infiltration of polluted outdoor air is also a major source of PAHs in indoor air. Many studies have identified traffic emissions as the main outdoor source of PAHs in indoor air for occidental cities (Dubowsky *et al.*, 1999, Fischer *et al.*, 2000, Fromme *et al.*, 2004b), but cooking emissions have also been identified as a major source of PAHs in terms of health effects in outdoor air in countries with different cooking habits that differ from the West. Li *et al* (2003) have identified that although cooking emissions were lower than those from traffic sources, the emission rates of total BaP_{equ} for cooking sources were much higher than traffic sources. Infiltration of polluted outdoor air by wood smoke may also contribute significantly to indoor PAH concentrations during winter periods in countries where wood-burning in fireplaces are used (CARB, 1993).

(ii) Concentration levels

PAHs with two rings are found mainly in the gaseous phase, whereas PAH with 5 or 6 cycles are essentially adsorbed onto particulate matter. PAHs with an intermediate number of cycles are distributed between both phases. A typical PAH gas/particles partitioning is shown in **Figure 1**.

Table 2 presents the indoor and outdoor concentration levels from various studies. It can be observed that Naphthalene is the dominant PAH in both indoor and outdoor air and can represent up to 90% of total PAHs. Naphthalene concentrations can reach up to several µg/m^3, whereas other PAHs found exclusively in the gaseous phase are found at only several tens of a ng/m^3 at the maximum concentrations. PAHs found exclusively in the particulate phase are generally of the order of several ng/m^3 or less, whereas PAHs partitioned between both phases are in the order of several ng/m^3.

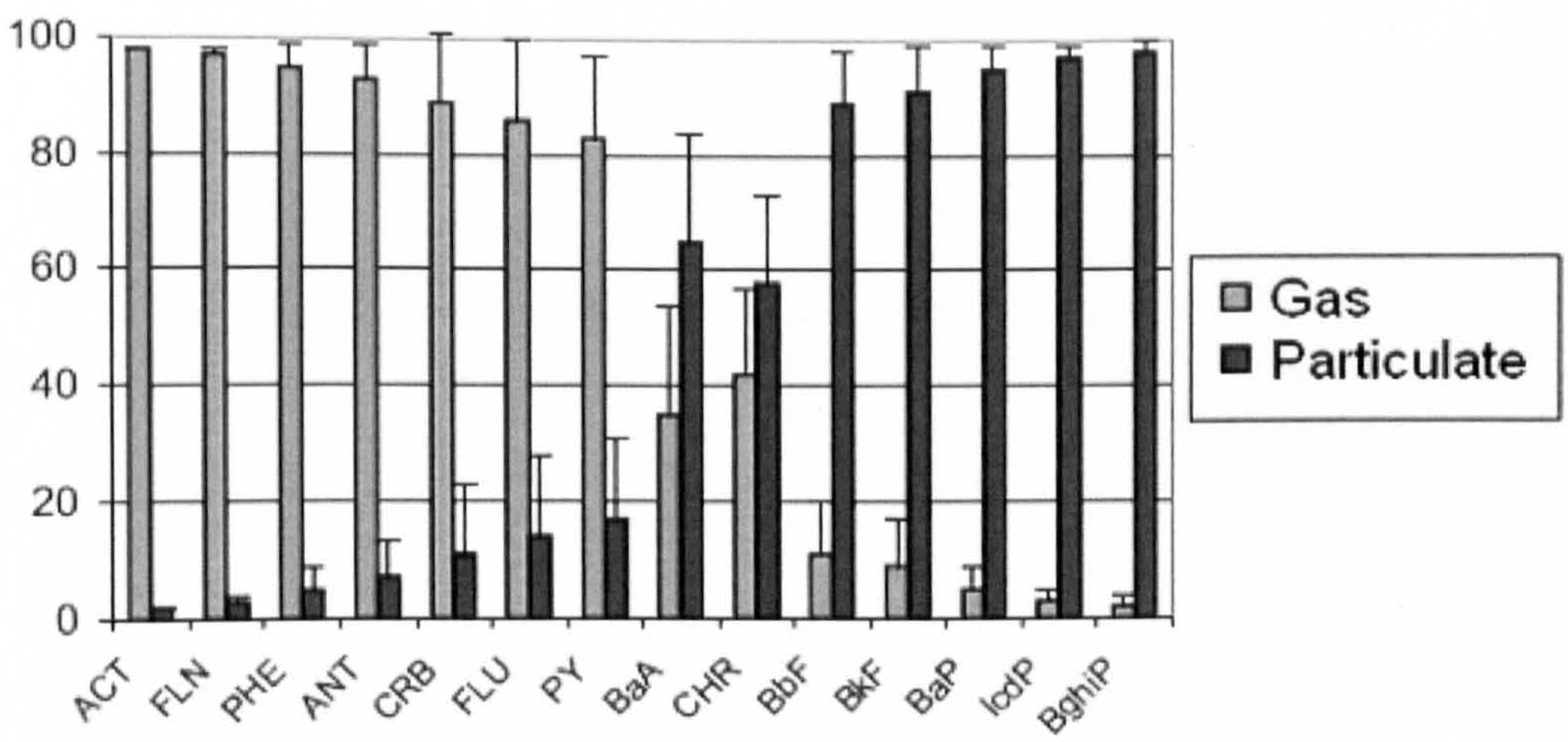


Figure 1: Gas/Particles partitioning in the atmosphere (From Odabassi et al (1999))

(iii) Indoor versus outdoor concentrations

The relationship between indoor and outdoor for PAHs has been investigated in several studies. The indoor/outdoor relationships (I/O) for individual PAHs are generally quite different. In many studies, the I/O ratio is generally greater than 1 for low molecular weight PAHs (PAHs predominantly in the gas phase) whereas it is close to 1 for compounds predominantly associated with the particle phase (Chuang *et al.*, 1999, Li *et al.*, 2000, Mitra *et al.*, 1995, Naumova *et al.*, 2002).

Naumova *et al* (2002) measured the indoor and outdoor concentrations of 30 PAHs in 55 non-smoking residences in three US cities (Los Angeles, Houston and Elizabeth). They found that the signature of 5-7 ring PAHs in the three cities was similar to the outdoor profiles, which suggests that indoor concentrations of exclusively particle-bound PAHs were dominated by outdoor sources. In contrast, indoor to outdoor ratios of PAH concentrations showed that indoor sources had a significant effect on indoor concentrations of 3-rings PAHs and a smaller effect on 4-rings PAHs. The same conclusions were drawn in a study of 10 non-smokers homes over a 14-month period (NUATRC, 2005). They found a strong correlation between indoor and outdoor concentrations for heavy PAHs (mostly or exclusively particle-bound) and a weak correlation between indoor and outdoor air concentrations for light compounds (mainly gaseous PAHs). These results suggest that the impact of indoor activities and indoor sources is greater than the influence of the penetrating outdoor air for gaseous PAHs. On the contrary, indoor air concentrations of particle-bound PAHs are greatly influenced by outdoor concentrations.

Table 2: PAHs concentrations (ng/m^3) in indoor and outdoor air from various studies (Min-Max (Median))

	USA – 10 Chicago homes (N=120) [1] June 2000-July 2001			USA – 24 North Carolina low-income homes (N=24) [2] 1995		Japan – 22 homes in an industrial town [3] 2004		
	Indoor	Outdoor	I/O	Indoor	Outdoor	Indoor	Outdoor	I/O
Nap	4.2-2340 (177)	ND-1857 (168)	0.1-18 (1.0)	334-9700 (2190)	56.8-1820 (433)	94-29000 (955)	89-540 (210)	0.6-93 (3.7)
AcN	ND-33.3 (3.6)	ND-44.1 (5.6)	0-967 (1.0)	8.3-298 (96.0)	2.3-129 (21.4)	1.4-56 (5.2)	1.3-10.0 (2.8)	0.5-34 (1.6)
Fl	ND-52.7 (4.2)	ND-49.4 (9.3)	0-222 (0.4)	6.8-196 (49.7)	3.1-84.1 (16.4)	1.1-10 (4.2)	2.1-9.4 (3.7)	0.4-3.4 (1.2)
Phe	0.01-61.8 (0.7)	0.01-78.9 (9.7)	0-718 (0.3)	9.9-184 (66.3)	4.8-147 (30.4)	3.4-38 (8.8)	4.1-21 (8.0)	0.4-3.4 (1.1)
Ant	ND-51.54 (9.5)	ND-14.9 (1.2)	0-296 (12.3)	0.8-16.7 (6.2)	0.2-11.0 (1.9)	0.12-1.4 (0.19)	0.12-1.0 (0.31)	0.1-6.4 (0.4)
Flu	0.02-17.2(1.8)	0.2-15.4 (3.5)	0-45 (0.6)	1.2-19.3 (8.6)	1.1-23.1 (5.8)	0.41-4.1 (1.11)	0.97-4.1 (1.6)	0.3-2.5 (0.6)
Pyr	0.01-8.3 (1.5)	0.1-16.0 (2.2)	0-27 (0.6)	0.8-29.4 (6.7)	0.5-10.7 (2.9)	0.31-3.3 (0.84)	0.59-3.3 (1.3)	0.3-2.1 (0.6)
BaA	ND-1.5 (0.06)	0.01-2.7 (0.11)	0-51 (0.7)	0.11-3.13 (0.6)	0.07-2.18 (0.4)	0.02-0.66 (0.16)	0.1-1.5 (0.35)	0.1-3.5 (0.5)
Chr	ND-2.1 (0.16)	0.01-2.9 (0.27)	0.1-4.8 (0.5)	0.03-3.38 (0.8)	0.12-3.1 (0.7)	0.06-1.0 (0.33)	0.22-2.3 (0.73)	0.2-3.4 (0.5)
BbF	ND-1,3 (0,08)	ND-5.3 (0.13)	0-129 (0.5)	0.17-5.80 (1.3)	ND-1.36 (0.08)	0.09-1.7 (0.30)	0.36-2.9 (0.9)	0.2-1.7 (0.7)
BkF	ND-2.3 (0.06)	ND-1.2 (0.14)	0-5.7 (0.6)			0.03-0.54 (0.20)	0.15-0.94 (0.34)	0.2-1.7 (0.7)
BaP	ND-2.2 (0.10)	ND-4.9 (0.18)	0-6.4 (0.6)	0.05-4.49 (0.7)	0.04-2.49 (0.5)	0.06-0.96 (0.34)	0.16-1.5 (0.41)	0.2-2.3 (0.9)
IP	ND-0.9 (0.03)	ND-12 (0.10)	0-44 (0.8)	0.03-8.80 (0.9)	0.06-4.33 (0.6)	0.07-1.2 (0.43)	0.28-1.8 (0.63)	0.2-1.8 (0.8)
DahA	ND-0.5 (0.08)	ND-14 (0.08)	0-8.9 (0.9)	0.02-2.75 (0.5)	0.02-0.39 (0.2)	0.01-0.1 (0.04)	0.02-0.15 (0.05)	0.3-1.7 (0.7)
BghiP	ND-4.6 (0.19)	ND-6.9 (0.25)	0-77 (0.7)	0.04-20.9 (1.5)	0.05-4.62 (0.7)	0.09-1.0 (0.44)	0.32-1.9 (0.66)	0.3-1.9 (0.7)

[1] (NUATRC, 2005), [2] (Chuang et al., 1999), [3] (Ohura et al., 2004a)

ND: Not detected

1.1.3. Personal exposure concentration levels

To date, very little data on personal exposure to PAHs is available in the existing literature. **Table 3** summarises the findings of four studies.

Table 3: PAH concentrations in ng/m^3 measured by personal monitoring in winter (W) and summer (S)

Studies	France – Grenoble (1999)[1]		USA New York (1998-2001)[2]		Croatia-Zagreb (1996)[3]		Japan Shizuoka (2002)	
	Summer (S)	Winter (W)	S	W	S	W	S	W
Fl	0.4-1.4 **(0.9)**	1.26-3.17 **(2.27)**	-	-	-	-	0.10	0.11
Pyr	-	-	4.45	3.5	-	-	0.22	0.10
BaA	0.03-0.07 **(0.05)**	0.12-4.22 **(1.24)**	0.22	0.32	-	-	0.06	0.10
Chr/TriP	-	-	0.3	-	-	-	0.27	0.18
BbF	0.06-0.17 **(0.12)**	0.62-2.65 **(1.17)**	0.36	0.68	0.39	3.82	0.29	0.46
BkF	0.05-0.08 **(0.06)**	0.3-1.1 **(0.52)**	0.09	0.17	0.39	2.02	0.13	0.19
BaP	0.05-0.09 **(0.07)**	0.5-2.34 **(1.05)**	0.2	0.63	0.13	4.34	0.24	0.32
IP	0.39-0.52 **(0.46)**	0.99-6.33 **(2.88)**	0.33	0.82	-	-	0.36	0.45
DahA	ND	ND	-	-	-	-	0.04	0.03
BghiP	0.15-0.45 **(0.3)**	0.62-1.33 **(1.05)**	0.56	1.45	0.36	3.4	0.35	0.43

[1] *(Zmirou et al., 2000), 37 participants, particulate phase concentrations (Min-Max (Mean))*
[2] *(Tonne et al., 2004), 348 pregnant women, mean concentrations (gaseous and particulate)*
[3] *(Sisovic et al., 1996), 15 participants, mean concentrations (gaseous and particulate)*
[4] *(Ohura et al., 2005), 55 participants, mean concentrations(particulate phase)*

It can be seen from these studies that concentrations levels are quite different depending on the sampling location. Personal exposure to most PAHs was lower in New York than that measured in Zagreb and Grenoble. For instance, in winter, the personal exposure to BaP measured in Zagreb and Grenoble was approximately 7 and 2 times higher than that measured in New York City, respectively.

It can also be seen that wintertime personal exposures were higher than their summer counterparts. This trend is particularly marked for both European studies, where BaP winter exposure is 3 to 25 times and 5 to 35 times greater than summer value for the Grenoble and Zagreb studies respectively. In the New York study, personal exposure in winter increased only threefold for BaP and less for other compounds. The severe seasonal patterns of personal exposure in the European studies are related to the addition of combustion sources for heating, less effective dispersion conditions and the decrease in photochemical reactions in the atmosphere in winter.

1.2. Oxygenated PAH (OPAHs)

1.2.1. Health effect

The toxicological properties of OPAHs are much less documented than PAHs. However, OPAHs are semivolatile organic air pollutants of concern because of their demonstrated genotoxic effects. Studies of OPAH in bacterial cell mutation assays using the Ames test have found some of these compounds to be mutagenic (Kaden *et al.*, 1979, Møller *et al.*, 1985, Sakai *et al.*, 1985). The Ames test is used to determine the mutagenic potential of a substance based on the mutation rate of bacteria that are exposed to the substance. The significance of this test can be questioned, since the toxicity with bacteria may not be relevant for more complex organisms and due to the fact that this test is carried out with synthetic substances that may not be representative of real atmospheric samples. Durant *et al* (1996) have investigated the mutagenic properties of 20 OPAHs by human cell bioassay-directed chemical analysis using an extract of urban aerosol rather than synthetic compounds. They found that the semivolatile fraction containing oxygenated PAH was mutagenic to human cells.

1.2.2. Sources and concentrations levels

While PAHs are emitted directly from combustion processes, oxygenated PAH are both primarily emitted and formed in the atmosphere either by chemical reactions of PAH compounds with atmospheric oxidants (OH, 0_3...) or by photo-degradation of their parent PAHs compounds (Allen, 1997, Barbas *et al.*, 1996, Perraudin, 2004). Very few studies can be found in the existing literature regarding the occurrence of OPAHs in ambient air. They have been identified in ambient air in North American cities since the early 1980s (Allen, 1997, Fraser *et al.*, 1998, Hawthorne *et al.*, 1992, Ligocki *et al.*, 1989, Wilson *et al.*, 1995) and in European cities (Alastair *et al.*, 1995, Albinet, 2005, Albinet *et al.*, 2006, Albinet *et al.*, Submitted, Leoz-Garziandia, 1998, Niederer, 1998, Schnelle-Kreis *et al.*, 2001). The identified compounds are ketones, quinones, carboxaldehydes, and hydroxyl-PAHs.

Some data for the most recurrent OPAHs (1-naphthaldehyde, 9,10-anthraquinone, 9-fluorenone, benzanthrone, benz(a)anthracene-7,12-dione) found in the existing literature is provided in **Table 4**. As with PAHs, the partitioning of OPAHs between the gaseous phase and the particulate phase depends on the temperature via the vapour pressure. Therefore, the lighter OPAHs are preferentially in the gaseous phase whereas heavier OPAHs are in the particulate phase. An gas/particles partitioning diagram from air samples collected in Marseille (France) is presented in **Figure 2** (Albinet, 2005). It can be seen that 1-naphthaldehyde and 9-fluorenone are present exclusively in the gaseous phase whereas benzanthrone and benz(a)anthracene-7,12-dione are exclusively in the particulate phase. 9,10-anthraquinone is partitioned between both phases.

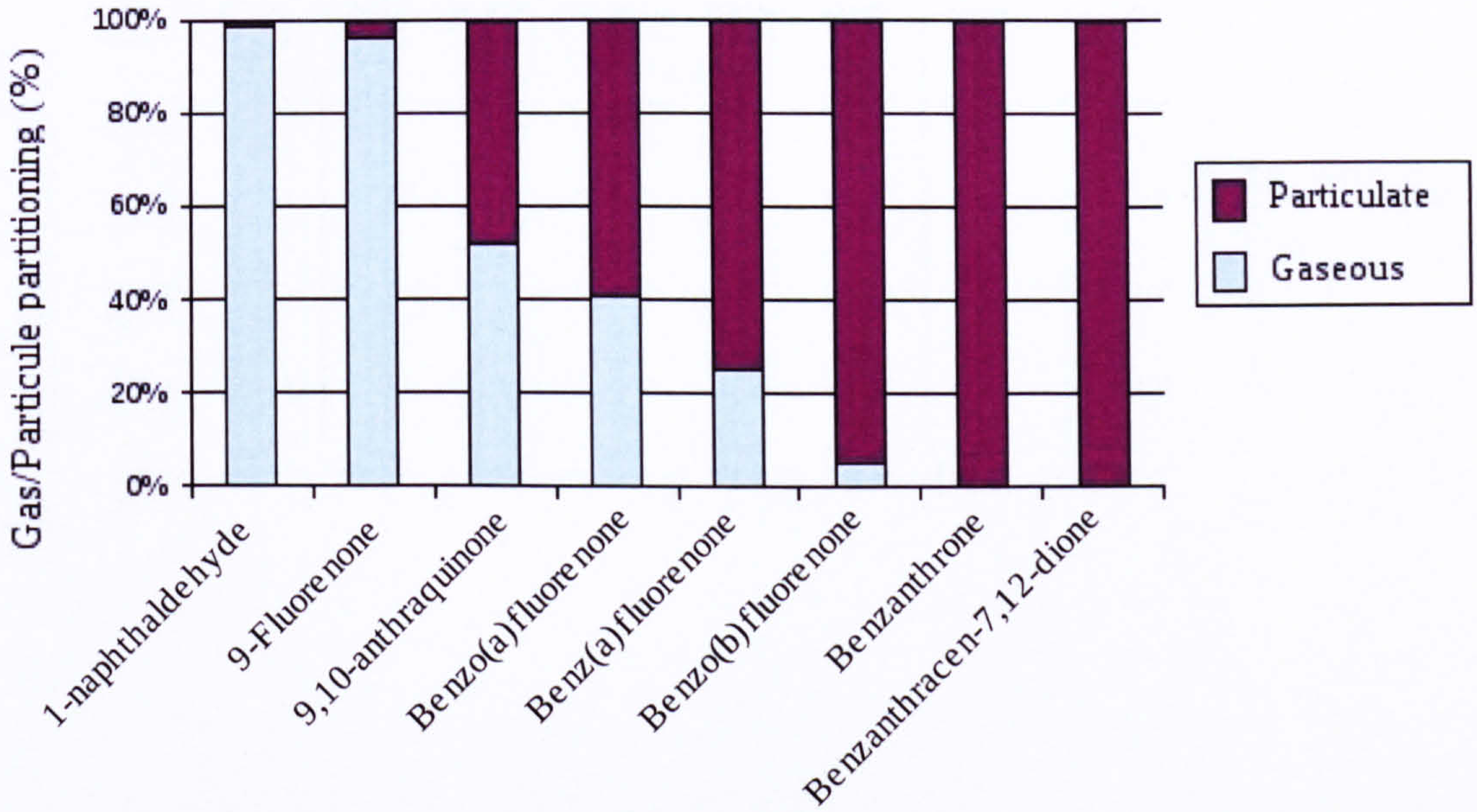


Figure 2: Gas/Particles partitioning of PAHs in ambient air sample from Marseille (32°C) (From Albinet *et al* (2005))

Typical concentrations determined in the particulate phase are around the ng/m^3 and about ten times higher in the gaseous phase (concentrations of 9,10 anthraquinone and 9-fluorenone up to 40 ng/m^3 measured in Paris by Leoz-Garzandia (1998).

Regarding the seasonal variations of OPAHs, the concentrations levels seem more significant in summer than in winter. The photo-chemical origin of OPAHs (photo-degradation and photo-oxidation of PAH parents) could explain this phenomenon. This behaviour was observed by Yassaa *et al* (2001) for 9,10-anthraquinone in an urban site of Algiers (Algeria) and by Wilson *et al* (1995). In this study, the concentration levels of the 4 OPAHs quantified (Naphthalene-1,8-dicarboxylic acid, pyrene carboxaldehyde, pyrene-3,4-dicarboxylic acid and benz(a)anthracene-7,12-dione) were systematically more significant in summer and autumn compared to winter and spring periods.

Regarding the indoor air concentrations levels of OPAHs, only one publication was found in the body of literature (Chuang *et al.*, 1991). They measured the indoor and outdoor concentrations of five OPAHs as well as 15 PAHs and 5 nitro-PAHs in an eight-home study. They found higher average indoor levels compared to the average outdoor levels for all the compounds with the exception of 2 OPAHs (Naphthalene-1,8-dicarboxylic acid and Pyrene-3,4-dicarboxylic acid) and one nitro-PAH (2-nitrofluoranthene). It was suggested that these three compounds were formed by oxidation reaction/photo-degradation of PAHs parents. These reactions are expected to be more significant in outdoor air due to hydroxyl radical concentrations and more significant UV radiation in outdoor air.

Table 4: Atmospheric concentrations of the most recurrent OPAHs in the body of literature (ng/m^3)

Ambient air studies										
Studies	USA - Houston (1990-1991) [1]				Algeria Algiers (1998-99) [2]		Germany Munich (1996-1998) [3]	France – Marseille (July 2004) [4]		
Site characteristics	S	A	W	S	S	W	Urban	Urban	Sub-urban	Rural
1-naphthaldehyde	-	-	-	-		-	-	0-1.47 (0.48)	0.11-2.13 (0.81)	0-0.43 (0.18)
9,10-AQ	-	-	-	-	6.2	1	0.51-1.47 (0.96)	0.37-2.57 (1.39)	0.07-2.79 (0.77)	0.04-0.45 (0.18)
9-fluorenone	-	-	-	-	-	-	0.22-0.46 (0.35)	1.4-6.9 (3.6)	0.19-5.27 (2.1)	0.38-1.24 (0.88)
Benzanthrone	-	-	-	-	-	-	1.07-5.05 (2.50)*	0.1-0.54 (0.22)	0.02-0.48 (0.14)	0.004-0.06 (0.02)
BaA-7,12-O	0.07	0.13	0.08	0.04	-	-	0.16-0.85 (0.41)	0.06-0.23 (0.12)	0.01-0.19 (0.06)	0.005-0.03 (0.01)

Indoor and outdoor study		
Study	USA (1999) [5] 8 homes winter 86/87 (Mean indoor/Mean outdoor (ratio))	
Sampling characteristics	Non smokers homes	Smokers homes
9-fluorenone	7.19/4.55 (1.6)	14.27/3.63 (3.9)
Naphthalene-1,8-dicarboxylic acid	3.95/10.35 (0.8)	3.89/8.20 (0.5)
Pyrene carboxaldehyde	0.04/0.08 (0.5)	0.17/0.04 (4.2)
Pyrene-3,4-dicarboxylic acid	0.17/0.22 (0.77)	0.16-0.36 (0.4)
Benz(a)anthracene-7,12-dione	0.33/0.25 (1.3)	0.42/0.18 (2.3)

[1] *Wilson et al (1995), OPAHs concentrations in summer (S), autumn (A) and winter (W)*

[2] *Yassaa et al (2001), OPAHs concentrations in summer (S) and Winter (W)*

[3] *Schnelle-Kreis et al (2001), urban air concentrations, min-max (Mean)*

[4] *Albinet et al. (Submitted), urban (n=12), sub-urban (n=14) and rural (n=14) air concentrations (min-max (Mean))*

[5] *Chuang et al. (1991, 1999)*

* *Sum of benzanthrone and 1-Pyrenecarboxaldehyde*

1.3. Flame retardant (organophosphate esters)

1.3.1. Health effects

Although organophosphate esters are commonly found in indoor environments (Carlson *et al.*, 1997, Otake *et al.*, 2001, Salthammer *et al.*, 2003, Sjodin *et al.*, 2001), knowledge of the toxicity of this class of compounds is still limited. Tris(2-chloroethyl)phosphate (TCEP) has been known to cause acute toxicity of the central nervous system in experimental animals (Tilson *et al.*, 1990) and have carcinogenic properties (Matthews *et al.*, 1993). Contact allergy was demonstrated for triphenylphosphate .

1.3.2. Sources and concentration levels

Organophosphate esters (OPs) are used extensively as flame retardants or plasticizers. They are also used as additives in the manufacture of plastic materials, polyurethane, rubbers, cellulose derivatives or lubricants and may represent up to 30% of the weight of manufactured goods. Because organophosphate esters are not covalently bonded to the material, they are likely to migrate out from the material and to be released in the air in indoor environments.

Organophosphate flame retardant includes both halogenated and non-halogenated compounds. The global consumption of OPs was estimated at 186,000 tons in 2001, and consumption has increased sharply in recent years (Marklund *et al.*, 2005). Tris (2-chloroisopropyl) phosphate, Tri-n-butyl phosphate, Tris(isopropylphenyl) phosphate, 2,2-Bis(chloromethyl)trimethylene, bis(bis(2-chloroethyl)phosphate) and Tris (2-chloroethyl)phosphate are used extensively in Europe with annual tonnages exceeding 2000 tonnes/years and up to 23,000 tonnes/year for Tris (2-chloroisopropyl) phosphate (Fisk *et al.*, 2003).

Typical concentrations found in indoor air are provided in **Table 6**. It can be seen that some of these compounds, such as tributylphosphate (TBP), tris(2-chloroethyl)phosphate (TCEP) or Tri(chloropropyl)phosphate are ubiquitous in indoor air. Concentrations ranged from several ng/m^3 to thousands of ng/m^3. In a 50-building study including homes, school buildings and offices, Ingerowski *et al* (2001) found concentrations of TCEP up to 6000 ng/m^3 (data not shown).

Table 5: Concentrations levels in ng/m^3 of various OPs from several studies (min-max (occurrence))

Study	Sweden [1] (1997)	Japan [2] (2003)	Sweden [3] (2005)	Sweden [4] (2003)	Germany [5] (2003)	
Date and sampling site	**3 schools, day care, office (n=5)**	**27 houses**	**19 microenvironments including Homes, offices, library, prison, Plastic factories, hotel…**	**Library, New car, home, laboratory**	**Eight different new cars (car test stand**	
					Room temperature	**65°C**
Tributylphosphate	NQ	<1-100	<0.2-120 (95%)	4.1-138 (100%)	<10-150	160-2118
Tri(2-chloroethylphosphate)	11-250 (100%)	<1-380	0.4 -730 (100%)	11.4-110 (100%)	<50	<10-100
Tri(chloropropyl)phosphate:1	14-41 (100%)	NQ				
Tri(chloropropyl)phosphate:2	5.1-12 (100%°	NQ	10-570 (100%)	10-112 (100%)	<10-480	70-11100
Tri(chloropropyl)phosphate:3	ND-2.9 (80%)	NQ				
Triphenylphosphate	ND-0.8 (60%)	<1-70	<0.1-23 (68%)	0.5-35 (100%)	<10-90	<10-2230
Tri(2-butoxyethyl)phosphate	2.9-5.9 (100%)	NQ	<0.4-55 (52%)	0.7/45 (100%)	<50	<50-690
Tri(2-ethylhexyl)phosphate	ND-10 (20%)	NQ	<0.2-14 (20%)	2.75 (100%)	<10-90	<10-190
Tris(1,3-dichloro-2-propyl)phosphate	NQ	NQ	<0.2-150 (30%)	NQ	<10-200	70-8640
Di-n-octylphenyl phosphate	NQ	NQ	<0.3-4.8 (5%)	NQ	NQ	NQ
Tripropyl phosphate	NQ	NQ	<0.1-8.4/12	NQ	NQ	NQ

[1] *(Carlson et al., 1997)*, [2] *(Otake et al., 2004)*, [3] *(Marklund et al., 2005)*, [4] *(Sanchez et al., 2003)*, [5] *(Wensing et al., 2003)*
NQ: Not quantified

1.4. Phthalates

1.4.1. Health effects

The adverse health effects of phthalic esters have been the subject of a decade of controversy. While several phthalates, particularly diethyl hexyl phthalate (DEHP), have been shown to be testicular toxicants (Peters *et al.*, 1997), a recent study involving juvenile primates did not show testicular effects.

Other studies have shown that dibutylphthalate (DBP) act as an endocrine disrupter, and damages the reproductive system of male rats at low exposures (Foster *et al.*, 1997, Mylchreest *et al.*, 1999). DEP was also suspected of exhibiting endocrine disrupting effects and BBP appeared weakly oestrogenic in vitro .

Regarding the carcinogenic properties of phthalates, DEHP, which accounts for ca 50% of the total production of phthalic esters, was classified as possibly carcinogenic to humans (group 2B). Its downgrade to being classified as not carcinogenic to humans (Group 3) in 2000 resulted in considerable debate in the scientific community.

1.4.2. Sources and concentration levels

Phthalate is the generic name given to esters of 1,2 benzendicarboxylic acid. There are approximately 50 different phthalates esters which are used in industry, but only 8 of them are commercially significant , namely: dimethylphtalate (DMP), diethylphthalate (DEP), di-*i*-butylphthalate (DiBP), dibutylphthalate (DBP), benzylbutylphthalate (BBP), di-(2-ethylhexyl)phthalate (DEHP), di-*i*-nonylphthalate (DiNP) and di-*i*-decylphthalate (DiDP). The last two are not pure compounds, but consist of several isomers with alkyl carbon number of 9 and 10, respectively.

World global production has been estimated to be $2.7*10^6$ tonnes annually. The major use is as plasticisers for the production of polyvinyl Chloride (PVC), but they are also used extensively in industrial paints, inks, adhesives, defoaming agents and lubricating oils. Plasticisers are necessary to manufacture flexible PVC products and may constitute between 15 and 60% of the weight depending on the final application. Phthalates constitute the vast majority of plasticisers for PVC (93% in 1997) and approximately 900,000 tonnes are used annually in Western Europe (European Commission, 2000).

While the phthalates with low molecular weights (DMP, DEP, DiBP, DBP, BzBP) are used for their emulsifying properties, DEHP, DiNP and DiDP are principally incorporated in polymers (especially PVC) as plasticizers. Phthalates are not chemically bound to the end-products to which they are added. This has led to their significant spread throughout the environment. Typical concentration levels found in indoor air are presented in **Table 5.** It can be seen that phthalates are ubiquitous compounds in indoor air. Concentrations for most of the phthalates are around one $\mu g/m^3$, but concentrations levels of up to 15 $\mu g/m^3$ can be found in some homes.

Table 6: Indoor air phthalates concentrations in ng/m³ from various studies *

Study	USA (2001-2003) [1]	Japan (2004) [2]	Germany (2000) [3]		USA/Poland (2003) [4]	
	120 homes	27 homes	59 homes	74 kindergarten	30 participants from New-York	30 homes participants from Krakow
Diethylphthalate	130-4300 (100%) **590**	10-610 **100**	>10-5480 (100%) **643**	>10-1263 (100%) 353	1500-7100 **2700**	260-2900 **840**
Di-n-butylphthalate	52-1100 (100%) **220**	10-6180 **390**	>10-5586 (100%) **1083**	>10-13305 (100%) **1188**	110-4100 **400**	750-15000 **2300**
Benzylbutylphthalate	<31-480 (44%) **<DL**	<1-110 18	<10-575 (85%) <DL	<10-391 (25%)	10-630 40	ND-190 20
Bis(2-ethylhexyl)phthalate	<59-1000 (68%) **77**	<1-3130 **156**	>10-615 (100%) **156**	>10- 2253 (100%) **458**	50-410 **220**	80-1100 **370**
Dicyclohexylphthalate	-	<1-750	-	-	-	-
Dimethylphthalate	-	-	>10-13907 (100%) **436**	>10-13233 (100%) 331	-	-
Dimethylpropylphalate	-	-	>10-5887 **459**	>10-2659 **505**	-	-
Di-iso butylphthalate	-	-		-	30-1130 **370**	310-8100 **810**

* *Min-max (occurrence)* ***Median***

Occurrence: Number of samples above detection limit/total of samples (%)

[1] *Rudel et al (2003),*

[2] *Otake et al (2004)*

[3] *Fromme et al (2004a)*

[4] *Adibi et al (2003)*

1.5. Alkylphenols

1.5.1. Health effects

Despite the fact that some alkylphenols have been identified as hormonally active agents, the determination of these compounds has received little attention. The hormone disrupting effect of alkylphenol was first demonstrated in the 1930s (Dodds *et al.*, 1938), but concerns for human health really began in 1991 when the oestrogenic effect of nonylphenol was accidentally discovered (Fenske *et al.*, 1990). The same conclusion was drawn by White *et al* (1994).

1.5.2. Sources and concentration levels

Alkylphenols (APs), like organophosphates and phthalic esters, are used as polymer additives and hence they are likely to be released in indoor environments. They act as heat stabilizers for polymer resins. They are also used in the manufacture of varnish and lacquer resins, disinfectant and fungicide for impregnation of fruit wrappers, and household disinfectants. Alkylphenols can also be released into the environment by the microbial breakdown of alkylphenol ethoxylates (APEs), which are used in household detergents, dispersing agents in papers, emulsifying agents in the latex paints, glue and pesticides preparation.

The main route of exposure to humans appears to be via contaminated drinking water, but their occurrence in the atmosphere could also be an important source. A study carried out in the New York and New Jersey urban atmosphere has found that alkylphenol can be transferred to the air by vaporisation from river water (Dachs *et al.*, 1999). The authors found concentrations of nonylphenol varying from 2.2 to 70 ng/m^3.

Very little information is available in the existing literature about APs in indoor air. The first data found in the literature were published by Rudel *et al* (2001). They found several APs and APEs in residential air at concentrations up to 100 ng/m^3. A recent study by Saito *et al* (2004) carried out in both indoor and outdoor air has shown that compounds such as 4-tertbutylphenol, 4-tert-octylphenol or 4-nonylphenol are ubiquitous in indoor air and that concentration levels as high as 600 ng/m^3 could be found in homes (**Table 7**). Outdoor concentrations were much lower, thus confirming that the main pathway to human exposure for this chemical class is in indoor environments.

Table 7: Concentration levels in ng/m^3 of several APs (min-max (occurrence) Median)

Studies	Japan [1]			USA [2]	USA [3]
	45 Houses (n=90)	19 Office buildings (n=38)	Outdoor (n=33)	120 homes	Mobile trailer, office buildings, residence (n=6)
4-t-BP	<2.4-387 (99%) 69	10.3-88.4 (100%)30.8	<2.4-6.1 (26%)	NQ	11-48 (100%) 31
4-OP	<3.2-45.7 (52%) 7.6	<3.2-30.5 (71%) 5.7	<3.2-5.3 (6%)	NQ	7 (30%) 7
4-NP	<4.5-680 (98%) 125	11.0-555 (100%) 95.2	<4.5-53.1 (42%) 7.5	21-420 (100%)110	ND-118 (30%)

[1] Saito et al (2004), [2] Rudel et al (2003) [3] Rudel et al (2001)
ND: Not detected
Occurrence: Number of samples above detection limit/total of samples (%)

1.6. Pesticides

1.6.1. Health effects

The full health risks associated with pesticides are unknown. Most pesticides have never been systematically reviewed for their full range of potential human health effects.

However, it is recognised that many pesticides may have adverse health effects for humans such as potential carcinogens, reproductive effects, and damage to the nervous, endocrine, or immune systems. Laboratory studies conducted on animals have linked chronic exposure to pesticides to birth defects, tumour development and cancers. The EPA has classified approximately 165 chemical pesticides as known, probable or possible human carcinogens.

It is now recognised that infants and children are more susceptible to the effects of pesticides than adults. They are less tolerant to chemicals and they are generally exposed to greater doses than adults. Early developmental stages of their organs, nervous systems, and immune systems, greater rates of cell division and their lower body weight increase their vulnerability to pesticide exposure. Children have a tendency to explore their environment with their mouths, and are consequently exposed to high concentrations of pesticide residues contained in house dust. Concentrations in children's breathing zones are also generally higher than in adult's breathing zones.

1.6.2. Sources and concentration levels

Little is known about pesticide use and exposure in indoor environments despite the fact that pesticides are widely used in homes. They are used to reduce many household pests, including those associated with indoor plants, pets, and wood and woollen products. Polluted outdoor air due to agricultural pesticide application can also penetrate indoors. They are sold as sprays, powders, crystals, balls, and foggers. The majority of household pesticides belong to 4 chemical classes, namely organophosphates, carbamates, pyrethroïds and organochlorines. Organochlorine pesticides were used extensively in the past because they were effective against a wide range of pests. However, nowadays most of them are prohibited for use as household pesticides because they are not readily broken down in the environment and accumulate in humans and animals.

Table 8 summarises concentration levels and occurrence of the target compounds from the study by Rudel *et al* (2003), as well as concentrations for these pesticides from various studies.

Table 8: Concentrations of selected pesticides from various studies in ng/m³ (min-max (Occurrence) median)

Study	USA (2002)[1] (n=72)	USA (2003)[2] (n=120)	France (2001)[3] (n=9)
	Organophosphates		
Chlorpyrifos	0.7-193 (100%) 9.9	ND-92 (38%) ND	(0%)
Diazinon	2.0-6100 (100%) 159	ND-550 (40%) ND	ND-45 (22%) ND
Methyl parathion	ND-0.9 (4%) ND	ND-92 (6%) ND	ND-3.7 (22%) ND
	Carbamates		
Propoxur	3.9-1380 (100%) 33.1	ND-110 (47%) ND	0-282 (22%) ND
Carbaryl	ND-0.7 (2%) ND	ND-22 (11%) ND	(0%)
	Pyrethroids		
Pyperonyl butoxide	ND-11.1 (83%) 0.5	ND-110 (6%) ND	NQ
Permethrin cis	ND-2.8 (33%) ND	ND-3.7 (3%) ND	(0%)
Permethrin trans	ND-7.0 (47%) ND	ND-5.4 (3%) ND	(0%)
	Organochlorines		
4,4'-DDT	ND-4.0 (68%) 0.3	ND-30 (10%) ND	(0%)
4,4'-DDE	ND-2.2 (68%) 0.2	ND-5.1 (3%) ND	
4,4'-DDD		ND-3.5 (3%) ND	ND-0.7 (11%) ND
γ-chlordane	ND-2.5 (78%) 0.3	ND-83 (53%) 0.22	(0%)
α-chlordane	ND-1.8 (58%) 0.1	ND-61 (51%) 0.1	(0%)
Carbaryl		ND-22 (11%) ND	(0%)
Hepatchlore	(0%)	ND-71 (44%) ND	ND-0.1 (22%) ND
Lindane	ND-3.2 (2%) ND	ND-110 (1%) ND	ND-0.9 (88%) 1.0
Endosulfan	(0%)		0.1-2.3 (77%) 0.2
	Fungicides		
2-phenylphenol	5.7-743 (100%) 23.7	71-970 (100%) 71	NQ

[1] Whyatt et al (2002), [2] Rudel et al (2003), [3] Blanchard (2001)
ND: Not detected
Occurrence: Number of samples above detection limit/total of samples (%)

Pesticide residues in indoor air are generally of the order of several ng/m^3 but can reach levels of several $\mu g/m^3$ in some homes. Very high concentrations are generally found after application in the homes. Fenske *et al* (1990) have measured concentrations of Chlorpyrifos of 60 $\mu g/m^3$ 5 hours after application of this pesticide for flea treatment. They also found that concentrations in infants' breathing zones were substantially higher (94 $\mu g/m^3$) than in adults breathing zones, thus confirming that children are more exposed to pesticides than adults.

1.7. Selected target compounds

The chemical families selected for this study include a huge number of molecules. In order to demonstrate the feasibility of the method for personal and indoor air measurements, a limited number of molecules were selected based on several criteria:

- ✔ molecules likely to be present in indoor air at concentrations detectable with the developed method
- ✔ molecules that are potentially harmful to human health
- ✔ cover a broad range of volatility in each chemical family in order to include gaseous and particulate molecules

Target molecules selected for this study are listed in **Table 9.**

Table 9: Selected target compounds

Chemical	ACR	MW	Boiling point (°C)	Toxicity	Chemical	ACR	MW	Boiling point (°C)	Toxicity
Polycyclic aromatic compounds (PAHs)									
Naphthalene	Nap	128	218	Class C	Triphenylene	TriP	228	438	Class D
Acenaphthylene	AcNP	152	265	Class D	Chrysene	Chr	228	448	Class B2
Acenaphthene	AcN	154	279	Class D	Benzo(b)fluoranthene	BbF	252	457	Class B2
Fluorene	Fl	166	295	Class D	Benzo(j)fluoranthene	BjF	252	470	Class B2
Phenanthrene	Phe	178	340	Class D	Benzo(k)fluoranthene	BkF	252	480	Class B2
Anthracene	Ant	178	340	Class D	Benzo(a)pyrene	BaP	252	495	Class B2
Fluoranthene	Flu	202	375	Class D	Indeno(1,2,3-cd)pyrene	IP	276	525	Class B2
Pyrene	Pyr	202	404	Class D	Dibenzo(a,h)anthracene	DahA	278	527	Class B2
Benzo(a)anthracene	BaA	228	437	Class B2	Benzo(g,h,i)perylene	BghiP	276	532	Class D
Oxygenated polycyclic aromatic compounds (OPAHs)									
1-naphthaldehyde	1-Nap	156	292	mutagen	9-phenanthrenecarboxaldehyde	9-PheC			mutagen
9-fluorenone	9-FlO	180	342	mutagen	Benzanthrone	BAO	230	-	mutagen
9,10-anthraquinone	9,10-AQ	208	380	mutagen	Benz(a)anthracene-7,12-dione	BaA-7,12-O	258	-	mutagen
Organophosphate esters									
Tributylphosphate	TBP	266	289	HAA	Tris(2-chloroethylphosphate)	TCEP	285	330	HAA
Phthalalic esters									
Dimethylphthalate	DMP	194	284	HAA	Butylbenzylphthalate phthalate	BBP	312	370	HAA
Diethylphthalate	DEP	222	298	HAA	Bis(2-ethylhexyl)phthalate	DEHP	390	387	HAA
Dibutylphthalate	DBP	278	340	HAA					
Alkylphenols									
4-tertbutylphenol	4-t-BP	150	237	HAA	4-nonylphenol	4-t-NP	220	-	HAA
4-octylphenol	4-t-OP	206	-	HAA					
Pesticides									
2-phenylphenol	2-PP	170	282	HAA	Methyl parathion	MPara	263	-	HAA
Propoxur	ProP	209	-	HAA	Endosulfan I	End II	407	-	HAA
Diazinon	DiaZ	304	306	HAA	Permethrin cis/trans	Perm	391	-	HAA

[1] *USEPA, Class B2: probably carcinogen to human, Class D: Not Classifiable as to Human Carcinogenicity, HAA: Hormonally active agents*

Chapter 2: Sampling and analytical method for personal and indoor air SVOCs measurements

Personal sampling refers to the procedure whereby air is sampled within the person's breathing zone. Both human activity and time is taken into account when sampling with personal samplers. A sensitive analytical technique should be used to compensate the low sampling volume available with personal pumps. The limits of the traditional solvent extraction based method and a review of the studies based on a thermal procedure to analyse semivolatile compounds are presented in this chapter.

2.1. Personal sampling method for SVOCs

2.1.1. Criterion to select the personal sampler

The sampler should be equipped with a filter and an adsorbent cartridge to collect both the particulate and gaseous phases, respectively. Association between particulate matter concentrations and morbidity has primarily been demonstrated for Total Suspended Matter (TSP) and the coarse fraction PM_{10} (particles with the mean diameters smaller than 10 μm) (Schwartz *et al.*, 1992). The $PM_{2.5}$ fraction is now considered to cause even more serious health treat because fine particles can be inhaled and deposited more deeply in the lung than the coarse fraction (Dockery *et al.*, 1993, Pope *et al.*, 1995). In addition, particle organic mutagens have been shown primarily in association with fine particles (Allen *et al.*, 1996, Hughes *et al.*, 1998, Pagano *et al.*, 1996). It was therefore decided to use a $PM_{2.5}$ sampling head in this study.

2.1.2. Available personal samplers

The first sampler devoted to SVOCs sampling was developed in the early 1980s. Lewis *et al* (1982) developed a personal sampler for pesticides and related semivolatile compounds. This sampler was equipped with a filter and PUF cartridge, but no particle size selector was available. Other samplers specially designed for the collection of SVOCs for both the gaseous and particulate phases were also developed, but none of them were equipped with a particle size selector (Clausen *et al.*, 1997, Noto *et al.*, 1996). Development of personal particle size selector began in the late 1990s when it started to be accepted that the fine fraction $PM_{2.5}$ represented a more serious threat to human than larger particles. Available personal $PM_{2.5}$ sampling monitors found in the literature are listed in **Table 10.**

To date, the URG corp samplers (URG-2000-25 and URG-2000-15T) are the only ones specially designed to collect both phases. Details of these sampling head/samplers are provided in **appendix 2.** Other particles size selectors were only developed to collect the particulate phase. The MSP $PM_{2.5}$ was fitted with a PUF cartridge to sample PAHs in both fractions. Up to now, none of the available samplers designed to collect both gaseous and particulates semivolatile organic compounds are compatible with a thermal desorption procedure.

Table 10: Available personal sampling equipped with a $PM_{2.5}$ sampling head

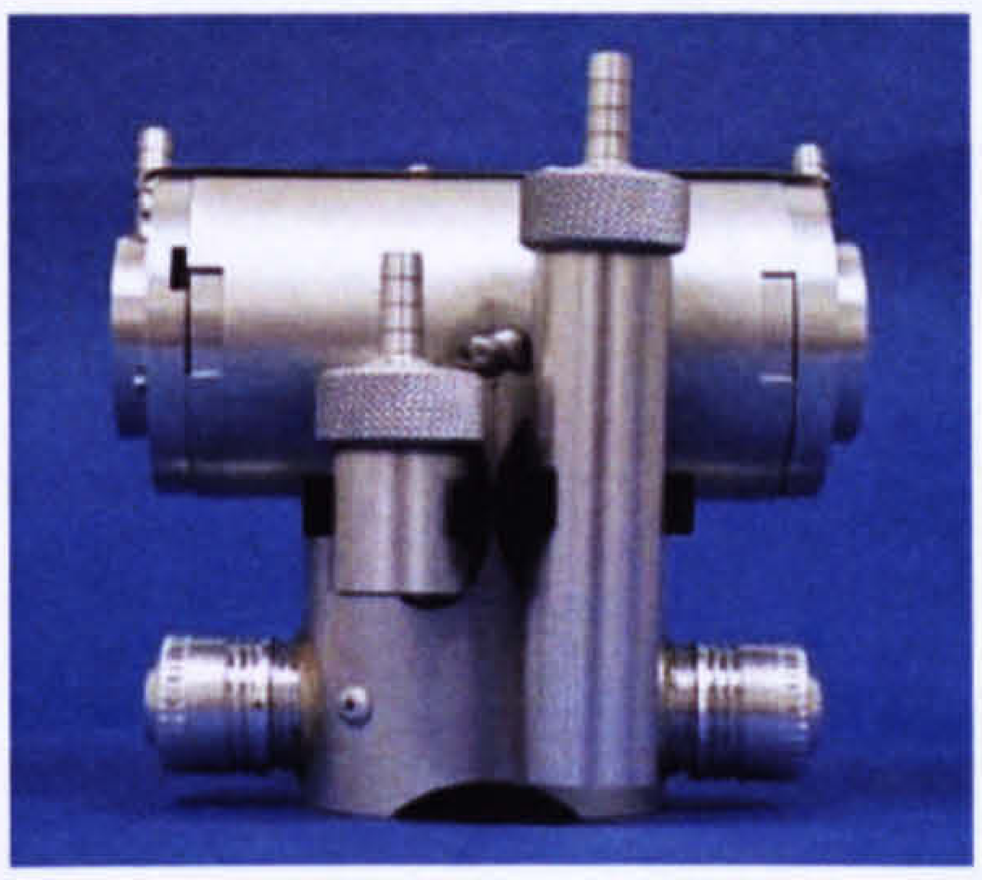
Sampler	Sampling conditions	Sampling media		References
	Flow rate (LPM)	Filter diameter	Adsorbent	
Chempass	2.0 or 4.0	37	No	Liu *et al.*, 2003, Meng *et al.*, 2005
BGI GK2.05	4	37	No	Expolis study (e.g. Koistinen *et al.*, 1999
SIBATA ATPS-20	1.5	37	No	Ohura *et al.*, 2005
Modified MSP	2.0/4.0/10	37	PUF	Naumova *et al.*, 2002 Naumova *et al.*, 2003
MSP (PEM)	2.0/4.0/10	37	No	Fischer *et al.*, 2000 Meng *et al.*, 2005
URG-2000-25	2.0 or 4.0	25	PUF	Rudel *et al.*, 2001 Rudel *et al.*, 2003 Tonne *et al.*, 2004
URG-2000-15T	1.5/1.7/2.0	25	XAD-2 (2.0 g)	Williams *et al.*, 1999

2.1.3. Description of selected personal sampler

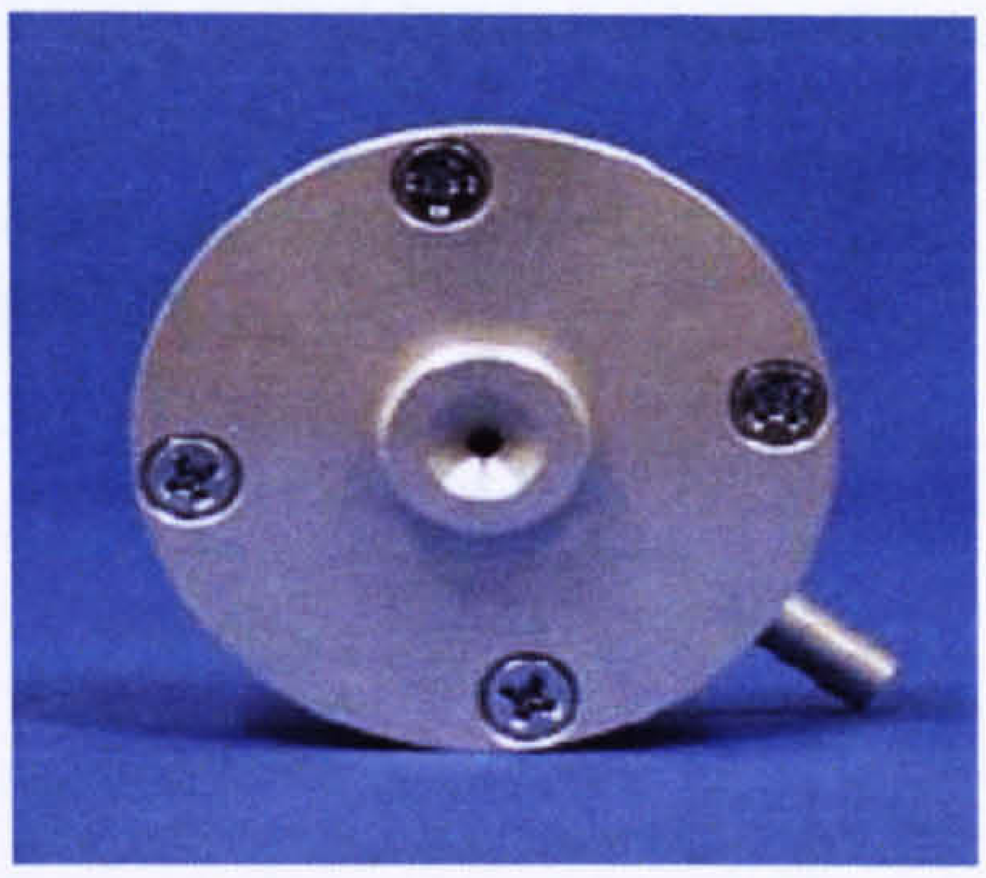
It was first thought to use the URG-2000-15T samplers because this sampler specially designed for SVOCs collection could be easily modified to replace the solvent extraction cartridge by a thermal desorption tube. Connection between the filter holder and the thermal desorption tube could be done by mean of a SVL fitting. However, an evaluation by the US-EPA (Williams *et al.*, 1999) has shown that the aerodynamic cut-point of the impactor was only of 1.7 µm. Since one of the criterion to select the sampling head was the collection of the $PM_{2.5}$ fraction, it was decided to select another one for true $PM_{2.5}$ measurements.

The $PM_{2.5}$ impactor of the multi-pollutant Chempass sampler Model 3400 **(Picture 1)** was selected. In its original configuration the Chempass sampler consists of two impactors ($PM_{2.5}$ and PM_{10}) for gravimetric measurements on 37 mm diameter filters, a $PM_{2.5}$ impactor for organic and elemental carbon measurements onto 15 mm diameter filter, a denuded $PM_{2.5}$ impactor for particulate and sulphate measurements onto 15 mm diameter filter and a two Ogawa passive samplers to measure gaseous co-pollutants such as nitrogen dioxide (NO_2), sulphur dioxide (SO_2) or ozone (O_3).

(a)



(b)



Picture 1: (a) Chempass sampler (b) $PM_{2,5}$ impactor of the Chempass sampler

This impactor was selected for this study for the following reasons:

- ✔ Among all the commercially available personal sampling heads, the impactor of the Chempass sampler is the the most thoroughly studied. The performances of this impactor have been well characterised in both laboratory tests and field studies (Demokritou *et al.*, 2001, Li *et al.*, 2003).
- ✔ Minor modifications of the impactor were required to incorporate a thermal desorption tube to collect the gaseous phase.
- ✔ This sampler was available at INERIS, thus no extra investment was necessary to perform the demonstration study.

The modified sampling system is depicted in **Picture 2**. It consists of a single stage inertial impactor with a 50% cut point of 2.4 at 1.8 l/min, a Teflon T to limit the flow through the sampling tube in order to prevent exceeding the safe sampling volume and to limit the backpressure so that battery capacity can be extended for long sampling periods. The Teflon T and the outlet of the impactor were connected by means of a 6 mm Teflon tubing. A manifold is used to finely regulate the flow through the bypass and sampling tubes. It is equipped with a high capacity NiMH battery and a highly consistent pump design to maintain constant volumetric flow rate with increasing back pressure due to filter loading. The sampling system was placed in an insulating box for noise reduction and to protect the system. The overall weight of the sampling system in the backpack is less than 3 kg. The total volume for a 24-hour sampling period is 2.6 m^3 for the particulate phase and 0.72 m^3 for the gaseous phase (only 0.5 l/min were passed through the sample tube to limit backpressure). Although the Chempass sampler is not accredited as a reference sampler (none of the developed personal samplers are currently accredited as standard reference samplers in both the EU and US), the

Chempass sampler was fully evaluated by Demokritou *et al* (2001) through a series of laboratory tests. They found that collection efficiency approached nearly 100% for particles larger than the $PM_{2.5}$ cutpoint when using grease as an impaction media.

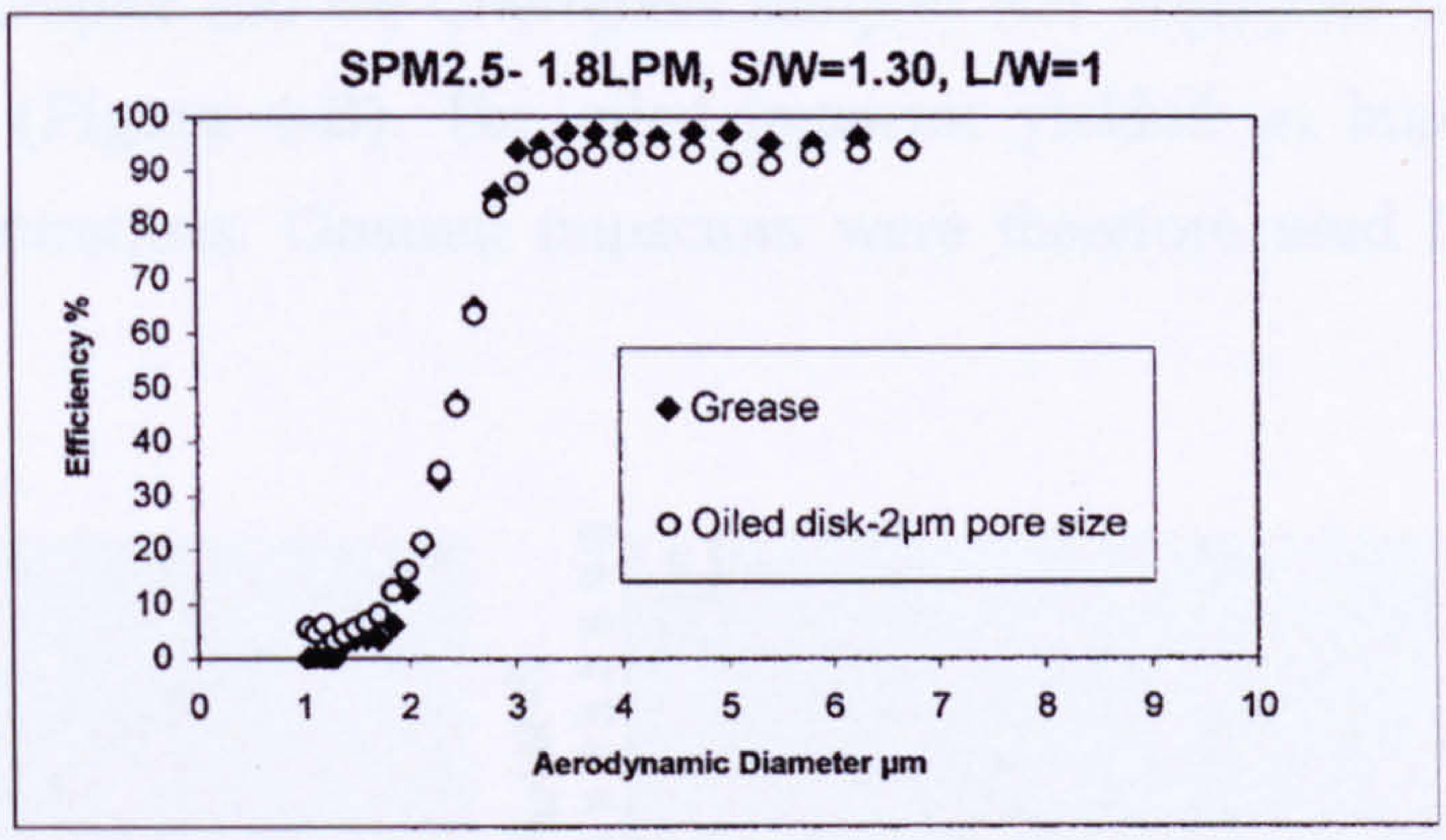
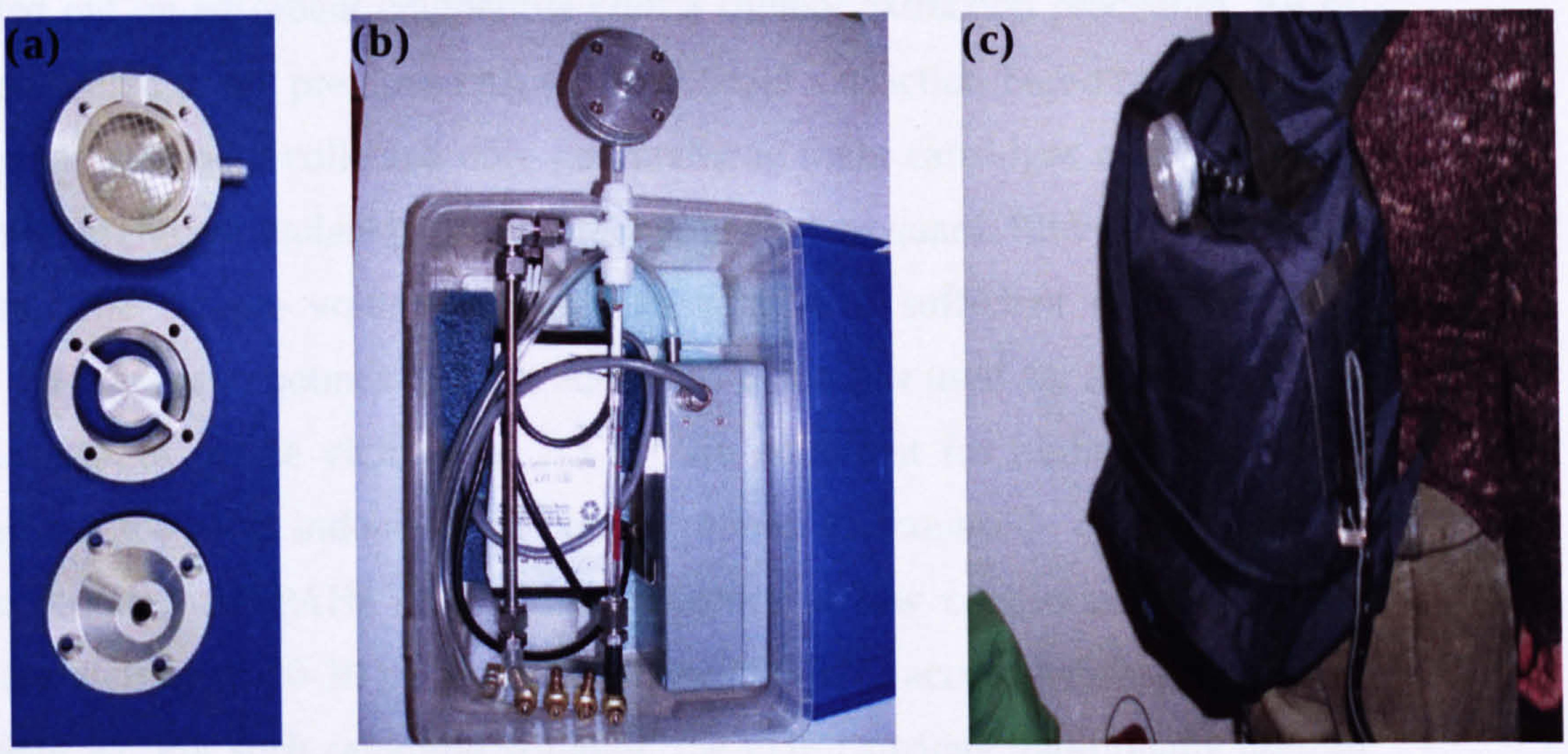


Figure 3: Collection efficiency for the $PM_{2.5}$ Chempass sampling head (From Demokritou *et al* (2001))

It can be seen **Figure 3** that this impactor has reasonable sharp cut characteristics with cut-off points close to the theoretical design value of 2.5 µm. Particle nozzle and wall losses were below 5% (data not shown). Liu *et al* (2003) have conducted a two-year comprehensive exposure assessment study that examined PM exposure and health effects in 108 participants. During this campaign, they compared the performance of the Chempass sampling (4 l/min) head with a Federal reference method (FRM) sampler for ambient air collection of PM. The design of the 4 l/min Chempass sampler is identical to the sampler used in this study (1.8 l/min); it can therefore be expected that both samplers will behave similarly in terms of performance.



Picture 2: Description of the sampling system used in this study (a) Inner components of the impactor (b) Sampling system with impactor, sampling tube, bypass tube, manifold, pump and battery (c) sampling system in the backpack for sample collection

They found that Chempass concentrations were underestimated by 12% compared to the reference sampler (**Figure 4-A**). The size of the difference between these two samplers is acceptable and is common between collocated samplers. They found that the bias between the low flow sampler and the Chempass sampler was negligible when a greased impactor was used (**Figure 4-B**). The oiled impactor yielded an important overestimation of the concentrations. Greased impactors were therefore used in this study.

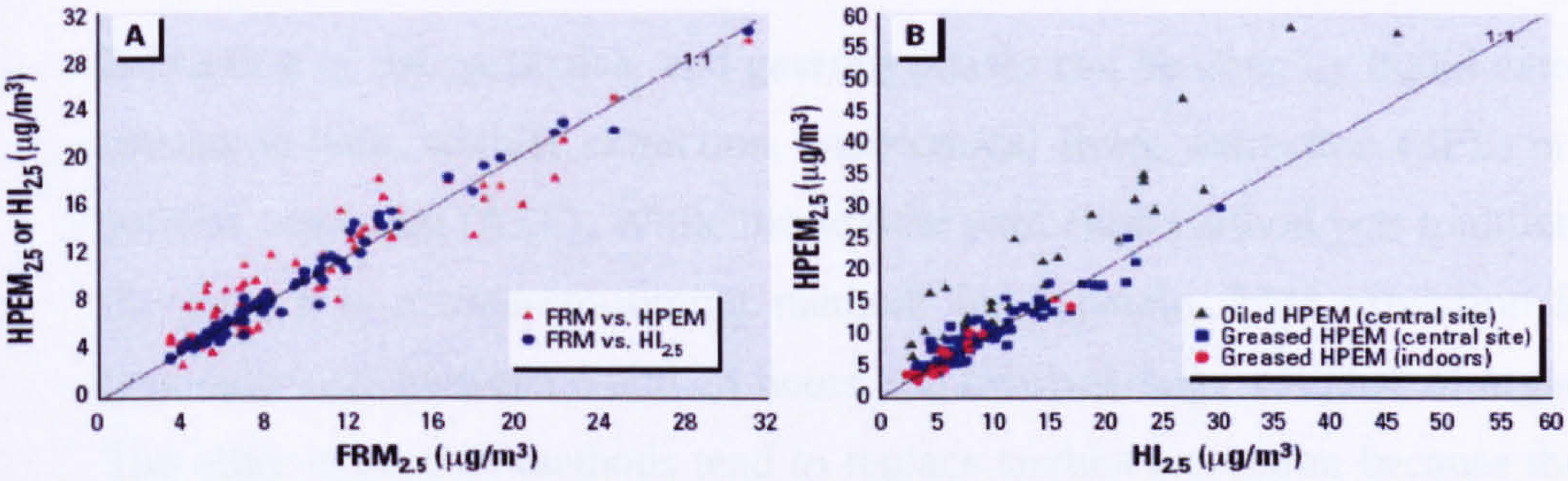


Figure 4: Comparison between a low flow sampler (HI), the Chempass sampler (HPEM) and a federal reference sampler (from Liu *et al* (2003))

2.2. Analytical method for SVOCs measurements in indoor or personal air samples

2.2.1. Solvent extraction based method

Collection of SVOCs present in the gas phase in indoor or personal sampling studies is mainly carried out on adsorbent compatible with a solvent extraction procedure. All of the studies presented in the previous chapter are solvent extraction-based methods. The gaseous phase is generally collected onto polyurethane foam cartridges or XAD resins to a lesser extent. The particulate phase is either collected on quartz filter fibre (QFF) or Teflon filters. The sample volume required to achieve a sufficient detection limit depends on the target compounds and the analytical technique used for analysis. While low sample volumes in the vicinity of 2-3 m^3 are sufficient for phthalates analyses because they are found in indoor air at concentrations of thousands of ng/m^3, larger volumes are required for PAHs due to their presence at low concentrations. Sample volumes in the vicinity of 20-30 m^3 are generally required for accurate measurements of PAHs in indoor air. For such sampling volumes, the PUF cartridge traditionally used to collect the gaseous phase is prone to breakthrough for low boiling point compounds. Naumova *et al* (2002) observed a severe breakthrough for the lowest PAHs.

Breakthroughs varied between 42% and 56% for the four lightest PAH (naphthalene, acenaphthylene, acenaphthene and fluorene).

Sample collection generally lasts 2 days due to the low flow rate sampling pumps used in indoor air. Low sampling pumps are used in indoor microenvironments such as homes because high volume samplers equipped with high flow sampling pumps are noisy and cumbersome. In addition, sampling of high volumes in a closed environment often results in a reduction of the concentration because of the air exchange between indoor and outdoor air.

Extraction of the particulate and gaseous phases can be done by liquid extraction using ultrasonic bath, soxhlet extraction, supercritical fluids extraction (SFE) or accelerated solvent extraction (ASE). While the soxhlet extraction method was traditionally used in the past, it is a time-consuming method; for example, PAH extraction from a filter generally lasts between 6 and 24 hours and involves large volumes of organic solvents. The other extraction methods tend to replace soxhlet extraction because they are much faster (extracting time can be reduced to between 30 minutes and 2 hours) and they are consume less solvent. Extracts are then evaporated and made up to a known volume of solvent. Purification steps using a solid phase extraction cartridge (SPE) or other purification technique are sometimes used to eliminate interfering compounds.

Two techniques are commonly used to analyse SVOCs: (i) gas chromatography (GC) and (ii) high performance liquid chromatography (HPLC).

PAH analyses in indoor air studies are based exclusively on HPLC coupled to a fluometric detector (HPLC-fluo) or on GC coupled to a mass spectrometer detector (GC/MS). Hot split/splitless injection is traditionally used as the injection technique for GC/MS injection, but recently a newly injection technique referred to as large volume injection has been applied for PAH measurements by GC/MS (Bornehag *et al.*, 2005, Norlock *et al.*, 2002). The method quantifiable limits (MQL) from various studies in indoor air as well as estimated MQL achievable with the personal sampler used in this study for these 3 analytical techniques are provided in **Table 11.** By comparing the concentration levels obtained in the various indoor air studies **(Table 2)** and the MQL provided in **Table 11,** it can be observed that these three methods are sufficiently sensitive for indoor air studies, but only the GC/MS method, based on large volume injection, could be applied for accurate measurement of personal samplings.

As stated before, solvent extraction based methods are very time consuming (even if modern extraction techniques such as ASE greatly reduce extraction time) and the detection limit achieved with the conventional HPLC or GC/MS analytical techniques are not sufficiently low for accurate personal sampling measurements at the low ng/m^3

level. This method also suffers from being prone to evaporation of low volatile during the volume reduction procedure and high molecular species may adsorbed over the glassware during the extraction steps. Careful attention should be paid to the sample preparation procedure and recovery factors must be accurately determined to compensate these losses. Recovery factors correspond to the percentage of analyte recovered during the solvent extraction step. An example of recovery factors for different support media calculated for n-alkanes and PAHs using a rapid vacuum evaporator is provided in **Figure 5.**

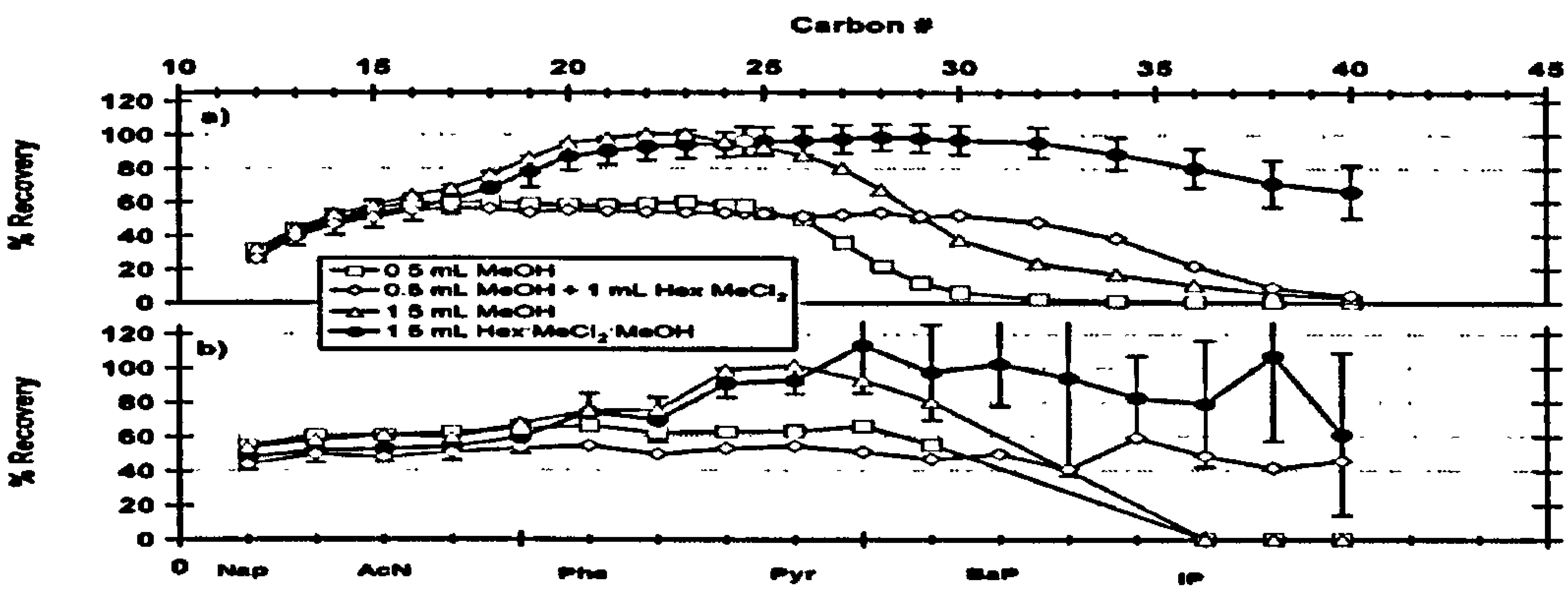


Figure 5: Recovery of n-alkanes (a) and PAHs (b) from a solvent extraction procedure (from Swartz *et al* (2003))

The recovery for both n-alkanes and PAHs increases with molecular weight until they reach a plateau and then decrease steadily. Poor recovery of low volatile is the result of irreversible losses during the reduction of the volume, while poor recovery of high molecular weight compounds is accounted for by adsorption over the wall of the flask. Spiking filters is not recommended to determine recovery factors for n-alkanes and PAHs associated to PM because n-alkanes more volatile than n-C17 and PAH more volatile than fluoranthene evaporate during the spiking procedure. These losses increase the detection limit of low volatile species and increase the uncertainty and precision of this method.

Table 11: Method detection limit (MQL) for three analytical techniques based on solvent extraction (ng/m³)

	HPLC-Fluo [1]		GC/MS (split/splitless injector) by TO13-A [2]		GC/MS (large volume injector) [3]	
Final volume of the extract (ml)	0.5		0.2		2	
Injection volume (µL)	20		1		60	
Sample volume (m³)	24	2.5 *	19 (48 hrs)	2.5 *	28.8 (24 hrs)	2.5 *
Naphthalene	-		-	-	0.136	1,57
Acenaphthene	0.01	0.08	-	-	0.015	0,17
Acenaphthylene	0.02	0.19	1.2	9.12	0.008	0,09
Fluorene	0.02	0.15	-	-	0.145	1,67
Phenanthrene	0.04	0.34	2.1	15.96	0.027	0,31
Anthracene	0.01	0.13	0.16	1.21	0.016	0,18
Fluoranthene	0.04	0.41	0.56	4.18	0.05	0,58
Pyrene	0.04	0.38	0.28	2.12	0.02	0,23
BaA	0.02	0.23	0.08	0.61	0.011	0,13
Chrysene	0.01	0.10	0.08	0.61	0.012	0,14
BbF	0.03	0.24	0.08		0.007	0,08
BkF	0.01	0.13	0.08	0.69	0.004	0,05
BaP	0.01	0.13	0.04	0.31	0.004	0,05
IP	0.03	0.24	0.07	0.53	0.012	0,14
DahA	0.02	0.22	-	-	0.008	0,09
BghiP	0.02	0.17	0.12	0.92	0.011	0,13

** Estimated method quantifiable limit (MQL) estimated for the personal sampler used in this study (sample volume of 2.5 m³ for the particulate phase)*
[1] Albinet, (2005). MQL= 10 x signal/noise of the lowest concentration standard.
[2] CARB (1992), [3] Norlock et al(2002). MQL=sd x $t_{0.99}$ from cartridges spiked with low levels of analytes. Loaded cartridges went through the entire sample procedure.

2.2.2. Thermal desorption based method

Solvent extraction-based methods are labour intensive and time consuming. They are also prone to contamination from solvent impurities and large quantities of solvent make this approach an environmentally unfriendly practice. Due to the low sample volume available with personal pumps, the analytical methods traditionally used lack sensitivity. The large volume injection method combined with GC/MS analysis is sufficiently sensitive for low volume samples, but the sample preparation is demanding. The alternative method to the solvent extraction approach is to use elevated temperatures as a means to transfer organics from filters or adsorbents to the analytical system.

2.2.2.1. Thermal desorption of the gaseous phase

While thermal desorption is used extensively to analyse VOC, collection of SVOCs on adsorbents compatible with a thermal desorption procedure has been carried out on very few occasions. Most of the studies have been carried out on specific compounds such as pesticides in contaminated atmospheres (Briand *et al.*, 2002, Cessna *et al.*, 1993, Clement *et al.*, 2000) or phthalic esters in artificial atmospheres or indoor air (Afshari *et al.*, 2004, Kang *et al.*, 2005, Uhde *et al.*, 2001). Analysis of a wider range of compounds is even rarer (Chan *et al.*, 1990, Clausen *et al.*, 1997, Ligocki *et al.*, 1985). In these studies, sampling of the gas phase was performed using Tenax TA. Clement *et al* (2000) found, in a comparative study, that Tenax TA yielded better result than other adsorbents tested (Carbopack Y, Carbopack B, Carbotrap B, Carboxen and chromosorb 106) in term of desorption recovery for volatile and semivolatile pesticides. Although little is know about the performance of Tenax TA for semivolatile measurements, its thermal stability is well-recognised and as a consequence, it is the preferred adsorbent for the analysis of SVOCs by thermal desorption.

Tenax TA belongs to the porous polymeric adsorbent family originally synthesised for use as resin in HPLC. It is a macroporous, semi-crystalline polymer manufactured from diphenyl-p-phenylene oxide. Its structure is shown in **Figure 6.**

It has a relatively low surface area (about 35 $m^2\ g^{-1}$); as a consequence, it is inadequate in high concentration atmospheres, but very appropriate when monitoring ambient or relatively unpolluted indoor air.

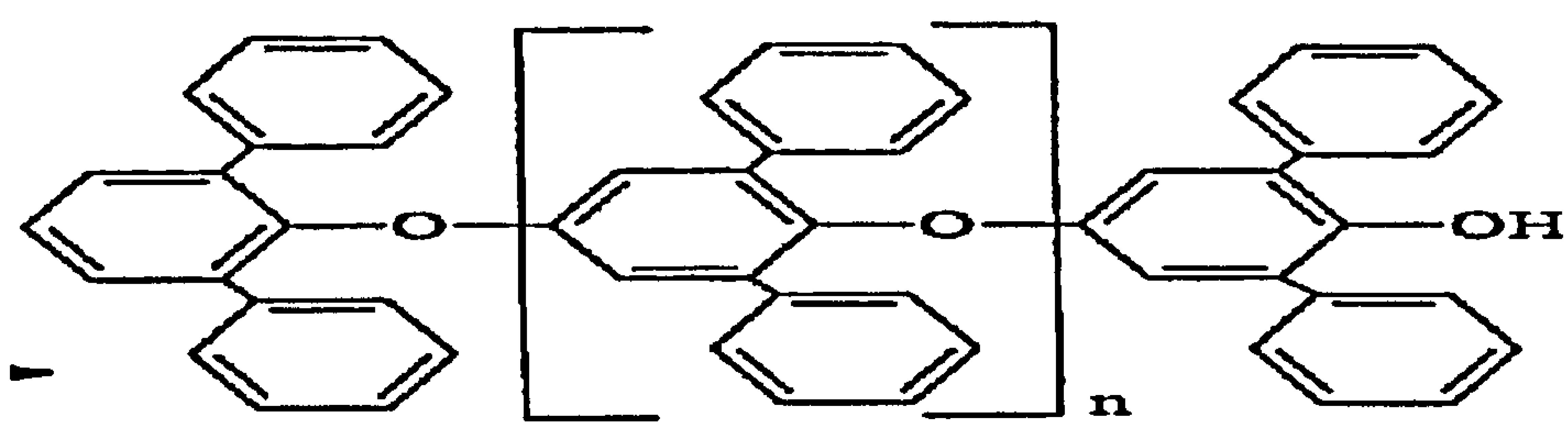


Figure 6: Chemical structure of Tenax TA

The suitability of an adsorbent for air sampling depends on the physical and chemical properties of both the adsorbent and the analytes. The first criterion that an adsorbent should satisfy when it is selected for an application is its sampling capacity. A sufficient volume of air should be quantitatively sampled to meet the desired detection limit, but there are also other important parameters:

✓ ***Sampling capacity of an adsorbent can be evaluated*** by placing two tubes in series and sampling the desired volume of air. A quantitative sampling is performed if no analytes are present in the second tube. This method is useful but does not give any indication of the maximum sampling achieved on the adsorbent. Afshari *et al* (2004) were able to sample 440 l onto Tenax TA (200 mg) tubes without breakthrough for di(ethylhexyll)phthalate (DEHP).The sampling capacity of an adsorbent is generally determined experimentally in artificial atmospheres through breakthrough volume studies. Contrary to field experiments, breakthrough volume enables estimation of the determination of the maximum sample volume that provides a quantitative sampling. Details of breakthrough measurements methods are described in detail in **chapter 3.1.**

Many studies can be found in the literature regarding BTV determination on this adsorbent for VOCs, but data for SVOCs is limited. A breakthrough volume (BTV) of 100 l per gram of adsorbent at 20°C for naphthalene was estimated using an indirect method (SIS scientific, Online). Care should be taken when breakthrough volume are estimated through this method because the influence of environmental parameters is not taken into account (e.g. competitive effects of other molecules or humidity). However, this data indicates that this adsorbent seems sufficiently strong for large volume sampling of naphthalene, which is the lightest PAH target compounds.

✓ ***Desorption or recovery efficiency*** is defined as the percentage of analyte recovered by the desorption step. Tenax TA has been shown to have a good desorption recovery for selected PAHs. Brussol *et al* (1999) efficiently recovered naphthalene and phenanthrene from this adsorbent. Good desorption recovery seems possible for heavier PAHs. Clausen *et al* (1997) obtained good recovery for pyrene on the same adsorbent. Efficient recovery was obtained for 16 semivolatile pesticides by Briand *et al* (2002). The adsorbent Tenax TA also appears suitable for phthalic esters (Afshari *et al.*, 2004, Clausen *et al.*, 1997, Kang *et al.*, 2005, Uhde *et al.*, 2001).

✓ ***Storage stability*** is defined as the ability of an adsorbent to retain an analyte without appreciable losses over a period of time and under normal storage conditions. Samples taken in the field can not be analysed immediately and are often stored for a couple of days or even weeks. The bibliographic search did not give any indication on the storage stability of Tenax TA for SVOCs. De bortoli *et al* (1992) found good recovery of VOC after fifty days of storage at room temperature and –15°C. SVOCs being less volatile than VOCs, it can be reasonably assumed that no significant losses will appear during storage.

✓ ***The affinity of the adsorbent for water*** is an important parameter when analysing the sample tube with a system using a cryogenic trap. The capillary used in the cryogenic trap is prone to blockage or breaking due to freezing of water. In theory, for a spherical ice plug, the minimum water amount that would cause column clogging for 0.53, 0.32 and 0.23 mm i.d capillary column are 77.9, 17.1 and 6.4 µg of water, respectively. In practice, the water will freeze out as an elongated volume rather than a sphere, thus the volume of water. It has also been reported that the presence of water can reduce the adsorption efficiency for individual compounds during sampling (Helmig *et al.*, 1995).

✔ ***The inherent artefact level*** is important when working on traces. The conditioning procedure should be optimised in order to increase the sensitivity. The minimum background achievable varies with the adsorbents. Background levels on the adsorbent Tenax TA are generally low but may be significant for some compounds. Clausen *et al* (1997) found several ng of DEHP on blank tubes intensively conditioned.

✔ ***Artefact formation during sampling.*** Oxidising species present in the air flow may cause degradation of organic compounds adsorbed on the adsorbent or degradation of the adsorbent itself resulting in the formation of artefact compounds. Tenax TA is prone to degradation in the presence of oxidant compounds during sampling. In a study aiming to characterise degradation products in the presence of oxidant species, Kleno *et al* (2002) identified 23, 13 and 12 degradation products in the presence of ozone (200 ppb), nitrogen dioxide (1.4 ppm) and hydroxyl radicals respectively. None of the selected target compounds were identified, but it can be presumed that the adsorption characteristic of this adsorbent might evolve over a long sampling period. To summarize, Tenax TA seems to be appropriate for collecting SVOCs over a long sampling period for the following reasons:

(i) It is hydrophobic, meaning that adsorption of water over a long sampling period should be limited and analysis therefore should not be problematic.

(ii) Efficient desorption recovery was obtained for several chemical classes in several studies

(iii) Efficient collection over a long sampling period seems possible

However, this adsorbent need further characterisation for long sampling period for a broad range of SVOCs because it has only been used for specific applications for a limited number of compounds.

2.2.2.2. Thermal desorption of the particulate phase

Thermal desorption of particulate matter from air samples has been done in a number of limited studies. The first publication found in the existing literature was published by Wauters *et al* (1979). They used a conventional split/splitless injector to desorb a fraction (1:77) of a filter from a high volume sampler. The accuracy of the method was not tested, but they positively identified a number of PAHs, alkanes and phthalates.

Greaves *et al* (1985) developed an injection system to analyse alkanes and PAHs from low flow samples. Laboratory-made particulate collection devices could be inserted in the injector block, thereby avoiding manipulating the filter after collection of the sample in order to reduce possible contamination. The temperature of the column was -60°C to prevent significant movement of the compounds of interest through the chromatographic column during thermal desorption. The accuracy and precision of the methods was evaluated by parallel collection of airborne particulate matter by both the flow sampler (in duplicate) and a high flow sampler. The collected samples were subsequently analysed by thermal desorption for low flow samples and the standard extraction method for the high flow samples. The accuracy of the method was also evaluated by analysing certified reference particulate matter (SRM 1649). They found that both methods agree within a factor of 2.5 for 98% of the 87 individual measurements and by a factor of 1.25 for half of the compounds quantified. The concentrations determined on the collected low flow samplers were in agreement. The PAH values measured using the thermal desorption method were in agreement with the certified value of the reference material, but the precision was quite poor. The authors concluded that the SRM1649 particulate matter was inhomogeneous at the μg levels, since the precision of the concentration measurements in the low flow field experiment was much better.

More recently, thermal desorption based methods have been developed to determine PAH composition in size segregated aerosols from residential wood combustion (Hays *et al.*, 2003), to characterise SVOCs in time-resolved (few hours) or size segregated ambient aerosol air samples (Falkovich *et al.*, 2001, Jeon *et al.*, 2001, Waterman *et al.*, 2000, Waterman *et al.*, 2001), to analyse various SVOCs in ambient air aerosols (Demokritou *et al.*, 2004, Schnelle-Kreis *et al.*, 2005) or indoor air aerosols (Clausen *et al.*, 1997) on a daily basis, to identify organics compounds from household dust or to determine nitro-PAHs in very polluted air samples (Beiner *et al.*, 2003). Thermal desorption of PM from the cited publications is based on three forms of thermal desorption, i.e. in-injection port, micro-scale sealed vessel (MSSV) thermal desorption and thermal desorption with conventional thermal desorption apparatus.

In the in-injection port method, filter strips are placed inside the GC liner and the liner is subsequently placed inside the injection port. This method requires no modifications of the GC injector if the liner is placed manually in the injector port. Liners should be replaced and cleaned after each analysis to prevent potential carry-over to the next analysis and irreversible adsorption due to deposit of carboceneous materiel over the wall of the liner. The Direct sample introduction device (DSI) used by Falkovitch *et al* (2001) overcomes this problem because the thermal extraction takes place inside a disposable vial placed inside the injector.

The sample throughput can be improved with modified injectors that automatically place the liner in the injection port of the chromatographic system (Schnelle-Kreis *et al.*, 2005, Welthagen *et al.*, 2003). The main advantage of this method is that no transfer line is used between the injector port and the column, thus eliminating possible adsorption effects.

The main drawback of this method is that desorbed compounds are refocused at the head of the capillary column, thus limiting desorption flow to a the column flow rate. In addition, the injector should be sufficient to avoid losses of volatile compounds during the loading step. Ho *et al* (2004) noticed that n-alkanes more volatile than n-C13 and PAHs more volatile than phenanthrene were lost during the loading step if an injector temperature of 100°C was used. A temperature of 30°C was efficient to avoid losses of n-C12 and naphthalene. Rapid cool down can be achieved if the injector is equipped with a cooling device, otherwise the cool down process is very slow (1 to 2 hours).

Both the MSSV and thermal desorption apparatus work on the same principle. Thermal extracted compounds are focused in a separate cold trapping system equipped with a split valve at the outlet of the trap. High desorption flow while keeping a low flow in the capillary is possible because the exceeding flow is vented through the outlet split valve. The drawback of these systems is the use of a transfer line between the cold trap and the thermal desorption oven, thus increasing the possibility of compound losses by wall adsorption. The length of the transfer line in the MSSV system is limited to a few centimetres, while it varies from a few centimetres to 1.5 meters in commercially available thermal desorption systems.

Evaluation of the performance of the thermal desorption method used in the cited publications has been performed on very few occasions. The accuracy of the method was evaluated by Falkovitch *et al* (2001) and Waterman *et al* (2000, 2001) by comparison with certified reference material SRM1649A, while Ho *et al* (2004) compared their method with a solvent extraction method. Hays *et al* (2003) also performed a comparison with the SRM1649A urban dust, but no results were reported.

Results of the studies reporting concentrations determined in the certified reference material SRM1649A are reported in **Table 12.** It can be seen that the determined concentrations in the different studies are close to the certified value. The ratio of the certified value to that of the concentrations determined in these three studies ranges from 0.77 to 1.16. Such a level of agreement is acceptable because one must keep in mind that the SRM1649A reference material was certified with a solvent extraction method, thus the desorption efficiency from both methods may be different.

The incomplete solvent extraction efficiency was demonstrated by Falkovitch *et al* (2001). They analysed the SRM1649A particulates by thermal desorption that were previously extracted by soxhlet solvent according the extraction procedure cited in the SRM1649A certificate of analysis. Traces of PAHs are observed in **Figure 7-c** illustrating incomplete solvent extraction (note the change of the Y-axes). Repeated thermal desorption of urban dust previously thermally extracted did not show any traces of PAHs **(Figure 7-b),** thus indicating complete recovery of the thermal extractable fraction of the PAHs analysed. As noted previously, PAH concentrations determined in the urban dust SRM16491A in the different studies are close to the certified value; however, it should be noted that the precision of the TD methods tends to decrease with high molecular weight PAHs.

Table 12: SRM1649A concentrations from various studies in mg.kg^{-1} (mean confidence 95%)

	NIST (Certified value)	Waterman (2000)[1]	Falkovitch (2001)[2]	Waterman (2001)[3]
N° of samples		n=5	n=5	n=5
Sample weight (mg)		3	0.5	3
TD method		MSSV	DSI	MSSV
Phenanthrene	4.14 (0.37)	4.62 (0.11)	4.05 (0.13)	4.56 (0.24)
Anthracene	0.43 (0.08)			
Fluoranthene	6.45 (0.18)	6.67 (0.16)		6.4 (0.23)
Pyrene	5.29 (0.25)	5.06 (0.18)	4.61 (0.24)	4.56 (0.61)
BaA	2.21 (0.07)	2.86 (0.17)	2.2 (0.40)	2.39 (0.44)
Chrysene	3.05 (0.06)	3.66 (0.20)		3.66 (0.41)
BbF	6.45 (0.64)	6.20 (0.68)		6.43 (0.87)
BkF	1.91 (0.03)			
BaP	2.51 (0.09)	2.79 (0.81)		2.47 (0.69)
IP	3.18 (0.072)			
DahA	0.29(0.02)			
BghiP	4.01 (0.91)			

[1] Waterman et al (2000), [2] Falkovich et al (2001), [3] Waterman et al (2001)

Waterman *et al* (2001) attributed the greater standard deviation for the high molecular weight to increased co-elution due to the unresolved complex mixture (UCM) (**Figure 8**).

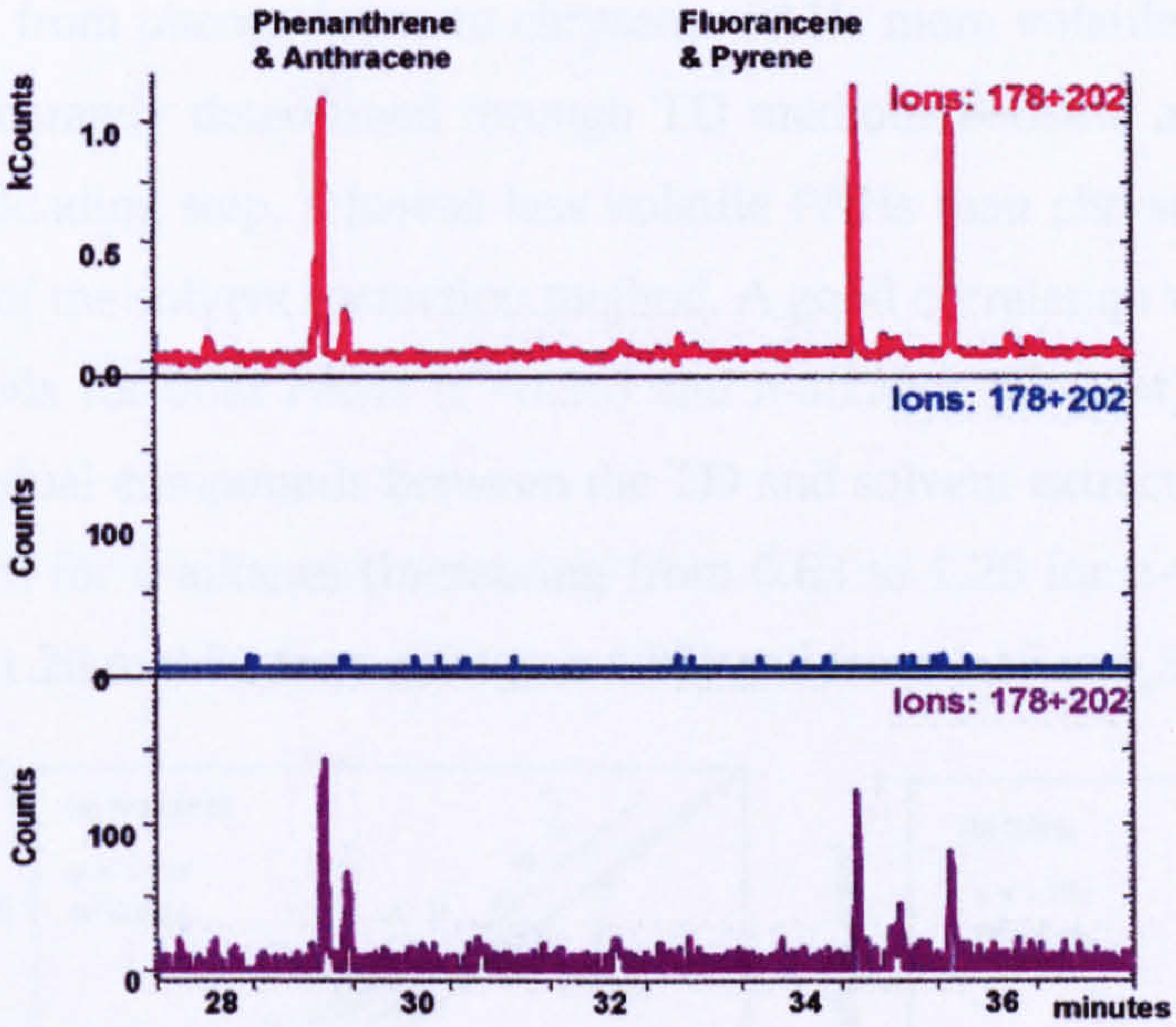


Figure 7: Thermal desorption of 0.5 mg urban dust (b) 2nd desorption of the same sample (c) Thermal desorption of 0.5 mg of urban dust previously soxhlet solvent extracted (From Falkovitch et al (2001))

Finally, it can be observed that no concentrations were given for the MW=178 $g.mol^{-1}$ (anthracene), MW=252 $g.mol^{-1}$ (BkF), MW=276 $g.mol^{-1}$ (IP and BghiP) and MW=278 $g.mol^{-1}$ (DahA) in the studies performed by Waterman *et al* (2000, 2001). Compounds with MW=276 and MW=278 were not quantified due to poor response and the increased background interference from the UCM for these compounds. The non-quantification of anthracene and benzo(k)fluoranthene was not explained. Likewise, no explanations were given by Falkovitch *et al* (2001) for the quantification of only 3 PAHs.

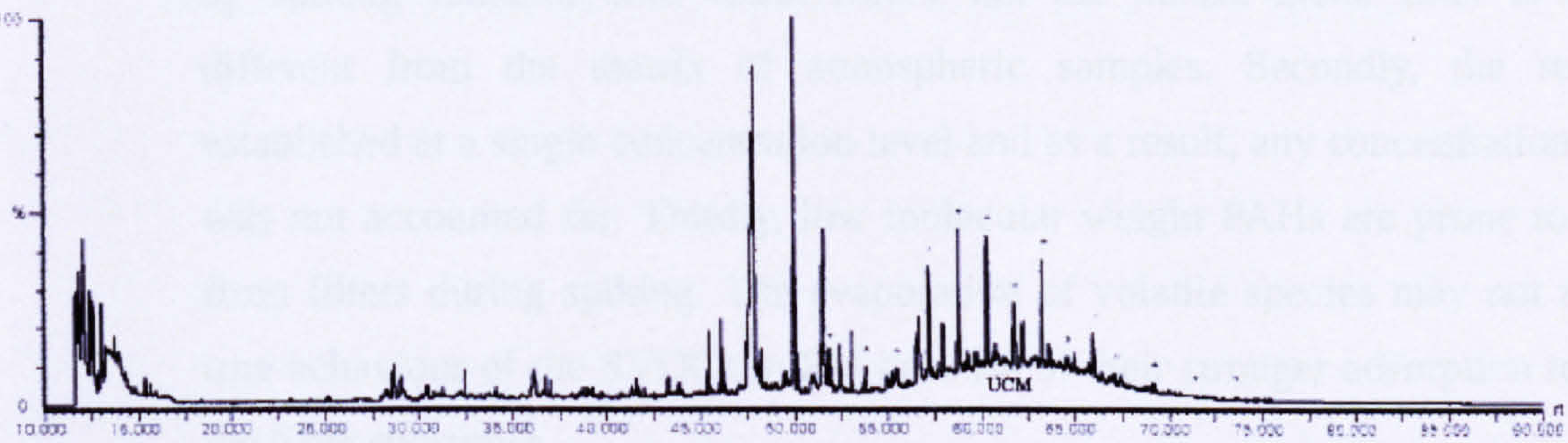


Figure 8: Chromatogram of 2.90 mg of thermally desorbed SRM1649A urban dust (from Waterman *et al* (2000))

Ho *et al* (2004) evaluated the accuracy of their TD method (manual in-injection port) by analysing filters strips cut from aerosols filter collected by high volume sampling (n=16). The remaining portion of the filter was analysed by a conventional soxhlet extraction method and GC/MS analysis. The extent of the agreement between the two methods is reported in**Figure 9**. n-alkanes include compounds from n-C17 to n-C35 and PAHs from phenanthrene to chrysene. PAHs more volatile than phenanthrene could not be accurately determined through TD methods because a fraction was lost during the filter loading step, whereas less volatile PAHs than chrysene were below the detection limit of the solvent extraction method. A good correlation was obtained between the two methods for both PAHs (r^2=0.95) and n-alkanes (r^2=0.94). The concentration ratio for individual compounds between the TD and solvent extraction method ranged from 0.63 to 1.26 for n-alkanes (increasing from 0.63 to 1.26 for n-C17 to n-C28 and decreasing from 1.26 to 0.76 for n-C28 to n-C35) and from 1.15 to 1.33 for PAH compounds.

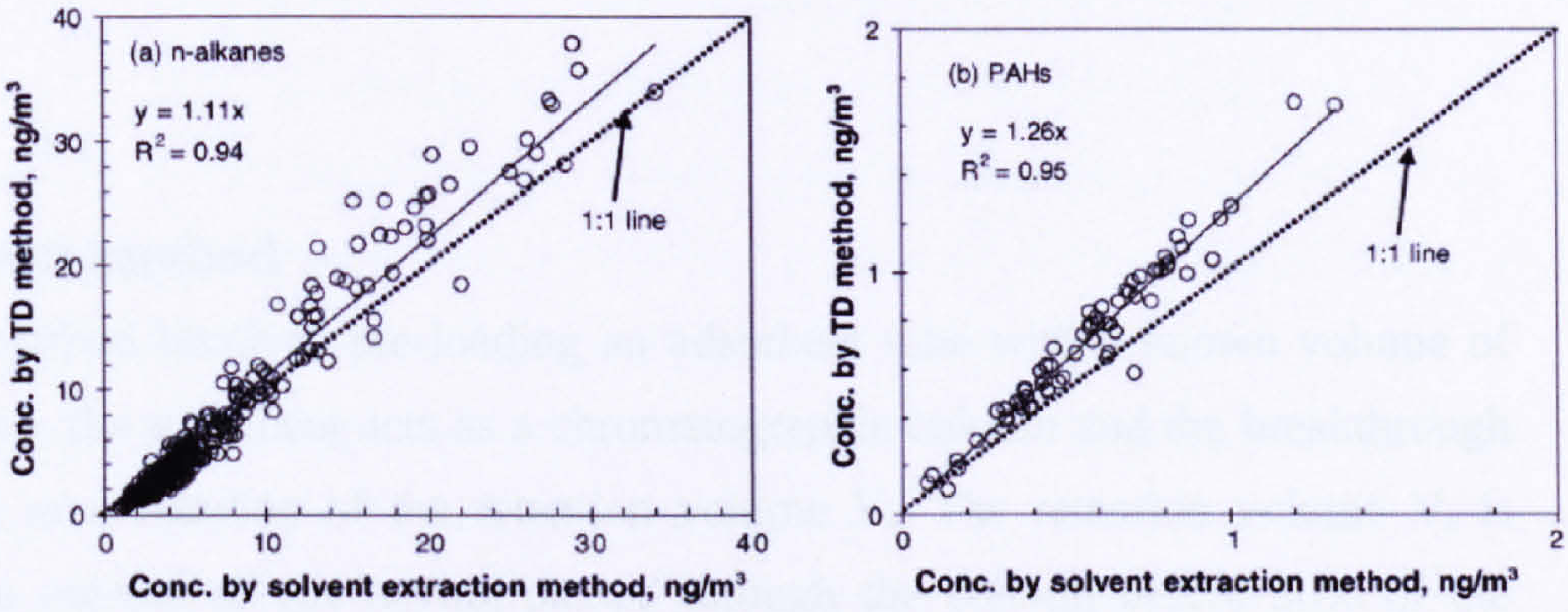


Figure 9: (a) Comparison of air concentrations of n-alkanes and PAHs (b) measured by a solvent extraction and a TD method (from Ho *et al* (2004))

A possible explanation suggested by the authors to explain the under estimation by the TD method for n-alkanes from n-C17 to n-C28 and the over estimation for n-C-28 to n-C35 and for PAHs is the use of erroneous recovery factors for the solvent extraction method. Firstly, the authors determined the recovery for the solvent extraction method by spiking standard onto blank filters, but the matrix blank filter is considerably different from the matrix of atmospheric samples. Secondly, the recovery was established at a single concentration level and as a result, any concentration dependence was not accounted for. Thirdly, low molecular weight PAHs are prone to evaporation from filters during spiking. The evaporation of volatile species may not represent the true behaviour of the SVOCs in PM because of their stronger adsorption to PM than to the filter substrates.

In conclusion, the level of agreement between both methods was reasonably good when considering the uncertainty of the recovery factors of the solvent extraction method. The incomplete recovery from the TD method was not discussed by the authors, but this factor could also contribute to differences between the two methods.

Chapter 3: Breakthrough volume measurements methods theory

The breakthrough volume enables estimation of the determination of the maximum sample volume that ensures a quantitative sampling. Breakthrough volume (V_b or BTV) is defined as the volume of gas that passes through an adsorbent bed before a fraction of the analyte is eluted from the adsorbent .

3.1. Breakthrough volume measurement methods

Breakthrough volume measurements can be performed using a direct or an indirect method.

3.1.1. Indirect method

The indirect method involves pre-loading an adsorbent tube with a known volume of adsorbate. Then, the adsorbent acts as a chromatographic column and the breakthrough is determined as a function of the retention volume V_r. The retention volume V_r is defined as the volume of gas having passed through the column before 50% of the analyte is eluted from the adsorbent **Figure 10**.

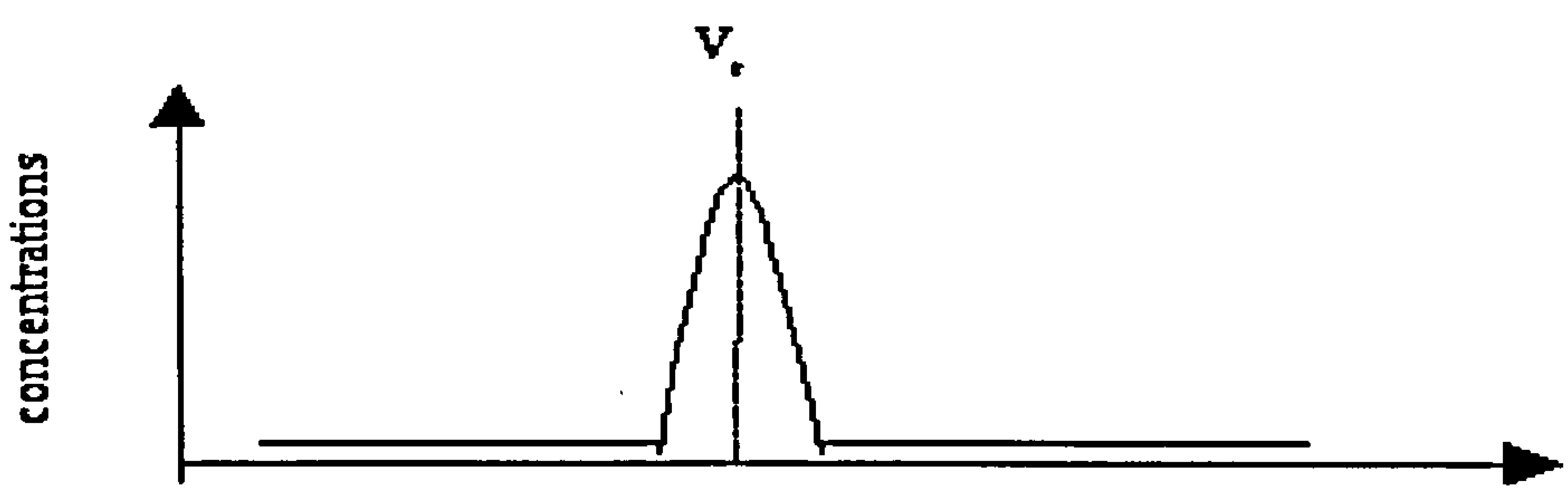


Figure 10: Relation between Vb and Vr using an indirect method

This method that has been shown to be useful to compare the performance of different adsorbents, but is not recommended to measure sampling capacity (Bertoni *et al.*, 1997) as the influence of environmental parameters is not taken into account (e.g. competitive effects of other molecules or humidity). The direct method generally yields much lower BTV values than the indirect method (Bertoni *et al.*, 1997, Mastrogiacomo *et al.*, 1998).

3.1.2. Direct method

The direct method consists in continuously loading a gas containing target compounds through an adsorbent bed at a defined temperature and controlled humidity.

Determination of the breakthrough can be determined online (Bertoni *et al.*, 1997, Brown *et al.*, 1979, Comes *et al.*, 1993, Foley *et al.*, 2001), off-line using a single sample tube (Bertoni *et al.*, 1997, Simon *et al.*, 1995) and off-line using two tubes in series.

3.1.2.1. Online detection

The effluent flow can be monitored on-line by means of a GC detector (Bertoni *et al.*, 1997, Brown *et al.*, 1979, Comes *et al.*, 1993, Foley *et al.*, 2001). This method is limited by the sensitivity of the detector. Foley (2001) was able to work in the mg/m^3 region using a FID detector.

Working with lower concentrations (µg/m^3) requires the use of a pre-concentration step. A cold trap or desorption unit can be placed between the sample and the detector. This method is very sensitive and intervention by the operator is limited except for the development of the system. This system permits BTV determination with concentrations similar to those of the ambient atmosphere.

The value of the breakthrough, V_b depends on the definition of breakthrough. It is marked by an increase of the baseline. Some studies have marked the breakthrough when the analyte in the effluent bed reaches 50 % of the inlet concentration (Van Der Straeten *et al.*, 1985), 10 % (Baya *et al.*, 1996, Comes *et al.*, 1993, Foley *et al.*, 2001) and 1 % (Brown *et al.*, 1979, Sturges *et al.*, 1993). A typical diagram is depicted in **Figure 11.**

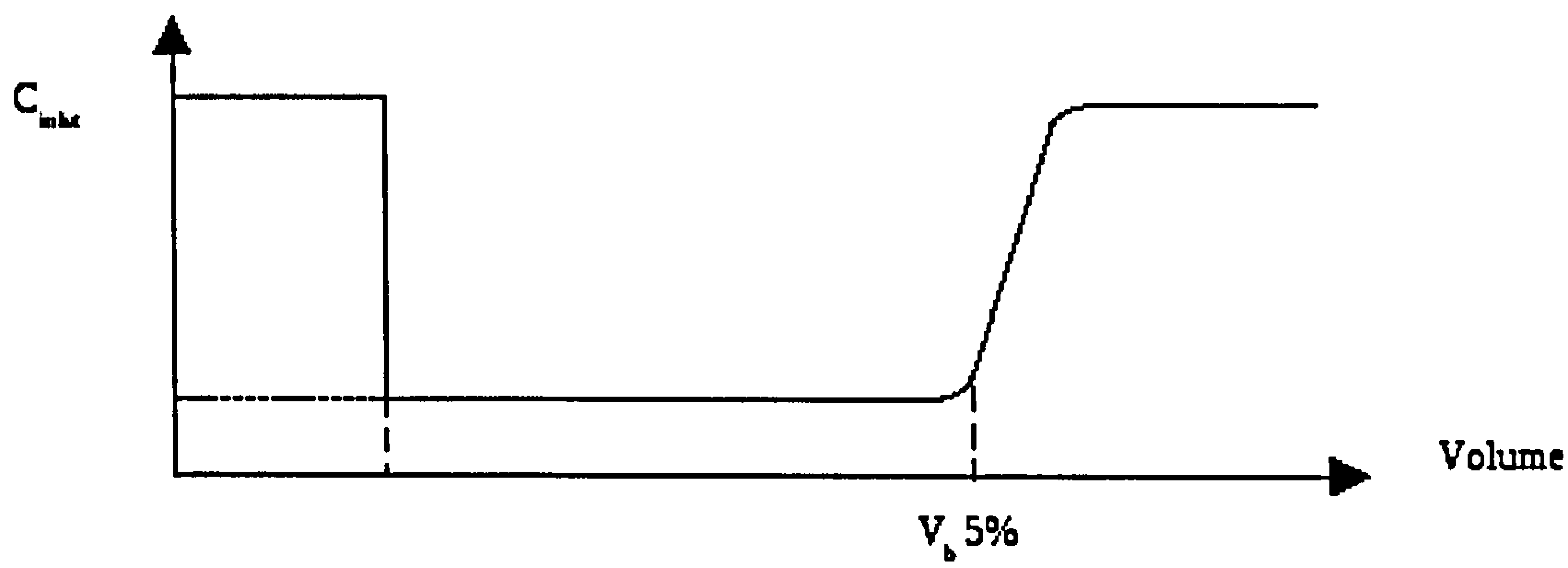


Figure 11: Typical diagram during Vb measurement with the online direct method

3.1.2.2. Off-line detection using two tubes in series

Two tubes can be placed in series and the second tube can be replaced and analysed at regular intervals. V_b is then determined once the analyte is detected in the second tube (Harper, 1993).

3.1.2.3. Off-line detection using a single sample tube

This method allows V_b measurement at low adsorptive concentrations ($\mu g/m^3$). This method involves passing various volume of a generated atmosphere through sample tubes. The sample tubes are subsequently desorbed, analysed and a graph representing the amount of adsorbed compounds against sample volumes can be plotted. A typical graph is shown in **Figure 12.** A linear relationship exists until breakthrough occurs. The end of the linear domain corresponds to V_b.

The linear domain is expressed as the function $y=ax$, which can be calculated with the least-squares method. The non-linear domain is expressed by the function $y=cx^d$, and the factors c and d can also be obtained using the least squares method (Simon *et al.*, 1995).

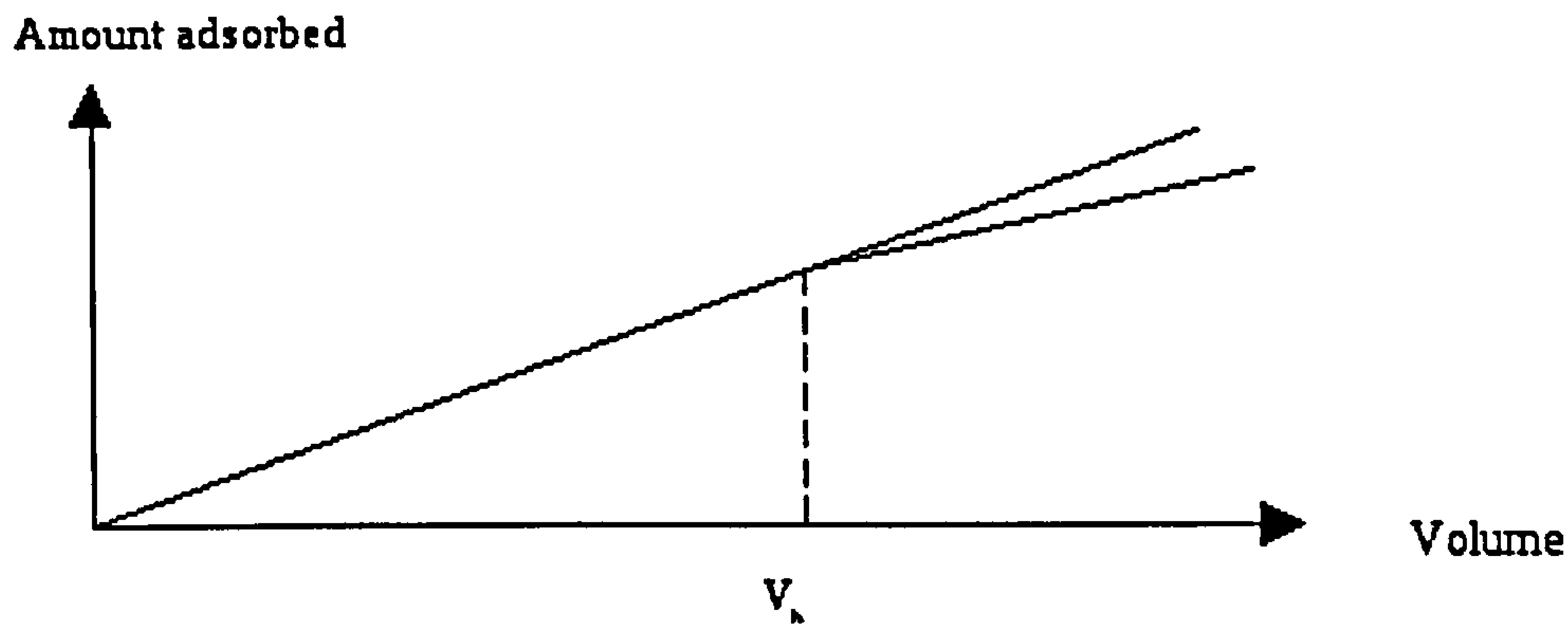


Figure 12: Typical graph representing the linear and non-linear relationship between amount adsorbed and volume sampled

3.2. Vapour generation systems

Determination of V_b values and evaluation of different parameters (sampling artefact) of the sampler involves developing a dynamic vapour generation system. This system should permit the generation of a continuous flow of vapours at concentrations varying from a few ng/m^3 to a few $\mu g/m^3$ at ambient temperatures and under controlled humidity. Vapour generation systems are generally divided into two categories, (i) static and (ii) dynamic systems. The most-employed dynamic methods for preparing standard organic gases are gas stream mixing, injection, permeation tubes, diffusion tubes, and evaporation.

Gas stream involves mixing two or more gases at known flow rates to produce the desired concentrations. This system can be controlled by any devices measuring flow rates accurately, but is limited to compounds present in the gaseous state.

Injection method involves injecting gases or liquids into a flowing gas stream. Any dispensing apparatus such as pumps (Foley *et al.*, 2001), motor-driven syringes (Harper, 1993), pistons or electronic nozzle (Meininghaus, 1999) can be used to inject stable flows of the components. Both injection and gas stream mixing methods cannot be used in this study because most of the SVOCs selected are in the solid state at ambient temperature.

Permeation systems work on the principle that liquefied gases enclosed in a vessel escape from it at a constant and reproducible rate through the wall of a permeable membrane commonly made of PTFE or other polymer material (Barratt, 1981). This system is suitable for producing vapours of very volatile organic compounds (Simon *et al.*, 1995) and was used on one occasion to produce Naphthalene vapour (Temime *et al.*, 2002). The authors found that permeation cells were effective to produce naphthalene vapours in the ppbv range at ambient temperature. They also noticed that a stable flow of naphthalene was reached after a period of 4 or 5 days.

The diffusion method was preferred in this study because diffusion cells can be laboratory made and because diffusion rates can be estimated from an empirical equation.

This method works on the principle that a liquid contained in the reservoir evaporates at a constant rate and the vapours diffused slowly through the capillary tube into a flowing gas stream.

Diffusion rates can be estimated by applying the equation describing the diffusion of a vapour in equilibrium through a capillary tube **(Equation 1)**. Possanzini *et al* (2000) have shown that theoretical and experimental values were closely related for n-C_6 to n-C_9 liquid carbonyl. This estimate of the diffusion rate is interesting because it makes it possible to determine the dimensions of the vessels and capillary for a given concentration prior to vapours generation.

$$r=DMPS\,\ln[P/(P-p)]\,(RTL)^{-1} \qquad \textbf{Equation 1}$$

r: Diffusion rate (g/s)
D: Coefficient of molecular diffusion (cm^2/s)
M: Molecular mass (g/mol)
P: Total pressure in the diffusion cell (kPa)
p : Partial pressure of the diffusion vapour at the absolute temperature (kPa)
T: Temperature of the diffusion cell (K)
R: gas constant ([ml kPa]/[mol K])
S: Cross sectional area of the cell (cm^2)
L: Length of the capillary (cm)

The coefficient of molecular diffusion can be estimated using **Equation 2.**

$$D_{ij}=(10^{-3}T^{1.75}(1/M_i+1/M_j)^{1/2})/(p(V_i^{1/3}+V_j^{1/3})^2) \qquad \textbf{Equation 2}$$

D: Diffusion coefficient of a compound i in the medium j (air)
T: Temperature (K)
M: Molecular weight (g/mol)
p: Pressure (atm)
V: Molecular volume (determined by addition of atomic volumes with bonding increments – **appendix 3).**

Part II: Experimental procedures

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Chapter 4: Breakthrough volume measurements experimental

The breakthrough volume measurement method used in this study was based on a direct method involving the development of a vapour generation system. A thermal desorption-gas-chromatography (TD-GC) method was developed in order to quantify the concentrations generated in the vapour generation system. Once validated, the vapour generation system will be used for breakthrough measurements and evaluation of the sampler performances.

4.1. Development and optimisation of the analytical method (TD-GC-FID) using a single tube thermal desorber

4.1.1. Material

Analyses were carried out on a Fisons GC8000 chromatograph coupled to a thermal desorber single tube (Envirochem model 851). A diagram of the experimental set-up is depicted in **Figure 13** and a photograph of the analytical chain is presented **Picture 3**.

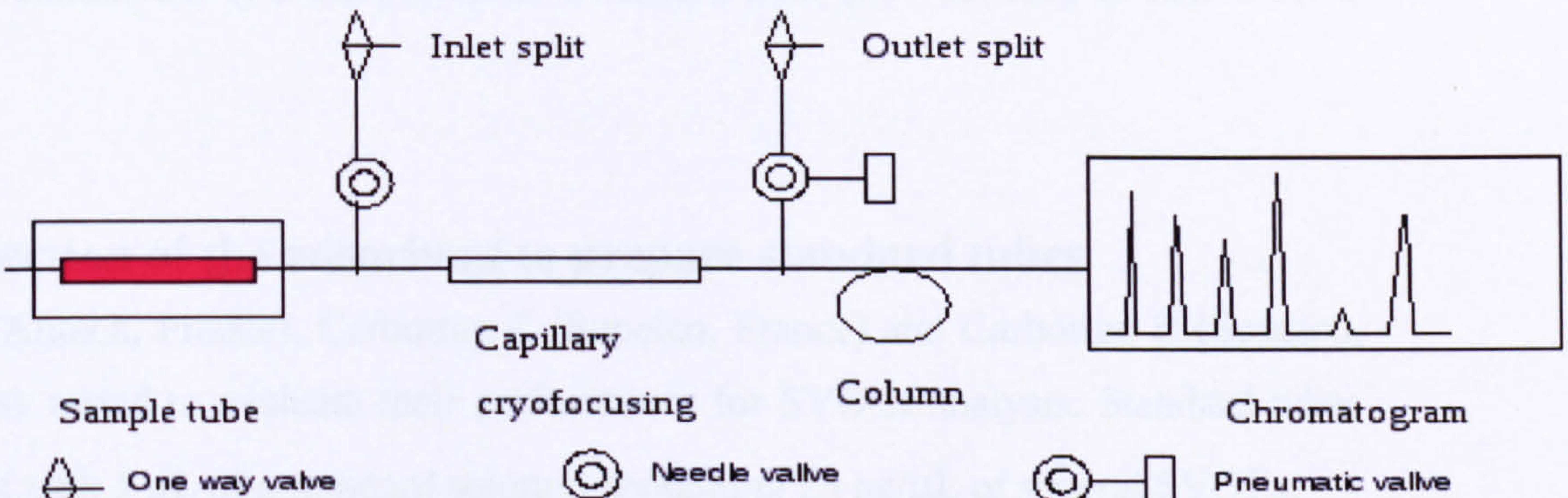


Figure 13: A Schematic diagram of a thermal desorption with capillary cryofocusing

Picture 3: Thermal desorption unit mounted on the top of a GC-8000/MD800 chromatograph

- **Thermal desorption unit (Envirochem)**
  - → Desorption temperature up to 400°C
  - → Switching valve heated up to 240°C
  - → The transfer line is a 1 meter long capillary silica column (0.53 mm i.d) and can be heated to 290°C
  - → The cold trap (deactivated silica column) can be cooled down to –150°C (liquid nitrogen) and heated up to 400°C

- **Gas chromatograph**
  - → Mobile phase: Helium
  - → Stationary phase: DB-XLB capillary column (25m × 0.25 mm i.d. × 0.25 µm film thickness)
  - → Detector
  - → FID at 300°C controlled by Chrom-Card V3.1

- **Adsorbent tubes**

Glass tubes (11.5 mm in length, 4 mm i.d and 6 mm o.d) from Supelco were used in all of the experiments. Tubes were loaded with approximately 40 mg of Tenax TA (60/80 mesh from Supelco) or Carbotrap C (20/40 mesh from Supelco). The adsorbent bed was held in place with two plugs of silanised glass wool. Tubes were conditioned on a Dynatherm conditioner (Model 60) under a Helium flow (100 ml/min) at 330°C for 2 hours.

4.1.2. Selection of the adsorbent to prepare standard tubes

Tenax TA (Alltech, France), Carbotrap C (Supelco, France) and Carbotrap B (Supelco, France) were tested to evaluate their performance for SVOCs analysis. Standard tubes were spiked with 1 µL of a standard solution containing 25 ng/µL of several SVOCs.

4.1.3. Standard tubes preparation

The two procedures commonly used to prepare standard tubes were tested to determine which was more convenient for spiking tubes with semivolatile organic compounds standards.

✓ Standard introduced onto tubes in the vapour phase (vaporisation method)

Standard tubes were prepared by means of a thermal desorption unit (Dynatherm Model 890). This thermal desorber unit is equipped with a septum at the inlet of a desorption chamber, a heated valve (up to 240°C) and a side port exit whereby the vaporised SVOCs were collected on the adsorbent tubes. Liquid solutions (25 ng/µL) were injected (1 µL syringe) in the desorption chamber (350°C) and transferred to the sample tube under a Helium flow (100 ml/min) for a given period of time.

✓ ***Standard introduced onto tubes directly as liquids (liquid method)***

The syringe needle was inserted halfway into the core of the adsorbent bed. Liquid standard were then injected and the excess of solvent was purged under a Helium flow of 100 ml/min during 10 minutes. Liquid standards were injected in the middle of the adsorbent bed in order to prevent losses of volatile compounds during the purge step.

4.1.4. Optimised TD and GC analytical method

After optimisation of the method, the analytical conditions presented in **Table 13** were retained and used for the breakthrough measurements experiments.

Table 13: Optimised analytical conditions

Events
Desorption of the sample tube at 310°C for 40 minutes. Trapping at –150°C
End of tube heating and valves switched to the trap desorption position
Trap heating at 350°C until the end of the run
Analytical program started
40°C to 100°C at 5°C/min; 100°C for 3 minutes;
100 to 190 at 10°C/min; 190°C for 3 minutes
190°C to 320°C at 15°C min; 320°C for 5 minutes

4.2. Development of the vapour generation system

A vapour generator based on the diffusion method was developed in order to perform a breakthrough volume study. This system should permit the generation of vapours at concentrations representative of ambient or indoor air levels. The vapour generation system was modified several times in order to more efficiently control the vapour generated.

4.2.1. Generation of atmosphere at a flow rate limited to 2 $l.min^{-1}$

This primary experiment was performed with two compounds from the US-EPA list of 16 priority PAH compounds. Naphthalene (bp. 230°C) was chosen because it is a lighter PAH and hence it is more prone to breakthrough, while pyrene (bp. 404°C) was retained because it is a heavier PAH that can be found in the gaseous phase at relatively significant concentrations.

4.2.1.1. Experimental set-up

The vapours escaping from the diffusion tubes at a constant rate are diluted in a flowing air stream. The system developed in this study is depicted schematically in **Figure 14** and presented in **Picture 4**. The air entering the generator was dried through a silica gel cartridge (30 cm in length and 10 cm in diameter) and purified through a charcoal stainless steel cartridge (60 cm in length and 20 cm in diameter) to remove volatile contaminants. The air was then filtered through a quartz fibre filter (0.07µm pore diameter) in order to remove any particles coming from the charcoal. The vapour generation system was placed in a fume cupboard located in a temperature-controlled room. 1/4-inch and 1/8-inch stainless steel and PTFE tubes were used in this generator. Connection was done by means of swagelock fittings equipped with either stainless steal or Teflon ferrules.

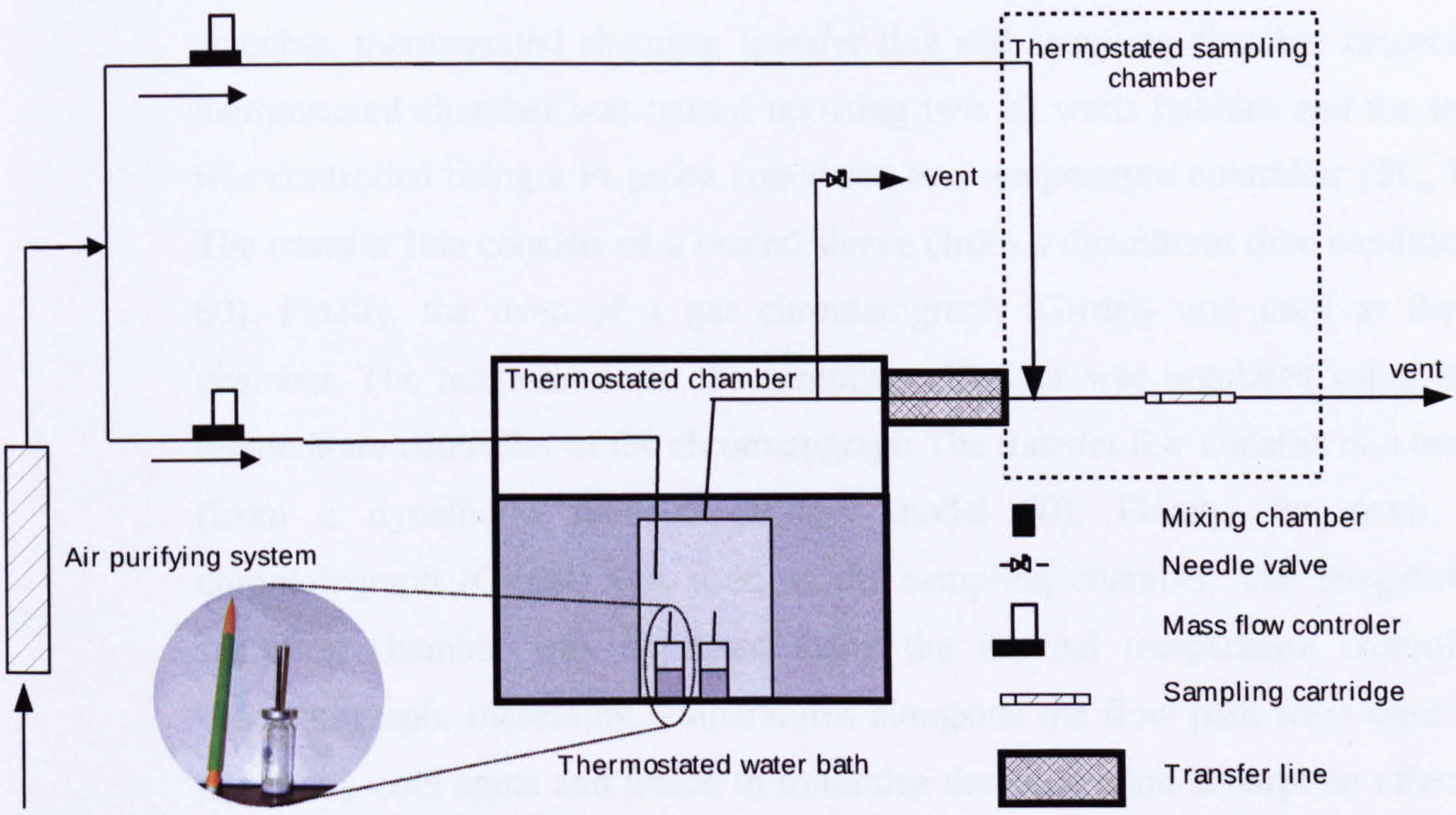
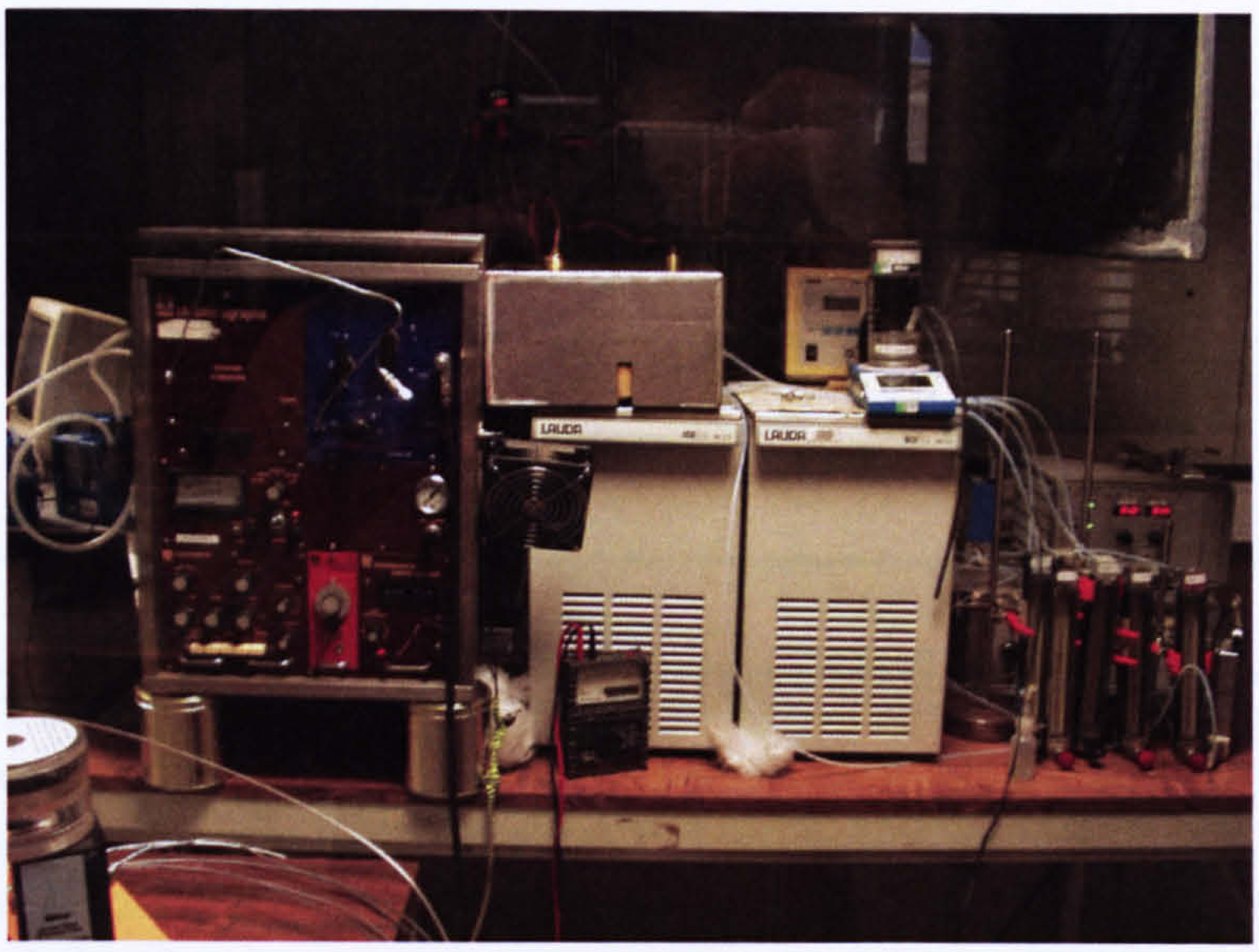


Figure 14: Schematic diagram of the vapour generation system with a single diffusion chamber (low flow rate)

Diffusion tubes were placed in a glass diffusion chamber (i.d. 15 cm and 20 cm in length). Diffusion tubes were made of a stainless steal or glass capillary inserted through the septum of a 10 ml glass vial or via an open cell (without capillary). The diffusion chamber was immersed in a temperature-controlled water bath (lauda). Vapours escaping from diffusion tubes were diluted in the incoming purified airflow controlled by means of a mass flow controller (millipore). The enriched flow was then directed to the sampling chamber by successively passing through a thermostated chamber and a heated transfer line.



Picture 4: Vapour generation with sampling chamber (gas chromatograph), thermostated water bath and thermostated chamber

In order to avoid any cold spots, increasing temperature was set in the diffusion chamber, thermostated chamber, transfer line and sampling chamber respectively. The thermostated chamber was heated up using two 20 watts bubbles and the temperature was controlled using a Pt probe connected to a temperature controller (TC, REX 100). The transfer line consists of a heated sleeve (from a dynatherm tube conditioner model 60). Finally, the oven of a gas chromatograph (Girdel) was used as the sampling chamber. The temperature in the sampling chamber was regulated using the internal temperature controller of the chromatograph.The transfer line consists of a heated sleeve (from a dynatherm tube conditioner model 60). Finally, the oven of a gas chromatograph (Girdel) was used as the sampling chamber. The temperature in the sampling chamber was regulated using the internal temperature controller of the chromatograph. Increasing temperatures alongside the flow path were used in order to avoid any cold spots and hence to minimise the adsorption-desorption effects onto the wall the system.

In this system, the concentrations of the vapour generated were controlled by the temperature of the diffusion chamber, and diffusion cell dimensions. Dimensions of the diffusion cells were estimated using **equations 1** and **equation 2** provided in **chapter 3.2.**

4.2.1.2. Vapour generation conditions

Dimensions of the diffusion cells and vapour generation conditions are reported in **Table 14** and **Table 15**, respectively. Crystals were finely ground in a mortar in order to obtain a homogeneous powder.

Table 14: Dimensions of the diffusion cells

Compounds	Capillary length (cm)	Capillary diameter (mm)
Naphthalene	5.1	2
Pyrene	Open cell	21

Table 15: Vapour generation conditions

Parameters	Set-up
Flow rate through diffusion line	1 $l.min^{-1}$
Flow rate through the humidity line	1 $l.min^{-1}$
Temperature of the thermostated water bath (humidity)	20°C
Temperature of the thermostated water bath (humidity)	20°C
Temperature thermostated chamber	21°C
Temperature transfer line	22°C
Relative humidity	20%
Temperature sampling chamber	23°C to 27°C*

**At the start of the experiment, the temperature in the sampling chamber (gas chromatograph) was set to 23°C, but the system warmed up to 27°C due to the heating of the gas chromatograph electric devices.*

4.2.2. Generation of atmosphere with a high flow rate

The flow rate in the initial set-up was limited to 2 $l.min^{-1}$. In this experiment, it was decided to use a higher flow rate in the dilution line (5 $l.min^{-1}$) in order to permit the collection of multiple sample tubes during the breakthrough volume experiment. This experiment was performed with six compounds from various chemical families.

4.2.2.1. Experimental set-up

The general set-up depicted in **Figure 15** is similar to the first experiment except that a flow meter of higher flow rate was used to control the flow rate through the dilution line. In order to control more efficiently the temperature in the sampling chamber and to avoid temperature fluctuations due to the heating of the electric devices, the sampling chamber was swept with a air flow cooled down to -5°C. The air was cooled down to -5°C by passing 2 meters of the tube through a portable freezer.

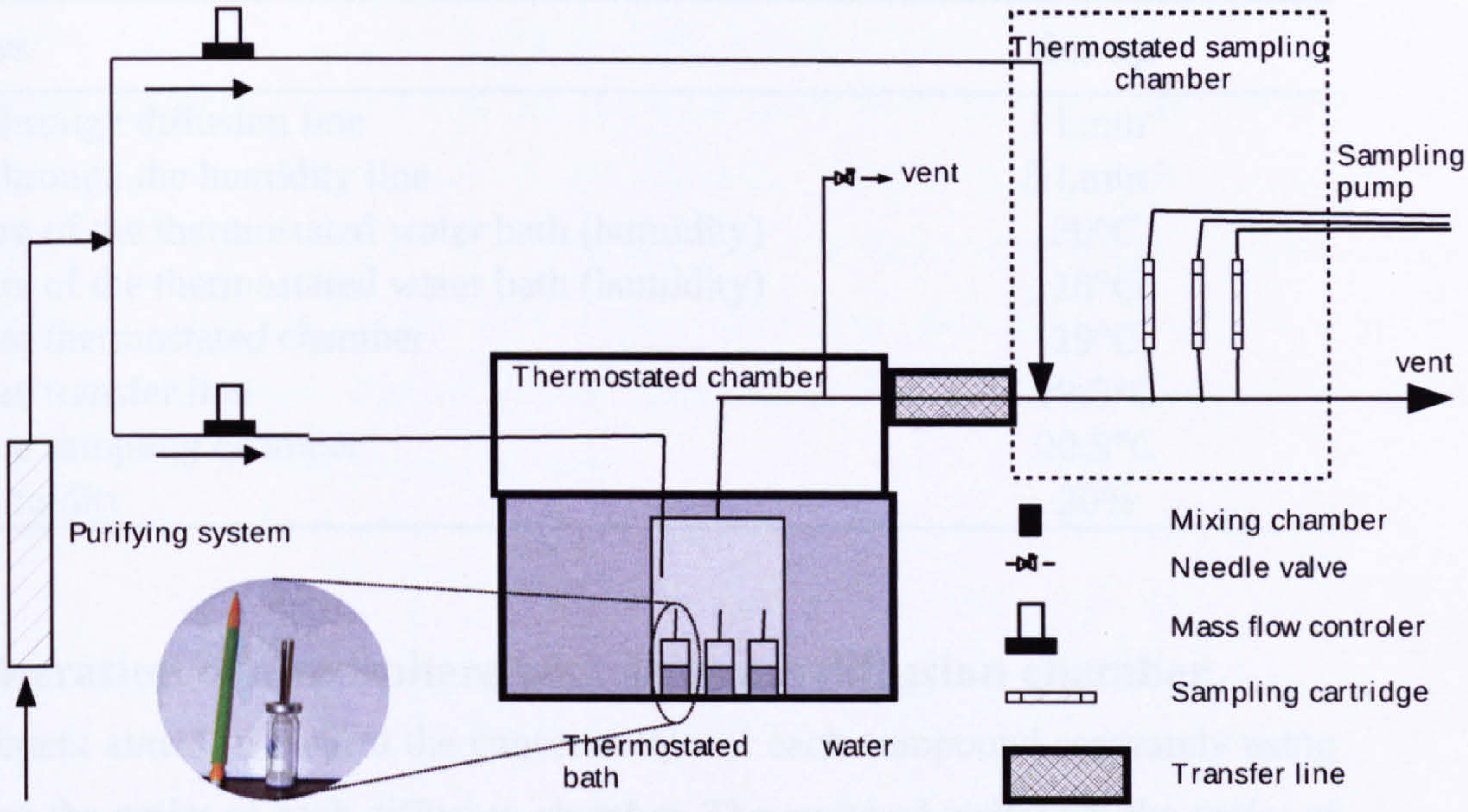


Figure 15: Schematic diagram of the vapour generation system with a single diffusion chamber (high flow rate)

4.2.2.2. Vapour generation conditions

Six different compounds were studied in this experiment. Dimensions of the capillary tubes and conditions of the generator are given in **Table 16** and **Table 17** respectively. The dimension of the capillary tubes were determined using **equation 1** and **equation 2 (chapter 3.2)** in order to generate concentrations representative of indoor air samples. Open cells were used for pyrene and DEHP since the calculated capillary diameter were larger than the diameter of the vial for reasonably short capillary. For instance, a capillary of 2.2 cm i.d x 0.5 cm length would be required for an estimated concentration of 200 ng/m^3.

Table 16: Dimension of the diffusion cells

Compounds	Capillary length (cm)	Capillary diameter (mm)	Estimated concentrations (ng/m^3)
Naphthalene	5	1	580
4-tertbutylphenol	6	0.8	130
TBP	4.7	2	300
Phenanthrene	1	2	127
Pyrene	Open cell		-
DEHP	Open cell		-

Table 17: Conditions in the vapour generation system

Parameters	Set-up
Flow rate through diffusion line	1 $l.min^{-1}$
Flow rate through the humidity line	5 $l.min^{-1}$
Temperature of the thermostated water bath (humidity)	20°C
Temperature of the thermostated water bath (humidity)	18°C
Temperature thermostated chamber	19°C
Temperature transfer line	19.5°C
Temperature sampling chamber	20.5°C
Relative humidity	20%

4.2.3. Generation of atmosphere with separate diffusion chamber

This experiment aimed to control the concentration of each compound separately using a split line at the outlet of each diffusion chamber. The enriched airflow at the outlet of the diffusion chambers was mixed and diluted in a dilution chamber.

4.2.3.1. Experimental set-up

Diffusion vials were placed in separate diffusion chamber **Figure 16**. A stable flow of purified air in each line connected to the diffusion chambers was obtained by splitting the airflow at the outlet of two mass flow meters (millipore). The airflow in each line was regulated by means of needle valves and controlled using glass tube flow meters.

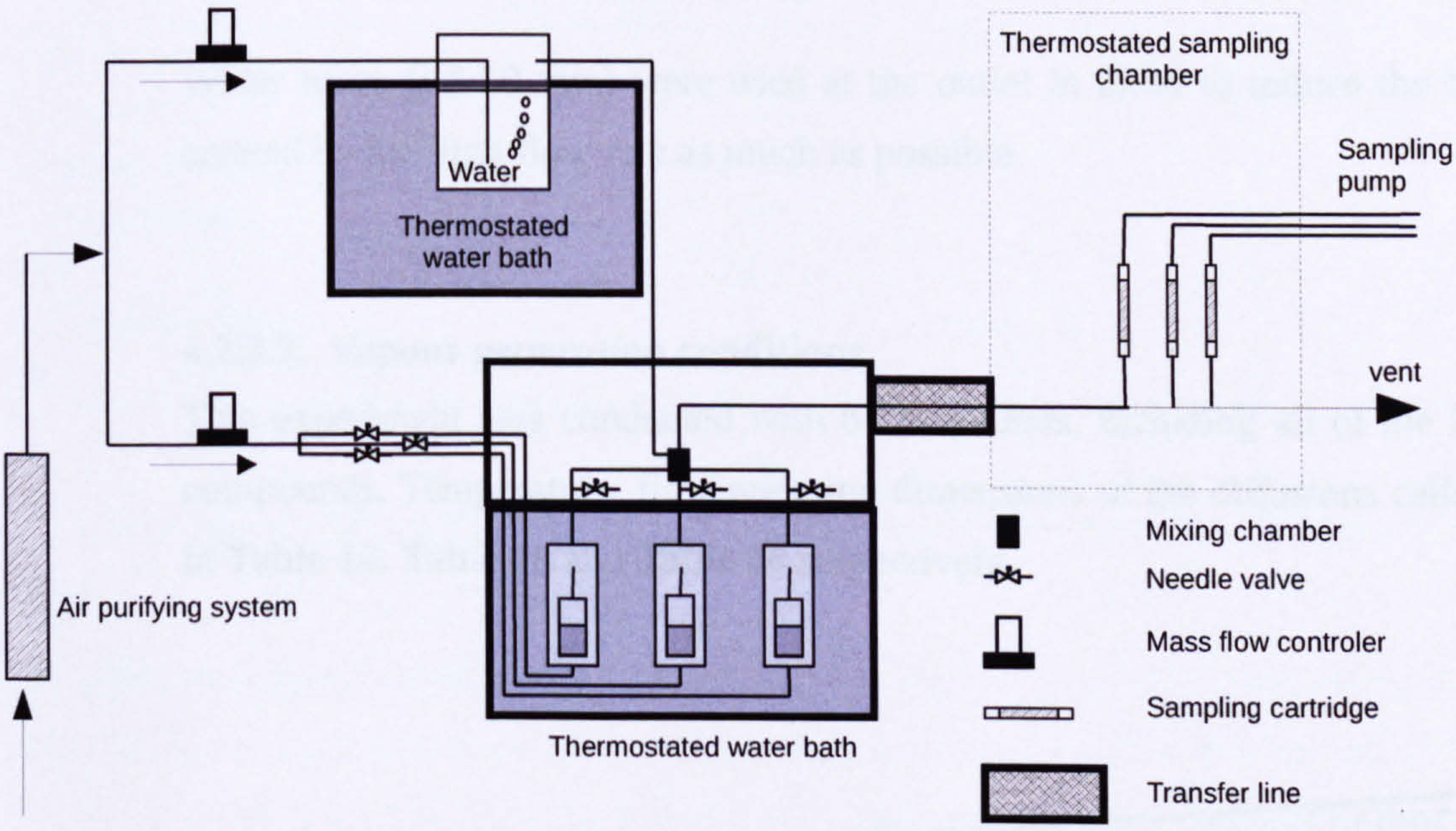


Figure 16: Schematic diagram of the vapour generation system with separate diffusion chamber

Diffusion chambers were made of stainless steel tubes (10 cm in length and 10 mm of i.d). Diffusion tubes were placed over a grid located at the bottom of the diffusion chamber. Vapours escaping the diffusion tubes were diluted in the flowing air stream entering from the bottom of the dilution chamber. A split line consisting of a T connector and a needle valve was added at the outlet of diffusion chamber in order to regulate dilution factors. The vapour generated were then mixed using a dilution chamber shown in **Figure 17** and **appendix 4**. This dilution chamber was used in the past at INERIS for another purpose.

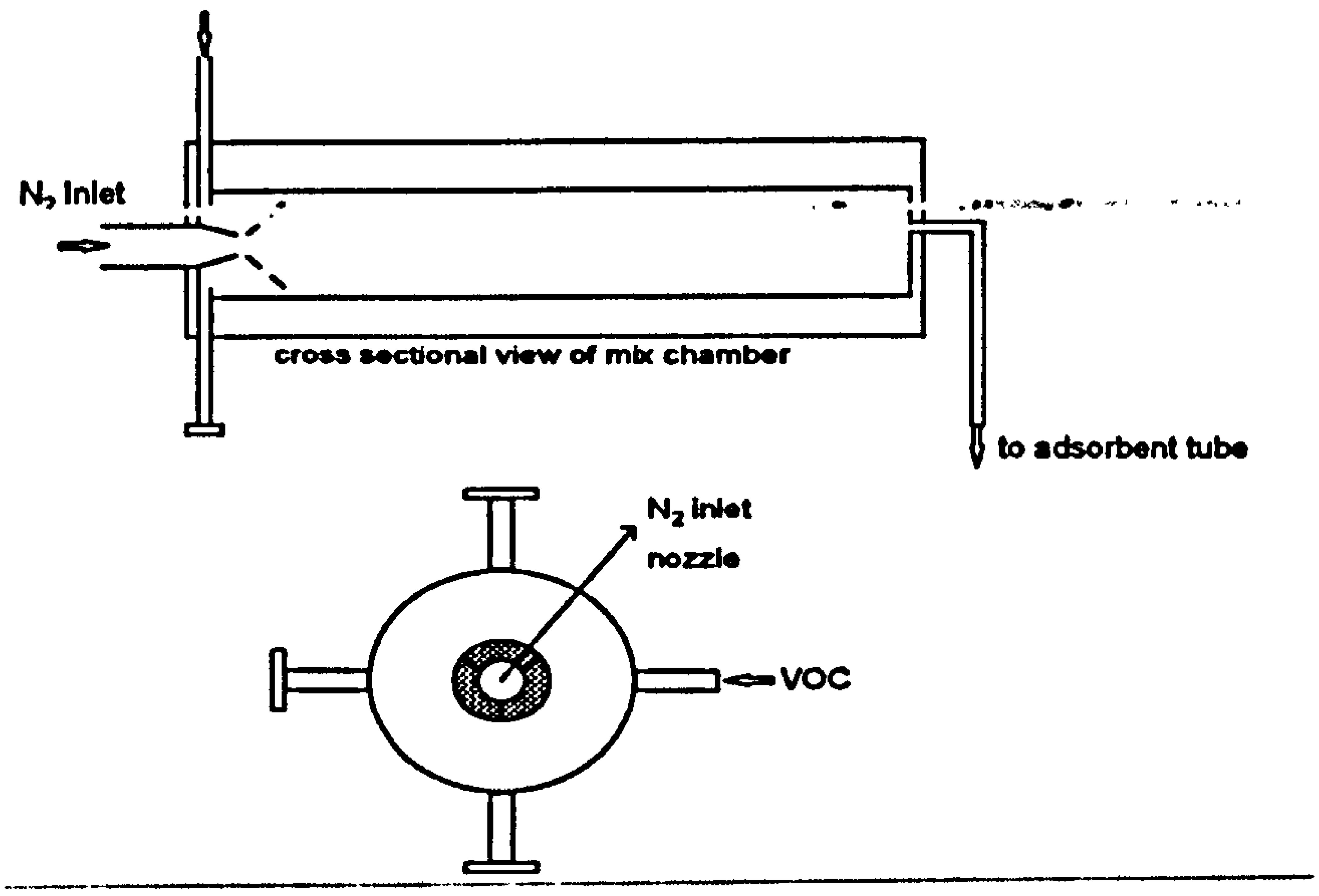


Figure 17: Modified dilution chamber (source: Foley *et al* (1999))

Wider tubes (i.d 10 mm) were used at the outlet in order to reduce the back pressure created by the high flow rate as much as possible.

4.2.3.2. Vapour generation conditions

This experiment was conducted with 8 compounds, including all of the lightest target compounds. Temperature, flow rates and dimensions of the diffusions cells are reported in **Table 18, Table 19** and **Table 20** respectively.

Table 18: Vapour generation temperature and humidity

Parameters	Set-up
Temperature of the thermostated water bath (humidity)	20°C
Temperature of the thermostated water bath (diffusion)	18°C
Temperature thermostated chamber	19°C
Temperature transfer line	19.5°C
Temperature sampling chamber	20.5°C
Relative humidity	20%

Table 19: Flow rates through the vapour generation system

Compounds	Flow rate inlet diffusion cell (ml/min)	Flow rate through split line outlet diffusion cell (ml/min)	Flow rate through dilution line (l/min)
Naphthalene	302	0	
4-tertbutylphenol	317	0	
DEP	506	0	
TBP	509	0	4.5
Pyrene	399	0	
DEHP, 2-phenylphenol, phenanthrene	493	0	

Table 20: Dimensions of the diffusion tubes

Compounds	Capillary length (cm)	Capillary diameter (mm)
Naphthalene	5.1	2.0
Phenanthrene	1.55	4.0
4-tertbutylphenol	5.13	1.4
2-phenylphenol	1.97	3.0
DEP	0.96	4.8
DEHP and Pyrene	Open cell	
TBP	1.82	4.8

Gilian personal air flow pumps (Gilair 5, Sensidyne inc) were used instead of the Buck pumps.

This pump is equipped with an outlet that can be used to check the flow rate while sampling. Flow rates were controlled with a Gilian gilibrator at the beginning and at the end of the sampling event. The sampling was validated if the flow variation was no more than 5%.

4.3. Breakthrough volume study

Breakthrough volume for several SVOCs on the adsorbent Tenax TA was measured using a direct method. A single measurement was carried out under high humidity (70% RH), temperature (30°C) and concentrations levels.

4.3.1. Experimental set-up

The vapour generator was modified in order to control the humidity rate of the air flow. The experimental set-up used for the breakthrough measurement experiment is presented in **Figure 18**. Wet air was obtained by bubbling through a large flask filled with deionised water heated in a water bath at 32°C. The humidified air was then passed through a condenser placed in the heated chamber (30°C) before entering the dilution chamber. Condensation in the condenser indicated saturation at this temperature. The relative humidity was controlled by the flow rate of wet air and the dry air containing the enriched air flow. Diffusion cells dimensions and flow rate through the generator are listed in **Table 23** and **Table 22**.

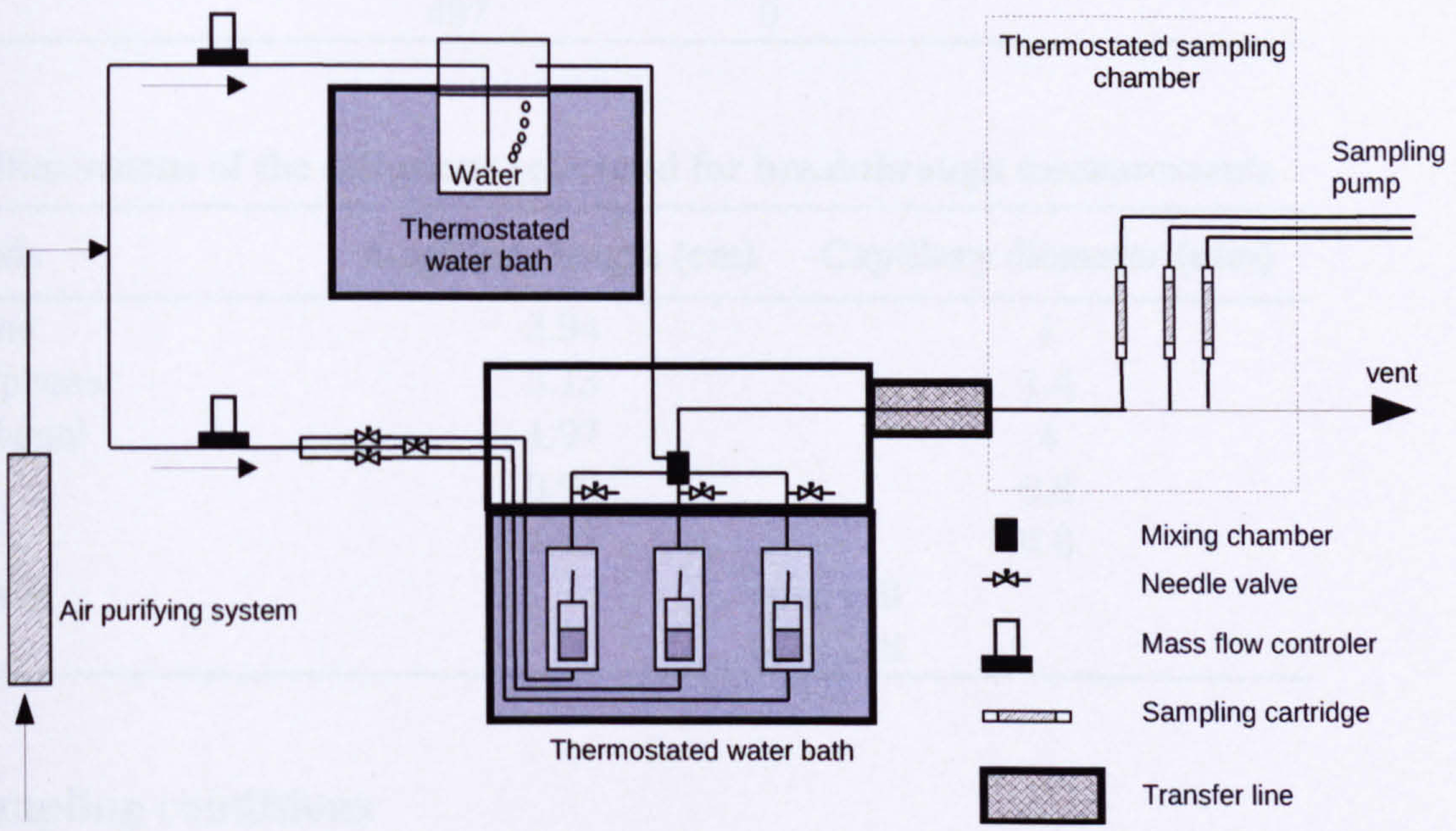


Figure 18: Schematic diagram of the vapour generation system with separate diffusion chamber and humidified air

4.3.2. Vapour generation conditions

The breakthrough volume experiment was performed with 7 compounds. Temperature, flow rates, and estimated generated concentrations are reported in **Table 21, Table 22** and **Table 23** and respectively.

Table 21: Vapour generation temperature and humidity

Parameters	Set-up
Temperature of the thermostated water bath (humidity)	20°C
Temperature of the thermostated water bath (diffusion)	18°C
Temperature thermostated chamber	19°C
Temperature transfer line	19.5°C
Temperature sampling chamber	20.5°C
Relative humidity	20%

Table 22: Flow rates conditions and estimated concentrations during breakthrough measurements

Compounds	Flow rate inlet diffusion cell (ml/min)	Flow rate through split outlet diffusion cell (ml/min)	Flow rate through dilution line (l/min)
Naphthalene	288	0	
4-tertbutylphenol	310	0	
DEP	509	0	
TBP	492	0	3.55
Phenanthrene	395	0	
2-phenylphenol	497	0	
Pyrene	497	0	

Table 23: Dimensions of the diffusions cells used for breakthrough measurements

Compounds	Capillary length (cm)	Capillary diameter (mm)
Naphthalene	3.94	1
4-tertbutylphenol	5.13	1.4
2-phenylphenol	1.97	4
DEP	0.96	9.8
TBP	1.82	4.8
Phenanthrene	open cell	
Pyrene	open cell	

4.3.3. Sampling conditions

Sample tubes compatible with a Gerstel TDS2 thermal desorption apparatus (Gerstel GmbH) were employed. Sample tubes (17 cm x 6 mm O.D. x 4 mm I.D.) were filled with 140 mg of 20/35 mesh Tenax TA (Alltech, France). The adsorbent was held in placed with two stainless steel grids.

Discrete volumes of the generated atmosphere were collected with a pump (Gilair 5, Sensidyne inc) operating at a flow rate of 500 ml/min. A cartridge filled up with silica gel was placed upstream of the pump to prevent water condensation inside it. Sampling was validated if the flow rates at the beginning and end of the sampling did not differ by more than 5%.

4.3.4. Analytical conditions

The analytical set-up described in **chapter 4.1.1** was used to determine the concentrations of the vapour generated whereas samples tubes used for breakthrough measurements were analysed via a Gerstel thermal TDS-2 desorption unit mounted on the top of a Fisons GC8000 with a flame ionization detector. The thermal desorption unit is coupled to a CIS-3 PTV injector (Gerstel GmbH) via a 15 cm long fused silica column for cold trapping. The injector was equipped with an empty baffled liner. The separation was performed on a DB5-MS (30 m L x 0.25 mm I.D x 0.25 µm, J&W, scientific, USA) capillary column.

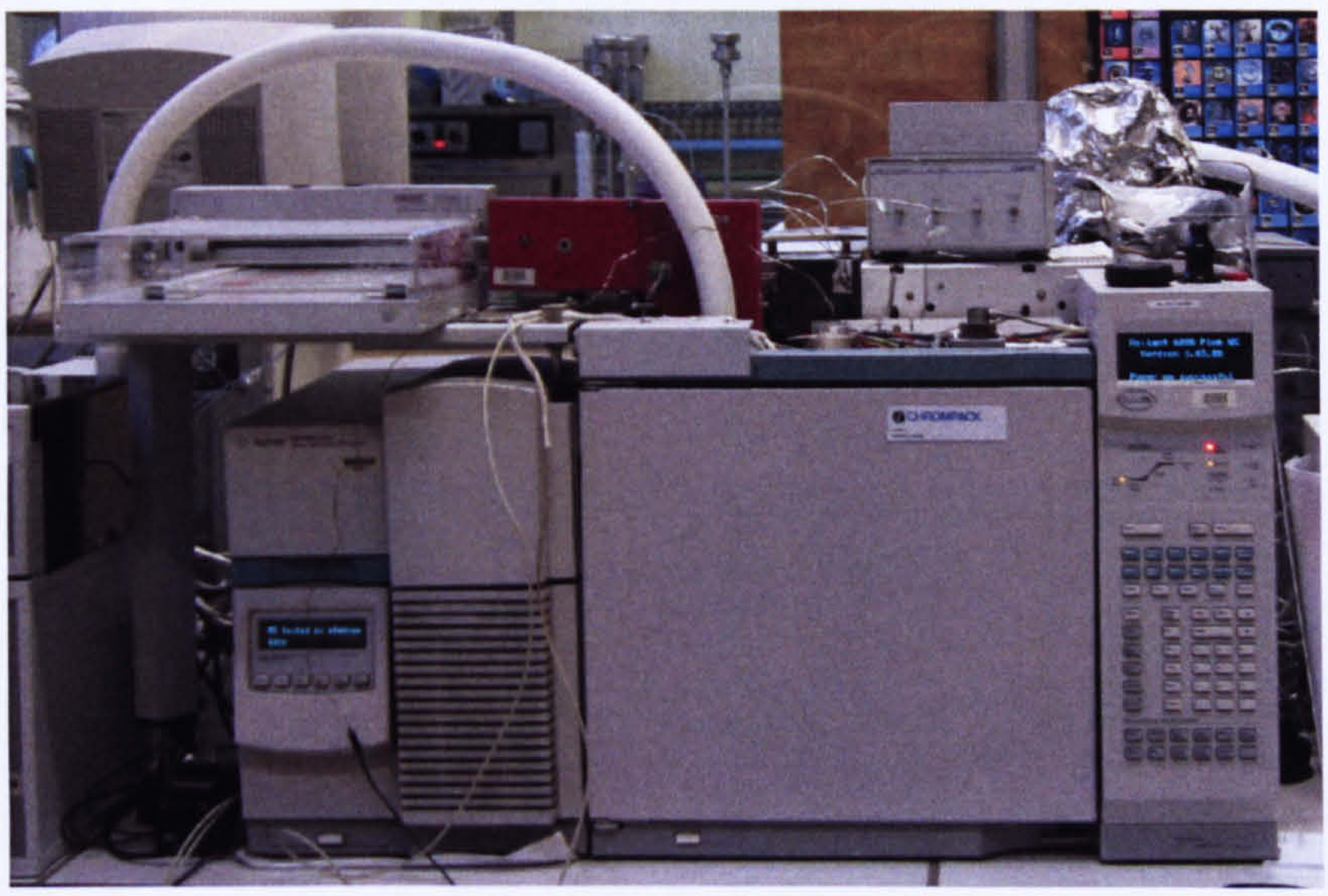
The thermal desorption unit was programmed from 40°C to 300°C at 60°C and held for 15 minutes. Analytes were transferred to the cold injector set at -150°C in splitless mode (40 ml/min) through the transfer line heated at 300°C. After desorption, the analytes were transferred to the capillary column in split mode (1/40) and the injector was heated to 300°C at 600°C/min. The oven temperature was programmed from 40°C (5 minutes) to 300°C at 10°C/min and held at this temperature for a further 5 minutes.

Chapter 5: Development of the analytical method

5.1. Instrumental set-up and GC/MS conditions

The analytical method was developed using a TDS-2 desorption unit mounted on an Agilent GC/MS system consisting of a 6890 model chromatograph and an Agilent 5973N mass selective detector (MSD). The thermal desorption unit is coupled to a CIS-4 PTV injector (Gerstel GmbH) via a 15 cm long fused silica column for cold trapping **Picture 5**. The separation was performed on a DB5-MS (30 m L x 0.32 mm I.D x 0.25 µm, J&W, scientific, USA) capillary column. The GC temperature was held at 60°C for 5 minutes, then ramped to 310°C at 10°C/min. The final temperature was then held for a further 10 minutes. The MS interface, ion source and quadrupole temperatures were set at 310°C, 230°C and 150°C respectively.

The MSD operated in electron impact mode with electron energy of 70eV. The acquisition was run in selected ion monitoring (SIM). The ions selected for the quantification as well as the secondary ions used for the identification are listed in **Table 24**. The MSD dwell time for each ion was between 40 and 100 ms in order to obtain a minimum of 10 data points at the lower concentration of the calibration.



Picture 5: Gerstel TDS-2 desorption unit (in red) mounted on the top of an agilent GC/MS system

5.2. Chemicals and standard tube preparation

Solvents used in this study were purchased from Fisher scientific. Dichloromethane, hexane and acetone were GC grade. Analytical standards were purchased from

Cambridge isotope, Sigma Aldrich and Acros Organics. Suppliers for each chemical are listed in **Table 24**.

✓ ***Standard solution preparation***

All glassware was cleaned by ultrasonication prior to use with dichloromethane and acetone. Stock solutions for each chemical family were prepared by weighting with a microbalance and made up to volume in 10 ml volumetric flasks. Stock solutions were prepared in acetone at 1000 ng/µl with the exception of phthalates, which were prepared at 3000 ng/µl. A stock solution containing the deuterated compounds was prepared at 1000 ng/µl with dichloromethane.

Standard solutions were prepared from the stock solutions in 10 ml volumetric flasks and made up to volume with n-hexane.

✓ ***Standard tube preparation***

Standard tubes were prepared by liquid spiking. Standard solutions were injected to the front of the sample tube and the excess of solvent was eliminated by passing 5 L of He (>99.999 %).

Table 24: Supplier, purity, retention time and characteristic ions of target compounds and internal standards

Compounds	Supplier	Purity (%)	Retention time	Primary ion	Secondary ion
		Group 1			
Naphthalene d8	Cambridge Isotope	99	10.23	136	
Naphthalene	PAH mix, Accustandard		10.27	128	129
4-tertbutylphenol	Puriss, Sigma Aldrich	99	11.97	135	107
Acenaphthylene	PAH mix, Accustandard		14.16	152	153
Dimethylphtalate	Sigma Aldrich	99	14.14	163	164
Acenaphthylene	PAH mix, Accustandard		14.16	152	153
		Group 2			
Acenaphthene d10	Cambridge Isotope	99	14.52	164	
1-naphthaldehyde	Acros Organics	95	14.87	156	128
2-phenylphenol	Pestanal, Sigma Aldrich	99	14.98	170	141
Fluorene	PAH mix, Accustandard		15.83	166	165
Diethylphthalate	Sigma Aldrich	99	15.86	149	177
Propoxur	Pestanal, Sigma Aldrich	99	16.08	110	152
		Group 3			
Tributylphosphate	Sigma Aldrich	99	16.51	99	155
9-fluorenone	Acros Organics	99	17.58	180	152
Tris(2-chloroethyl)phosphate	Sigma Aldrich	97	17.79	248.9	204.9
4-octylphenol	Sigma Aldrich	99	17.87	107	206
Phenanthrene d10	Cambridge Isotope	99	18.01	188	
Phenanthrene	PAH mix, Accustandard		18.05	178	179
Anthracene	PAH mix, Accustandard		18.17	178	179
Diazinon	Pestanal, Sigma Aldrich	99	18.11	179	137
		Group 4			
4-octylphenol	Sigma Aldrich	99	18.96	107	220
Methyl parathion	Pestanal, Sigma Aldrich	99	19.12	108.9	262.9
Dibutylphthalate d4	Oekanal, Sigma Aldrich	98	19.77	153	

Compounds	Supplier	Purity (%)	Retention time	Primary ion	Secondary ion
Dibutylphthalate	Purum, Sigma Aldrich	98			
9,10-anthraquinone	Acros Organics	99	19.99	208	180
Fluoranthene	PAH mix, Accustandard		20.85	202	101
Pyrene d10	Cambridge Isotope	99	21.31	212	
Pyrene	PAH mix, Accustandard		21.34	202	101
9-phenanthrenecarboxaldehyde	Sigma Aldrich	97	21.40	206	178
		Group 5			
Endosulfan β	Pestanal, Sigma Aldrich	99	22.51	194.9	236.8
Benzylbutylphthalate	Sigma Aldrich	98	23.30	149	191
Benzo(a)anthracene d12	Cambridge Isotope	99	24.18	240	
Benzo(a)anthracene	PAH mix, Accustandard		24.21	228	113
Chrysene d12	Cambridge Isotope	99	24.23	240	
Chrysene	PAH mix, Accustandard		24.29	228	113
Benzanthrone	Acros Organics	99	24.57	230	202
		Group 6			
Bis(2-ethylhexyl)phthalate	Purum, Sigma Aldrich	97	24.81	149	167
Benz(a)anthracene-7,12-dione	Acros Organics	99	25.30	258	202
Cis-Permethrin	Pestanal, Sigma Aldrich	99	26.04	183	163
Trans-Permethrin	Pestanal, Sigma Aldrich	99	26.18	183	163
Benzo(j)fluoranthene	PAH mix, Accustandard		26.59	252	253
Benzo(k)fluoranthene	PAH mix, Accustandard		26.64	252	253
Benzo(a)pyrene d12	Cambridge Isotope	99	27.17	264	
Benzo(a)pyrene	PAH mix, Accustandard		27.21	252	253
Perylene d12	Cambridge Isotope	99	27.34	264	
		Group 7			
Indeno(1,2,3-cd)pyrene	PAH mix, Accustandard		29.30	276	278
Dibenzo(a,h)anthracene	PAH mix, Accustandard		29.38	278	139
Benzo(g,h,i)Perylene d12	Cambridge Isotope	99	29.69	288	
Benzo(g,h,i)Perylene	PAH mix, Accustandard		29.71	276	278

5.3. Quantification

The MSD was tuned with perfluorotributylamine at the start of a series of runs. The SVOCs in the gaseous and particulate phases were determined using the internal standard method. Relative response factors (RRF) were calculated for each analyte with a minimum of five calibration points. The following equation was used to calculate RRF for each compound.

$$RRF = \frac{A_x * C_{is}}{A_{is} * C_x}$$

where A_x is the response of the primary ion of the analyte, counts
A_{is} is the response of the primary of the internal standard, counts
C_x is the concentration of the analyte, ng/µl
C_{is} is the concentration of the internal standard, ng/µl

The calibration was accepted if the relative standard deviation of the mean relative response factors ($\overline{RRF}$)for the five standards was less than 30%.

The concentrations of the target analyte were calculated using the following equation.

$$Concentrations\ (ng/m^3) = \frac{A_x * C_{is}}{A_{is} * \overline{RRF} * V}$$

Where V is the volume of air sampled (m^3)

A continuing calibration standard (middle range of the calibration standard) was processed every 15 samples to check the performance of the system. Calibration was accepted when the continuing calibration standard was within 30% of the initial calibration value.

Chapter 6: Performance of developed method

6.1. Performance of the analytical procedure for the organic analysis of particulate matter

The performance of the developed method was evaluated with a standard reference material and by comparison of indoor air filter analysed using the thermal desorption method and a well-established solvent extraction method.

6.1.1. Evaluation with a standard reference material

6.1.1.1. Sample preparation

Urban dust SRM1649a (National Institute of Science and Technology) was used to evaluate the performance of the developed method. This reference material was prepared from atmospheric particulate (sieved to < 125 μm) collected in the late 1970's in Washington D.C. This reference material has a certified value determined with soxhlet extraction methods for a number of PAHs.

Approximately 3 mg of urban dust material was distributed over half of a 37 mm Whatman QMA quartz fibre filter. The filter was rolled up using two pairs of clean stainless steel tweezers and inserted into clean thermal desorption tubes (conditioned at 350°C for two hours under a Helium flow of 100 $ml.min^{-1}$). The other half of the filter was spiked with the deuterated solution, and transferred to the TD tube once the solvent had evaporated after a few seconds. The pair of tweezers was cleaned with acetone before each use.

6.1.1.2. Analysis

Filters and standard sample tubes were analysed using the instrumental set-up and chromatographic conditions presented in **chapter 5.1**. The thermal desorption unit was programmed from 40°C to 350°C at a rate of 60°C/min and held at this temperature for 15 minutes. The analytes were transferred in splitless mode to the cold injection system (CIS) cooled at -150°C. After desorption, the analytes were transferred to the capillary column in split mode (1:10) by heating the CIS to 350°C at a rate of 12°C/s. The CIS was held at this temperature for further 10 minutes.

6.1.2. Comparison with a solvent extraction method

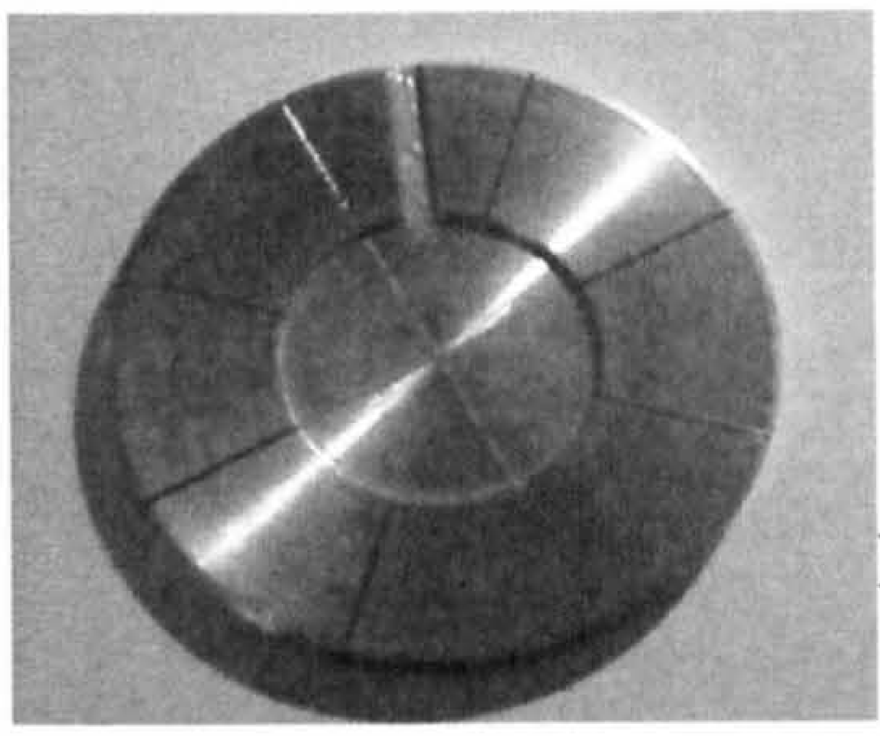
6.1.2.1. Indoor air sample collection

Twenty four hours indoor air samples were collected onto 47 mm quartz fibre filters using a Partisol sampler equipped with a $PM_{2.5}$ sampling head (Model 2000, 1 $m^3.h^{-1}$). The sampling was carried in a building located in the city of Verneuil en Hallate, France which can be considered as a suburban area.

Prior to sampling, quartz fibre filters (Waterman, QMA quality) were calcinated at 500°C for 12 hours to remove any organic contaminants and stored in a dessicator. Collected samples were stored at -18°C until analysis.

6.1.2.2. Filter cut procedure

Filters were cut in eight portions of identical dimensions using a 47 mm filter holder specially designed and manufacture for this purpose **(Picture 6)**.



Picture 6 : Filter holder designed at INERIS

This filter holder made of aluminium was designed so that a stainless steel blade could be inserted through the slots allowing a clean and precise cut. One eight of the filter was analysed by TD/GC/MS and the remaining portions were solvent extracted and the concentrated extract were analysed by HPLC.

6.1.2.3. Solvent desorption analysis

Filters were extracted with dichloromethane (Carlo Erba, HPLC grade) by Pressurised liquid extraction (ASE 200, Dionex). Before extraction, the extraction cells (33 ml) were filled with Fontainebleau sand (150-210µm, VWR) and cleaned at 120°C under 140 bars for 1 cycle (heat time and static time set to 6 minutes). Filter portions were then inserted into the extraction cell and the cell dead volume was filled up with pre-cleaned Fontainebleau sand. The extraction was performed at 120°C under 140 bars for 3 cycles (heat time and static time set to 6 minutes). Extract were concentrated under a nitrogen stream (Zymark Turbovap II) and made up to volume to 1 ml with acetonitrile.

The extract were analysed by a Dionex P580 equipped with a fluorometric detector (RF 200). Two reverse phase columns (Supelco Supecosil LC-PAH C18, 250 mm x 4.6 mm x 5 μm and Alltech Alltima C8, 250 mm x 4.6 mm, x 5 μm) placed in series were used to obtain a good separation. The separation was performed at 1 $ml.min^{-1}$ with a binary solvent gradient (acetonitrile/Water) detailed in **Table 25.**

The injection volume was 20 μL and the column temperature was controlled at 30°C in a Croco-sil oven to reduce retention time shifting.

Table 25: Binary solvent program

Time (minutes)	Water (%)	Acetonitrile (%)
0	70	30
30	70	30
100	0	100
120	0	100

6.1.2.4. Thermal desorption analysis

Filters and standard sample tubes were analysed using the instrumental set-up and chromatographic conditions presented in **chapter 5.1.** The thermal desorption unit was programmed from 40°C to 350°C at a rate of 60°C/min and held at this temperature for 15 minutes. The analytes were transferred in splitless mode to the cold injection system (CIS) cooled at -150°C. After desorption, the analytes were transferred to the capillary column in split mode (1:10) by heating the CIS to 350°C at a rate of 12°C/s. The CIS was held at this temperature for further 10 minutes.

6.2. Performance of the developed method (sampling and analysis)

6.2.1. Conditioning and storage of sample tubes and filters

Prior sampling, QFF filters (Waterman, QMA quality) for both the Partisol and the modified Chempass sampler were calcinated at 500°C for two hours.

PUF cartridges were conditioned with dichloromethane (Carlo Erba, HPLC grade) by Pressurised liquid extraction (ASE 200, Dionex) at 90°C under 100 bars for 3 cycles (heat time and static time set to 5 minutes). Tenax TA sample tubes were conditioned 2 hours at 350°C and stored at ambient temperature in storage containers equipped with PTFE caps (Gerstel, inc).

Collected filters and PUF were stored at -18°C until analysis. Before storage, PUF cartridges were wrapped in pre-cleaned aluminium foil and placed in opaque sealed polypropylene bags whereas filters were placed in individual calcinated glass Petri dishes.

Collected Tenax TA samples tubes were replaced in their storage containers and stored at 4°C.

6.2.2. Parallel sampling between the developed sampler and a low volume sampler

To evaluate the accuracy of the developed method including sampling and analysis, a Chempass sampler and a low volume sampler were operated concurrently. The low volume sampler used for this study was a Partisol model 2000 equipped with a VSCC $PM_{2.5}$ fractionator (1 $m^3.h^{-1}$). This sampler in combination with the VSCC cyclone has been recognized as a Federal equivalent method (FEM) by the US-EPA. A Polyurethane foam (PUF) was placed downstream of the filter to collect the gaseous phase.

Two sampling campaigns were carried out. The sampling was carried in a building located in the city of Verneuil en Hallate, France which can be considered as a suburban area. Each sampling campaign involved six 24 hours parallel samplings.

The first campaign was carried with Tenax TA sample tubes that were previously used for sampling.

The second campaign involved parallel sampling between a Partisol sampler and two Chempass samplers. One Chempass sampler was equipped with freshly packed Tenax TA sample tubes. The other was equipped with Tenax TA sample tubes that had been used for 5 sampling events of 24 hours.

6.2.3. Parallel sampling between the developed sampler and a low volume sampler

The precision of the method was evaluated from six co-located samplers **(Picture 7)**. Samples were collected during 24 hours inside the living room of a flat located in central Paris. The mean temperature was 26 °C.

Picture 7: Co-located samplers inside the apartment

6.2.4. Solvent extraction analysis

Partisol filters were analysed using the procedure detailed in **chapter 6.1.2.3**. PUF cartridges were extracted with dichloromethane (Carlo Erba, HPLC grade) by Pressurised liquid extraction (ASE 200, Dionex) at 90°C under 100 bars for 3 cycles (heat time and static time set to 5 minutes). Extracts were concentrated under a nitrogen stream (Zymark Turbovap II) and made up to volume to 1 ml with acetonitrile.

6.2.5. Thermal desorption analysis

Chempass filters were cut in two portions of identical dimensions using the same type of filter holder as the one described in **chapter 6.1.2.2 (Picture 6)**. This filter holder was designed to incorporate 37 mm filters.

One half of the filter was then divided into two portions to facilitate the introduction of the filter into the desorption tubes. Each portion of the filter was rolled up using two pairs of clean stainless steel tweezers and inserted into clean thermal desorption tubes (conditioned at 350°C during two hours under a Helium flow of 100 $ml.min^{-1}$). A quarter of a clean 37 mm QFF was spiked with the deuterated solution, and transferred to the TD tube once the solvent had evaporated after a few seconds. The pair of tweezers was cleaned with acetone before each use.

Filters, sample tubes and standard sample tubes were analysed using the instrumental set-up and chromatographic conditions presented in **chapter 5.1**. The thermal desorption unit was programmed from 40°C to 350°C at a rate of 60°C/min and held at this temperature for 15 minutes. The analytes were transferred in splitless mode to the cold injection system (CIS) cooled at -150°C. After desorption, the analytes were transferred to the capillary column in split mode (1:10) by heating the CIS to 350°C at a rate of 12°C/s. The CIS was held at this temperature for further 10 minutes.

Chapter 7: Demonstration study

The applicability of the developed method for human exposure measurements was demonstrated during a 6-day sampling study. Indoor, outdoor and personal samples from a 24-hour period were collected simultaneously. Five samples were collected during working days and one on the week-end. This demonstration campaign carried out during 6 non consecutive days was conducted in spring 2006 (from 29 March to 11 April).

7.1. Home description

The demonstration campaign was carried out in a third floor 'non-smokers' flat measuring about 65 square meters located in the centre of Paris. The building is one century old with poorly fitted single glazing windows located adjacent to a non-busy road with virtually no traffic **(Picture 8)**.

The major road with continuous traffic throughout the day is approximately 150 meters away from the building. The flat comprises two bedrooms, one living-room, and a separate kitchen overlooking a patio. The kitchen is equipped with an induction cook top and an electric oven; therefore, the only combustion sources in the kitchen were cooking fumes. The kitchen window was open and the kitchen door was left open during cooking, which is a common practice of the inhabitant. No other combustion sources, such as candles and incense burning, were used during the sampling period. Hardwood varnished floors and painted walls are present in the flat.

Picture 8: Picture of the street and patio taken from the flat

7.2. Sampling strategy

Integrated indoor, outdoor and personal air samples from a 24-hour period were collected simultaneously. Inside the flat, sampling equipment was placed in the living room and in the kitchen at about 1.5 meters high to simulate the breathing zone. The outdoor air sampler was placed on the balcony facing the street at about 0.5 meters from the window. A schematic diagram of the studied flat is presented in **Figure 19**.

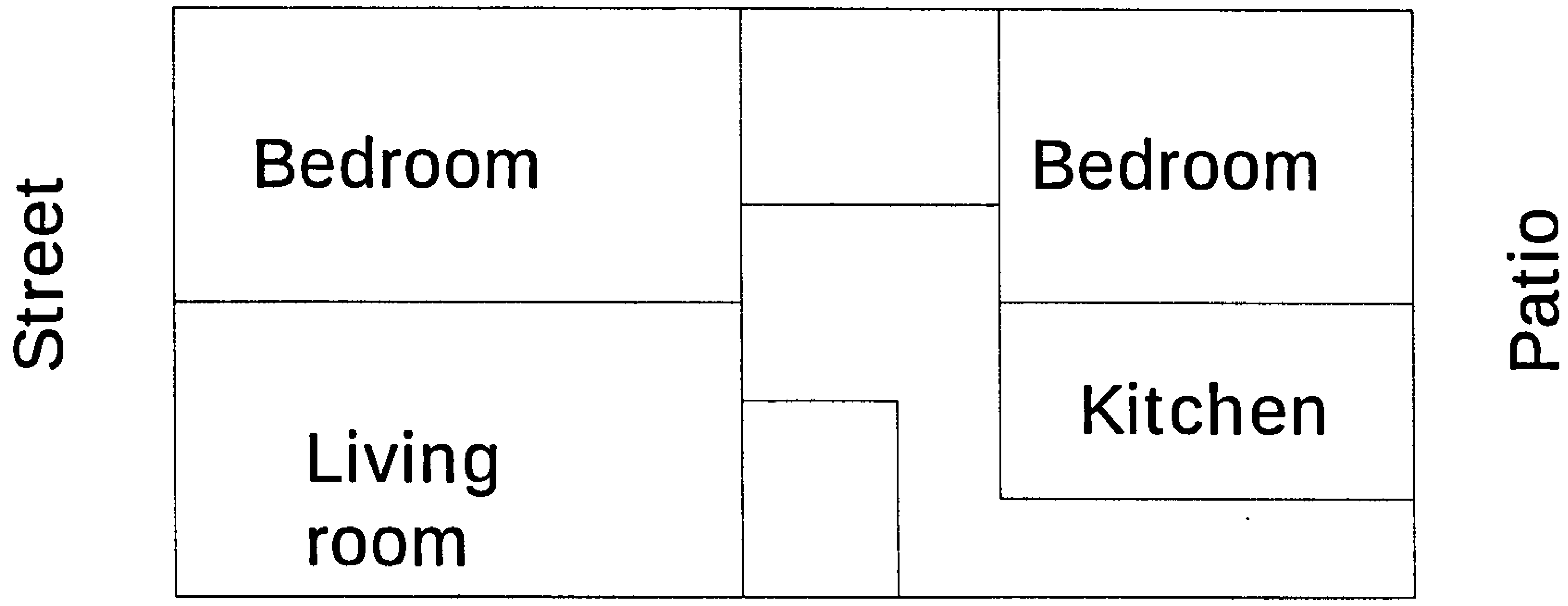


Figure 19: Schematic diagram of the studied flat

The personal air sample was collected by placing the equipment in the backpack that was worn throughout the day, except during sleeping and driving. The personal sampling during the working day included 120 km of motorway driving (60 km in urban and near-urban area and 60 km in a rural area), the working shift in a rural area and the time spent at home. The time activity patterns and major events during sampling are summarised in **Table 26**.

Table 26: Time activity patterns and major events during the sampling campaign

	Weather	Events	Personal sampling Event* (Hrs)
Day 1	Sunny with light rain	Frying eggs	D (2h10), W (9h40), H (12h10)
Day 2	Sunny	No cooking	D (2h30), W (9h30), H (12h00)
Day 3	sunny	No cooking Bedroom window inadvertently left open throughout entire sampling event	D (2h40), W (9h20), H (12h00)
Day 4	Sunny spells	Oven (20 min), Week-end	H (21h30), O (2h30)
Day 5	Cloudy	No cooking	D (2h40), W (9h20), H (12h00)
Day 6	Sunny spells	Oven (20 min)	D (2h30), W (9h30), H (12h00)

** D (driving), W (work environment), H (Home), O (outside)*

The mean indoor, outdoor and personal sampling temperatures over the sampling period were 20.2°C, 10.4°C and 20.1°C respectively. There was no rain during the sampling period except during the first sampling day.

7.3. Sampling method

Sample were collected using the modified $PM_{2.5}$ Chempass sampling head described in **chapter 2.1.3**. Particles associated SVOCs were collected on 37 mm quartz fibre filters (QFF) and gaseous compounds were retained on the thermal desorption tube filled with Tenax TA (mesh size 20/35). The pump were operated at a flow rate of 1.8 $l.min^{-1}$ to achieve a cut-off at 2.5µm and the manifolds were regulated to obtain a flow rate of 0.4 $l.min^{-1}$ (±10%) through the sample tubes. Flow rates were controlled at the beginning and end of each sampling events.

Before sampling, Tenax TA samples tubes were conditioned for 2 hours at 350°C, whereas QFFs were baked at 500°C for 2 hours. Clean Tenax TA sample tubes were stored in storage containers (Gerstel, inc). Clean QFFs were stored in petri dishes placed in a dessicator. After sampling, both QFFs and sample tubes were returned to their original containers. QFFs and Tenax TA samples tubes were stored at -18°C and 4°C respectively until they were analysed. Fields blanks were collected to determine potential contamination during transport and storage (6 filters and 6 Tenax TA tubes)

7.4. Analysis

Filters and Tenax TA sample tubes were analysed within a period of two months after sampling. Each QFF filter was split in 2 equivalent fractions using the filter holder described in **Picture 6 (chapter 6.1.2.2)**. Filters and sample tubes were analysed using the instrumental set-up presented in **chapter 5.1**.

The thermal desorption unit was programmed from 40°C to 350°C at a rate of 60°C/min and held at this temperature for 15 minutes. The analytes were transferred in splitless mode to the cold injection system (CIS) cooled at -150°C. After desorption, the analytes were transferred to the capillary column in split mode (1:10) by heating the CIS to 350°C at a rate of 12°C/s. The CIS was held at this temperature for further 10 minutes.

Part III: Results and discussion

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Chapter 8: Breakthrough volume measurements results

The first task of this study was to determine an appropriate adsorbent for the measurement of gaseous semivolatile compounds with a broad range of volatility from several chemical families. The appropriate adsorbent should permit a safe collection and a complete recovery by thermal desorption. Among three adsorbents potentially suitable for the analysis of SVOCs, one of them was retained based on a recovery study and its sampling capacity was evaluated via a breakthrough volume measurement study. The measurement method involves passing various volumes of a generated atmosphere through sample tubes filled with the retained adsorbent. A vapour generation system based on a diffusion method was therefore developed to generate stable concentrations at ambient air concentrations levels. The concentrations were verified by sampling discreet volume of the generated atmosphere and the collected tubes were subsequently analysed by thermal desorption-gas chromatography with a flame ionisation detector.

8.1. Choice of the adsorbent

Since very little informations could be found in the scientific literature regarding the suitability of adsorbents compatible with a thermal desorption procedure for the collection and analysis of SVOCs, it was decided to evaluate the performance of the adsorbent Carbotrap B which is extensively used for the collection of VOCs of intermediate volatility, the adsorbent Carbotrap C supposed to extend its range to less volatile compounds owing to its physical properties (lower surface area than Carbotrap B) and the adsorbent Tenax TA which as been found to be suitable for some SVOCs such as pesticides and phthalates.

Sample tubes were desorbed during 40 minutes at recommended temperature (310°C for Tenax TA sample tubes and 350°C for Carbotrap B and Carbotrap C sample tubes).

Results of this comparison study are presented in **Figure 20** as histograms of the mean detector response with their respective standard deviation (error bars). It can be observed in this figure that the adsorbent Carbotrap B and Carbotrap C are not adequate to analyse SVOCs. Most of the compounds are only partially desorbed from these adsorbents or irreversibly adsorbed.

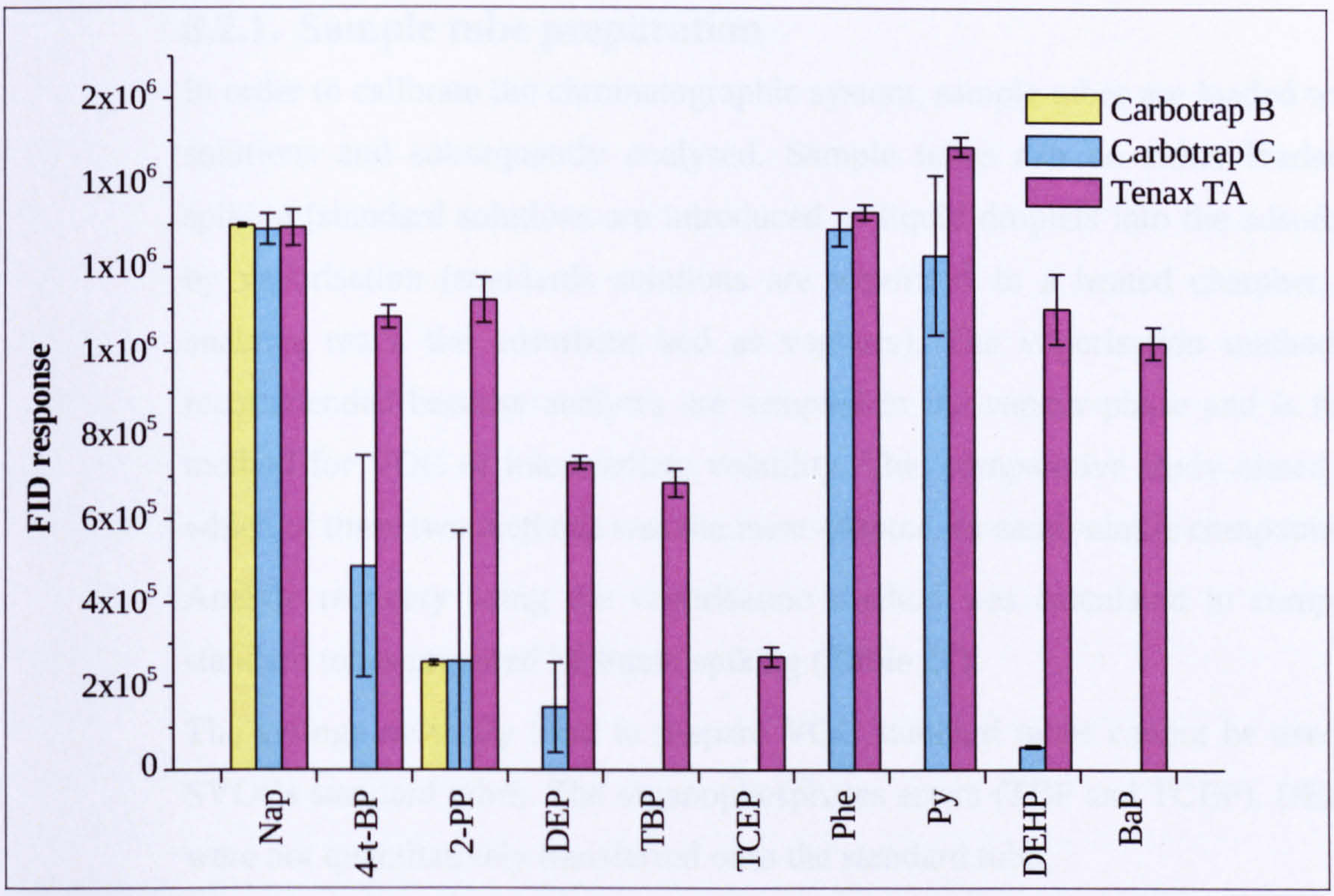

Figure 20: Comparison of the recovery for three adsorbents spiked at the 25 ng level (n=5 for the three adsorbents)

Naphthalene is the only compound that can be desorbed efficiently from the adsorbent Carbotrap B. 2-phenylphenol can be desorbed to a lesser extent and the other compounds are irreversibly adsorbed under the thermal desorption conditions used.

Desorption from the adsorbent Carbotrap C is improved for PAH compounds, since compounds up to pyrene can be desorbed efficiently from this adsorbent, but other compounds are only partially desorbed. Even if the adsorbent Tenax TA has some drawbacks (such as a potential degradation), it appeared from this experiment that it was the best adsorbent tested. It was therefore decided to use this adsorbent for this study.

The degradation product of Tenax TA sample tubes was checked by mass spectrometry. Degradation products positively identified were 2.6-diphenylphenol, 2.6-diphenyl-p-benzoquinone (DPQ) and 2.6-diphenyl-p-hydroquinone (DPQH), but these compounds were not problematic since none of them overlapped with the retention times of the studied compounds.

8.2. Development and optimisation of the analytical method (TD-GC-FID)

The optimisation of the analytical method involved the optimisation of the spiking procedure and optimisation of the desorption time.

8.2.1. Sample tube preparation

In order to calibrate the chromatographic system, sample tubes are loaded with standard solutions and subsequently analysed. Sample tubes can be either loaded by liquid spiking (standard solutions are introduced as liquid droplets into the adsorbent bed) or by vaporisation (standards solutions are vaporised in a heated chamber so that the analytes reach the adsorbent bed as vapours). The vaporisation method is usually recommended because analytes are sampled in the vapour phase and is the preferred method for VOC of intermediate volatility. This comparative study aimed to evaluate which of these two methods was the most adapted for semivolatile compounds.

Analyte recovery using the vaporisation method was calculated in comparison with standard tubes prepared by liquid spiking **(Table 27)**.

The syringe normally used to prepare VOC standard tubes cannot be used to prepare SVOCs standard tubes. The organophosphates esters (TBP and TCEP), DEHP and BaP were not quantitatively transferred onto the standard tube.

In order to improve the transfer, it was attempted to use a syringe that fit in the middle of the desorption chamber (hottest part) and to increase the desorption time. The modified method improved the recovery, but was still not quantitative. Increasing the desorption time to 60 minutes was still insufficient for quantitative transfer. Increasing the desorption flow rate would have been a solution to improve the transfer but it was finally decided to use liquid spiking as a standard tube procedure.

Table 27: Analyte recovery using the vaporisation method (%)

Compounds	Syringe normally used to prepare VOC standard tubes (10 minutes)	Syringe that fit in the middle of the desorption chamber (30 minutes desorption)	Syringe that fit in the middle of the desorption chamber (Further 30 minutes)
Naphthalene	100.7	95.0	0.0
4-tertbutylphenol	108.3	108.5	0.0
2-phenylphenol	100.2	103.1	0.0
DEP	98.0	98.5	0.0
TBP	2.3	66.2	0.0
TCEP	5.9	74.8	0.0
Phenanthrene	104.1	103.1	0.0
Pyrene	64.3	87.4	0.0
DEHP	8.9	61.7	20.7
BaP	1.6	28.1	5.7

8.2.2. Optimisation of the desorption time

The performance of the analytical procedure to transfer the analytes into the chromatographic column is influenced by many parameters. Due to the low volatility of the target compounds, all the parameters influencing the transfer to the analytical column were set at the maximum operating limits (i.e. desorption flow (30 ml/min^{-1}), desorption temperature (310°C), transfer line temperature (290°C) and desorption trap temperature (350°C)). The only parameters that could be optimised was the desorption time. Preliminary experimental work has demonstrated that carry over and possibly incomplete desorption were likely to occur under standard desorption conditions (20 minutes, 310°C) for organophosphate esters, DEHP and BaP (data not shown). It was therefore decided to increase the desorption time in order to reduce the carryover and enhance the desorption. Carry-over is likely to be reduced because the transfer line and the valve in the desorption unit were flushed with a high flow rate of carrier gas (i.e. equal to the desorption flow) for a longer period of time. Increasing the desorption time is also likely to enhance the desorption since more time is left for the transfer. Results of this experiment are presented in **Figure 21** that show histograms of the FID response per ng injected at three concentrations levels and raw data are given in **appendix 5**.

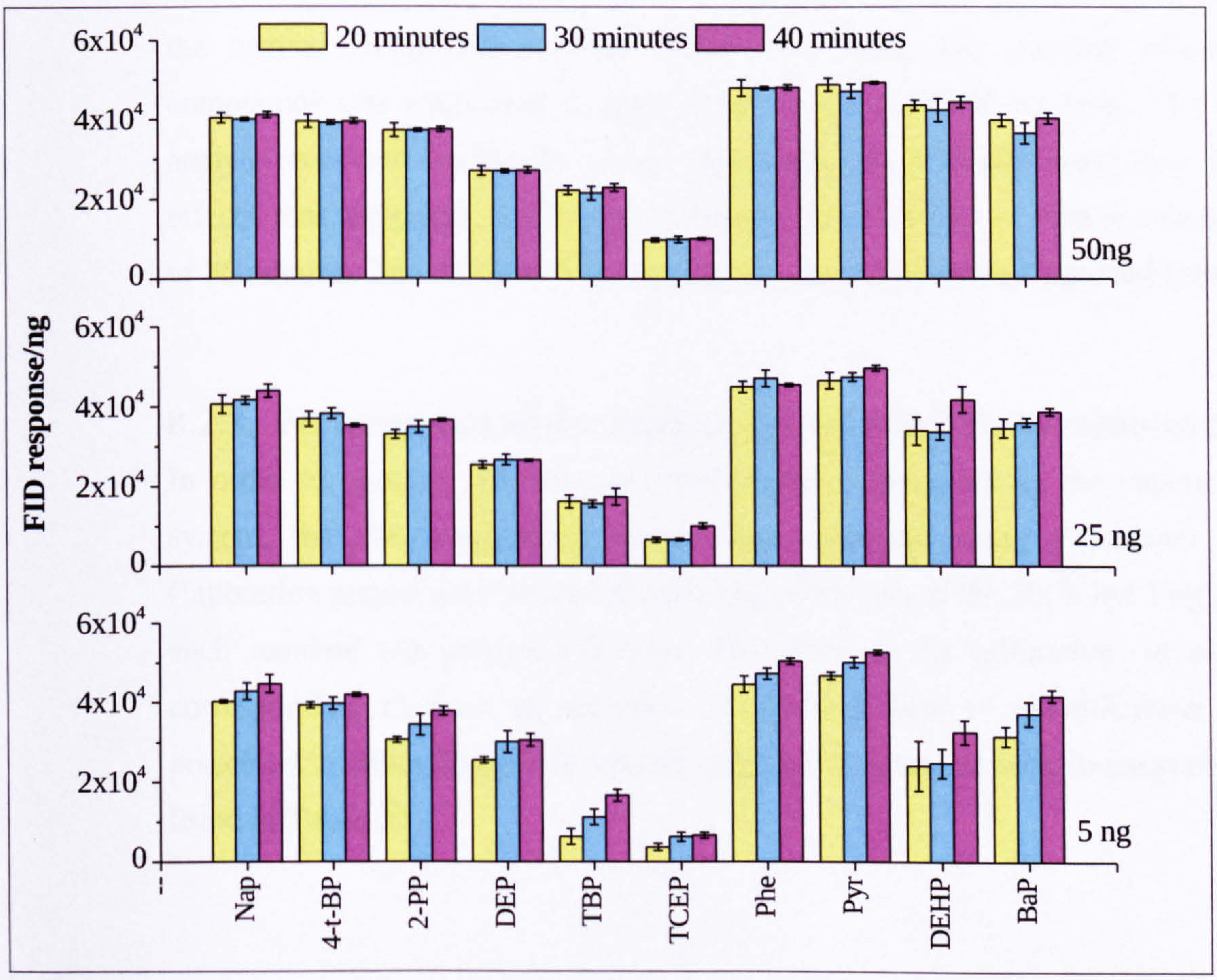

Figure 21: Response factors at different concentrations levels and desorption time (5 replicates at each concentration level)

It can be observed that the response factors for most of the analytes overlapped at the 50 ng and 25 ng on-tube levels. At the 5 ng on-tube level, the response factors tended to increase by increasing the desorption time. This effect was the most significant for the organophosphate and phthalate esters, 2-phenylphenol and benzo(a)pyrene. The response factor between 20 and 40 minutes desorption time was increased by a factor of 2.63 and 1.82 for TBP and TCEP, respectively. The response factors of other compounds, with the exception of naphthalene, 4-tertbutylphenol, phenanthrene and pyrene, were increased by a factor more than 1.2. Adsorption of a fraction of the analytes in the sample flow path (active site or cold spots) or incomplete desorption/irreversible adsorption from the Tenax TA samples tubes are possibly the reasons explaining lower response factors for shorter desorption time at low concentrations. By increasing the desorption time, more time is left for transferring the analytes to the cold trap. At high concentrations, response factors were similar regardless of the desorption time, since even if a fraction of analytes were retained in the sample flow path or Tenax TA sample tubes, the quantities retained were negligible compare to loading. Desorption recovery was checked for each desorption temperature by repeating the analysis of one tube spiked with 50 ng after analysis of an empty tube. A memory effect from the desorption of a previous sample was noticeable primarily for the heavier compounds (pyrene, DEHP and BaP). The memory effect for these compounds was equivalent to approximately 1% at the 50 ng level. The quantity of analyte recovered during the second desorption was generally lower than the memory effects, thus suggesting that complete desorption was achieved even at a desorption time of 20 minutes. The 40-minute desorption time was retained as a standard condition.

8.2.3. Performance of the analytical method (TD: 40 minutes at 310°C)

In order to quantify the vapours concentrations generated in the vapour generation system, the chromatographic system was calibrated using a external calibration. Calibration graphs were plotted at concentration levels of 50, 25, 5 and 1 ng on-tube and each standard was analysed 5 times. The slope of the calibration curves with their corresponding r^2, limit of detection (LOD) and limit of quantification (LOQ) are presented in **Table 28** and the relative standard deviation at each concentration level are listed in **Table 29**.

Table 28: Linearity, detection limit and blank quality of the analytical method

Compounds	Calibration range (ng)	Slope	R^2	LOD (ng)	LOQ (ng)	Blank mean (n=5)
Nap	1-55	y = 41126x + 23492	0.998	0.1	0.2	ND
4-t-BP	1-50	y = 39018x - 12948	0.996	0.1	0.4	ND
2-PP	1-50	y = 37390x - 2298	0.999	0.2	0.9	0.14
DEP	1-50	y = 27605x + 5719	0.999	0.3	0.9	0.08
TBP	1-50	y = 236.81x2 + 11126x + 14503	0.999	0.3	0.9	0.36
TCEP	5-60	y = 10576x - 19115	0.999	1.5	5.0	ND
Phenanthrene	1-50	y = 47932x - 11563	0.998	0.1	0.4	ND
Pyrene	1-50	y = 49091x + 13031	1.000	0.2	0.5	0.06
DEHP	1-50	y = 44376x - 19079	0.998	1.0	3.4	0.28
BaP	1-50	y = 39986x - 2163	0.999	0.1	0.4	0.06

Limit of detection; LOD= mean blank + 3 sd blank (n=5)
Limite of quantification, LOQ= mean blank +10 sd blank (n=5)
ND= not detected

It can be observed in **Table 28** that a linear response was obtained for the target compounds at the exception of TBP. The quadratic response for this compound is the result of its incomplete transfer into the capillary column due to its adsorption onto the wall of the sample flow path. The regression coefficients were really good with values ranging from 0.998 to 1.000 and limit of detections (mean blank + 3sd) ranged between 0.1 ng and 1.5 ng on-tube. Limit of detections were influenced by the quality of the blank and the response of individual target compounds. The detection and quantification limits presented in **Table 28** are achievable with a clean system. However, in real sampling with high concentrations, the memory effect will prevent reaching such levels. It is therefore recommended to analyse an empty tube between two samples in order to reduce the carry-over of analytes on subsequent analysis.

The method is less repeatable at low concentrations for many compounds as indicated with higher relative standard deviation **(Table 29).** This is not uncommon in chromatography, since peak areas approach the background level. The background level in gas chromatography (liquid injection) is mainly influenced by the solvent impurities and residues left in the injection port. In thermal desorption, the memory effect and the blank of the adsorbent itself are the chief influences on the background level.

Table 29: Repeatability of the analytical method based on relative standard deviation (5 replicates at each concentration levels)

Compounds	RSD (%) at 1ng level	RSD (%) at 5 ng level	RSD (%) at 25 ng level	RSD (%) at 50 ng level
Naphthalene	1	5	4	2
4-tertbutylphenol	4	1	1	2
2-phenylphenol	8	3	1	2
DEP	8	5	1	3
TBP	10	9	12	4
TCEP	-	10	7	3
Phenanthrene	4	2	1	1
Pyrene	4	1	2	1
DEHP	28	9	8	3
BaP	4	4	2	3

8.2.4. Summary

The adopted thermal desorption procedure is efficient for most of the compounds. Analytical difficulties are mainly encountered for DEHP and organophosphate esters. The precision of the method for organophosphate esters and DEHP is not as good as for other compounds. The developed analytical method was deemed satisfactory and was used to determine the concentrations generated in the vapour generation system.

8.3. Results of the vapour generation system

8.3.1. Results of the vapour generation system (VGS) with a single diffusion chamber at low flow rate

A blank of the system was performed before starting the generation **(Figure 22)**. It can be seen that the purifying system was effective in removing most of the contaminants present in the ambient air used to dilute the vapours. The dilution air did not interfere on the vapour generated since the concentrations generated were much higher than background levels.

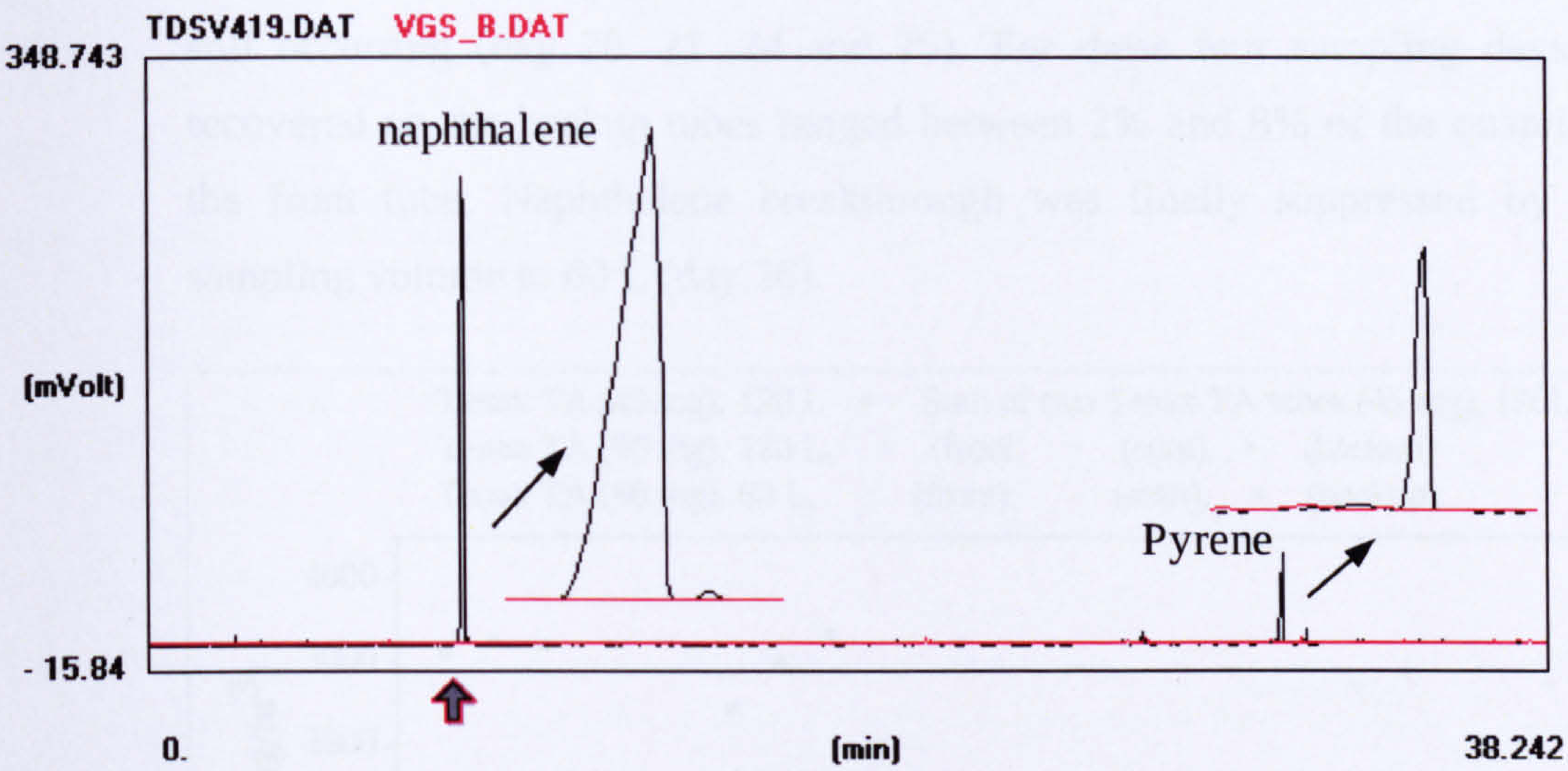

Figure 22: Vapour generation blank (red line) and vapour of naphthalene and pyrene (black line)

Evolution of the concentrations for both naphthalene and pyrene are shown in **Figure 23**. Samples to control the vapour generated were collected by forcing the entire flow to pass through Tenax TA sample tubes (mesh 60/80). Sample tubes were subsequently analysed using the developed analytical method.

Vapours for both pyrene and naphthalene were detected even after 2 days, but it was observed that the concentrations were still not stable on day 9. Suspected reasons for this instability arise from:

- equilibrium in the VGS not being reached
- incomplete desorption
- sampling procedure not safe (i.e. breakthrough occurring)

The first hypothesis could not be excluded, but equilibrium should be reached quickly in such system. Temime *et al* (2002) developed a vapour generator to generate naphthalene vapours using the permeation method in the 2 ng/m^3 to 150 ng/m^3 range. They found that the concentration was stable from the first control (2 days). Even if the designs of both generators were different (length and material of the sample flow path), it was expected that the concentrations would stabilise more quickly. The second hypothesis was rejected since a second desorption of a sample tube did not show any traces of the target compounds. The third hypothesis was suspected on day 10, since the concentration of naphthalene (sum of two tubes placed in parallel sampled at 1 $l.min^{-1}$) was higher than in the previous days. Breakthrough for both naphthalene and pyrene was demonstrated by placing two tubes in series at the outlet of the VGS (day 12, data not shown). The amount found on the backup tube represented 34% and 5% of the front tube for naphthalene and pyrene respectively. Doubling the load of Tenax TA in the sample tubes did suppress breakthrough for pyrene, but naphthalene breakthrough was still occurring (day 20, 21 ,24 and 25). For these four sampling days, the amount recovered on the backup tubes ranged between 2% and 8% of the quantities found on the front tube. Naphthalene breakthrough was finally suppressed by reducing the sampling volume to 60 L (day 26).

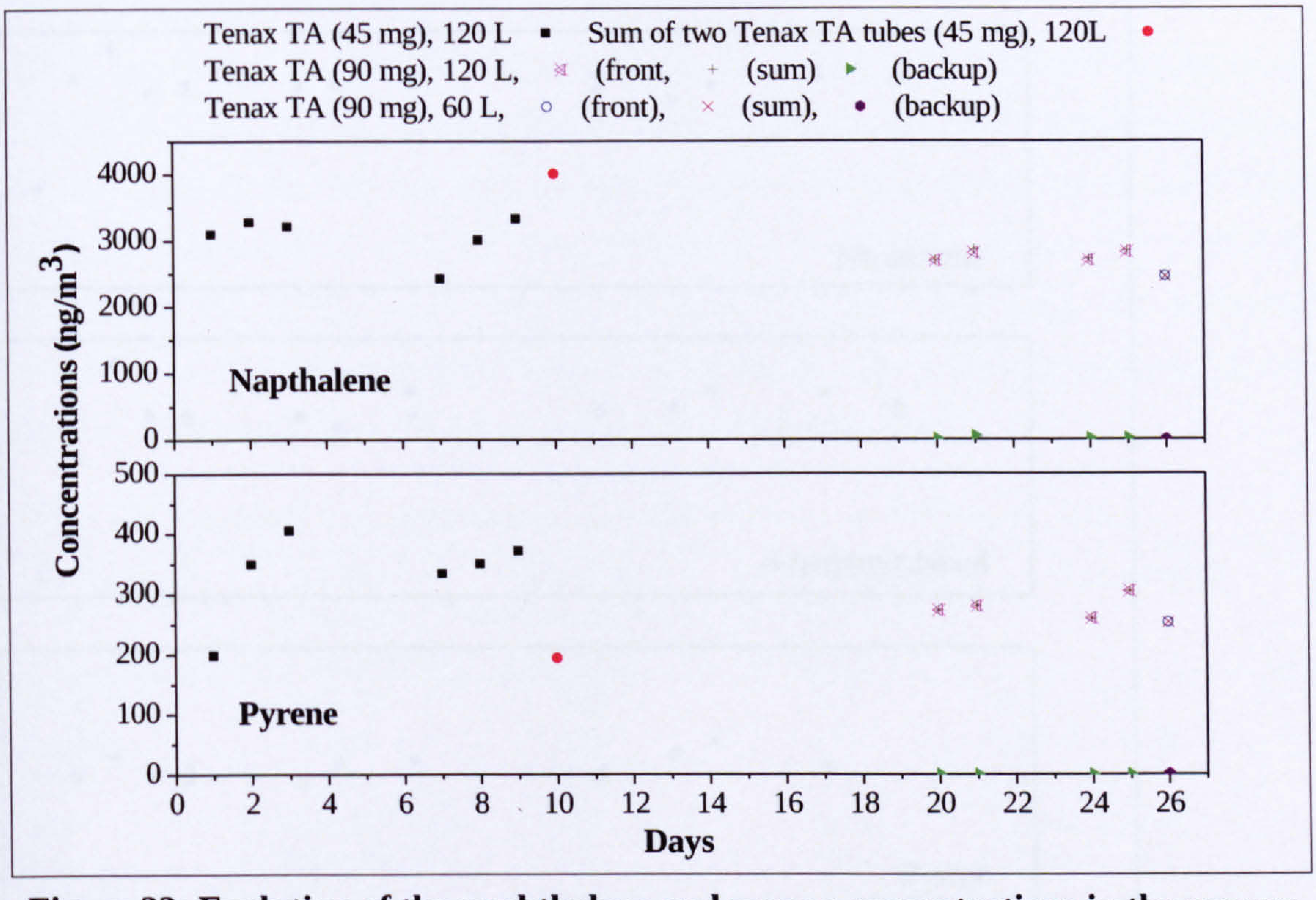

Figure 23: Evolution of the naphthalene and pyrene concentrations in the vapour generation system (ng/m³)

The procedure to control the vapour generated and the set-up of this generator suffered from several drawbacks. Firstly, placing the tube at the outlet of the generator results in pressure variation in the generator. Any change in pressure results in variation of the diffusion rate **(equation 2)** and hence variations of the concentrations. The flow rate at the outlet of the generator is not sufficient to perform replicate measurements. It was therefore decided to repeat the experiment with a higher flow rate through the dilution line and to include compounds from different chemical families.

8.3.2. Results of the vapour generation system (VGS) with a single diffusion chamber at high flow rate

This experiment aimed to generate vapours for various compounds. Concentrations of the vapours were determined by pumping rather than forcing the air to pass through the sample tube. Samples were collected at 1 $l.min^{-1}$ onto Tenax TA (mesh 60/80) with a Buck VSS 5 pump (A.P buck, France) for a final volume of 60 L. Vapour generation was attempted for 6 compounds, including at least one compound for each chemical family (PAH, alkylphenol, organophosphate esters and phthalates). The evolution of the concentrations for the vapour generated is shown in **Figure 24.**

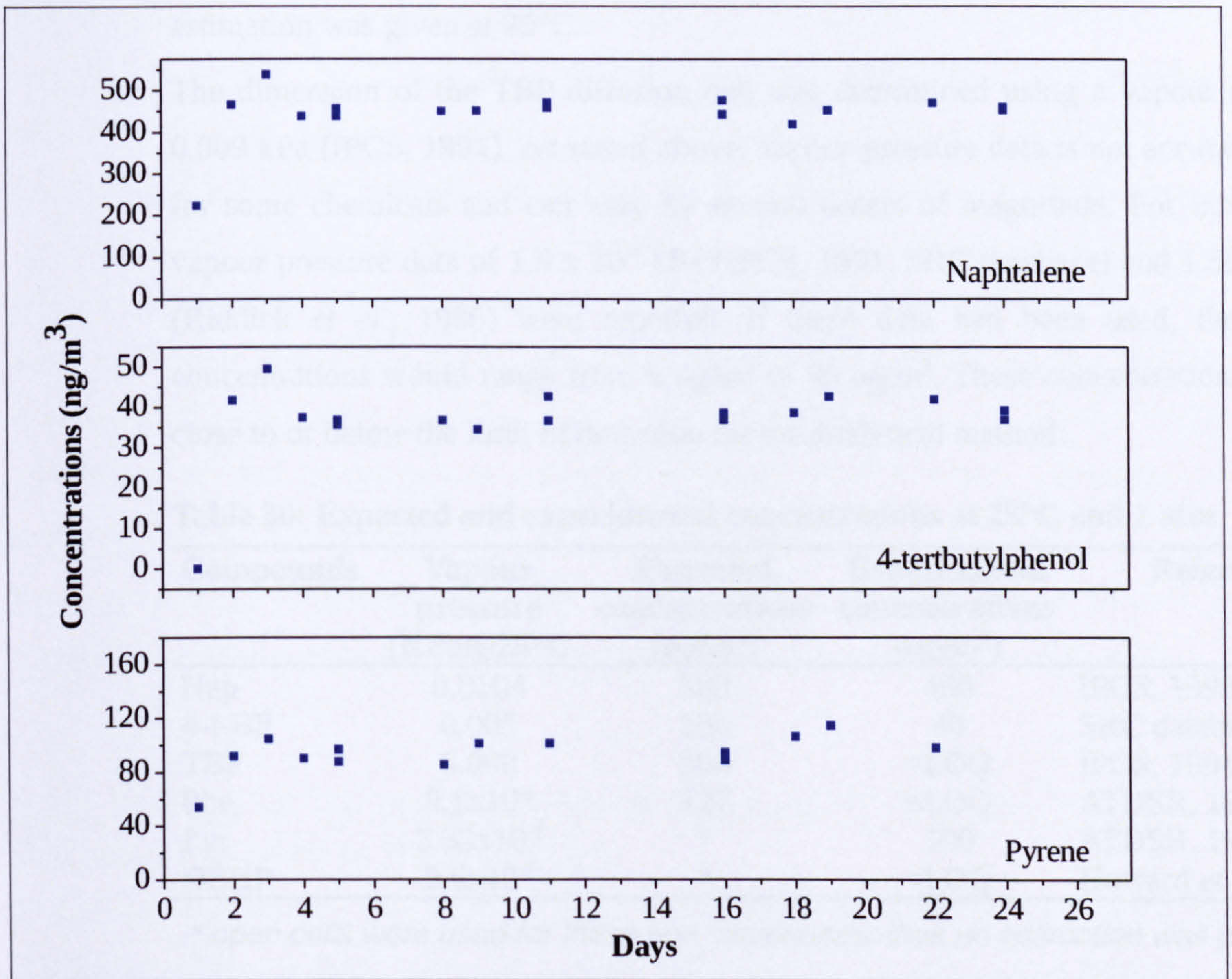

Figure 24: Evolution of the concentrations in the VGS (60 L sampling volume using sample tubes filled with 90 mg of Tenax TA)

It can be seen that vapours were generated for 3 compounds out of 6. One explanation for the non-generation of DEHP, TBP and phenanthrene is that the vapour generated for these compounds adsorbed to the wall of the generator. This is not unlikely for DEHP and TBP, since these two compounds are known as 'sticky compounds'. For phenanthrene, the lack of generation was surprising since vapours were generated for two of its congeners (naphthalene and pyrene). The dimension of the capillary should have permitted the generation of phenanthrene vapours. Among the different parameters entering into the calculation of diffusion rates **(equation 1)**, the vapour pressure can strongly affect estimates. Vapour pressure for semivolatile compounds at ambient temperature are often extrapolated from measurements at higher temperatures. Consequently, vapour pressure data found in the existing literature can vary greatly depending on the authors. For instance, if a vapour pressure of 1.62×10^{-5} at 25°C (Mackay *et al.*, 1992) is used in the calculation, the expected phenanthrene concentrations would be only 20 ng/m^3. This concentration corresponds to 1.2 ng on-tube for a 60 litres sampling volume, which is very close to the limit of quantification. In addition, lower diffusion rates were expected than those provided in **Table 30**, since the temperature in the water bath was 18°C whereas the vapour pressure used for estimation was given at 25°C.

The dimension of the TBP diffusion cell was determined using a vapour pressure of 0.009 kPa (IPCS, 1991). As stated above, vapour pressure data is not accurately known for some chemicals and can vary by several orders of magnitude. For instance, TBP vapour pressure data of 1.5×10^{-4} kPa (IPCS, 1991, SRC database) and 1.59×10^{-5} kPa (Riddick *et al.*, 1986) were reported. If these data had been used, the estimated concentrations would range from 5 ng/m^3 to 50 ng/m^3. These concentrations levels are close to or below the limit of detection for the analytical method.

Table 30: Expected and experimental concentrations at 25°C and 1 atm

Compounds	Vapour pressure (KPa@25°C	Expected concentrations (ng/m^3)	Experimental concentrations (ng/m^3)	References
Nap	0.0104	580	450	IPCS, 1998
4-t-BP	0.005	130	40	SRC database
TBP	0.009	300	<LOQ	IPCS, 1991
Phe	9.1×10^{-5}	127	<LOQ	ATDSR, 1995
Pyr	3.33×10^{-7}	*	100	ATDSR, 1995
DEHP	8.6×10^{-7}	*	<LOQ	Howard *et al.*, 1995

* *open cells were used for these two compounds; thus no estimation was possible*

It can also be seen that the calculated and experimental concentrations are quite different for 4-tertbutylphenol. The capillary tube was inspected at the end of the experiment and it was found that the diameter was only 0.8 mm at one end of the tube (stainless steel ring created by tube cutter). Inaccurate vapour pressure data cannot be excluded, since this chemical is poorly documented. Overall, naphthalene was the only compound in agreement with theoretical concentrations.

The stability of the vapour generated is more than acceptable for the three compounds. Variation of the concentrations from day to day and over the one-month experiment is roughly less than 10 %, 15 % and 15 % once the equilibrium is reached for naphthalene, 4-tertbutylphenol and pyrene respectively. Fluctuations in the concentrations are the results of the instability of the generator (flow rate fluctuation and temperature fluctuations) and the uncertainty of the measurements (analytical procedure and volume sampled). Fluctuation of the flow rate through the vapour generation line is suspected to be negligible, since a mass flow controller was used (±2%). Fluctuations through the dilution line may be higher because a simple manometer and needle valve was used. Uncertainty of the volume sampled is given to be ±5 %.

✔ **Summary**

This experiment has confirmed that a stable flow of vapour can be generated for some SVOCs. However, the dimensions of the diffusion cells for a given desired concentration were difficult to predict. The concentrations of the vapour generated in this system are controlled by the dimensions of the diffusion cells, the temperature of the water bath and dilution factor. Modifying the temperature or dilution factor will affect concentrations of all compounds. Vapours at different concentrations can be generated using diffusion cells of different sizes. However, this procedure has the drawback of breaking the equilibrium of the generator and does not allow accurate controlling of the concentrations generated because SVOCs vapour pressures are generally not well characterised.

In order to more efficiently control the concentrations generated, it was decided to modify the system so that different dilution factors could be set for each compounds.

8.3.3. Results of the vapour generation system (VGS) with a separate diffusion chamber at high flow rate

It was demonstrated in the previous experiment that it was difficult to estimate the dimension of the capillary tubes for a given concentration because vapour pressure of most semivolatile compounds is often inaccurate. Vapour pressure at ambient temperature for semivolatile compounds are often derived from measurements at elevated temperature and extrapolation using Clausius-Clapeyron or Antoine equation. This method of measurement results in important inaccuracies and only data based on the saturation technique can be trusted (Howard *et al.*, 1995).

It was therefore decided to use wider and shorter capillary tubes than those used in the previous experiment for 4-t-butylphenol, TBP and phenanthrene. Generation of 2-phenylphenol and diethylphthalate vapours was also attempted using wide and short capillary tubes. Generation of vapour at a desired concentration can be done in two steps using this experimental set-up. Vapours are generated at "unknown" concentrations using wide and short capillary tubes. Then, desired concentration levels can be reached using the split line located at the outlet of each diffusion chamber.

The evolution of the concentrations generated over a 2-week period is presented **Figure 25**.

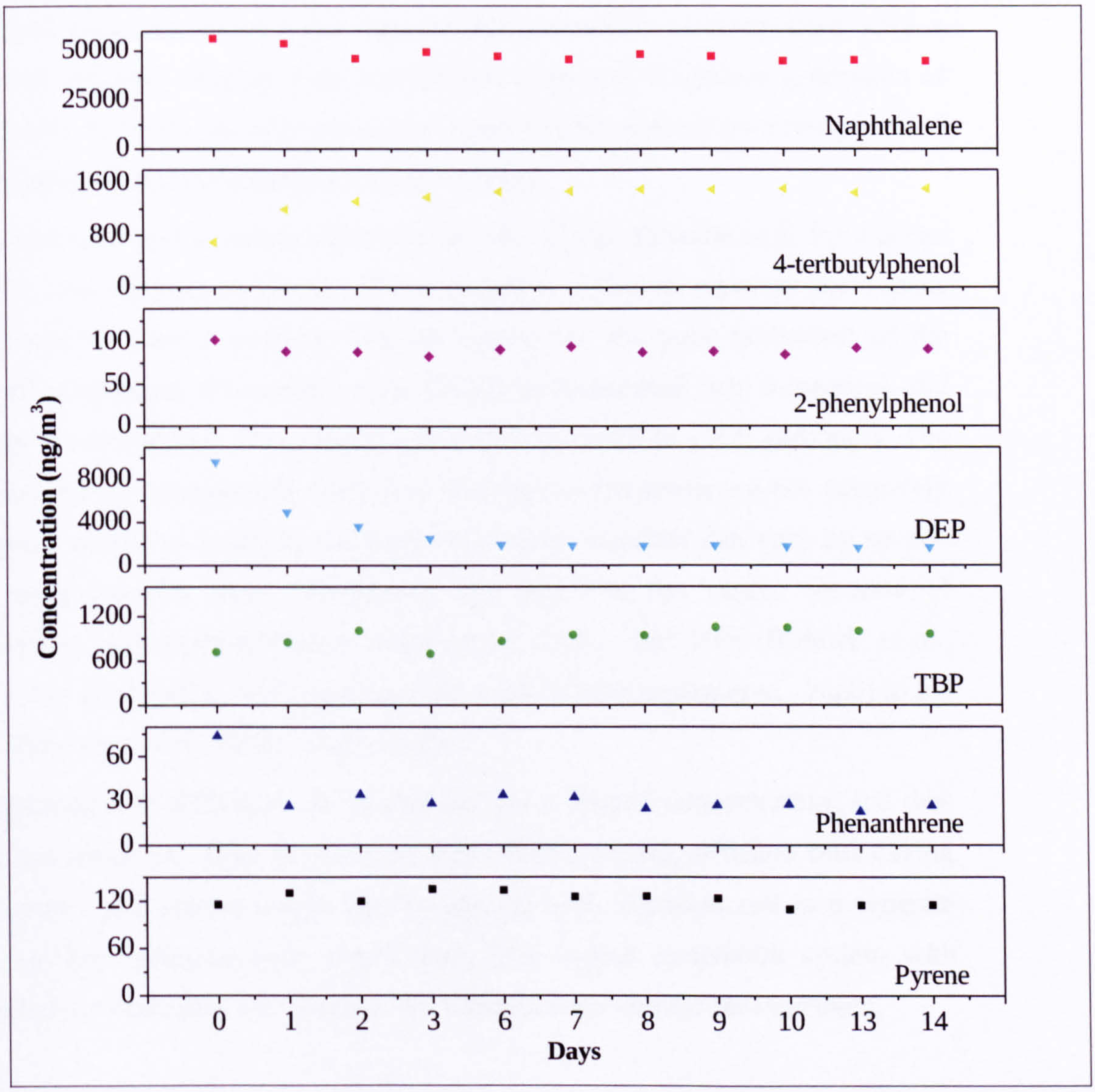

Figure 25: Evolution of the concentration over a two weeks period

It can be seen that vapours were generated for all the compounds with the exception of DEHP, which is the least volatile. The vapour concentrations were stable once equilibrium was reached. The average concentration (SD, ng/m^3) was 46000±1500 for naphthalene, 1460±80 for 4-tertbutylphenol, 90±5 for 2-phenylphenol, 1750±90 for diethylphthalate, 950±130 for tributylphosphate, 28±4 for phenanthrene and 126±8 for pyrene.

It can be seen that naphthalene concentrations were generated at concentrations of 46 μ g/m³, which is much higher than expected (diffusion cell identical to the one used in the vapour generation system with single chamber at low flow rate). It is thought that the high generation of naphthalene was the result of a vial that was not properly tightened.

8.3.4. Vapour generator conclusions

The developed apparatus enables the reproducible generation of compounds with a broad range of volatility ranging from naphthalene to pyrene. It enables generation of vapours not only of PAHs, but also phosphate esters (TBP), phenols (4-tertbutylphenol and 2-phenylphenol), and phthalates (diethylphthalate).

The results obtained tend to demonstrate that the size of the diffusion cells for a given concentration was difficult to predict. The theoretical diffusion equation for vapour through a capillary tube is probably not the reason for the poor estimation of the diffusion cell dimension. Possanzini *et al* (2000) demonstrated that theoretical and experimental concentrations were closely correlated for n-C6 to n-C9 carbonyls. The main problem for the compounds studied is that vapour pressures are not accurately known. Vapour pressures found in the body of existing literature can vary by several orders of magnitude for some compounds. For instance, the vapour pressure of tributylphosphate and diethylphthalate ranges from 1.59 x 10^{-5} KPa (Riddick *et al.*, 1986) to 9 x 10^{-3} KPa (IPCS, 1991) and from 6.5 x 10^{-5} KPa (Cousins *et al.*, 2000) to 2.8 x 10^{-4} KPa (Hinckley *et al.*, 1990), respectively.

The poor estimation of diffusion cell dimensions for a desired concentration, and thus the lack of generation for some compounds, was solved by using diffusion cells having a wider diameter and shorter length and by placing each diffusion cell in a separate diffusing chamber equipped with a split line. The vapour generation system with separate diffusions chambers was used for the breakthrough volume measurement.

8.4. Breakthrough volume measurements at 30°C and 70% RH

A direct method was used to determine the breakthrough volume of selected target compounds on the adsorbent Tenax TA. This method was preferred to the indirect method based on retention volume because it is much closer to a real sampling procedure. A thorough evaluation of the parameters (vapour concentrations, humidity, temperature, sampling flow rate and co-pollutants) influencing the sampling capacity of an adsorbent is conceivable when breakthrough volumes are in the order of few litres, but is nevertheless very time consuming. Breakthrough volumes were expected to be much larger for the target compounds. Based on an indirect method, breakthrough volumes of naphthalene on the adsorbent Tenax TA of 100 m^3 per gram and 9.5 m^3 gram were determined at 20°C and 40°C respectively. It was therefore decided to the measure the breakthrough volume under the worst conditions that may be encountered during field sampling. This method is recommended by the European standard for the measurement of benzene concentrations in ambient air via pumped sampling followed by thermal desorption and gas chromatography (CEN-EN14662-1).

8.4.1. Selected sampling conditions

The temperature and the relative humidity of the vapour generation system were set at 30°C and 70%, respectively. This temperature and relative humidity are likely to be in the upper range of those found in field sampling. For instance, the indoor air quality observatory (OQAI) reported temperature of 24.8°C (P95) and relative humidity of 64.7% (P95) in the homes of 567 French families between 2003 and 2005 (OQAI, 2007). The concentrations levels generated for this study are presented in **Figure 26.**

The concentration of naphthalene, which is the compound suspected to have the lowest sampling capacity, was set at 4 µg/m3, which is in the upper range of the concentrations found in the literature. Breakthrough measurements were performed between day 6 and day 14. The average concentration (SD, ng/m^3) was 4590±220 for naphthalene, 1750± 90 for 4-tertbutylphenol, 1450±120 for 2-phenylphenol, 1900±100 for diethylphthalate, 950±90 for tributylphosphate, 72±4 for phenanthrene and 37±3 for pyrene.

The flow rate was set at 500 ml.min^{-1} which is the maximum flow rate that could be tolerated by the personal pumps. Higher flow rates result in excessive noise and pump overheating.

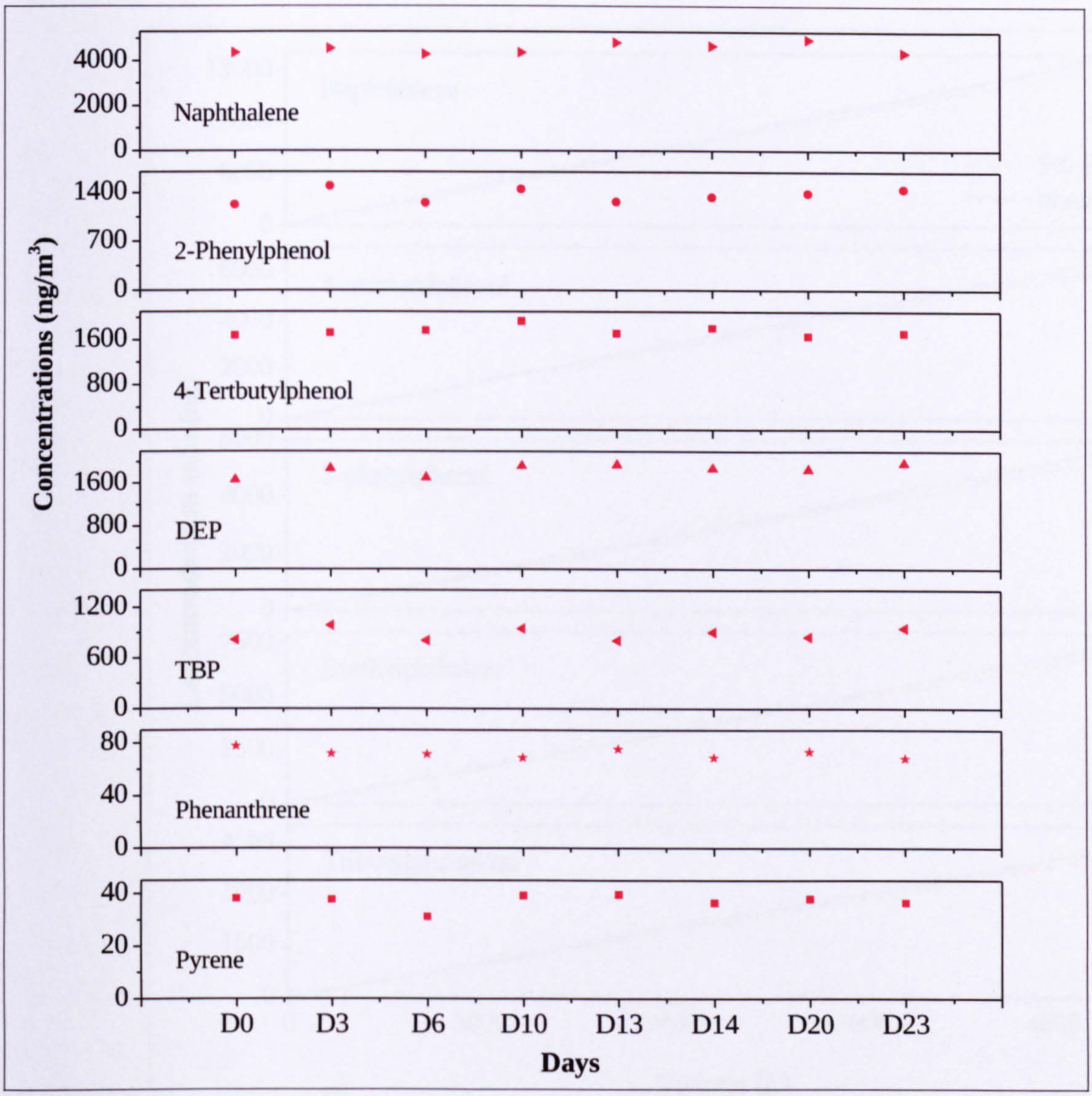

Figure 26: Evolution of the concentrations over a period of one month

8.4.2. Breakthrough volume determination

Multiple discrete volumes from the vapour generation system were collected and the amount of analytes sampled versus the sampled volumes was plotted **(Figure 27)**. A linear curve is obtained until breakthrough occurred. The linear equation y=ax was fitted by a least square method and the liner curve corresponding to a breakthrough of 5% was plotted.

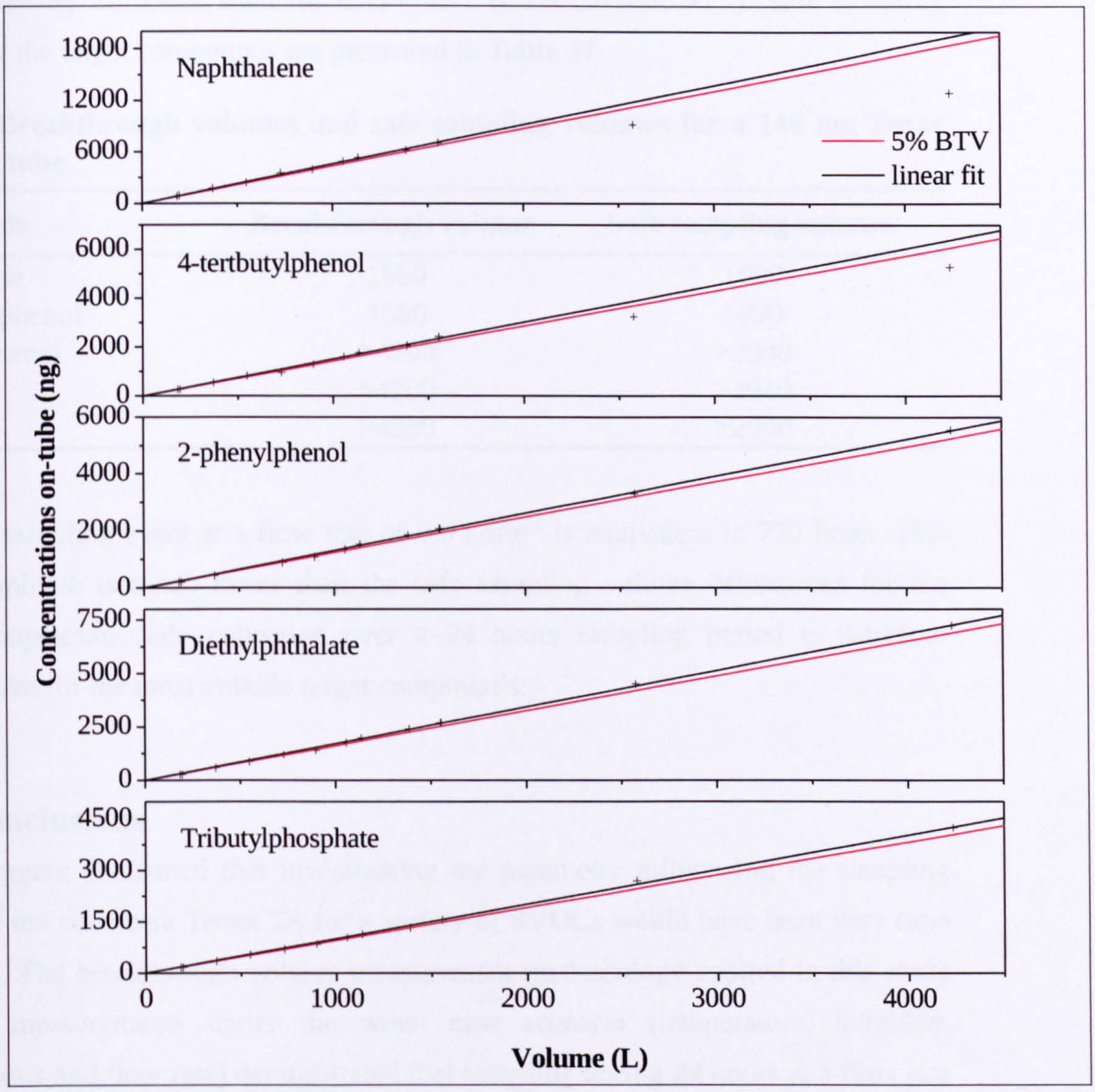

Figure 27: BTV on Tenax TA at 30°C and 70% relative humidity

The 5% BTV value correspond to the intersection between the 5% BTV line and the non-linear domain. It can be seen that breakthrough occurred for both naphthalene and 4-tertbutylphenol. Not enough data points were available to fit the non-linear domain; the 5% BTV value therefore could not be determined accurately. The 5% BTV value could have been refined by sampling a series of discrete volumes between the extreme value above the 5% BTV line and the first value below the 5% BTV line, but this was not deemed necessary, since the aim of the experiment was to ensure safe sampling for a 24-hour sampling period.

The 5% breakthrough volume was therefore defined as the last data point before the non-linear domain crossed the 5% breakthrough line, which corresponds to a sampling volume of 1550 L.

To allow a suitable margin of safety, a safe sampling factor corresponding to 70% of the 5% breakthrough volume is generally applied. For instance, this safety factor is recommended by European standard EN14662-1 (CEN-EN14662-1,). Safe sampling volumes for the target compounds are presented in **Table 31.**

Table 31: Breakthrough volumes and safe sampling volumes for a 140 mg Tenax TA sample tube

Compounds	Breakthrough volume	Safe sampling volume
Naphthalene	1550	1090
4-tertbutylphenol	1550	1090
2-phenylphenol	>4200	>2940
DEP	>4200	>2940
TBP	>4200	>2940

A 24-hour sampling event at a flow rate of 0.5 $l.min^{-1}$ is equivalent to 720 litres. This sampling volume is much lower than the safe sampling volume determined for the lightest compounds. Safe collection over a 24 hours sampling period is therefore expected even for the most volatile target compounds.

8.4.3. Conclusions

This experiment confirmed that investigating the parameter influencing the sampling capacity of the adsorbent Tenax TA for a variety of SVOCs would have been very time consuming. The breakthrough volume measurement methodology applied in this study based on measurements under the worst case scenario (temperature, humidity, concentrations and flow rate) demonstrated that sampling during 24 hours at a flow rate of 0.5 $l.min^{1}$ onto Tenax TA sample tubes filled with 140 mg of the adsorbent was safe.

Chapter 9: Development of the analytical method (TD-GC-MS)

Factors affecting the desorption and transfer of the analytes to the capillary column were optimized. The optimised method aimed to calibrate the system for the analyse of both the particulate and gaseous phases.

9.1. Choice of the column, liner and outlet split

A liner filled with a small plug of deactivated glass wool was selected for this study. This inert liner was preferred to an empty liner or baffled liner to increase the trapping of volatile compounds. An outlet split of 1:10 was selected to prevent column overloading due to the very high load of the samples. In addition, target compounds likely to be present at the $\mu g/m^3$ (e.g. phthalates) would be outside the linear calibration range if a splitless injection was performed. The analytical method with a split ratio of 1:10 was still sufficiently sensitive to quantify compounds present at low concentrations (sub ng/m^3). For instance, a 0.2 ng/m^3 concentrations of BaP in the particulate phase correspond to 25 pg injected into the capillary column (for a sample volume 1.3 m^3 equivalent to half of a filter collected during 24 hours) which is still much higher than the limit of detection of the MS detector.

A capillary column having an internal diameter of 0.32 mm was preferred to a conventional 0.25 mm i.d to reduce the risk of column saturation due to the high load of the samples injected.

9.2. Optimisation of the desorption time, temperature and flow

9.2.1. Desorption temperature

Desorption temperature of 300°C and 350°C were compared at a fixed desorption time of 15 minutes, a flow rate of 50 $ml.min^{-1}$ and transfer line temperature of 300°C. It can be seen **Figure 28** that the same peak areas were obtained for PAHs. For the other chemical families, peak areas at 350°C where generally higher than those obtained at 300°C. The influence of the desorption temperature is generally more pronounced for the less volatile compounds and for polar compounds such as alkylphenols and OPAHs. A desorption temperature of 350°C was therefore retained.

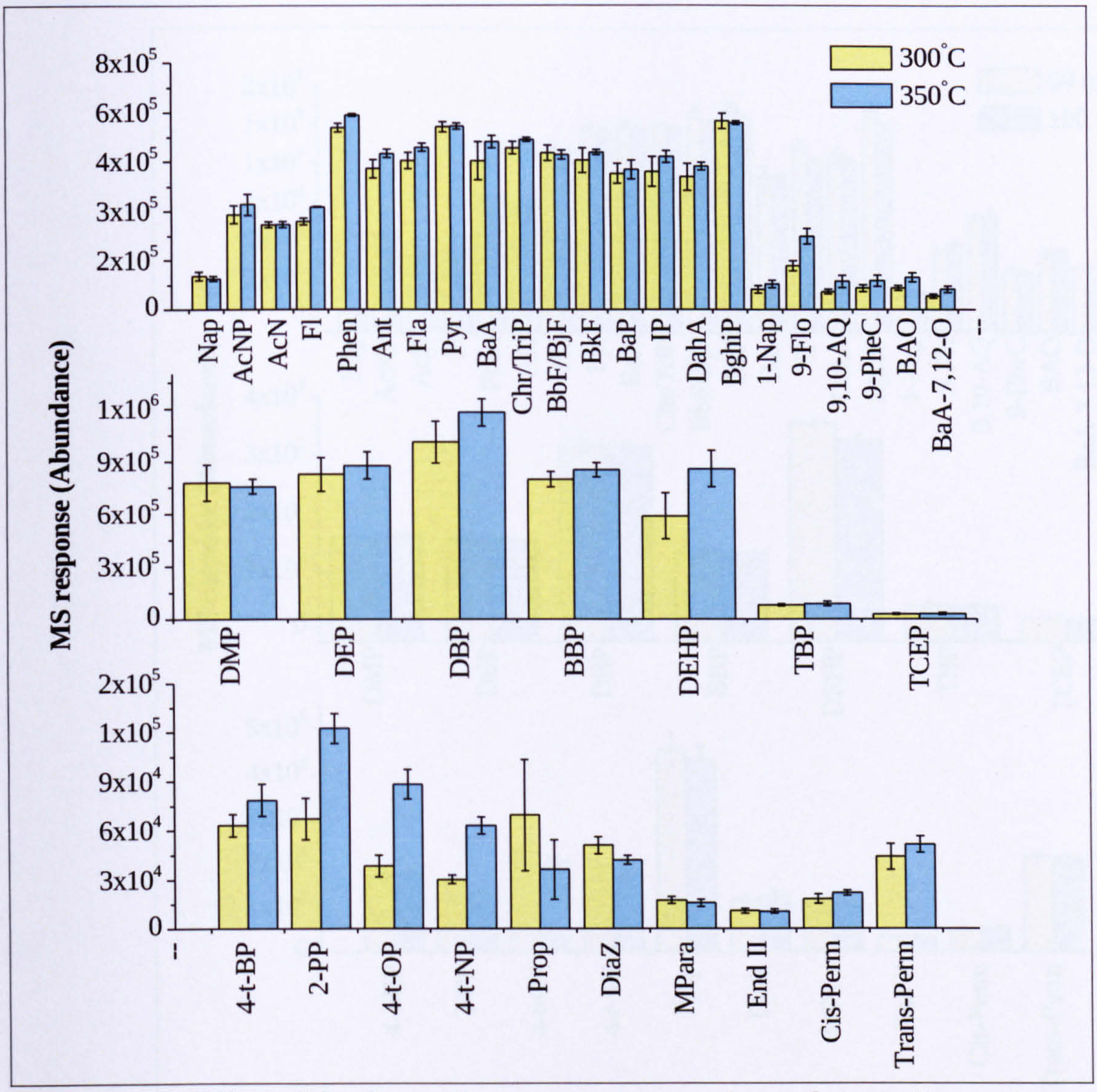

Figure 28: Effect of the desorption temperature on the peak area. Desorption during 15 minutes at 50 ml.min^{-1} (3 replicates)

9.2.2. Optimisation of the flow rate

The influence of the desorption flow was studied at a standard desorption flow (50 ml.min^{-1}) and at the maximum desorption flow available with the system (100 ml.min^{-1}). A capillary column with a smaller inner diameter is required to use higher flow rates. An empty tube was analysed between each sample tube to check the carryover. The influence of the desorption flow is presented in **Figure 29**. No significant difference was observed between the two flow rates. Peak areas were very similar and the carryover was negligible for both flow rates. For instance, at a flow rate of 50 ml.min^{-1}, the carryover was 0.013% and 0.060% for BaP and BghiP respectively. A flow rate of 100 ml.min^{-1} was however selected in order to desorb more efficiently high boiling points compounds from filter extracts that have been shown difficult to desorb.

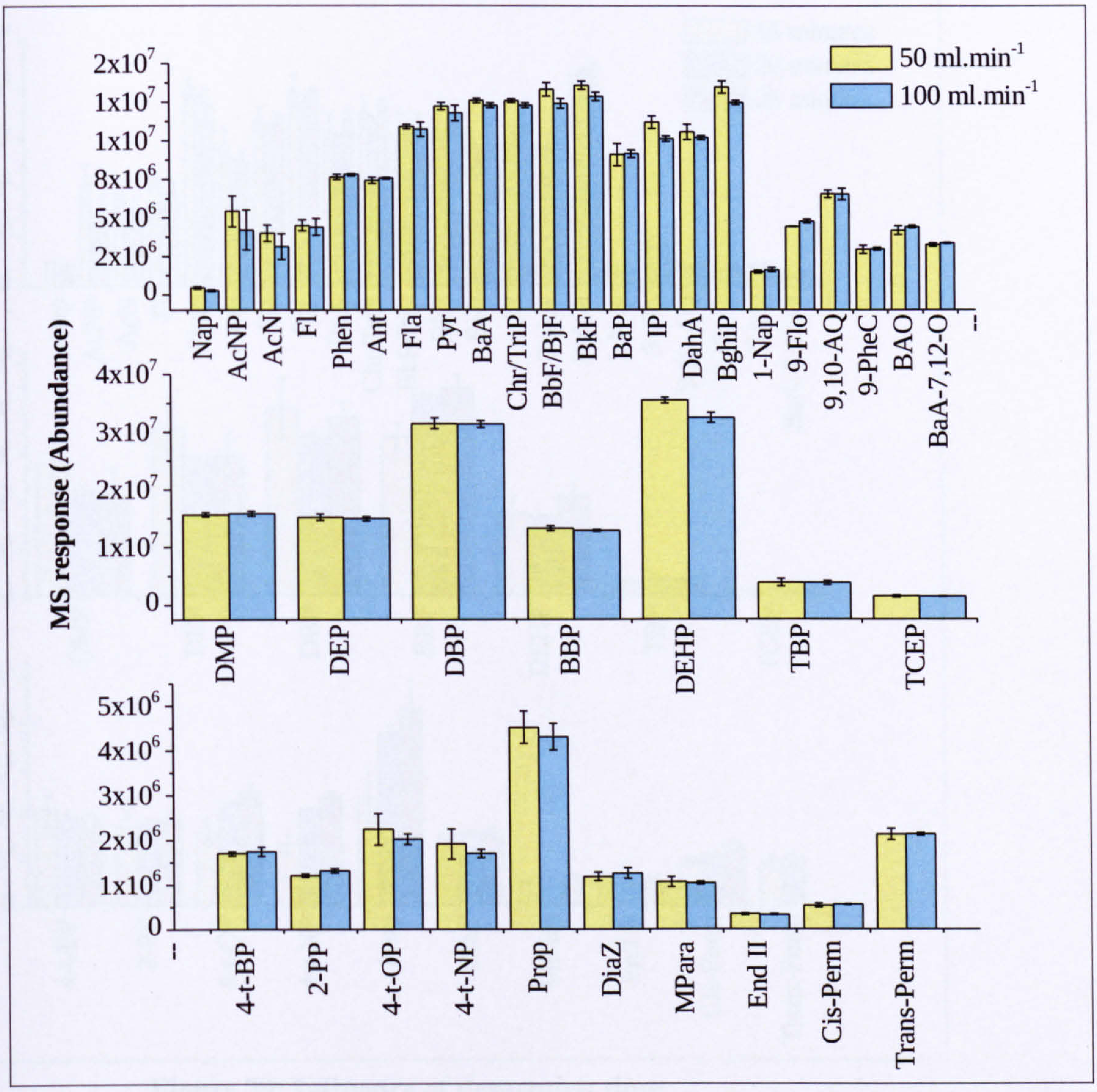

Figure 29: Influence of desorption flow. Desorption at 300°C for 15 minutes (3 replicates)

9.2.3. Desorption time

Desorption time of 15, 20 and 25 minutes (at a desorption temperature of 300°C) were tested to evaluate the influence of this parameter **(Figure 30)**. Peak areas were generally similar at the exception of some polar compounds (4-t-OP and 4-t-NP) and some low volatile compounds (permethrins and BBP). For the more volatile compounds, the response decreased with time because the compounds were not quantitatively trapped. A desorption time of 15 minutes was retained in order to limit the GC run time.

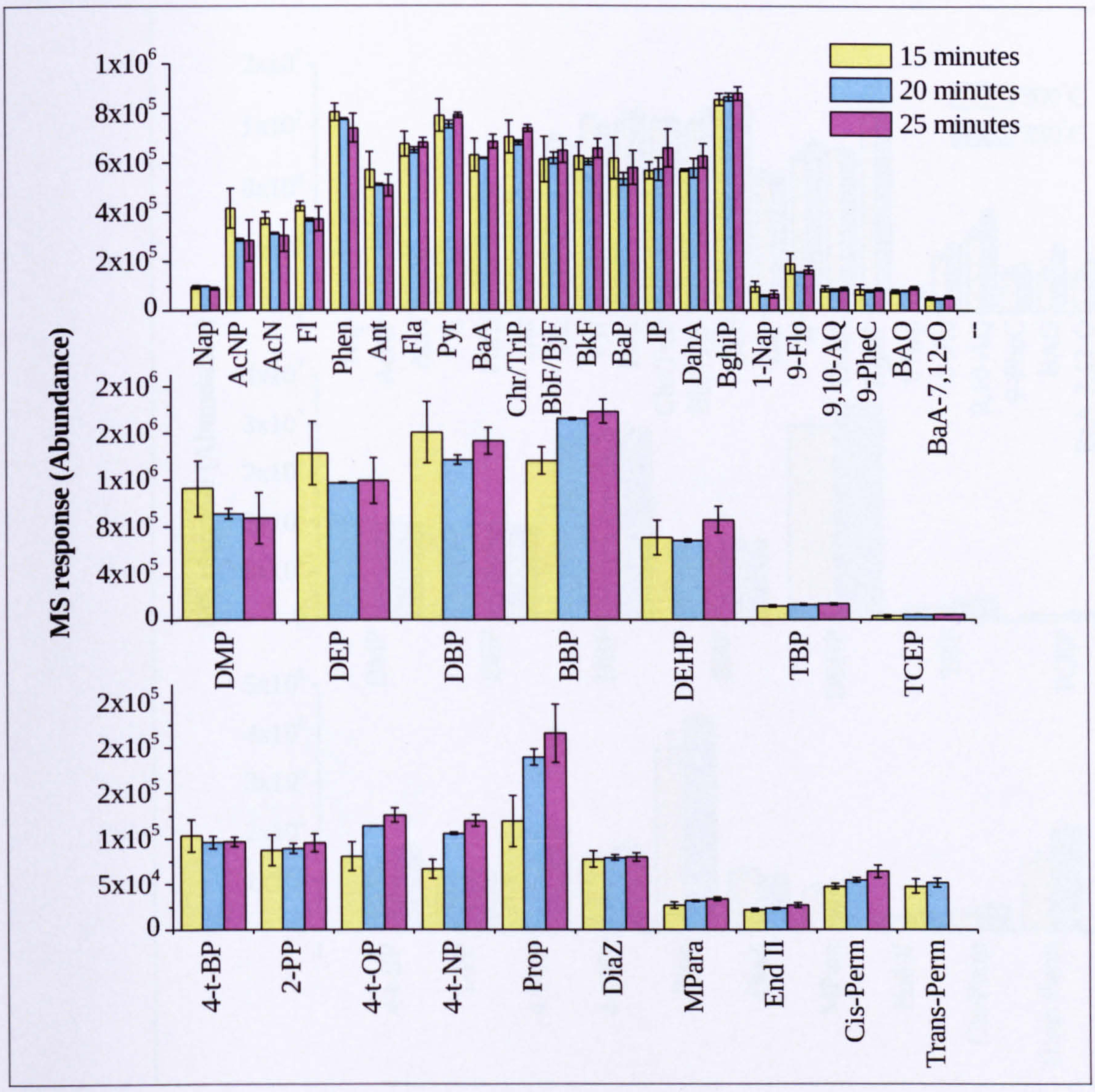

Figure 30: Influence of desorption time

9.3. Optimisation of the cold injection system (CIS) and transfer line temperature

9.3.1. Optimisation of the transfer line temperature

The transfer line temperature influence was evaluated at a standard temperature (300°C) and the temperature limit of the transfer line (350°C). The desorption time was set at 15 minutes and the desorption temperature at 300°C. The influence of the transfer line temperature on the transfer of the analyte into the analytical column is presented in **Figure 31**.

The difference between the two temperature was not huge however higher peak areas were noted for some compounds at 350°C.

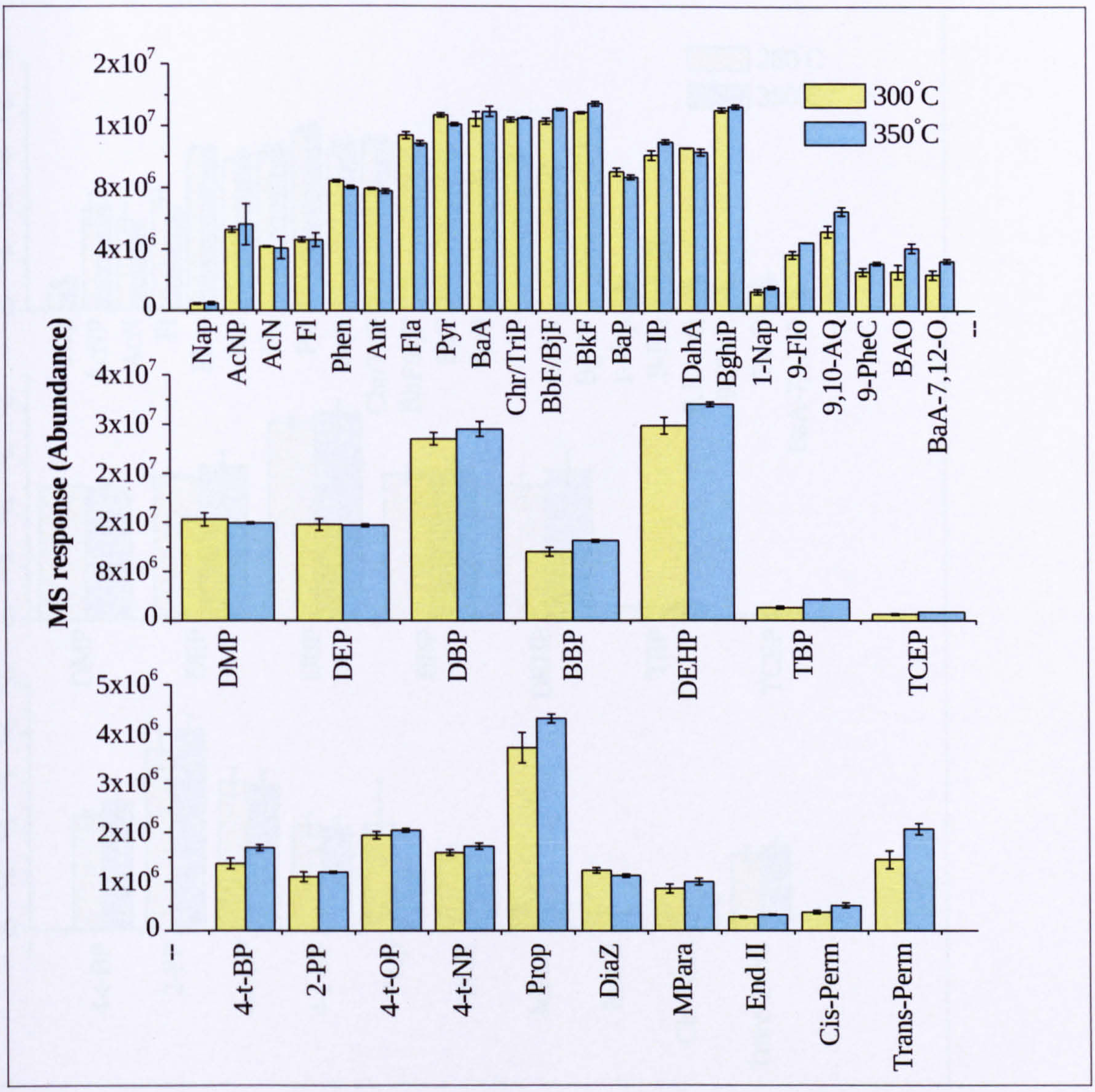

Figure 31: Influence of transfer line temperature (3 replicates)

9.3.2. Desorption temperature

The effect of the desorption temperature of the cold trap to transfer the analytes into the capillary column was evaluated at 280°C and 350°C. The trap was flash heated at 600°C/min and the temperature was held during 10 minutes. It can be seen in **Figure 32** that a temperature of 280°C is sufficient to re-desorbed the compounds cryofocused onto the glasswool liner. A temperature of 350°C was however retained in order to enhance the desorption from liners contaminated with particulate matter (i.e. particulate matter from filter samples tend to accumulate in the sample flow path and liner thus making the desorption and transfer more difficult).

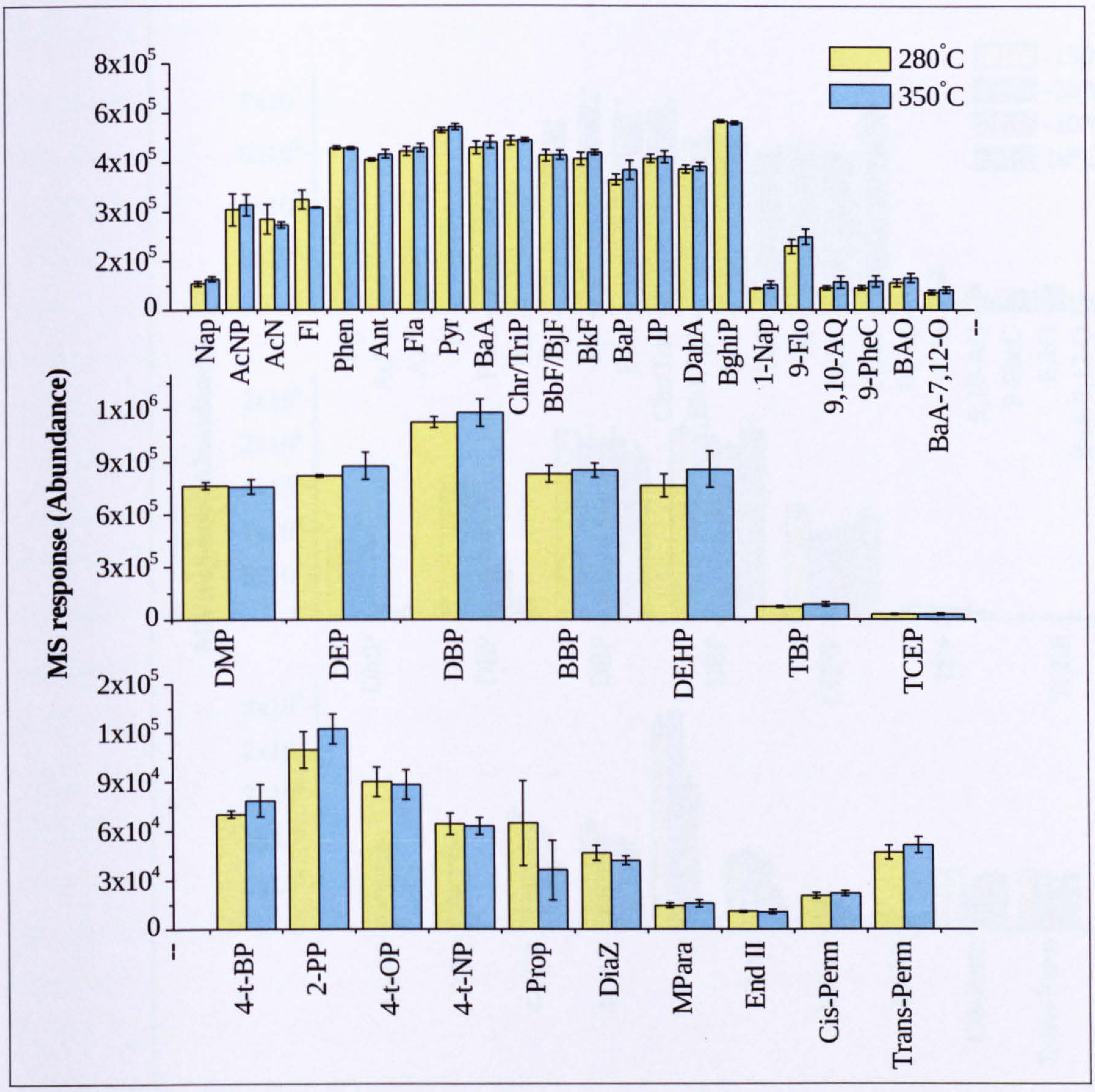

Figure 32: Effect of the desorption temperature of the PTV on the peak area

9.3.3. Cold trapping temperature

The trapping efficiency was studied at -150°C, -50°C, -10°C and 10°C while the helium flow rate was maintained at 100 ml.min^{-1} **(Figure 33)**. No significant differences were encountered between -150°C and -50°C at the exception of the most volatile PAHs up to acenaphthene. Higher cold trapping temperatures were not sufficient to retain high volatile from other chemical families. A temperature of -150°C was therefore retained.

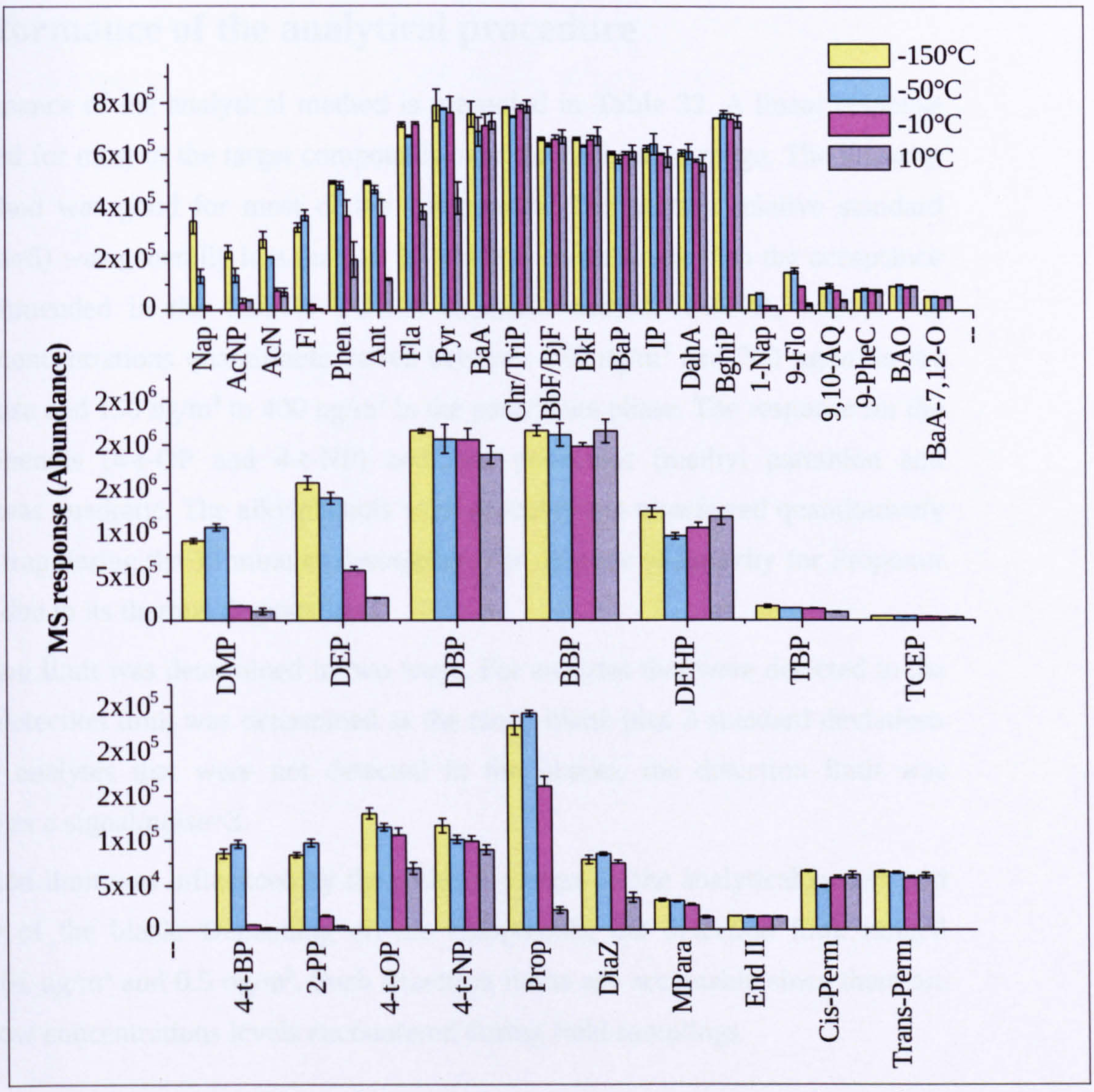

Figure 33: Effect of the cryofocusing temperature on the peak areas

9.3.4. Retained analytical conditions

The retained analytical conditions were as follow. The thermal desorption unit was programmed from 40°C to 350°C at a rate of 60°C/min and held at this temperature for 15 minutes. The analytes were transferred in splitless mode to the cold injection system (CIS) cooled at -150°C. The temperature between the TDS and the CIS was set at 350°C. After desorption, the analytes were transferred to the capillary column in split mode (1:10) by heating the CIS to 350°C at a rate of 12°C/s. The CIS was held at 350°C for 10 minutes.

9.4. Performance of the analytical procedure

The performance of the analytical method is presented in **Table 32.** A linear response was obtained for most of the target compounds over the calibration range. The linearity of the method was good for most of the compounds. The percent relative standard deviation (n=5) was generally less than 10 % which is much lower than the acceptance level recommended in the USEPA TO13A standard method (USEPA, 1996). The maximum concentrations quantifiable varied between 270 ng/m^3 and 700 ng/m^3 in the gaseous phase and 150 ng/m^3 to 400 ng/m^3 in the particulate phase. The response for the two alkylphenols (4-t-OP and 4-t-NP) and two pesticides (methyl parathion and Propoxur) was quadratic. The alkylphenols were probably not transferred quantitatively to the cold trap during the 15 minutes desorption. The absence of linearity for Propoxur is possibly due to its thermal degradation.

The detection limit was determined in two ways. For analytes that were detected in the blank, the detection limit was determined as the mean blank plus 3 standard deviations (n=6). For analytes that were not detected in the blanks, the detection limit was determined as a signal/noise=3.

The detection limit was influenced by the residues present in the analytical system and the quality of the blank. Depending on the compounds, the detection limit ranged between 0.01 ng/m^3 and 0.5 ng/m^3. Such detection limits are acceptable since there are still far below concentrations levels encountered during field samplings.

Table 32: Performance of the analytical method (gaseous phase)

Compounds	IS	Calibration range (ng)	Mean RRF	%RRF	LOD gaseous (ng/m^3) *	LOD particulate (ng/m^3)**
Nap	Nap-d8	0.1-200	1.13	6.3	0.41	0.03
AcNP	Nap-d8	0.1-200	1.14	8.6	0.05	0.01
AcN	Nap-d8	0.1-200	1.32	1.1	0.05	0.01
Fl	AcN-d8	0.1-200	1.46	4.9	0.08	0.02
Phe	Phe-d10	0.1-200	1.41	7.2	0.12	0.03
Ant	Phe-d10	0.1-200	1.40	4.8	0.08	0.01
Flu	Pyr-d10	0.1-200	1.21	2.8	0.03	0.01
Pyr	Pyr-d10	0.1-200	1.43	3.8	0.03	0.01
BaA	BaA-d10	0.1-200	1.37	4.8	0.04	0.01
Chr/TriP	BaA-d10	0.1-200	1.50	5.0	0.05	0.01
BbF/BjF	Per-d12	0.1-200	1.34	7.1	0.03	0.01
BkF	Per-d12	0.1-200	1.30	4.4	0.02	0.01
BaP	Per-d12	0.1-200	1.14	4.6	0.01	0.01
IP	BghiP-d12	0.1-200	1.07	3.1	0.01	0.01
DahA	BghiP-d12	0.1-200	1.15	2.7	0.01	0.01
BghiP	BghiP-d12	0.1-200	1.24	5.5	0.01	0.01
1-Nap	AcN-d8	0.1-200	0.53	6.9	0.05	0.01
9-FlO	AcN-d8	0.1-200	1.52	3.1	0.34	0.03
9,10-AQ	Phe-d10	0.1-200	0.41	8.6	0.23	0.01
9-pheC	Pyr-d10	0.1-200	0.32	10.8	0.02	0.01
BAO	BaA-d10	0.1-200	0.64	2.3	0.07	0.01
BaA-7,12-O	BaA-d10	0.1-200	0.39	4.7	0.02	0.01
DMP	DBP-d4	1.5-500	1.55	4.0	0.08	0.2
DEP	DBP-d4	1.5-500	1.50	1.2	0.41	0.4
DBP	DBP-d4	1.5-500	1.45	5.6	0.35	0.2
BBP	DHP-C13	1.5-500	0.78	6.6	0.12	0.2
DEHP	DHP-C13	1.5-500	0.92	11.1	0.51	0.5
TBP	Phe-d10	0.5-200	1.11	6.7	0.08	0.1
TCEP	Phe-d10	0.5-200	0.22	9.2	0.07	0.1
4-t-BP	Nap-d8	0.1-200	0.70	1.9	0.14	0.07
4-t-OP			Quadratic function			
4-t-NP			Quadratic function			
2-PP	AcN-d8	0.1-200	1.13	5.2	0.4	0.6
Propoxur			Quadratic function			
Diazinon	Phe-d10	0.5-200	0.27	7.1	0.01	0.01
Methyl parathion			Quadratic function			
β-endosulfan	Pyr-d10	0.5-200	0.03	7.4	0.02	0.02
Permethrin cis	BaA-d10	0.5-200	0.37	5.2	0.01	0.01
Permethrin trans	BaA-d10	0.5-200	0.52	3.3	0.01	0.01

** Sample volume of 0.72 m^3 (sampling at 0.5 Lpm during 24 hours)*

*** Sample volume of 1.30 m^3 (sampling at 1.8 Lpm during 24 hours-half of the filter)*

Chapter 10: Performance of the developed method

After the optimisation of the analytical method to calibrate the GC/MS system, the performance of the method for the organic analysis of particulate matter was evaluated. The performance of the TD technique was evaluated by analysing samples of urban dust standard reference material and by analysing a set of 6 indoor air samples using both the TD technique and a traditional solvent extraction method. In order to estimate the performance of the developed method for the gaseous phase and to detect any bias resulting from the sampling apparatus, a field method comparison between the personal sampler and a low flow sampler/solvent extraction method was conducted.

10.1. Performance of the analytical method for the airborne analysis of organic matter

10.1.1. Analysis of certified reference material SRM1649a

The performance of the developed analytical method was evaluated by analysing NIST standard reference material SRM1649a (approximately 3 mg). Although the sample weight was not representative of the load that would be obtained with the developed sampler for a 24-hour sampling period, 3 mg of the standard reference was used because the material lacks homogeneity at the low mg level. For instance, the median $PM_{2.5}$ mass concentrations found during the recent large scale study RIOPA in three different area of the united states were 14.4, 15.5 and 31.4 mg/m^3 for indoor, outdoor and personal measurements. These $PM_{2.5}$ mass concentrations would correspond to a sample load of 37.4, 40.3 and 81,6 µg/m^3 with the developed sampler for indoor, outdoor and personal measurements, respectively.

A 3 mg sample load was demonstrated to be relatively homogeneous and the results obtained in this study could be directly compared with the value reported by other studies based a thermal desorption procedure.

The quantitative results of PAH and OPAH compounds are presented in **Table 33** and are compared with other studies based on a thermal desorption procedure **(Table 34)**. Target compounds other than OPAHs and PAHs are not presented here because this reference material is not certified for these compounds and because no data was found in the literature regarding the concentrations of these compounds.

Table 33: Concentrations measured by TD/GC-MS in the reference material SRM 1649a (n=5)

Compounds	1	2	3	4	5	mean	rsd (%)	Primary desorption efficiency (%)*	Target identification **
Fl	0.844	0.747	0.780	0.792	0.734	**0.779**	5.5	99.4	Yes
Phe	4.240	3.445	4.064	3.701	3.698	**3.830**	8.3	98.6	Yes
Ant	1.038	0.871	0.958	0.923	0.861	**0.930**	7.7	98.7	No
Flu	6.324	5.412	5.360	5.699	5.360	**5.629**	7.4	98.8	Yes
Pyr	5.074	4.970	4.399	4.654	4.255	**4.671**	7.6	98.2	Yes
BaA	2.475	1.853	1.948	2.187	1.959	**2.085**	12.0	98.3	Yes
Chr/TriP	3.929	3.594	3.563	3.623	3.628	**3.668**	4.0	97.2	Yes
BbF/BjF	8.166	7.326	6.777	7.332	7.017	**7.324**	7.2	99.1	Yes
BkF	1.639	1.690	1.412	1.479	1.496	**1.543**	7.5	99.0	Yes
BaP	2.848	2.325	2.341	2.505	2.288	**2.462**	9.4	98.5	Yes
IP	2.695	2.439	2.299	2.158	2.176	**2.353**	9.4	97.8	Yes
DahA	0.526	0.393	0.360	0.343	0.368	**0.398**	18.6	97.3	No
BghiP	2.949	2.705	2.541	2.254	2.365	**2.563**	10.8	99.2	Yes
9-FlO	1.861	1.594	1.583	1.552	1.483	**1.517**	9.5	96.9	Yes
9,10-AQ	2.445	2.339	2.288	2.163	2.201	**2.223**	5.1	96.6	Yes
9-PheC	0.245	0.243	0.301	0.274	0.290	**0.259**	8.2	100.0	Yes
BAO	3.382	3.192	3.232	2.996	2.989	**3.065**	5.4	99.0	Yes
BaA-7,12-0	3.711	3.470	3.532	3.425	3.292	**3.380**	4.5	99.3	Yes

* *Primary desorption defined as* $\frac{\text{primary desorption concentration}}{\text{primary and secondary concentration}} \times 100$

** *Relative abundance of target compounds within ±25% of the expected abundance determined from the standard*

The precision of the method is good and is in the same neighbourhood or better than other studies based on a thermal extraction procedure. The relative standard deviation (n=5) is less than 10% for all PAHs and OPAHs except for dibenzoanthracene.

Although no sample clean up is possible with thermal desorption procedures, the analysis by mass spectrometry is sufficiently selective to limit interferences. For instance, target compounds were positively identified when the relative abundance of the qualifier ions was within the acceptance criteria of ± 25% of the expected abundance determined from the standard. It can be observed in **Table 33** that with the exception of Ant and DahA, the target PAHs and OPAHs were positively identified. The relative abundance of the qualifier ions was within the acceptance criteria of ± 25% of the expected abundance determined from the standard.

The level of agreement between the certified value and the determined concentration for the positively identified PAHs is reasonably good. The ratio of the NIST value to that by the developed method ranged between 1.02 to 1.24 for PAHs from phenanthrene to benzo(a)pyrene. For the heavier compounds, the ratio was 1.35 and 1.56 for IP and BghiP respectively.

The very low fluorene ratio is certainly the result of losses during the evaporation step of the NIST procedure. In addition, the NIST fluorene value might be biased because the concentration is provided as a reference value, contrary to the concentrations of other PAHs provided as certified values.

The anthracene concentration obtained by TD/GC/MS was nearly twice as high as the certified concentration. Although the peak shape of the quantifier ion **(Figure 34-b)** is quite symmetrical, a co-elution with an interference is not impossible because the relative abundance could not be determined (co-elution). Another speculative explanation is the formation of anthracene due to the thermal degradation of an anthracene derivative. Anthracene is one of the most reactive PAHs and is rapidly converted to derivatives (Nitro and Oxy) in the atmosphere.

Finally, the lower concentrations determined for IP and BghiP through the TD method is certainly the result of the irreversible adsorption of these compounds. Increasing the desorption time is not sufficient to increase the recovery, as indicated by a primary desorption efficiency close to 98% for these compounds. A higher temperature is certainly needed to efficiently desorb these compounds. This was not possible because the desorption was performed at the temperature limit of the thermal desorber.

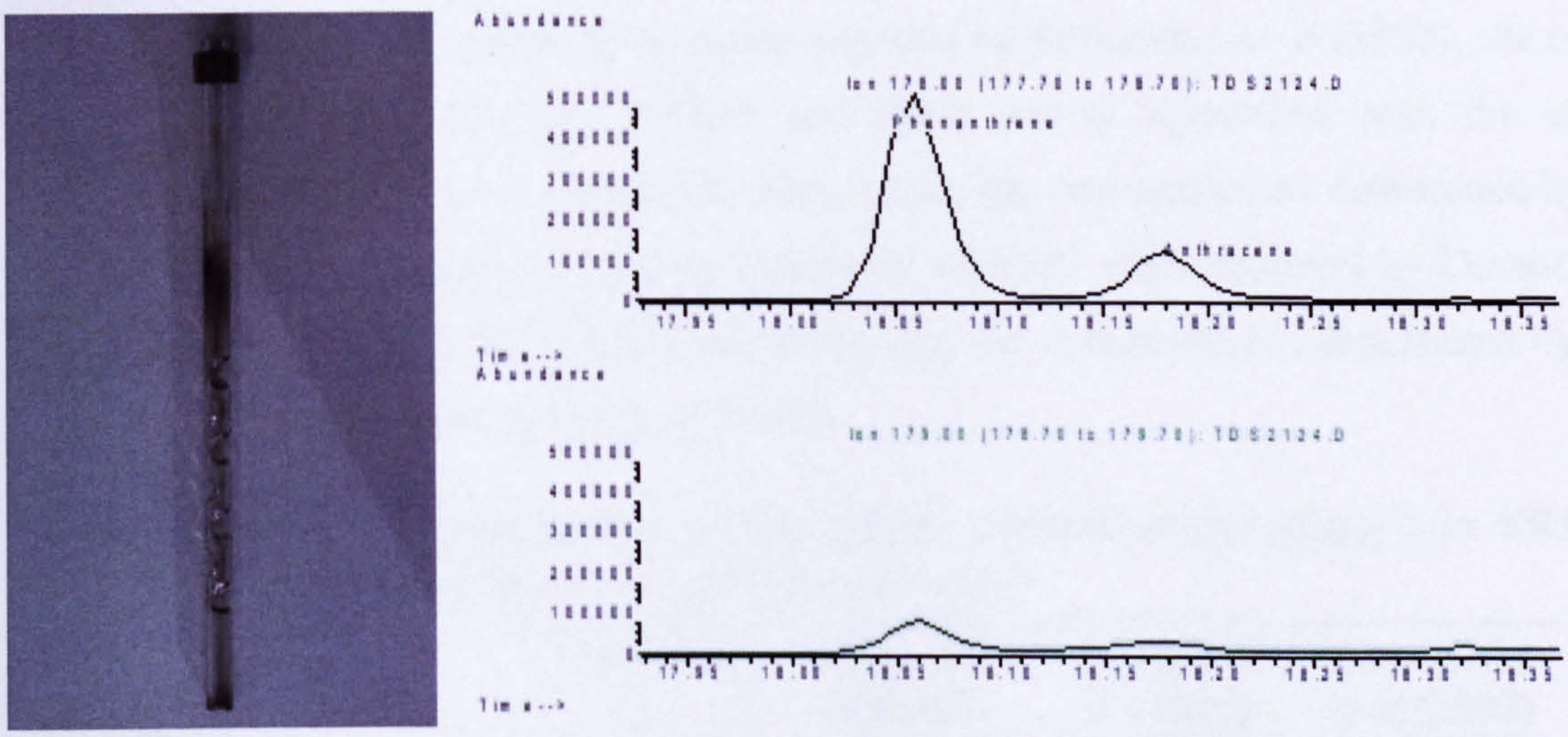

Figure 34: (a) Contaminated liner after SRM1649a (b) analysis anthracene in SRM1649a at m/z= 178 and 179

The reference material is not certified for OPAHs; however, the concentrations determined by the TD method were compared with concentrations reported from previous studies in an attempt to determine the accuracy of the developed method (**Table 35**). The comparison is not straightforward because of the spread of the results between previous studies.

Table 34: Determined PAH concentrations (µg.g-1) in SRM1649a compared with NIST reference value and data from other studies based on a thermal desorption procedure

Study	This study	NIST	NIST STUDY	Waterman (2000)	Falkovitch (2001)	Waterman (2001)
Extraction method	TD	Solvent extraction		TD	TD	TD
Fl	0.78 (0.04)	0.23 (0.05)*	0.25	-	-	-
Phe	3.83 (0.31)	4.14 (0.37)	1.08	4.62 (0.11)	4.05 (0.13)	4.56 (0.24)
Ant	0.93 (0.07)	0.43 (0.08)	0.46	-	-	-
Flu	5.63 (0.36)	6.45 (0.18)	1.15	6.67 (0.16)	-	6.4 (0.23)
Pyr	4.67 (0.31)	5.29 (0.25)	1.13	5.06 (0.18)	4.61 (0.24)	4.56 (0.61)
BaA	2.08 (0.24)	2.21 (0.07)	1.06	2.86 (0.17)	2.2 (0.40)	2.39 (0.44)
Chr/TriP	3.67 (0.13)	4.40	1.20	3.66 (0.20)	-	3.66 (0.41)
BbF	-	6.45	-	6.20 (0.78)	-	6.43 (1.08)
BbF/BjF	7.32 (0.5)	7.95	1.09	-	-	-
BkF	1.67 (0.11)	1.91 (0.03)	1.24	-	-	-
BaP	2.46 (0.23)	2.51 (0.09)	1.02	2.79 (0.81)	-	2.47 (0.69)
IP	2.35 (0.29)	3.18 (0.07)	1.35	-	-	-
DahA	0.40 (0.07)	0.29 (0.02)	0.72	-	-	-
BghiP	2.57 (0.27)	4.01 (0.91)	1.56	-	-	-

* *Reference value*

With the exception of the value reported by Fernandez *et al* (1992), the concentrations of 9-FlO, 9,10-AQ, 9-PheC and BAO are in agreement with the concentrations determined in this work. For BaA-7,12-0, the concentrations determined by the thermal desorption method were in agreement with the value reported by Durant *et al* (1998), but approximately three times lower than the concentrations determined by Albinet *et al* (2006) and Fernandez *et al* (1992)

Table 35: Comparison of the OPAH concentrations ($\mu g.g^{-1}$) in SRM1649a with other studies based on a solvent extraction

Study	This study	Albinet *et al* (2006)	Durant *et al* (1998)	Fernandez *et al* (1992)	Cho *et al* (2004)
Analytical Method	TD-GC/MS	GC/MS (NICI)	GC/MS (EI)	GC/MS (EI)	GC/MS (EI)
9-FlO	1.52 (0.12)	1.11 (0.14)	1.60 (0.11)	0.3 (0.03)	
9,10-AQ	2.22 (0.09)	2.24 (0.36)	2.70 (0.12)	0.22 (0.04)	2.03 (0.19)
9-PheC	0.26 (0.02)	0.25 (0.03)			
BAO	3.06 (0.13)	3.71 (0.87)	4.50 (0.34)	1.31 (0.02)	
BaA-7,12-0	3.38 (0.12)	8.46 (0.79)	2.40 (0.25)	7.46 (1.1)	

✓ *Conclusions*

The concentrations determined by the TD method were in agreement with the certified value for most of the compounds, but irreversible adsorption of the heavier compounds was suspected. Increasing the desorption time to increase desorption recovery is not efficient to increase recovery, since more than 95% of the thermal extractable was desorbed during the primary desorption for all the PAHs and OPAHs. Increasing the desorption temperature was impossible, since the desorption was performed at the maximum temperature allowed by the system. It should be noted that analysing particle reference material resulted in a heavy contamination of the system **Figure 33**. Using less reference material (~ 0.7 mg) was attempted to reduce system contamination, but the concentrations determined were not reproducible **(appendix 6)**. The relative standard deviation ranged between 18 and 58% for the quantified PAHs. This result confirmed the finding of Greaves *et al* (1985) that the certified reference material lacks of homogeneity at the low mg level.

This problem might not be observed with the TD method based on in-injection port because the liner is replaced after each analysis. Since the SRM1649a were collected more than 30 years ago, it was decided to pursue the experiment with freshly collected filter and compare the TD results with a well-established solvent extraction procedure. The compounds adsorbed onto the SRM1649a may have penetrated more deeply in the particulate, resulting in a more difficult desorption, especially for heavier compounds.

10.1.2. Analysis of indoor air filters by a solvent extract method and the TD/GC-MS method

The thermal desorption procedure was compared with a traditional solvent extraction method. Twenty-four hour indoor air samples were collected using a Partisol sampler equipped with a $PM_{2.5}$ sampling head at a flow rate of 1 $l.min^{-1}$. Each filter was cut in eight strips of the same size. One-eighth of the filter was analysed by thermal desorption and the remaining portions were analysed using the solvent extraction method.

10.1.2.1. Filter homogeneity

This comparison method is only possible if the filter portions are homogeneous. This was verified by analysing six filter strips from the same filter **(Table 36)**. It can be seen that the concentrations determined on each portion of the filter were homogeneous. The relative standard deviation (n=6) was less than 10% with the exception of BghiP, TCEP and BBP. The primary desorption efficiency was also checked by a second desorption of the filters. The primary desorption efficiency for PAHs and OPAHs was in agreement with those determined for the SRM1649a reference material. For other compounds not analysed in the reference material (phthalates, organophosphate esters and phenols), the desorption time was sufficient to efficiently remove the thermal extractable fraction.

Table 36: Concentrations in ng/m^3 determined from 6 filters strips (47mm filter cut into 8 strips)

Compounds	run 1	run 2	run 3	run 4	run 5	run 6	mean	rsd (%)	Primary desorption efficiency (%)
Naphthalene	NQ	NQ	NQ	NQ	NQ	NQ	-	-	-
Acenaphthylene	NQ	NQ	NQ	NQ	NQ	NQ	-	-	-
Acenaphthene			co-elution				-	-	-
Fluorene	0.21	0.24	0.22	0.23	0.21	0.23	0.22	**4.0**	97
Phenanthrene	1.53	1.62	1.56	1.53	1.46	1.54	1.54	**3.4**	99
Anthracene	0.14	0.16	0.15	0.16	0.15	0.16	0.15	**5.3**	98
Fluoranthene	2.25	2.56	2.39	2.32	2.25	2.40	2.39	**4.4**	98
Pyrene	1.60	1.69	1.58	1.51	1.48	1.59	1.58	**4.7**	99
BaA	0.77	0.78	0.77	0.73	0.71	0.75	0.75	**3.5**	100
Chr/TriP	1.46	1.54	1.38	1.35	1.30	1.43	1.41	**6.1**	99
BbF/BjF	3.06	3.02	2.86	2.80	2.72	2.94	2.90	**4.4**	99
BkF	0.72	0.74	0.73	0.68	0.72	0.71	0.72	**3.0**	99
BaP	0.95	1.01	0.92	0.89	0.86	0.91	0.92	**5.4**	99
IP	1.51	1.46	1.38	1.40	1.37	1.40	1.42	**3.7**	99
DahA	0.18	0.16	0.15	0.16	0.16	0.15	0.16	**5.8**	100
BghiP	0.79	0.67	0.60	0.65	0.62	0.52	0.64	**13.8**	99
1-Nap	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
9-FlO	2.36	2.53	2.44	2.40	2.33	2.40	2.41	**2.8**	95
9,10-AQ	5.19	5.60	5.20	4.95	4.85	5.35	5.19	**5.2**	98
9-pheC	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
BAO	8.88	9.53	9.04	8.20	8.20	8.42	8.71	**6.1**	100
BaA-7,12-O	2.15	2.40	2.00	2.18	1.96	2.27	2.16	**7.7**	100
DMP	0.72	0.80	0.76	0.71	0.70	0.73	0.74	**4.8**	100
DEP	40.94	43.53	41.25	38.97	38.75	41.84	40.88	**4.4**	100
DBP	29.42	32.04	31.21	29.43	28.09	30.64	30.14	**4.8**	100
BBP	4.66	5.01	5.22	4.85	7.22	9.97	6.15	**33.9**	101
DEHP	100.2	104.8	102.7	100.9	101.7	117.5	104.7	**6.2**	100
TBP	89.57	96.16	93.18	88.84	85.67	93.25	91.11	**4.1**	100
TCEP	1.29	1.39	1.57	1.19	1.14	1.20	1.30	**12.3**	100
4-t-BP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
2-phenylphenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
2-octylphenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
4-nonylphenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-

10.1.2.2. Results of the comparison of the particulate phase concentrations measured by a solvent extract method and the TD/GC-MS method

The comparison was only possible for PAHs, since no analytical methods were validated for the other target compounds. The accuracy of the solvent extraction method was verified by analysing the standard reference material SRM1649a **(appendix 7)**.

The extent of agreement between both methods was evaluated by means of a linear fitting **(Figure 35)**. Compounds more volatile than phenanthrene were not included in the comparison because a fraction of these compounds (Naphthalene, acenaphthylene, acenaphthene and fluorene) is lost during the solvent reduction step of the solvent extraction method.

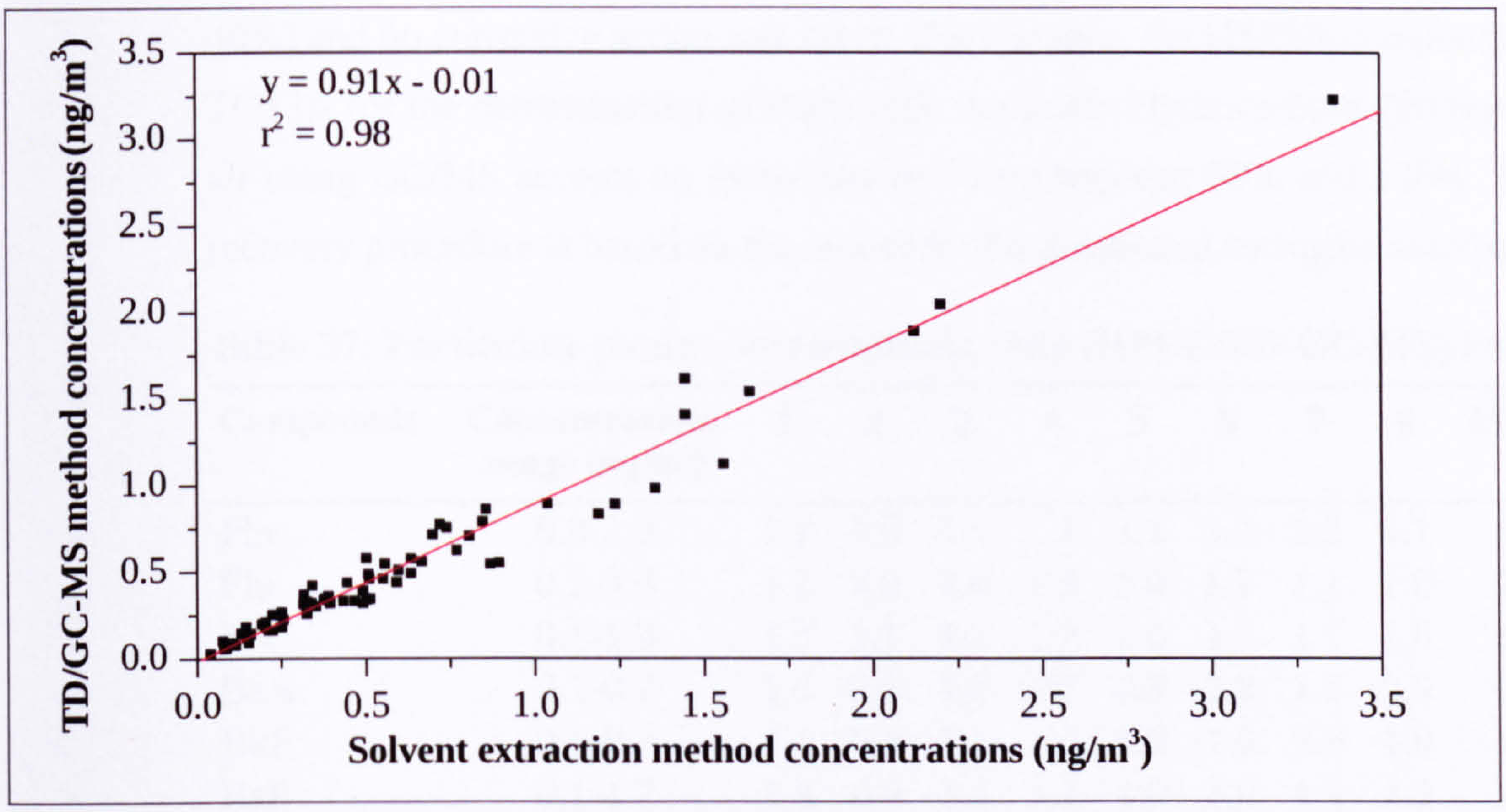

Figure 35: Comparison of the concentrations (ng/m³) between the solvent extraction and the TD/GC-MS method (Partisol filters)

The slope close to 1, the intercept close to zero and the r^2 equivalent to 0.9 indicate that the concentrations obtained by both methods were equivalent. However, individual PAH ratios **(Table 37)** indicate that the degree of agreement between the two methods is not equivalent to the same extent for all PAHs studied despite the good correlations. Ratios greater than 1 indicate that higher concentrations were obtained by the solvent extraction method.

Two distinct trends can be observed. The concentrations are equivalent by both methods for PAHs up to BaP. Mean individual ratios for these compounds are close to 1 and individual ratios ranged between 0.7 and 1.3 over the 8-day sampling period. Such a level of agreement is reasonably good and can be attributed to the analytical uncertainty of both methods.

For PAHs less volatile than BaP, mean individual ratios were equal to 1.4, 1.3 and 1.4 for IP, DahA and BghiP respectively. Individual ratios were all above 1 and ranged from 1 to 1.7. These results tend to confirm that the desorption conditions were not efficient to quantitatively desorb the heavy PAHs. It should be noted that the desorption efficiency did not show an analyte concentration dependency. The concentrations levels determined were broad with a tenfold factor for most of the compounds and it can be seen that the ratios were homogeneous, as observed with the low relative standard deviation (less than 15% for most of the PAHs). A correcting factor could be applied to compensate for the low recovery of heavy PAHs. However, it was judged that the level of agreement between both methods was reasonably good (the deviation did not exceed 40%) and no corrective action was taken. For instance, the USEPA compendium method TO13A for the determination of Polycyclic Aromatic Hydrocarbons (PAHs) in ambient air using GC/MS accepts an extraction recovery between 60% and 120%. The TO13A recovery procedure is based on the recovery of a deuterated surrogate standard.

Table 37: Particulate phase concentrations ratio (HPLC/TD-GC-MS) from 8 filters

Compounds	Concentrations range (ng/m^3)	1	2	3	4	5	6	7	8	Mean	RSD (%)
Phe	0.8-2.0	1.1	0.9	1.1	1.1	1.1	1.3	1.3	1.1	**1.1**	**11**
Flu	0.2-3.3	1.2	0.9	1.0	1.4	1.0	1.2	1.1	1.0	**1.1**	**16**
Pyr	0.1-1.9	1.3	1.1	1.1	1.2	1.1	1.3	1.1	1.0	**1.2**	**7**
BaA	0.1-0.7	1.0	0.9	1.0	0.7	0.8	0.8	1.2	0.9	**0.9**	**11**
BkF	0.1-0.7	1.1	0.9	1.1	1.1	1.0	1.0	1.0	1.0	**1.0**	**9**
BaP	0.1-1.7	1.2	0.9	1.2	1.1	1.0	1.0	1.1	1.2	**1.1**	**11**
IP	0.2-1.4	1.6	1.0	1.4	1.3	1.5	1.4	1.3	1.5	**1.4**	**14**
DahA	0.03-0.3	1.7	0.9	1.4	1.4	1.3	1.1	1.5	1.4	**1.3**	**18**
BghiP	0.2-1.6	1.6	1.1	1.4	1.4	1.5	1.4	1.2	1.4	**1.4**	**13**

✓ *Conclusions*

The procedure for cutting the filter was effective to obtain homogeneous sub-samples. The comparison between the well-validated solvent extraction and the TD method confirmed that the thermal desorption of heavy PAHs was incomplete. However, the degree of discrepancy between both methods was judged satisfactory and no corrective action was taken.

10.2. Performance of the developed method: sampling and analytical procedure

A field comparison between the developed sampler and a low flow volume sampler compatible with a solvent extraction was carried out during two sampling campaigns (6 sampling days for each campaign). Although, the low volume sampler (Partisol Model 2000) is not designed for indoor air measurements but rather for ambient air measurements (it is noisy and cumbersome), this sampler was used during this comparison because its performances have been well characterised. This sampler in combination with the sampling head used in this study (VSCC cyclone) has been recognised as a federal equivalent method (FEM) by the US-EPA. It should be pointed out that none of the indoor air samplers available on the market have been recognised as reference method.

10.2.1. Thermal desorption efficiency for Tenax TA sample tubes

After collection of five samples (twenty-four hour sampling), desorption tubes were desorbed twice to evaluate the efficiency of the primary desorption. Results of the desorption efficiency for the compounds detected are presented in **Table 38**. The primary desorption efficiency was calculated by dividing the concentration of the primary desorption by the sum of the primary and secondary desorption. It can be observed that the primary desorption was very efficient for desorption of PAHs and phthalates; the primary desorption was more than 99% for these compounds.

Table 38: Primary desorption efficiency for Tenax TA samples tubes (%)

Compounds	Concentrations range (ng/m^3)	1	2	3	4	5	Mean
Naphthalene	31.3-63.3	99.7	99.7	99.6	99.6	100.0	99.7
Acenaphthene	9.5-21.9	100.0	100.0	99.5	100.0	100.0	99.9
Fluorene	8.4-18.6	99.7	99.7	99.2	99.7	99.7	99.6
Phenanthrene	6.9-14.2	99.6	99.7	99.4	99.9	99.7	99.7
Anthracene	0.2-0.7	99.8	99.8	99.5	99.6	99.3	99.6
Fluoranthene	1.2-3.1	99.8	99.9	99.5	99.7	99.5	99.7
Pyrene	0.3-0.9	99.1	98.4	99.0	99.5	99.7	99.1
9-FlO	7.5-16.6	97.5	97.9	96.7	97.3	97.3	97.3
9,10-AQ	1.2-3.1	96.8	92.0	95.9	94.3	98.8	95.6
DMP	3.6-7.8	100.0	99.9	98.9	100.0	100.0	99.8
DEP	11.4-44.8	99.6	100.0	99.5	100.0	100.0	99.8
DBP	1.7-2.3	98.9	98.0	99.3	99.3	99.5	99.0
BBP	0.8-1.8	99.5	98.5	98.3	100.0	100.0	99.3
DEHP	5.7-6.9	99.6	100.0	100.0	100.0	100.0	99.9
2-phenylphenol	2.9-5.0	95.6	96.2	97.8	95.3	99.3	96.8

10.2.2. Reproducibility of filter cut

Only one half of the Chempass filters were used for the analysis. This procedure was adopted to overcome the one shoot process of thermal desorption procedure. TD-based techniques consumed the entire sample upon the first analysis and there is no "second chance" to re-run the sample if something goes wrong. For instance, the sample can be lost in case of poor separation, concentrations outside the calibration range or failure caused by the apparatus. The second portion of the filters can therefore be used in case of problems.

This procedure is only possible assuming that the two portions are representative of the entire sample. Indoor air samples were collected and the two portions of each filter were analysed to verify that the sample preparation was safe.

Results of this experimental study for the detected target compounds are presented as the ratio between both portions of the five filters **(Table 39)**.

Table 39: Ratios between the two portions of a Chempass filter (n=5)

Compounds	Concentrations range (ng/m^3)	1	2	3	4	5	Mean	RSD (%)
Fluorene	0.06-0.22	1.12	0.84	1.04	1.17	0.94	**1.02**	**13**
Phenanthrene	0.10-0.22	1.12	1.20	1.00	1.15	1.03	**1.10**	**7.7**
Fluoranthene	0.12-0.41	1.16	1.08	1.20	1.12	0.92	**1.10**	**10.1**
Pyrene	0.08-0.30	0.97	1.17	1.16	1.13	0.92	**1.07**	**10.9**
BaA	0.05-0.11	0.97	1.04	1.10	1.16	0.98	**1.05**	**7.5**
Chr/TriP	0.11-0.20	1.01	1.15	1.13	1.09	0.94	**1.06**	**8.2**
BbF/BjF	0.14-0.22	1.19	1.10	1.15	1.20	0.92	**1.11**	**10.3**
BkF	0.05-0.08	1.11	1.21	1.01	1.01	1.03	**1.07**	**7.8**
BaP	0.06-0.14	1.00	1.14	1.08	1.12	0.96	**1.06**	**7.1**
IP	0.10-0.23	1.14	1.12	1.10	1.05	0.94	**1.07**	**7.6**
DahA	0.01-0.02	1.49	1.14	1.10	0.98	0.95	**1.13**	**19.6**
BghiP	0.10-0.40	1.07	1.04	1.09	1.11	0.96	**1.05**	**5.6**
9-FlO	0.44-1.70	1.10	1.15	1.09	1.11	0.96	**1.08**	**6.7**
9,10-AQ	0.60-1.38	1.08	1.06	1.09	1.01	0.97	**1.04**	**5.1**
BAO	0.14-0.24	1.02	1.20	1.15	1.12	1.06	**1.11**	**6.3**
BaA-7,12-O	0.08-0.12	1.04	1.12	0.84	1.08	0.99	**1.02**	**10.6**
DMP	7-21	1.14	1.04	1.05	1.08	0.90	**1.04**	**8.4**
DEP	45-185	1.15	1.22	1.11	1.08	0.93	**1.10**	**9.8**
DBP	29-196	1.03	1.06	1.10	0.98	0.89	**1.01**	**8.1**
BBP	8-30	0.87	0.97	0.78	0.83	0.98	**0.89**	**9.7**
DEHP	10-62	0.86	0.94	0.90	0.85	0.93	**0.89**	**4.5**
TBP	5.8-13.1	0.79	0.95	0.83	0.77	0.87	**0.84**	**8.7**
TCEP	1.3-3.5	0.74	0.88	0.82	0.70	0.84	**0.80**	**9.3**

The ratios between the concentrations measured on the two portions of each filter for all compounds were comprised between 0.8 and 1.2 with the exception of the organophosphate esters. This level of agreement between the concentrations measured on each portion from the same filter is more than acceptable. This bias between the concentrations measured on each portion from the same filter includes both the uncertainty of the analytical techniques and the filter cut-out.

10.2.3. Comparative study between the developed sampler and a low flow sampler

10.2.3.1. 1st campaign

Results of the first campaign for both the particulate and the gaseous phases are presented in **Figure 36**.

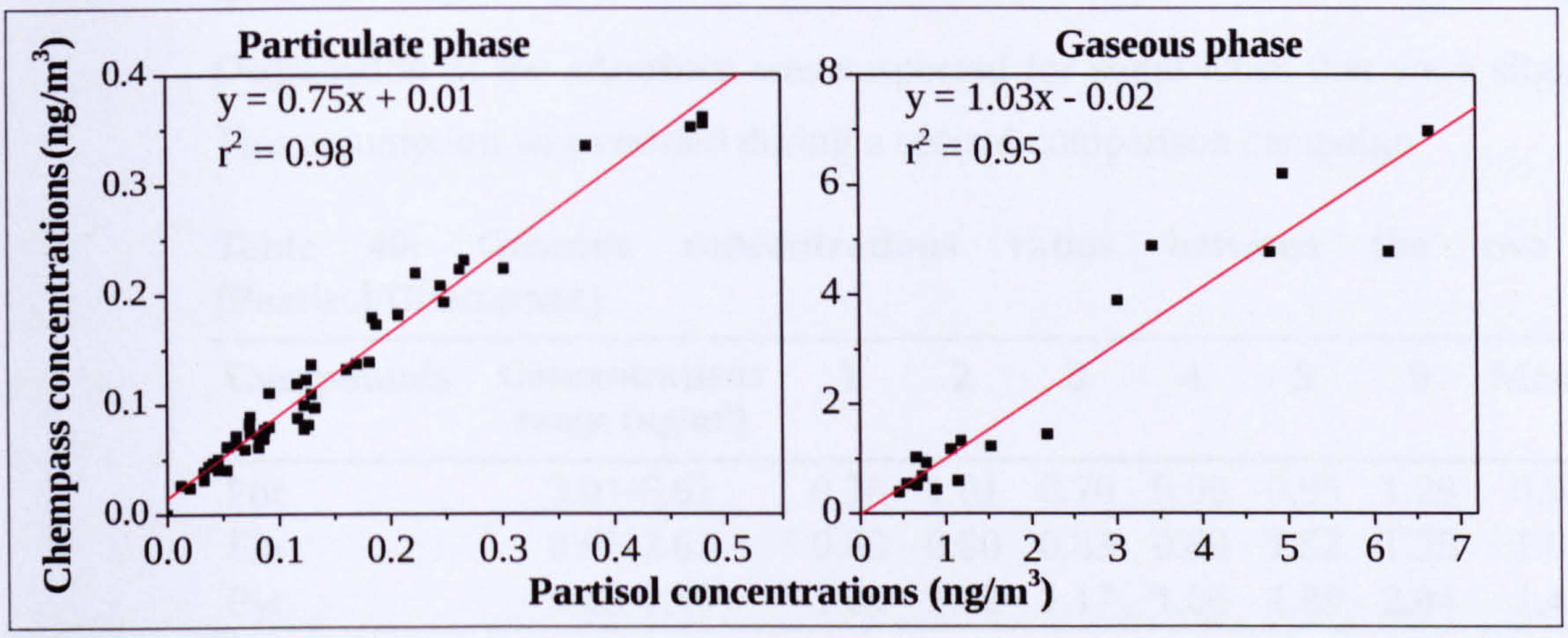

Figure 36: Comparison of the gaseous and particulate concentrations (ng/m³) between the Chempass and Partisol samplers

(i) Gaseous phase

The plot of the gaseous phase concentrations includes only phenanthrene, fluoranthene and pyrene. PAHs more volatile than phenanthrene are not retained efficiently on the PUF cartridge. Heavier compounds than pyrene were not detected.

The agreement between both methods for the gaseous phase was good. The slope is close to 1, the intercept close to 0 and the correlation coefficient was equal to 0.95. The difference between the two methods for individual compounds was less than 30% **(Table 40)** with the exception of three ratios highlighted in bold. Filter/adsorbent samplers are prone to sampling artefacts. A fraction of the gaseous PAHs may adsorbed onto the filter or onto particles collected at its surface. This artefact, defined as 'blow-on', reduced the apparent concentrations of the gaseous phase while the particulate phase concentrations are increased. A second artefact defined as 'blow-off' is also possible. A fraction of the PAHs adsorbed onto particles may be re-entrained by the gas flow, causing a decrease in the observed particulate concentrations and an increase of the gaseous concentrations. The Partisol sampler is likely to be more prone to blow-off than the Chempass sampler because of its higher sampling flow rate (10 times higher than the Chempass). This could be one of the reasons explaining the apparent higher concentrations by the Partisol sampler for fluoranthene and pyrene. However, this phenomenon should have been observed during the 6 sampling days. In addition, the particulate fraction of pyrene and fluoranthene represents only about 10% of the total fraction, hence even if blow-off occurred, the fraction re-entrained is not sufficient to explain the higher concentrations of fluoranthene and pyrene found with the Partisol sampler during two sampling days.

It was suspected that the low concentrations determined by the TD were due to the degradation of the adsorbent Tenax TA and the formation of active sites, which prevent good recovery.

Degradation of the adsorbent was suspected for some tubes that were slightly yellow. This assumption was verified during a second comparison campaign.

Table 40: Gaseous concentrations ratios between the two samplers (Partisol/Chempass)

Compounds	Concentrations range (ng/m^3)	1	2	3	4	5	6	Mean	RSD (%)
Phe	3.01-6.61	0.78	1.01	0.70	0.80	0.95	1.29	0.92	23.3
Flu	0.65-3.61	0.73	0.90	0.83	0.89	**1.52**	1.25	1.01	31.8
Pyr	0.45-1.95	1.01	1.32	1.17	1.06	**1.89**	**2.04**	1.42	31.2

(ii) Particulate phase

The two methods are highly correlated (r^2=0.98), but a bias exists, as evidenced by the slope equal to 0.75 and the positive intercept. This is the consequence of the heavy PAH concentrations being underestimated by the TD method **(Table 41)**. The concentrations ratios obtained in this comparison were similar to those determined during the analytical comparison between the HPLC and TD methods **(Table 37)**. This result suggests that sampling artefacts were limited or similar to those of the low volume sampler.

Table 41: Particulate concentrations ratios between the two samplers (Partisol/Chempass)

Compounds	Concentrations range (ng/m^3)	1	2	3	4	5	6	Mean	RSD (%)
Phe	<LOQ-0.12	0.84	-	1.29	0.86	1.08	-	1.02	20.1
Flu	<LOQ-0.19	1.18	0.86	1.12	1.28	-	0.90	1.07	16.7
Pyr	<LOQ-0.14	0.90	0.93	1.09	1.46	-	-	1.10	23.3
BaA	0.46-0.13	1.14	1.06	0.80	1.41	0.82	1.20	1.07	21.9
BkF	0.054-0.21	1.20	1.43	0.87	1.08	0.92	1.25	1.12	18.8
BaP	0.087-0.25	1.36	1.31	1.01	1.25	1.20	1.29	1.23	10.1
IP	0.11-0.48	1.59	1.22	1.41	1.34	1.17	1.46	1.37	11.4
DahA	<LOQ-0.13	1.18	-	-	1.72	-	-	1.45	26.2
BghiP	0.12-0.48	1.30	1.30	1.11	1.28	0.98	1.26	1.21	10.8

10.2.3.2. 2nd campaign

A second sampling campaign was carried out to verify that the aging of the Tenax sample tubes did not influence desorption recoveries. This campaign involved parallel samplings between a low volume sampler and two Chempass samplers. One Chempass was equipped with freshly packed tubes and the other with tubes that had already been used.

This sampling campaign also aimed to compare the OPAH concentrations determined by the TD method with the method developed by Albinet *et al* (2006). Unfortunately, the purified extracts were lost due to analytical problems on the GC/MS. The results of the low volume samplers for the particulate phase could not be used because the concentrations determined were all below the detection limits. Despite these analytical problems, the influence of the aging of the Tenax TA sample tubes was studied and the gaseous concentrations of the Chempass samplers were compared to those of the low volume sampler.

(i) Comparison between old tubes and tubes freshly packed

Results of the comparison between the concentrations measured with freshly packed tubes and tubes already used for sampling are presented in **Figure 37**. Concentrations between the two samplers are highly correlated (r^2=0.99) and the slope is close to the ideal value of 1. This result suggests that the apparent degradation of the adsorbent does not modify the adsorption/desorption properties of the adsorbent. The sampling capacities of the adsorbent did not appear to be reduced, since the concentrations between old and freshly packed tubes are similar. Fluoranthene and pyrene concentrations between the two samplers are also in good agreement. Hence, the assumption that the desorption of low volatile was incomplete due to the presence of active sites on old tubes was not validated.

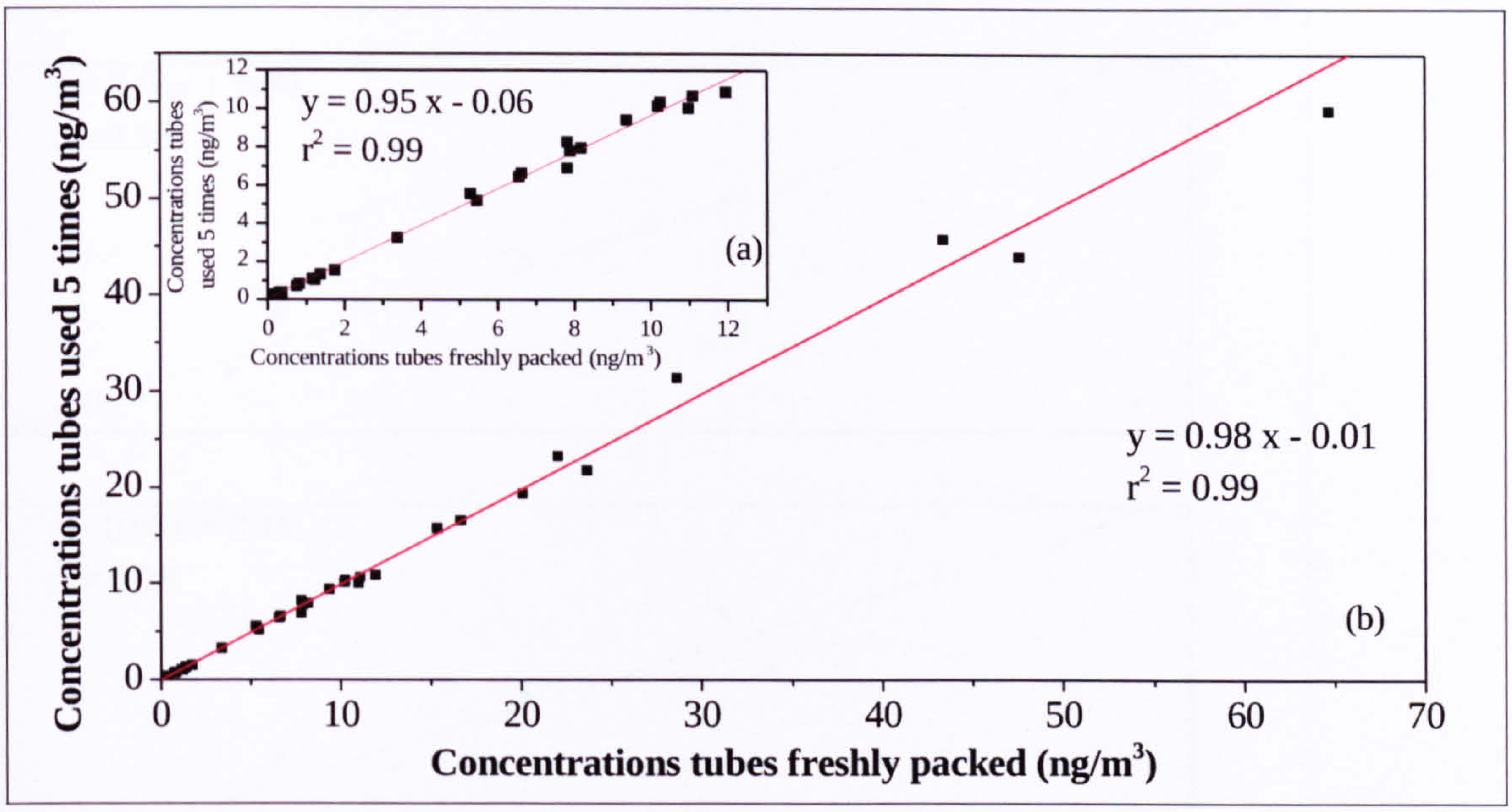

Figure 37: Comparison of the gaseous concentrations between a Chempass sampler equipped with used tubes and a Chempass sampler equipped with freshly packed tubes. (a) PAHs from naphthalene to pyrene, (b) PAHs from acenaphthene to pyrene

(ii) Comparison of the gaseous concentrations between the low volume samplers and the Chempass samplers

The results of the comparison between the two methods are presented in **Figure 38** as a simple linear fit between the gaseous concentrations measured by the Partisol sampler and the Chempass samplers. Contamination of the PUF cartridges led to elevated quantification limits for the Partisol measurements. As a result, the concentration of one sampling for fluoranthene and 4 samplings for pyrene were excluded from the comparison. The poor quality of the blank complicates the interpretation of the results because the blank concentrations represent an important fraction of the determined concentrations **(Table 42)** and **(appendix 8)**.

Table 42: Percent of the mean blank (n=3) to the concentration measured

Compounds	1	2	3	4	5	6
Phenanthrene	11	11	8	15	24	15
Fluoranthene	32	14	9	18	46	28
Pyrene	39	30	20	149	189	135

The elevated correlation and slope close to one indicate that the concentrations determined by the two methods were in agreement. However, since only very few data points were included in the comparison and because very few pyrene concentrations were above the limit of quantification, it is difficult to determine whether the TD method results in an underestimation of the concentrations of these compounds.

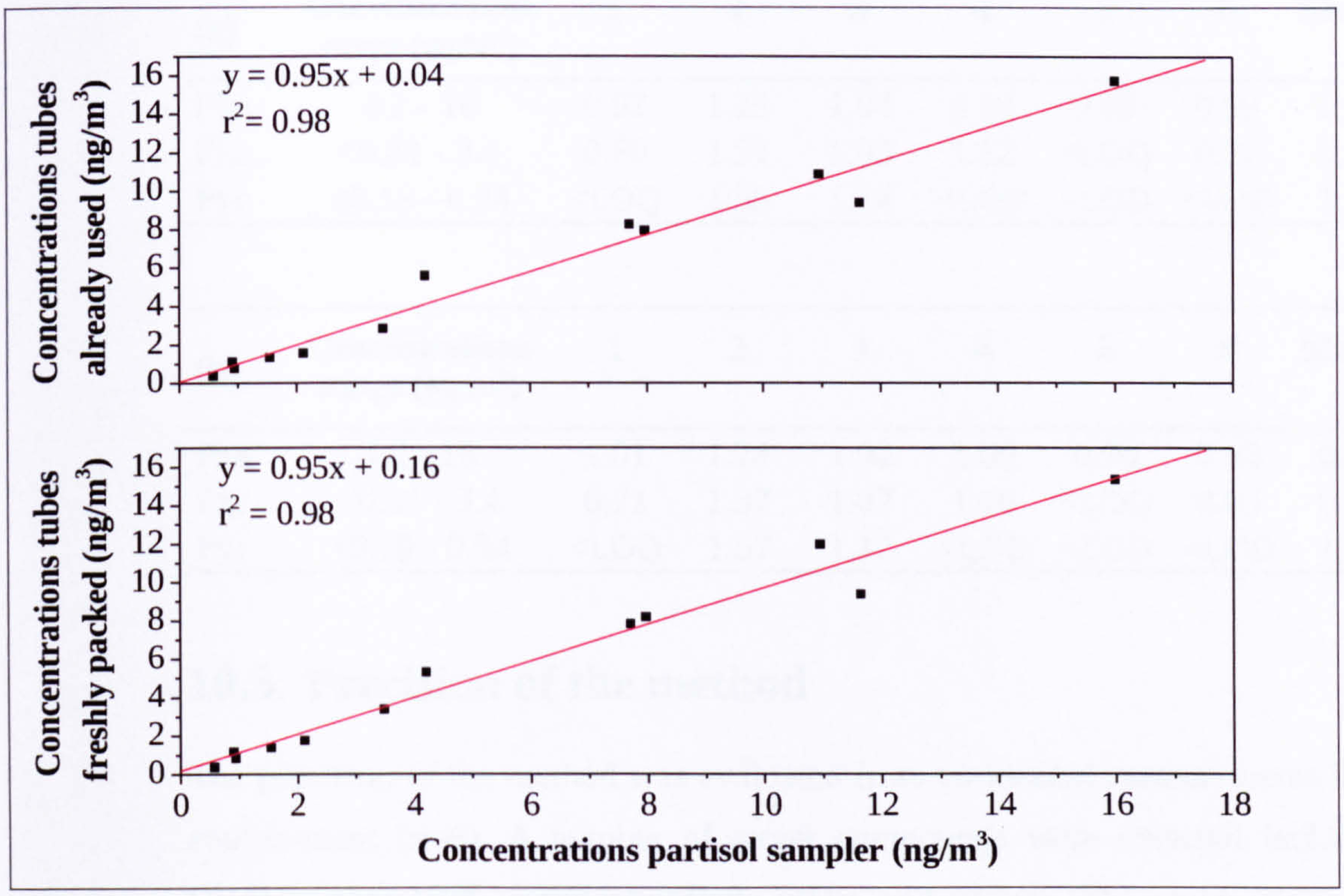

Figure 38: Comparison between the concentrations of the Chempass samplers and the Partisol sampler (phenanthrene, fluoranthene and pyrene)

By looking more closely at the individual concentrations ratios provided in **Table 43**, it can be observed that the difference between the two methods for phenanthrene is more than acceptable. Differences are less than 25% and the mean ratio is equal to 0.99 (n=6). For fluoranthene and pyrene, the difference is less than 40% and reached 56% for pyrene on the second sampling day. There are two possible explanations for the high pyrene ratio: incomplete thermal desorption of pyrene and contamination of the PUF cartridge. Incomplete thermal desorption was verified by performing a second and tertiary desorption. The sum of the secondary and tertiary thermal desorption represents only 0.2% and 2% of the primary desorption for fluoranthene and pyrene, respectively. Significant contamination of the PUF used during the second sampling day is not excluded and could be the reason for the underestimation of the pyrene concentration by the TD method. Only one PUF blank was verified during the first campaign. It cannot be excluded that abnormally elevated contamination of the PUF used for sampling days 5 and 6 was the origin of the difference between the two methods.

Table 43: Ratio of the concentrations measured by the Partisol sampler to that by the Chempass sampler (a) Tubes used and (b) freshly packed tubes

(a)	Concentrations range (ng/m³)	1	2	3	4	5	6	Mean	RSD (%)
Phe	4.2 - 16	0.92	1.25	1.04	0.98	0.80	0.99	0.99	15
Flu	<0.81 - 3.4	0.60	1.21	1.03	1.12	<LOQ	0.77	0.88	33
Pyr	<0.19 - 0.94	<LOQ	1.56	1.14	<LOD	<LOD	<LOD	1.25	22

(b)	Concentrations range (ng/m³)	1	2	3	4	5	6	Mean	RSD (%)
Phe	4.2 - 16	1.01	1.24	1.02	1.00	0.76	0.93	0.99	16
Flu	<0.81 - 3.4	0.71	1.37	1.07	1.16	<LOQ	0.83	0.94	33
Pyr	<0.19 - 0.94	<LOQ	1.57	1.17	<LOD	<LOD	<LOD	1.30	18

10.3. Precision of the method

The precision of the method was evaluated from co-located measurements in an indoor environment (n=6). A number of target compounds were detected including PAHs, OPAHs, phthalates, organophosphate esters and phenol. The mean concentrations as well as the relative standard deviation are presented in **Table 44** and **appendix 9.**

With the exception of gaseous phthalates, the relative standard deviations derived from the measurements were generally less than 10%. Reproducibility estimation using field measurements does not permit to estimate the concentration dependency effect. However, the precision determined during this measurement can be considered as the minimum that can be achieved with this method, since the concentrations determined were located at the low end of the calibration range. Better precision is expected at higher concentrations due to reduced analytical uncertainty.

For gaseous phthalates, the DBP, BBP and DEHP concentration levels were rather low. The origin of the poor reproducibility for these compounds is not well understood. One possible explanation is the contamination of the samples tubes by the sampling device, since these compounds are ubiquitous in the environment.

It can be seen in that gaseous concentrations of naphthalene, acenaphthylene and DMP were quantified. These compounds were detected but not quantified because of peak broadening and possible breakthrough through the cold trap.

Table 44: Particulate concentrations of 6 Chempass samplers placed in parallel over 24 hours

	Gaseous		Particulate	
	Concentrations (ng/m³)	RSD (%)	Concentrations (ng/m³)	RSD (%)
Naphthalene	NQ	NQ	<LOD	<LOD
Acenaphthylene	NQ	NQ	<LOD	<LOD
Acenaphthene	0.9	15.2	<LOD	<LOD
Fluorene	7.2	5.9	0.05	29.5
Phenanthrene	14.3	6.3	0.15	3.3
Anthracene	0.5	10.8	0.02	12.7
Fluoranthene	2.3	8.5	0.21	7.7
Pyrene	1.1	9.2	0.15	6.4
BaA	<LOD	<LOD	0.09	10.2
Chr/TriP	<LOD	<LOD	0.18	4.9
BbF/BjF	<LOD	<LOD	0.25	6.7
BkF	<LOD	<LOD	0.09	6.7
BaP	<LOD	<LOD	0.15	6.6
IP	<LOD	<LOD	0.18	6.3
DahA	<LOD	<LOD	0.04	9.3
BghiP	<LOD	<LOD	0.19	5.6
9-FlO	4.8	3.9	0.56	10.8
9,10-AQ	1.0	13.2	1.26	9.7
BAO	<LOD	<LOD	0.53	7.6
BaA-7,12-O	<LOD	<LOD	0.19	10.9
DMP	NQ	NQ	11.86	0.96
DEP	171.5	10.7	67.07	6.06
DBP	9.9	57.4	83.73	7.69
BBP	4.9	62.0	13.73	1.26
DEHP	5.3	35.0	55.86	2.99
TBP	<LOD	<LOD	7.02	14.7
TCEP	<LOD	<LOD	1.39	15.6
2-PP	18.3	5.7	<LOD	<LOD

NQ: not quantified due to cold trap breakthrough

Breakthrough through the cold trap did not occur with samples collected for the validation of the method because they were much less concentrated. Samples for validation of the method were collected at INERIS (in an office close to the laboratory), whereas samples collected for this experiment were collected in a flat located in Paris. An example of an indoor sample collected during this experiment and sample collected during the validation of the analytical method is presented in **Figure 39**. Breakthrough through the cold trap is very problematic because it prevents the determination of low boiling points compounds up to dimethylphthalate in this experiment, but it is likely that even less volatile would not be retained in more concentrated samples. There are three possible ways to prevent breakthrough through the cold trap:

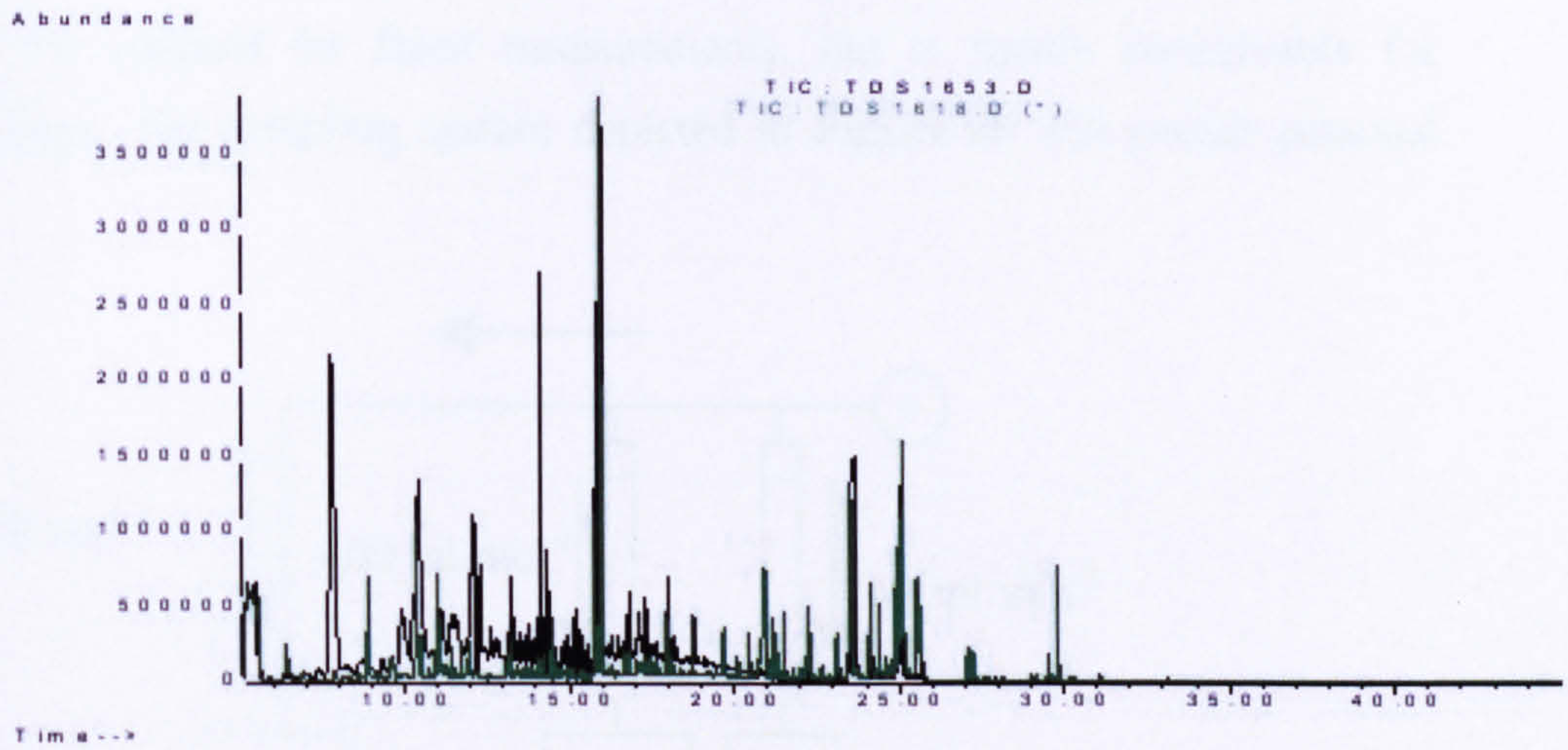

Figure 39: Chromatogram of an indoor air sample from this experiment (in black) and an indoor air samples from the validation of the method (in green)

- ***Use of a cold trap with a stronger adsorbent***

A trap filled with the adsorbent Tenax TA will certainly make it possible to eliminate breakthrough through the cold trap. However, the use of a stronger adsorbent increases the risk of carry over and poor desorption of low boiler.

- ***Use of an inlet split***

An inlet split can be used to reduce the sample load reaching the cold trap, thereby reducing possible breakthrough. This procedure reduces the sensitivity of the method and hence would prevent detection of compounds present at low concentrations. In addition, the reduction of the flow through the sample flow path may enhance carry-over.

- ***Reduction of the sampling volume***

Sampling at lower flow rates such as 40 ml/min through the Tenax TA desorption tube will make it possible to limit the sample loading by a factor of 10, thus reducing the risk of trap breakthrough. In addition, this method will also reduce the risk of breakthrough during sampling in very contaminated atmospheres. The drawback of this procedure is the same as the use of the inlet split, namely the lack of sensitivity for compounds present at low concentrations.

An alternative sampling method that will solve breakthrough problems in contaminated atmospheres while preserving good sensitivity is to collect samples in duplicate with distinct flow rates (400 ml/min and 40 ml/min). The tube collected at 400 ml/min should be analysed first and the second tube can be analysed if cold trap breakthrough occurred on the first tube. This solution will also overcome the limitation of sampling on only one tube when detected compounds are outside the calibration range. This procedure can be adopted for fixed measurements, but is hardly conceivable for personal samplings. The sampling system depicted in **Figure 40** will permit personal sampling.

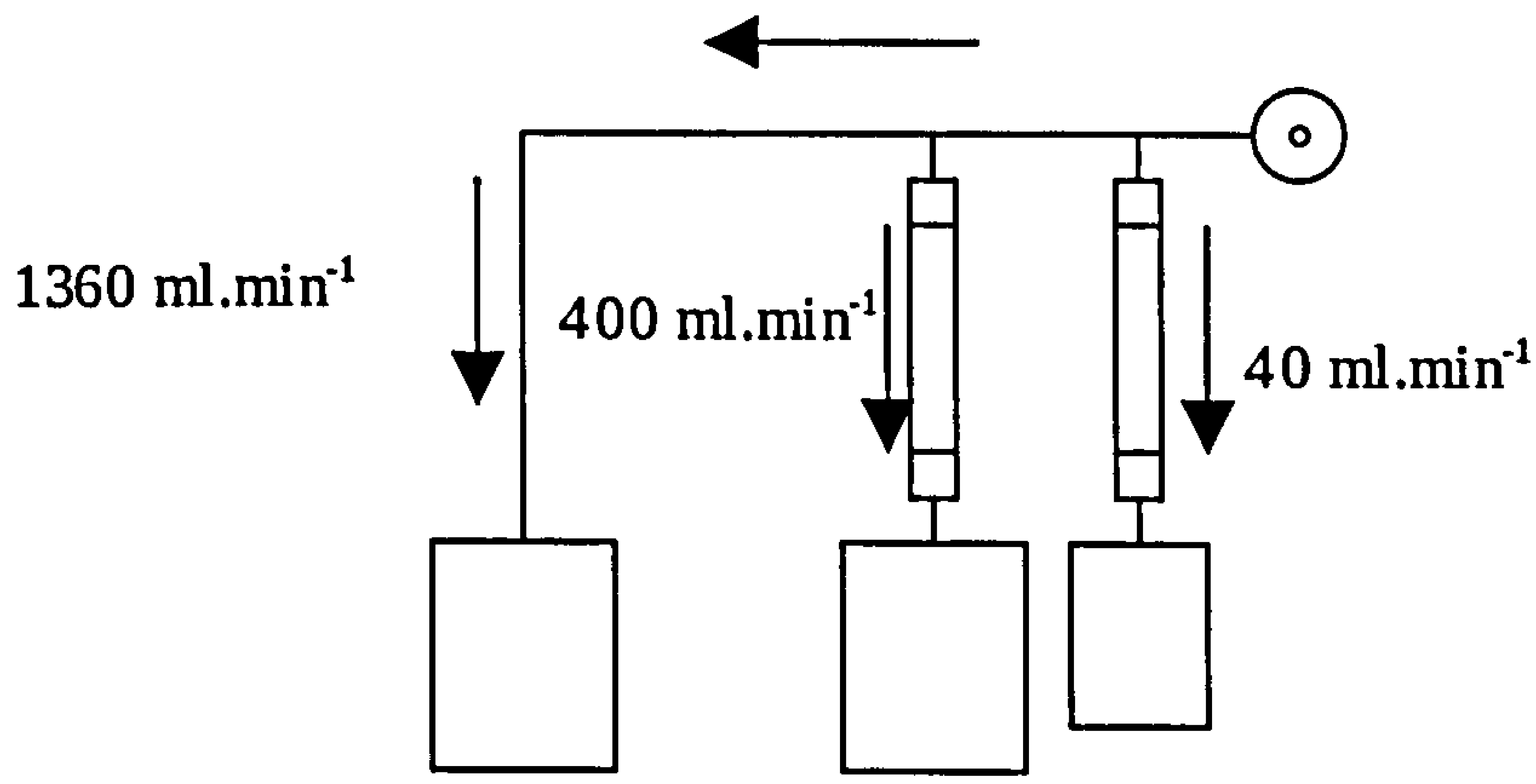

Figure 40: Schematic diagram of the sampling system equipped with two sample tubes

This sampling system tested in the laboratory requires three sampling pumps. This solution was tested in the laboratory by replacing the BGI pumps with a Gilair 5 $l.min^{-1}$ (Sensidyne, inc) and two Gilair low flow rate pumps (Sensidyne, inc). This solution was shown to be much more appropriate than the sampling method used during this experiment and demonstration campaign. Flow rates could be set in less than 5 minutes, whereas it required two hours to let the BGI pumps stabilise and approximately half an hour to set the flow rates. In addition, the modified sampling methodology was effective in reducing the noise of the sampling pumps. This is particularly interesting because the noise generated by sampling pumps is one of the limiting factors when performing personal measurement using active methods. The overall weight of the sampling equipment was not increased, as the Sensidyne pumps are much more lightweight than the BGI pumps.

10.4. Summary and conclusions

The performance of the developed method was evaluated in two steps. The first step involved evaluating the accuracy of the analytical method for PAH compounds to measure the particulate phase. The second step was to evaluate the overall method, including sampling and analysis. Different conclusions can be drawn from these experiments:

✓ *Analysis of particulate*

The accuracy of the analytical method to measure the particulate phase was performed in two ways: (i) using an ambient air reference material SRM1649a certified for a number of PAHs, and (ii) by measurement of indoor air filter portions using the TD method and a well-established solvent extraction method.

The results obtained with the standard reference material showed reasonable agreement with the certified values for PAHs from phenanthrene to benzo(a)pyrene. For these compounds the difference between the obtained and certified values was less than 30%. The concentrations of IP and BghiP were underestimated by the TD method due to a suspected irreversible adsorption under a desorption temperature of 350°C. For these two compounds the difference was 34% and 56%, respectively. Increasing the desorption time to enhance the recovery of these compounds is not inefficient, as demonstrated by a repeated analysis of the filter loaded with the reference material.

The concentrations determined in the reference material for OPAHs were compared with concentrations reported from other studies. The comparison was not straightforward because of the spread of the OPAHs concentrations reported from others studies. This spread demonstrates that further research is required for a better characterisation of this chemical class. Although it was not possible to draw definitive conclusions regarding the accuracy of the TD method for analysing OPAHs, the results tend to show that it is a promising technique.

The analysis of filter portions using the TD method and a well-established solvent extraction combined with HPLC analysis confirmed the results obtained with the standard reference material. The results obtained by the two methods are in good agreement for PAHs up to benzo(a)pyrene. For less volatile PAHs, the concentrations obtained by the TD method were about 40% lower than those obtained by the solvent extraction method.

Higher desorption temperatures are certainly required for thermal extraction of these compounds.

✓ *Analysis of the gaseous phase*

The accuracy of the TD method for analysing the gaseous phase was evaluated by parallel sampling with a Chempass sampler and a Partisol sampler. Twelve collocated samples were collected during two sampling campaign.

PAHs more volatile than phenanthrene are not retained on the PUF cartridge used in the Partisol sampler and PAHs less volatile than pyrene were exclusively present in the particulate phase. As a result, the concentrations of only three PAHs could be compared (phenanthrene, fluoranthene and pyrene). The phenanthrene concentrations were in good agreement between both methods. The fluoranthene and pyrene concentrations determined by the two methods were also generally in good agreement, but an apparent discrepancy was noted during a few sampling events. The reason for this discrepancy is not known. Secondary desorption of the Tenax TA sample tubes has shown that more than 98% of the compounds in question were desorbed during primary desorption. It was suspected that the degradation of the adsorbent by oxidants led to the formation of actives sites, thereby reducing recovery. A comparison between concentrations determined from old tubes and freshly packed tubes did not confirm this assumption. Concentrations determined on the PUF were blank corrected, but the possibility that abnormally contaminated PUF were used during the sampling events where higher concentrations were detected with the Partisol cannot be ruled out.

Chapter 11: Demonstration study

This demonstration study aimed to demonstrate the applicability of the method for personal and indoor measurements. Samples were collecting during 24 hours inside and outside a non smoker flat located in the centre of Paris. Personal samples from a flat inhabitant were also collected.

11.1. Data quality

11.1.1. Sampling

All the samples were within the criteria acceptance of flow rate fluctuation of ±5% between the beginning and end of the sampling. The personal sampling from sampling event day 6 was rejected, as the pump stopped due to a loose wire between the battery and power supply and the sample tube from the outdoor sampling of day 5 was broken.

11.1.2. Analysis

Identification was based on both relative retention time and relative abundance of the qualifier ion with the exception of anthracene and dibenzo(a,h)anthracene, which were identified based solely on their relative retention times. Chromatograms of the target compounds detected in this study for the particulate and gaseous phases are presented **appendix 10** and **appendix 11** respectively. The peak area of the quantifier ion was too low for these two compounds to permit their integration. The acceptance level for relative abundance was set to 30% as recommended by the European standard for the determination polycyclic aromatic hydrocarbons with gas chromatographic/mass spectrometric analyses (ISO/12884: 2000-04-01, 2000).

The mass found in the field blanks for both Tenax TA and QFF was negligible (less than 2%) compared to the mass in the samples and was not deduced from the mass in the samples.

The major problem with the analysis of Tenax TA sample tubes occurred with the lighter compounds in indoor and personal air samples. Peak broadening and possible breakthrough through the cold trap during thermal desorption due to high loading of these samples made the integration of naphthalene-d10, naphthalene, 4-tertbutylphenol, acenaphthylene and dimethylphthalate impossible. Reported concentrations for these compounds are provided as an indication and were not corrected for breakthrough.

11.2. Description of PAHs and OPAHs concentrations

Measurement results for the 16 PAH priory pollutants and 4 OPAHs are presented in **Table 45.** Naphthalene has the highest mean concentration outdoors and in outdoor air among the 16 PAHs. Naphthalene concentrations in indoor and personal samples were not reported because of analytical difficulties, but were much higher than outdoor concentrations levels. Following naphthalene, the three-ring PAHs, phenanthrene, fluorene and acenaphthene were found to have the highest concentrations in indoor, personal and outdoor air. The concentrations of phenanthrene reached up to 17.2 ng/m^3, 13.9 ng/m^3 and 5.9 ng/m^3 in indoor, personal and outdoor air respectively.

Table 45: PAHs and OPAHs concentrations in ng/m^3 (Mean (Min-Max))

Compounds	Living room (n=6)	Kitchen (n=6)	Personal sample (n=5)	Outdoor air (n=5)
Naphthalene	**234 (195-270)**	**208 (149-260)**	**199 (180-219)**	**85.4 (61.7-99.3)**
Acenaphthene	6.8 (4.47-7.77)	5.94 (4.58-7.8)	59 (4.14-9.98)	1.6 (0.85-1.67)
Fluorene	9.2 (5.48-12.54)	9.2 (5.78-13.6)	7.57 (3.1-10.7)	3.37 (2.36-4.05)
Phenanthrene	17.2 (15.8-19.1)	16.9 (13.5-18.9)	13.9 (12.3-16.4)	5.92 (4.25-7.88)
Anthracene	0.51 (0.37-0.60)	0.52 (0.44-0.64)	0.28 (0.19-0.47)	0.15 (0.16-0.17)
Fluoranthene	3.2 (2.8-3.81)	2.44 (1.97-3.07)	2.82 (2.6-3.07)	1.94 (1.31-2.36)
Pyrene	1.28 (1.15-1.41)	1.14 (0.93-1.48)	1.22 (1.13-1.28)	0.95 (0.69-1.22)
BaA	0.08 (0.05-0.13)	0.08 (0.04-0.12)	0.10 (0.03-0.14)	0.16 (0.06-0.29)
Chr/Trip	0.19 (0.10-0.26)	0.19 (0.09-0.25)	0.23 (0.09-0.29)	0.40 (0.18-0.64)
BbF/BjF	0.30 (0.21-0.43)	0.30 (0.16-0.40)	0.32 (0.16-0.44)	0.51 (0.24-0.80)
BkF	0.08 (0.06-0.13)	0.08 (0.05-0.13)	0.09 (0.05-0.13)	0.14 (0.07-0.22)
BeP	0.17 (0.12-0.26)	0.18 (0.10-0.24)	0.19 (0.09-0.27)	0.29 (0.14-0.47)
BaP	0.13 (0.07-0.21)	0.12 (0.06-0.18)	0.13 (0.05-0.19)	0.17 (0.07-0.26)
IP	0.15 (0.10-0.21)	0.14 (0.09-0.18)	0.15 (0.09-0.21)	0.21 (0.12-0.33)
DahA	0.02 (0.01-0.03)	0.02 (0.01-0.03)	0.02 (0.01-0.03)	0.03 (0.01-0.05)
BghiP	0.24 (0.16-0.29)	0.23 (0.14-0.30)	0.24 (0.14-0.38)	0.37 (0.20-0.52)
1-naphthaldehyde	NQ	NQ	NQ	NQ
9-fluorenone	5.4 (4.80-6.22)	5.2 (4.40-5.96)	5.17 (4.32-6.08)	5.9 (5.23-8.14)
9,10-AQ	1.56 (1.23-1.99)	1..55 (1.14-1.8)	1.90 (1.12-2.51)	1.88 (1.40-2.34)
9-PheC	<LOD	<LOD	<LOD	<LOD
Benzanthrone	0.17 (0.14-0.23)	0.19 (0.13-0.24)	0.21 (0.12-0.30)	0.31 (0.19-0.72)
BaA-7,12-O	0.08 (0.07-0.12)	0.09 (0.06-0.10)	0.09 (0.06-0.14)	0.11 (0.07-0.21)
$\sum$ PAH *	38.7 (30.9-47.2)	37.6 (27.9-47.4)	33.2 (24.7-43.9)	16.2 (10.6-21.2)
$\sum$ PAH gaseous	36.9 (34.1-43.5)	36.1 (29.9-43.8)	30.8 (28.7-34.2)	12.9 (9.3-14.4)
$\sum$ PAH particulate	1.8 (1.2-2.6)	1.9 (1.1-2.5)	2.1 (1.0-2.6)	3.3 (1.6-4.9)
$\sum$ OPAH	7.19 (6.2-8.56)	7.07 (5.7-5.15)	7.3 (5.6-9.03)	8.2 (6.8-11.4)

NQ: Not quantifiable due to cold trap breakthrough and peak broadening
** $\sum$ PAH: Sum of 14 PAHs from can to BghiP*
<LOD: Data below detection limit
Data reported in bold are given as an indication (injector breakthrough)

The larger PAHs (MW>228 g.mol^{-1}), covering most of the carcinogens, are much less concentrated and were present in sub ng/m^3 level. Intermediate molecular weight compounds (fluoranthene and pyrene) were found at concentration levels around the ng/m^3.

The concentration levels of cetone- and quinone-type OPAHs were of the same magnitude as their parent PAHs.

The concentrations were of the order of a few ng/m^3 for 9-fluorenone and anthraquinone and less than 1 ng/m^3 for the heavier OPAHs benzanthrone and benz(a)anthracene-7,12-dione. Carboxaldehyde-type oxygenated PAH 9-phenanthrenecarboxaldehyde was not detected in any of the samples.

With the exclusion of naphthalene and acenaphthylene, the total concentrations average of the 14 PAHs in the outdoor air was approximately half of the concentrations in the indoors and personal samples. The concentrations in the living room, kitchen, personal and outdoor samples were 38.7 ng/m^3, 37.6 ng/m^3, 33.2 ng/m^3 and 16.2 ng/m^3 respectively. The outdoor air ΣPAH concentrations were significantly lower than the indoors and personal samples because the concentrations of light PAH present in the gaseous phase were much lower outdoor.

The outdoor PAHs concentrations observed in this study are comparable with the ambient concentrations reported by the French air quality network AIRPARIF at the urban site Paris "les halles" in April 2003 and 2004 **(Table 46)**. Concentrations levels are also comparable with other European cities and north American cities (Los Angeles, Houston, Elizabeth and Chicago) but much smaller than concentrations found in the city of Taipei (Taiwan), Shimizu (Japan), Durham (USA) and Columbus (USA). The concentrations levels of OPAHs are also consistent with the data published in other studies at the exception of the German studies. Concentrations of 9-fluorenone and 9,10-anthraquinone were lower in the German study because the data reported are the concentrations in the particulate phase only. The concentration of benzanthrone is much higher in the German study probably because the concentration of this compound was given as the sum of benzanthrone and 1-Pyrenecarboxaldehyde.

Comparison of the coupled indoor and outdoor concentrations between the present study and other studies interested in the indoor/outdoor relationship in both the gaseous phase and particulate phases is also presented in **Table 46**. Naphthalene (2 rings), phenanthrene (3 rings), pyrene (4 rings) and benzo(a)pyrene (5 rings) were selected to include compounds with 2, 3, 4 and 5 rings and to make the comparison easier.

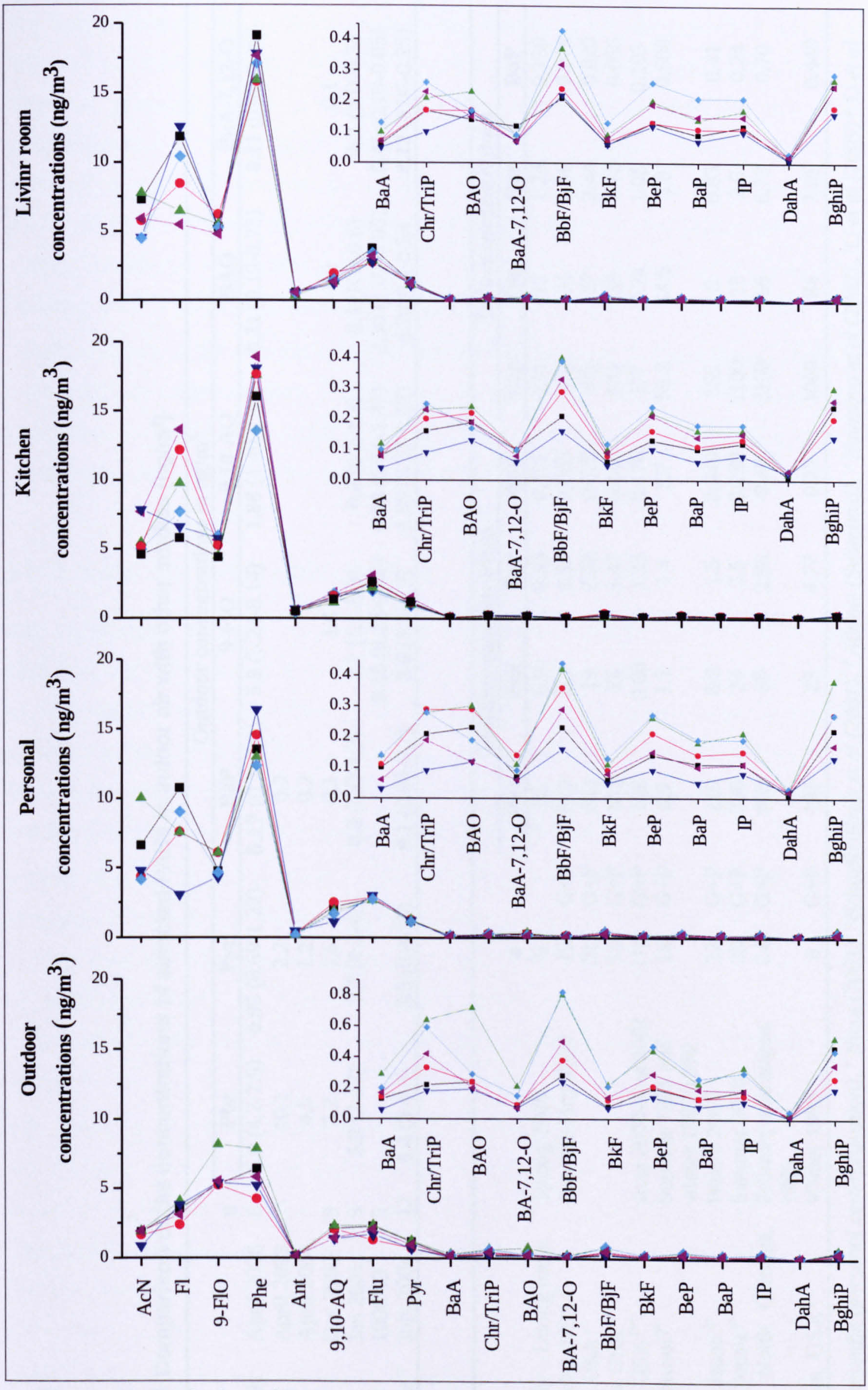

Figure 41: Evolution of PAHs and OPAHs during the 6 days sampling period

Table 46: Comparison of the concentrations of selected PAHs in indoor air with other studies (ng/m³)

			Outdoor concentrations in ng/m³						
		n	Phe	Pyr	BaP	9-FlO	9,10-AQ	BAO	BaA-7,12-O
This study	April 2006	6	**5.9** (4.2-7.9)	**0.95** (0.69-1.22)	**0.17** (0.1-0.2)	**5.9** (5.23-8.14)	**1.88** (1.40-2.34)	**0.31** (0.19-0.72)	**0.11** (0.07-0.21)
Paris [a]	April 2003		10.1	2.2	0.2				
Paris [a]	April 2004		4.5	1.2	0.2				
Paris [b]	Dec 2000	9	4.2	1.5	0,1	1.4		0.2	0.1
Paris [b]	Jan 2001	9	**5.9** (2-12)	**2.7** (0.3-4)	**0.3** (ND-1.3)	**3.7** (1.1-5.3)	**0.4** (0.2-1.3)	**0.1** (ND-0.6)	**0.1** (ND-0.3)
Munich [c]	1998/99	5				**0.35** (0.22-0.46)	**0.96** (0.51-1.47)	**2.50** (1.07-5.05)	**0.41** (0.16-0.85)
Marseille [d]	July 2004	12	**8.4** (3.4-5)	**3.5** (0.4-18)	**0.1** (0.04-0.2)	**3.6** (1.4-6.9)	**1.39** (0.37-2.57)	**0.22** 0.1-0.54	**0.12** (0.06-0.23)

				Outdoor concentrations				Indoor concentrations			
		n		Nap	Phe	Pyr	BaP	Nap	Phe	Pyr	BaP
This study – Living room	Spring 2006	6		85	5.9	0.95	0.171	234	17	1.28	0.130
Los Angeles, USA [e*]	June 99-May 2000	19	G+P	NQ	8.1	1.57	0.065	NQ	21	1.96	0.078
Houston, USA [e*]		21	G+P	NQ	19	2.33	0.025	NQ	27	2.44	0.020
Elizabeth, USA [e*]		15	G+P	NQ	26	3.47	0.140	NQ	33	2.42	0.055
Chicago, USA [f**]	June 2000-Aug 2001	115	G+P	168	9.68	2.22	0.176	177	0.74	1.05	0.103
Taipei, Taiwan [g*]	Summer 1995 and winter 1995/1996	14	G+P	0.9	1.2	1.4	3.7	59.2	14.5	2.9	0.500
Shimizu, Japan [h*]	Winter 2000	22	G+P	210	8.8	1.5	0.340	955	8	0.83	0.41
Shimizu, Japan [h*]	Summer 2000	25	G+P	380	23	3.5	0.230	1100	28	2.0	0.24
Durham, North Carolina, USA [i]	February and august 1995	24	G+P	433	30	2.95	0.46	2190	66	6.73	0.70
Columbus, USA [j]	Winter 1988	8	G+P	183	29	4.77	0.27	1060	84	7.01	0.440

[a] Leoz-Garziandia (personal communication), [b] Nicol (2001), [c] Schnelle-Kreis et al (2001), [d] Albinet (Submitted), [e] Naumova et al (2002),. [f] Li et al (2005) [g] Li et al (2000), [h] Ohura et al (2004b), [i] Chuang et al (1999), [j] Mitra et al (1995)

**Geometric mean **Median ***Arithmetic mean*

The coupled indoor and outdoor concentrations of most of the compounds in this study followed the trend generally observed in other studies. The concentrations of heavy PAH are generally higher or similar to indoor concentrations whereas light PAH concentrations tend to be higher indoor than outdoor. Indoor concentrations levels observed in this study are similar to those found in recent North American studies published by Naumova *et al* (2002) and Li *et al* (2005) but much smaller than those in Taipei, Taiwan (Li *et al.*, 2000), Shimizu, Japan (Ohura *et al.*, 2004a), Durham, USA (Chuang *et al.*, 1999) and Columbus, USA (Mitra *et al.*, 1995).

The fluctuation of the concentrations of individual PAHs and for the sum of 14 PAHs were small over the sampling period for both indoor and outdoor air. The maximum concentrations exceed the minimum concentrations by a factor of 2-3 folds for most of the compounds over the sampling period **(Figure 41).**

11.3. Gas/Particles partitioning

The partitioning between the gaseous and particulate phases obtained during the sampling study is reported in **Figure 42.** As observed in many studies, the gas phase partitioning is strongly dependent on the vapour pressure and ambient temperature. The lower molecular weight PAHs up to anthracene are mainly found in the gaseous phase. Fluoranthene and pyrene are partitioned between both phases, whereas compounds less volatile than anthracene are exclusively associated with particles.

OPAHs show a distribution similar to their analogue PAH. Vapour pressure data are not available in the existing literature for the OPAHs studied; however, it is likely that the oxygen atom in OPAHs causes a minor reduction in the vapour pressure. The gas phase to particulates ratio of three-ring OPAH 9-fluorenone (MW=180 $g.mol^{-1}$) thus corresponds to the ratio of the four-ring PAH fluoranthene and pyrene (MW=202 $g.mol^{-1}$).

The influence of ambient temperature on partitioning can be observed for both PAHs and OPAHs. The fraction in the particles for compounds partitioned between both phases is higher outdoors than it is indoors. This is consistent with respect to lower temperature outdoors than indoors. A number of studies interested in the characterisation of indoor air collect only the particles phase because most of the carcinogens are associated with particles. This study confirmed the findings from other studies reporting high concentrations of light PAHs and OPAHs in indoor air that are potentially harmful to human health. For instance, naphthalene was recently reassessed by the international agency for research on cancer (IARC) and reclassified as possibly carcinogenic to humans (group B2) (IARC, 2002). The toxic properties of OPAHs are poorly documented, but some of them are suspected mutagens.

Thus, it is essential to collect both phases to accurately characterise the human health effects associated with this class of compounds.

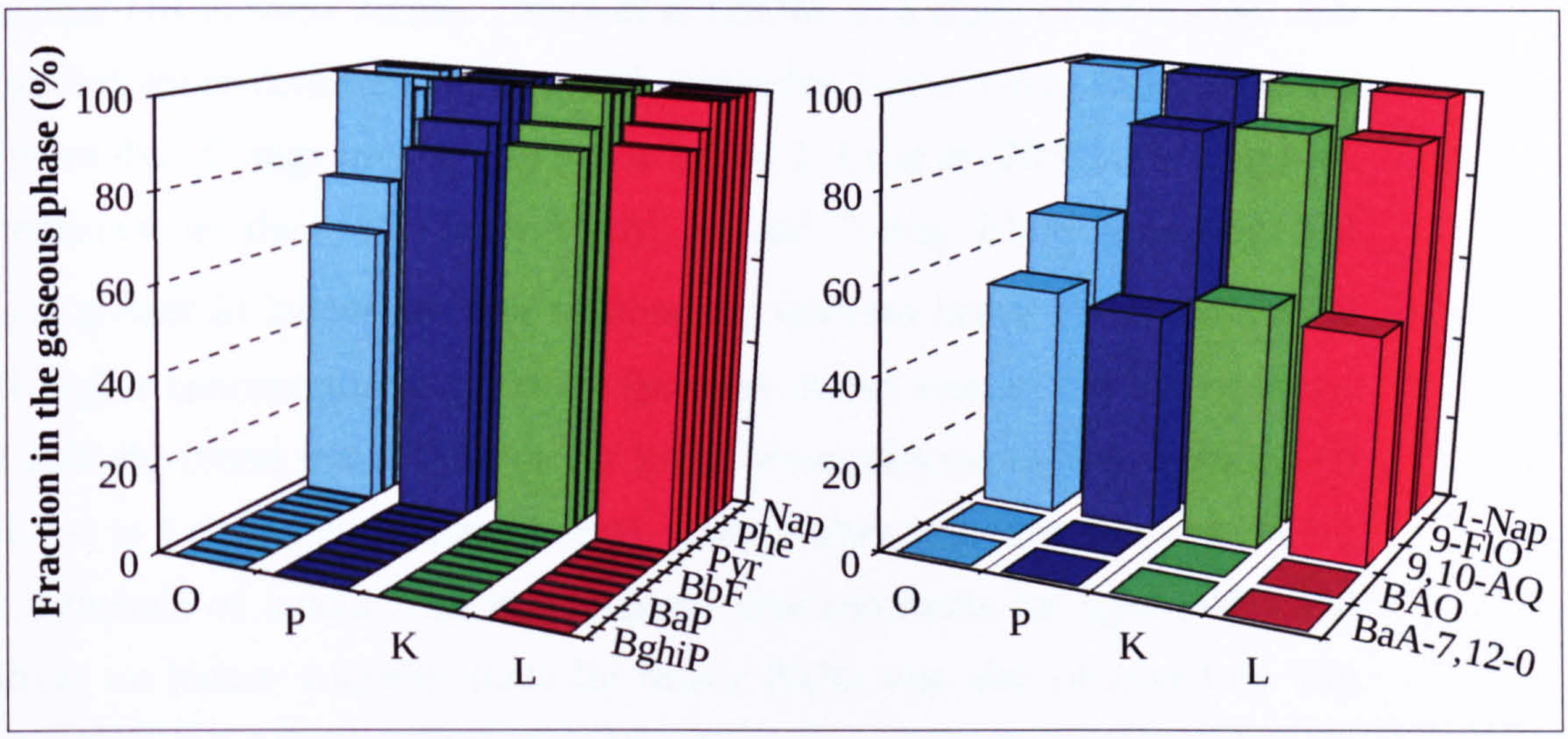

Figure 42: Gas/particles partitioning of PAHs and OPAHs (O=outdoor, P=personal, K=kitchen and L=living-room)

11.4. Source identification of PAHs

11.4.1. Relationship between indoor and outdoor

Boxplots of indoor to outdoor (I/O) ratios of PAH and OPAH concentrations determined in this study are presented in **Figure 43**. Ratios greater than one indicate that indoor sources contribute significantly to indoor concentrations, whereas ratios lower or close to one indicate the absence of indoor sources. Two clear distinct patterns can be observed for individual PAHs for both indoor and personal samples. I/O ratios greater than one were observed for light PAHs up to pyrene (MW=202 $g.mol^{-1}$), suggesting that indoor concentrations of these compounds were dominated by indoor sources. On the contrary, PAHs of higher molecular weight, exclusively particles associated, were dominated by outdoor sources. Their I/O ratios were all lower than one with the exception of dibenzo(a,h)anthracene in some samples. However, the concentrations of dibenzo(a,h)anthracene were very low (in the order of 0.02 ng/m^3) and the possibility that the difference in behaviour between dibenzo(a,h)anthracene and other heavy PAHs arise due to the analytical uncertainty at such concentration levels cannot be excluded. This difference in behaviour between high and low molecular weight PAHs obtained in this study is consistent with the data reported in other studies. Naumova *et al* (2002) observed, in a study of 55 non-smoking homes, that 3-ring PAHs were typically dominated by indoor sources, whereas concentrations in indoor air of high molecular weight PAHs with 5-7 rings were dominated by outdoor sources. 4-ring PAHs were generally dominated by outdoor sources, but indoor sources contributed significantly to indoor concentrations in some homes. Ohura *et al* (2004), in a study of 47 homes, also found I/O concentrations considerably greater than one for 2- and 3-ring PAHs, whereas PAHs with more than 5 rings usually had ratios below 1. Li *et al* (2005) also observed the same tendency in their 115-home study. 2- and 3-ring PAHs generally had concentrations greater in indoor air than outdoor air, whereas heavy PAHs (MW>228 $g.mol^{-1}$) had higher concentrations outdoor regardless of the season. On the contrary, Ohura *et al* (2004b) found that I/O ratios for PAHs were affected by the seasons. I/O ratios were close to 1 during the summer period, whereas they were less than one during winter. The influence of indoor sources on indoor concentrations for light PAHs and outdoor sources on indoor concentrations for heavy PAHs was also observed by Van Winkle *et al* (2001) and Chang *et al* (1991). Finally, numerous studies interested in the particle phase have only found I/O ratios close to or less than one suggesting that heavy PAHs concentrations indoors were dominated by outdoor sources (Chao *et al.*, 2002, Fromme *et al.*, 2004b, Li *et al.*, 2000, Li *et al.*, 2005, Ohura *et al.*, 2005). All of the cited studies tended to demonstrate that the indoor concentrations of heavy PAHs are dominated by outdoor sources whereas concentrations of light PAHs tended to be more influenced by indoor sources.

Finally, the influence of outdoor air on indoor air concentrations of heavy PAHs is also suggested by looking more closely at the I/O for each sampling period **(appendix 12)**. The window of the bedroom overlooking the patio was inadvertently left open through the entire sampling period of day 3 meanwhile the door of this bedroom was left closed. It can be seen that the lowest I/O (kitchen/outdoor and living room/outdoor) ratios for most of the heavy PAH was obtained that day. Heavy PAH concentration levels are likely to be lower in the patio than in the street because it is not directly influenced by traffic emissions. On the contrary, pollutants in the street are likely to become concentrated in that street, which can be considered a canyon street. Higher than usual ventilation with the air from the patio, suspected to be less concentrated, could be one explanation for the low I/O that sampling day. The assumption that heavy PAH concentration levels were lower in the patio than in the street could be one explanation for I/O ratios systematically lower than 1 for heavy PAHs.

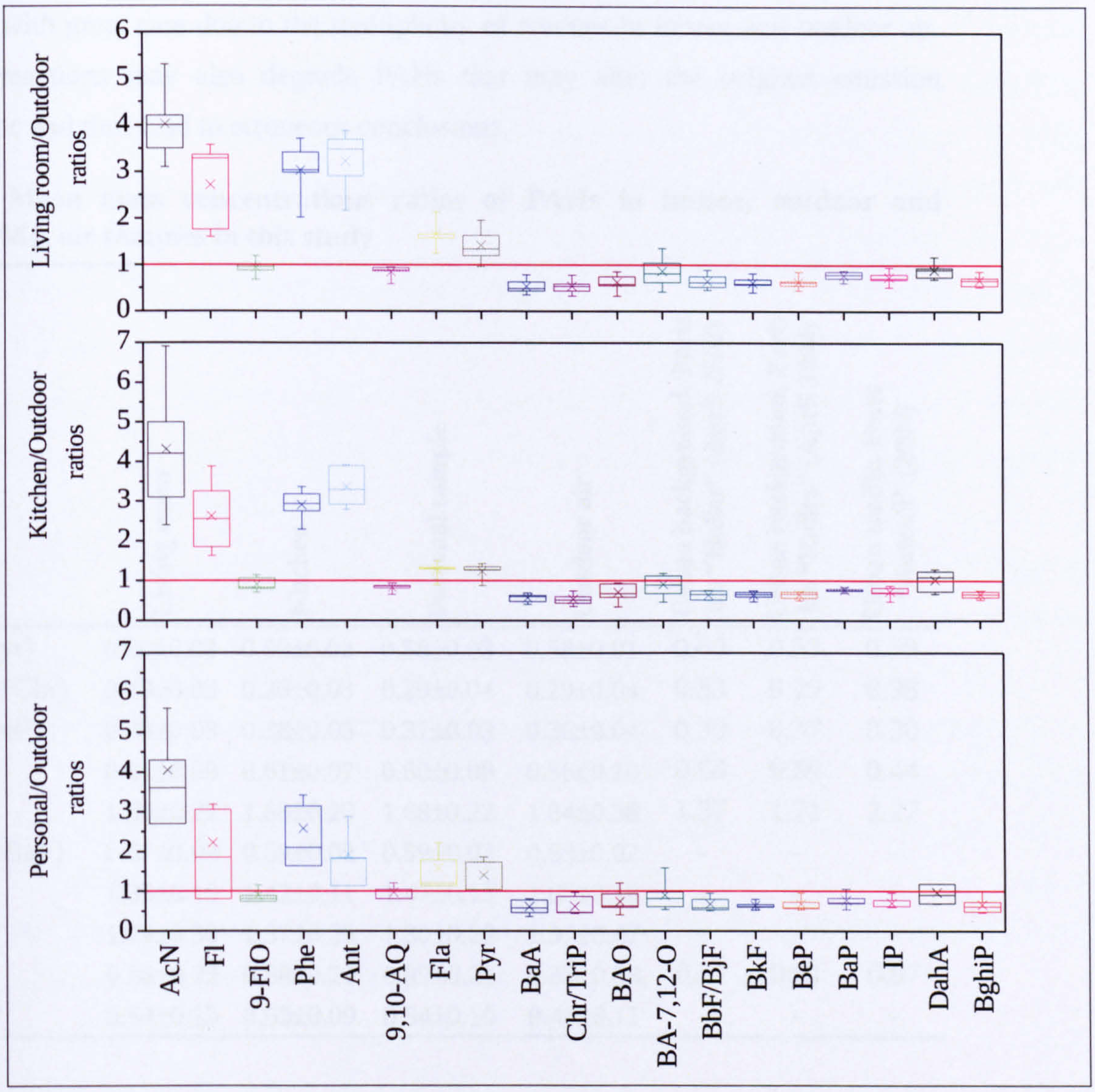

Figure 43: I/O ratios and P/O ratio (n=6 days)

In contrast to PAHs, I/O ratios suggest that indoor concentrations of the target oxygenated PAHs were influenced mainly by outdoor sources for both light and heavy OPAHs. I/O ratios were close to one for all of the target compounds. This finding was in agreement with Chang *et al* (1991), who found mean I/O ratios in non-smokers homes of 1.6 and 1.3 for 9-fluorenone and benz(a)anthracene-7,12-dione respectively.

11.4.2. Source identification of PAHs in outdoor air

Diagnostic ratios between individual PAHs has been suggested in many studies to obtain information about emissions sources or aging of air samples (Caricchia *et al.*, 1999, Chao *et al.*, 2002, Li, C. *et al.*, 2005, Pandey *et al.*, 1999, Panther *et al.*, 1999, Park *et al.*, 2002, Schauer *et al.*, 2003, Smith *et al.*, 1996). Diagnostic ratios found in this study as well as those found in the urban Paris site "les Halles" from previous years are presented in **Table 47**. It should be noted that use of the diagnostic ratio should be interpreted with great care due to the multiplicity of sources in indoor and outdoor air. Oxidation reactions may also degrade PAHs that may alter the original emission characteristic and thus lead to erroneous conclusions.

Table 47: Mean mass concentrations ratios of PAHs in indoor, outdoor and Personal $PM_{2.5}$ air samples in this study

Diagnostic ratios	Living room	Kitchen	Personal sample	Outdoor air	Urban background, Paris les "Halles" (April 2003)	Urban background, Paris les "Halles" (April 2004)	Urban traffic, Paris "Auteuil" (2004)
Flu/(Flu+Pyr)	0.60±0.03	0.58±0.02	0.58±0.03	0.58±0.01	0.60	0.53	0.59
BaA/(BaA+Chr)	0.29±0.03	0.30±0.03	0.29±0.04	0.29±0.04	0.33	0.29	0.38
IP/(IP+BghiP)	0.38±0.03	0.38±0.03	0.37±0.03	0.36±0.04	0.39	0.37	0.30
IP/BghiP	0.61±0.08	0.61±0.07	0.60±0.08	0.56±0.10	0.64	0.59	0.44
BghiP/IP	1.66±0.22	1.68±0.20	1.68±0.22	1.84±0.38	1.57	1.71	2.27
BeP/(BeP+BaP)	0.57±0.03	0.59±0.02	0.59±0.02	0.63±0.02	-	-	-
BeP/BaP	1.35±0.19	1.42±0.11	1.47±0.13	1.69±0.16	-	-	-
BghiP/BeP	1.44±0.30	1.37±0.25	1.30±0.20	1.37±0.47	-	-	-
BaP/IP	0.88±0.22	0.88±0.20	0.89±0.21	0.83±0.38	0.57	0.91	0.97
BaP/BghiP	0.54±0.13	0.53±0.09	0.54±0.10	0.46±0.11	-	-	-

It can be seen that ratios in outdoor samples found in this study were very close to those found in the Paris site "les Halles" in April 2003 and 2004, suggesting that the flat location is representative of the urban area of Paris and that no specific local emissions are present around the flat area.

The coupled BghiP/BeP and Cor/BeP are used as indicators of traffic with higher value indicating higher vehicular emissions. Coronene was not measured in this study; therefore, the conclusions can only be based on the BghiP/BeP ratio. The mean BghiP in outdoor air was equal to 1.37±0.04. Compared with BghiP ratio of 0.8 for non-traffic sources and 2.02 for traffic emissions (Nielsen, 1996), the results suggested that both traffic and non-traffic emissions contributed to PAHs in outdoor air. The contribution of traffic tends to be confirmed by the Flu/Flu+Pyr ratio. An indication of vehicular emission can be assigned when the ratio is higher than or equal to 0.4 (Rogge *et al.*, 1993). The mean ratio Flu/Flu+Pyr in this study was 0.58 in outdoor air.

Several PAH ratios have been proposed to distinguish gasoline and diesel emissions. Caricchia *et al* (1999) indicated that BaP/IP ratios of about 1 were characteristic of diesel engines, whereas ratios of approximately 0.4 were representative of gasoline engines. The mean outdoor air BaP/IP ratio found in this study was 0.83±0.14, corresponding roughly to the expected mixture of diesel and gasoline engines. In 2004, diesel-powered vehicles represented 50% of the registered vehicles in France (ADEME, 2006). An IP/IP+BghiP ratio of 0.18, 0.37, 0.56 were reported for gasoline cars, diesel cars and coal combustion (Grimmer *et al.*, 1983). The mean IP/IP+BghiP found in outdoor air was 0.36±0.04, suggesting diesel emissions. Li et kamens (1993) determined BghiP/IP ratios of 1.1-1.2 and 3.5-3.8 for diesel and gasoline engines, respectively. The ratio found in this study was 1.84±0.38, also suggesting a mix of diesel and gasoline engines.

Overall, the above diagnostic ratio suggested the contribution of traffic to the PAHs in the vicinity of the flat. Other emission sources such as domestic heating could not be identified in this study because the study was carried out during only one season.

Finally, the contribution of traffic to outdoor PAH concentrations is also suggested by the differences in concentration levels between weekdays and the sole sampling done during the week-end. The lowest concentrations for particulate PAHs for both indoor and outdoor particulate PAHs were obtained at sampling event 4, which corresponds to the week-end. Traffic emissions are likely to be lower during the week-end and it is not surprising that PAH concentrations were lower that sampling day.

11.4.3. Sources identification in indoor air

It can be observed that diagnostic ratios in outdoor samples were very close to indoor samples **(Table 47)**. This result tends to confirm that indoor, particles associated PAH concentrations are driven by outdoor concentrations. On the contrary, I/O ratios greater than 1 indicated that light PAH concentrations are dominated by indoor sources. Indoor sources identified as potential contributors to PAHs are tobacco smoking, cooking, incense burning, fireplaces and the use of naphthalene as moth repellent. Among these sources, the only one that could have generated PAHs during the sampling period was cooking.

The PAH concentrations in the living room and kitchen were similar during the 6 sampling events. Average living room to kitchen concentrations for individual PAH concentrations ranged from 0.9 to 1.31 **(appendix 12)**. Fluoranthene was the only compound with concentrations significantly higher in the living room than in the kitchen ($p<0.01$;t-test). This finding suggested that air mixing was fairly good in the flat and that cooking activities in this study did not significantly affect the air quality in the kitchen. PAH emission during cooking may have occurred, but PAHs were vented through the kitchen window that was left open during cooking or they were rapidly mixed in indoor air.

Assuming that substantial amounts of PAHs were generated during cooking and that the air in the kitchen was rapidly dispersed in the flat, greater I/O ratios should have been observed when cooking took place. It can be seen in **Table 48** that L/O or K/O ratios are not significantly different between cooking and non-cooking days, thus suggesting that the cooking activities in the flat did not generate substantial amounts of PAHs indoor. The source of light PAHs in indoor air could not be identified in this study. Possible indoor sources explaining higher concentrations of these light PAHs indoors than outdoors include the penetration of contaminated air generated by neighbour's activity. For instance, penetration of contaminated air could have occurred through the ventilation system, the front door or the window overlooking the patio.

Table 48: I/O ratios differences between cooking and no-cooking sampling events

	Living room/Outdoor (L/O)		Kitchen/Outdoor (K/O)	
	Mean cooking±sd*	No cooking**	Mean cooking±sd*	No cooking**
Acenaphthene	4.1±1.1	3.5	4.3±2.0	3.1
Fluorene	2.8±0.9	3.6	2.8±1.0	3.3
Phenanthrene	3.1±0.2	3.7	3.0±0.3	3.2
Anthracene	3.7±0.2	2.9	3.3±0.6	2.9
Fluoranthene	1.6±0.1	2.1	1.3±0.1	1.5
Pyrene	1.4±0.2	2.0	1.3±0.1	1.3
BaA	0.6±0.2	0.5	0.6±0.1	0.7
Chr/TriP	0.6±0.1	0.5	0.6±0.1	0.6
BbF/BjF	0.8±0.1	0.6	0.7±0.1	0.8
BkF	0.7±0.1	0.6	0.7±0.1	0.7
BeP	0.7±0.1	0.6	0.7±0.1	0.7
BaP	0.8±0.1	0.9	0.8±0.1	0.8
IP	0.8±0.1	0.7	0.8±0.1	0.9
DahA	1.0±0.1	0.9	1.2±0.1	1.1
BghiP	0.7±0.2	0.7	0.7±0.1	0.8
9-FlO	0.9±0.1	1.2	0.9±0.1	1.1
9,10-AQ	0.9±0.1	1.0	0.9±0.1	0.9
BAO	0.7±0.1	0.7	0.8±0.1	0.9
BaA-7,12-O	1.1±0.2	0.8	1.0±0.1	1.2

** Mean of 3 sampling days with cooking activities (day 1, 4 and 6)*

*** Only one sampling without cooking activities out of 3 reported. Day 3 was excluded because the window of the bedroom was left open and sample tube of outdoor air sampling of day 5 was broken.*

In the case of this flat, sampling could have been performed either in the kitchen or in the living room, since PAH concentrations in the living room were not substantially different from the kitchen. Very few studies have measured PAHs in different home microenvironments. Chuang *et al* (1991) found that the concentrations in the living room were higher than in the kitchens for most of the compounds. However, the difference was statistically different for very few compounds. Ohura *et al* (2005) measured PAHs in several home microenvironments, including the living room, kitchen, and bedroom. They also concluded that there were no significant differences between the various microenvironments. On the contrary, Zhu *et al* (2003) noticed elevated concentrations of Ant, Fl and Pyr in kitchens compared to bedrooms and living rooms in homes using gas liquefied petroleum gas as combustion fuels. The cooking activity during the sampling study was very limited and it is not surprising that PAHs were not generated in substantial quantities; thus no differences were observed between kitchen and living-room PAH concentrations. Among the different indoor sources, cooking is certainly one of the most home-to-home specific because there are so many factors influencing the generation of PAHs, including the quantity of food cooked, duration of cooking, cooking method (boiling, broiling, frying), combustion source used (gas, liquefied petroleum, electric), type of food (meat, fish, vegetable) and presence or absence of a kitchen fan, etc...

11.4.4. Sources identification in personal air samples

Personal samples diagnostic ratios **(Table 47)** were also close to indoor and outdoor ratios. Different ratios could have been expected, since personal samples combined three distinct microenvironments. The amount of time spent at home, inside the car and at the workplace located in a rural environment were approximately 12.5 hours, 2.5 hours and 9.5 hours respectively. Measurements inside the car and in workplace microenvironments were not available. However, the contribution of the workplace microenvironment to personal sample concentrations is expected to be weak because concentrations in the rural site are likely to be less than in the home which is located in Paris centre. On the contrary, although the inside car microenvironment represents only 10%, in time, of the personal samples, its contribution to the concentration of personal samples is expected to be higher than its time weight because concentrations are expected to be high. The inside car microenvironment included driving in a rural environment (50% of travel) and driving through a heavy traffic environment with traffic jam in a non ventilated tunnel. Concentrations levels of PAHs inside the tunnel can be very elevated compared to ambient air concentrations due to the poor dispersion of the pollutants (Pereira *et al.*, 2002, Wingfors *et al.*, 2001). Wingfors *et al* (2001) have reported tunnel concentrations one order of magnitude higher than urban concentrations.

The absence of sampling inside the car and in the workplace was clearly missing in order to identify major sources contributing to the personal exposure of the volunteer.

It should be pointed out that although personal measurements are the best mean to characterise human exposure, it is often difficult to measure the personal exposures of a significant number of people. The alternative is to measure concentrations in a number of microenvironments and to combine concentrations with the time spent by individuals in these microenvironments. Sources identification is also facilitated using the latter method since emission sources in microenvironments can be more easily identified than from microenvironment measurements. The bottleneck of this method based on microenvironments measurements is that microenvironments susceptible to have a major impact on the personal exposure should be precisely identified. Concentrations patterns within microenvironments should also be determined with precision in order to achieve an accurate estimation of the human exposure.

11.5. Risk assessment for PAHs

Assessing the toxicity of individual compounds in a complex mixture is complicated. One approach involves using toxic equivalent factors (TEF) based on a well-characterised compound, which is BaP for PAHs. It should be noted at this point that TEFs should be used with great caution, as TEFs are not true values and data available in the existing literature are very scanty **(Chapter 1.1.1, Table 1)**. BaP_{equ} concentrations presented in **Table 49** for indoor, outdoor and personal samples are based on TEFs from Doonaert *et al* (2003) .

It can be observed that the ΣPAH of BaP_{equ} are slightly lower indoors than outdoors when only the particles associated PAHs are included in the calculation. The same trend was observed in other studies **(Table 50)** and is related to indoor concentration levels of those PAHs generally lower than or similar to outdoors. The contribution of BaP to the ΣPAH represents approximately 50% to the total carcinogenic potential of PAHs in both indoor and outdoor air.

Table 49: Concentrations in indoor, outdoor and personal samples (BaP_{equ}, ng/m^3)

		Living room		Kitchen		Personal sampling		Outdoor air	
	TEF	Conc	BaP_{equ}	Conc	BaP_{equ}	Conc	BaP_{equ}	Conc	BaP_{equ}
Nap	0.001	>234	0.23	>208	0.21	>199	0.20	85	0.09
AcN	0.001	5.95	0.01	5.94	0.01	5.97	0.01	1.62	0.00
Fl	0.001	9.18	0.01	9.26	0.01	7.57	0.01	3.37	0.00
Phe	0.001	17.24	0.02	16.97	0.02	13.94	0.01	5.92	0.01
Ant	0.010	0.51	0.01	0.52	0.01	0.28	0.00	0.16	0.00
Flu	0.001	3.18	0.00	2.44	0.00	2.82	0.00	1.94	0.00
Pyr	0.001	1.28	0.00	1.14	0.00	1.22	0.00	0.95	0.00
BaA	0.100	0.08	0.01	0.08	0.01	0.10	0.01	0.16	0.02
Chr/TriP	0.100	0.19	0.02	0.19	0.02	0.23	0.02	0.40	0.04
BbF/BjF	0.100	0.3	0.03	0.30	0.03	0.32	0.03	0.51	0.05
BkF	0.100	0.08	0.01	0.08	0.01	0.09	0.01	0.14	0.01
BaP	1.000	0.13	0.13	0.12	0.12	0.13	0.13	0.17	0.17
IP	0.100	0.14	0.01	0.14	0.01	0.14	0.01	0.21	0.02
DahA	1.000	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03
BghiP	0.010	0.24	0.00	0.23	0.00	0.24	0.00	0.37	0.00
ΣPAH [a]			0.51		0.48		0.47		0.44
ΣPAH [b]			0.24		0.23		0.24		0.34

[a] *Sum of PAHs from Naphthalene to Benzo(g,h,i)Perylene*
[b] *Sum of PAHs from fluoranthene to Benzo(g,h,i)Perylene*

A contrasting result is obtained when both gaseous and particulate PAHs are included in the calculation. In that case, the ΣPAH of BaP_{equ} tends to be higher indoors than outdoors. Although the naphthalene concentrations given in **Table 45** are certainly underestimated (they were not corrected for possible breakthrough during thermal desorption), its contribution to ΣPAH of BaP_{equ} is significant. The low molecular weight PAHs contributes for more than 50% of ΣPAH of BaP_{equ} in indoor air and for 25% in outdoor air. The ΣPAH of BaP_{equ} is increased two fold when light PAHs are included in the calculation. These results demonstrate that BaP cannot be a sole indicator of the carcinogenic potency of PAH mixtures. Gaseous PAHs may contribute significantly to the carcinogenic potency of PAHs in indoor air. It is important, though, to sample both the particulate and gaseous phases when conducting risk assessment of PAHs.

Table 50: PAH concentrations in (BaP_{equ}, ng/m^3) in the present study compared with other studies

Studies	n	Sampling period and microenvironment	Concentrations of (BaP_{equ}) *	Concentrations of (BaP_{equ}) **
This study	6	Personal exposure	0.47$^{\alpha}$	0.24$^{\alpha}$
Japan [a]	17	Personal exposure winter	-	0.48$^{\alpha}$
Japan [a]	28	Personal exposure summer	-	0.38$^{\alpha}$
Japan [b]	20	Indoor air - Summer	1.63/0.87$^{\beta}$	0.44/0.45$^{\beta}$
Japan [b]	20	Indoor air - Winter	1.54/1.15$^{\beta}$	0.56/0.90$^{\beta}$
Chicago, USA [c]	10	June 2000 - August 2001	0.21/0.31$^{\beta}$	0.49/0.51$^{\beta}$
Los Angeles, USA [d]	19		-	0.12/0.14$^{\beta}$
Houston, USA [d]	21	June 1999 - May 2000	-	0.13/0.15$^{\beta}$
Elizabeth, USA [d]	15		-	0.20/0.35$^{\beta}$

* *ΣPAH of BaP_{equ} including PAHs from Naphthalene to benzo(g,h,i)Perylene*

** *ΣPAH of BaP_{equ} including PAHs from fluoranthene to benzo(g,h,i)Perylene*

$^{\alpha}$ *Personal sample concentrations,* $^{\beta}$ *Indoor/Outdoor air concentrations*

[a] *(Ohura et al., 2005),* [b] *(Ohura et al., 2004a),* [c] *(Li et al., 2005),* [d] *(Naumova et al., 2002)*

11.6. Other SVOCs

Concentrations of non-combustion-related SVOCs are discussed in the following chapter.

11.6.1. Description of SVOCs concentrations

Concentrations of detected non-related SVOCs found in this demonstration study are reported in **Table 51**. Among the 17 target non–combustion-related compounds, 8 of them were detected in all of the indoor, outdoor and personal air samples. These compounds include the five target phthalates, two phosphate esters and one compound presumably used as a disinfectant, namely, 2-phenylphenol (Rudel *et al.*, 2003). Pesticides (n=6) and alkylphenol (n=2) compounds were not detected in any of the samples, whereas phenol 4-tertbutylphenol could not be analysed due to its possible breakthrough through the cold trap during thermal desorption.

The concentration levels of phosphate and phthalate esters in both indoor and personal samples are similar, but much higher than outdoor levels. This finding confirmed that emission sources of these compounds are present mainly in indoor environments.

The outdoor air phthalate concentration levels found in this study are similar to concentration levels found in Paris by Teil *et al* (2006). The annual mean concentrations in outdoor air during the years 2002/2003 in the cited study were reported to be 9.1 ng/m^3, 21.9 ng/m^3, 4.7 ng/m^3 and 12.2 ng/m^3 for DEP, DBP, BBP and DEHP respectively. Similar outdoor concentration levels of DBP and DEHP were reported in Japan (Environmental Agency of Japan, 1999) and California (CARB, 1992). Elevated ambient phthalate concentrations may occur in industrial megalopolises. Higher outdoor concentrations than the indoor concentrations found in this study were reported by Wang *et al* (2007) in the mega city of Nanjiing (China). The authors reported mean winter outdoor concentrations of 132 and 158 ng/m^3 for DBP and DEHP, respectively. The low-level outdoor concentrations of organophosphate esters found in this study are consistent with the data published by Carlson *et al* (1997). TBP and TCEP outdoor concentrations were reported below the ng/m^3.

The indoor concentrations of phthalate levels found in the participant's home were generally lower than those reported in other studies, suggesting that the emission sources in the inhabitant's home were low compared to the homes of North American, European and Japanese families. Data on concentrations levels of phosphate esters in indoor environments are still limited. To the best of available knowledge, there is no data available in the literature regarding the occurrence of this chemical family in a large-scale study. However, the concentrations levels found in this study are comparable to the studies reporting values for TBP and TCEP.

Table 51: Concentrations of phthalates, organophosphate esters and 2-phenylphenol in ng/m^3 (Mean (Min-Max))

Compounds	Living room	Kitchen	Personal	outdoor
DMP	DNQ*	DNQ*	DNQ*	
DEP	277 (204 -376)	222 (165-338)	207 (141-342)	16.6 (14.6-18.4)
DBP	126 (80-194)	129 (92-196)	114 (106-141)	13.8 (7.9-20.1)
BBP	13 (9-19)	18 (14-30)	14 (13-20)	2.1 (2.1-5.7)
DEHP	48 (38-61)	46 (34-56)	64 (48-90)	9.6 (5.8-13.7)
TBP	23 (20-29)	22 (19-28)	17 (12-21)	2.1 (1.5-2.9)
TCEP	1.7 (1-2)	3.1 (2-4)	2.6 (2-3)	0.4 (0.3-0.6)
2-PP	15 (11-20)	16 (7-24)	13 (8-22)	3.4 (3.4-4.5)

**DNQ: Detected but not quantified (breakthrough through cold trap)*

Phosphate and phthalate esters are ubiquitous in indoor environments. Concentrations found in indoor homes vary greatly **(Table 5 and Table 52)** because the emissions sources are highly home-specific. Differences in concentrations between indoor microenvironments are influenced by building materials used, and the presence of consumer products and furniture containing these plasticizers/flame retardants. The emission rates from these manufactured products are likely to be related to the quantity of these additives added during manufacturing and other parameters such as the surface area, aging and ambient temperature.

Measurements in inhabitants' homes are clearly a better way to estimate human exposure to these chemicals; however, since people pass through various environments during the day, fixed-measurements in homes might still be inaccurate for proper estimates. Marklund *et al* (2005) in a 17 domestic and occupational environment study, observed that the public buildings tended to have organophosphate ester concentrations approximately 3-4 times higher in public buildings (offices, university lobby, hospital ward, library...) than domestic buildings. People might also be exposed to high concentrations of phosphate esters and probably phthalates while driving, and especially in brand new cars (Wensing *et al.*, 2003).

Personal measurements are therefore recommended to estimate the exposure of populations to these compounds.

Table 52: Concentrations of phthalates and organophosphates esters in indoor air (median concentration reported in ng/m³)

Study	n	DEP	DBP	BBP	DEHP	TBP	TCEP
This study (living room)	6	277	126	13	48	23	2
Rudel *et al* (2003)	120	590	220	<LOD	77	-	-
Otake *et al* (2004)	27	100	390	10	110	<1	<1
Otake *et al* (2001)	6	120	405	80	60	5	10
Fromme *et al* (2004a)	59	643	1083	18	156	-	-
CARB (1992)	125	350	410	35	103	-	
Sanchez *et al* (2003)	3	-	-	-		14	7

11.6.2. Conclusions

The aim of this demonstration study was neither to identify typical sources of exposure to SVOCs nor to estimate the exposure to these chemicals, but rather to demonstrate the feasibility of the method to conduct large-scale studies.

Personal and indoor sampling brought to the fore that the low volatile SVOCs could not be measured accurately. Peak broadening and possible breakthrough through the cold trap occurred due to the high loading of these samples.

The results in the studied flat were consistent with most previous studies reporting indoor heavy concentrations lower than or similar to outdoor PAH concentrations. Light PAH concentrations were higher indoors than outdoors, although no indoor sources were identified. This result suggested that indoor PAH concentrations are not only influenced by the flat inhabitants' activities, but also by the activities of the building inhabitants. The results of the OPAHs suggested that indoor concentrations are dominated by outdoor sources, while concentrations of organophosphates and phthalic esters confirmed that indoor concentrations are dominated by indoor sources.

Personal measurements could not provide conclusive answers for the microenvironment affecting the concentrations of target compounds. In the case of the volunteer spending more than 2 hours driving in a dense traffic, it can be expected that the inside car microenvironment contributed significantly to the PAH personal exposure.

The prediction of personal exposure is a complicated task because people pass through multiple microenvironments in the daytime. Concentrations levels in private homes are influenced by multiple factors such as building characteristics, sources, ventilation and air exchange rate. Concentrations in public buildings, personal cars and public transports are also expected to vary greatly. As a result, the variation of personal exposure concentrations is expected to be large between individuals and even larger between different minorities. Personal measurements combined with microenvironment measurements over a long period of time and at a large scale are clearly needed to estimate exposure of the population and identify key sources. Up to now, very little work has been done worldwide. In France, knowledge of the exposure of the population to the SVOCs targeted by this work is virtually non-existent. A large-scale study should be conducted to estimate the exposure of the French population to this chemical class and to take reduction measures if necessary.

Conclusions and perspectives

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The objective of this thesis was to develop an analytical method based on a thermal desorption procedure for the determination of semivolatile organic compounds (SVOCs) concentrations in indoor and personal air samples. The method was developed and evaluated for both the measurement of the gas and particles phases and a short demonstration study was performed to evaluate the applicability of the method for future larger field study.

The first task of this work was to verify that samples could be safely collected over a 24 hour sampling period. This was done through a breakthrough volume measurement study based on a direct method that required the development of a vapour generation system. The developed vapour generator based on a diffusion method is efficient to generate vapours at stable concentrations for compounds with a broad range of volatility. Measurements of breakthrough volumes were performed under the worst conditions (concentrations, humidity, temperature and flow rate) that may be encountered during field sampling. This experiment confirmed that the target compounds could be quantitatively sampled for 24 hours. The sample volume for a twenty-four hour sampling period (0.72 m^3) represents less than 50% of the 5% breakthrough volume for naphthalene and 4-tertbutylphenol.

The thermal desorption method was then developed for 38 target compounds including PAHs, OPAHs, alkylphenols, phthalates, organophosphate esters and pesticides. The retained analytical conditions permit most of the target compounds to be quantified with limit of detection ranging between 0.01 ng/m^3 and 0.5 ng/m^3. Such concentrations levels were far below the concentrations levels determined during the demonstration study.

Thermal desorption for aerosol measurements is an emerging subject in the scientific literature. This method has been evaluated in very few studies mainly to quantify PAHs and n-alkanes. The performance of the TD method was evaluated for PAH measurements with a standard reference material (SRM1649a, NIST) certified with solvent extraction procedure and with freshly collected in air filters analysed by both thermal desorption and a well-established solvent extraction procedure. These two comparative methods have demonstrated that the TD method is efficient to quantify PAHs with a MW≤252 g.mol^{-1}. For less volatile compounds, the concentration determined by the TD method were underestimated by approximately 40-50 % due to their incomplete desorption.

In order to evaluate the performance of the developed method for both the gaseous and particulate phases, parallel samplings were conducted between the modified Chempass sampler and a low volume PUF/filter sampler (n=6). This side by side comparison clearly demonstrate that the developed method was much more efficient than the low volume PUF sampler for the measurement of gaseous low molecular weight compounds (MW≤178 $g.mol^{-1}$). For the remaining gaseous PAHs (phenanthrene, fluoranthene and pyrene), the agreement between both method was generally good (deviation less than 20%).

Regarding the particulate phase, measured concentrations from both samplers were highly correlated at the exceptions of the heavy PAHs (MW≥252 $g.mol^{-1}$). The concentrations ratios obtained in this comparison were similar to those determined during the analytical comparison between the HPLC and TD methods thus suggesting that sampling artifact were limited or similar to those of the low volume sampler.

Finally a demonstration study consisting of twenty four hours indoor and personal measurements was carried during six days. The results in the studied flat were consistent with most previous studies reporting indoor heavy PAH concentrations lower or similar to outdoor PAH concentrations. Light PAH concentrations were higher indoors than outdoors, although no indoor sources were identified. This result suggested that indoor PAH concentrations are not only influenced by the flat inhabitants' activities, but also by the activities of the building inhabitants. This demonstration study also confirmed that phthalates and organophosphate esters are ubiquitous in indoor environments, although no specific source such as vinyl flooring was present in the studied flat.

This demonstration study as well as the comparison with the low volume sampler clearly demonstrate that this developed method based on a thermal desorption procedure is well suited for personal and indoor SVOCs measurements. This method is very sensitive, allows a high sample throughput and is environmentally friendly. However, this study revealed that the developed method also has some drawbacks and should be improved for future large scale study.

(i) The quantification of heavily contaminated samples is impossible because the MS detectors reached saturation at few ng. For instance, the upper quantification limit of the developed method for phthalates is approximately 700 ng/m^3 and 400 ng/m^3 for the gaseous and particulate phases, respectively. Since the thermal desorption procedure is a destructive method, there is no chance to re-run the sample. Such concentration levels are not uncommon and concentrations of up to dozens of $\mu g/m^3$ can be found in the literature. This is not directly a problem for the particulate phase because the second fraction of the filter can be analysed with a higher split ratio. On the contrary, only one sample tube is available for the gaseous phase. This means that the concentration levels of the most exposed population cannot be quantified. This problem can be solved by sampling in duplicate or by using the modified sampling system incorporating 3 sampling pumps when conducting personal measurements. However, these methods have the drawback of complicating the sampling methodology. Another alternative is the use of a thermal desorption apparatus equipped with a re-collection tube for multiple injection. It should be noted that commercial apparatus currently available are equipped with long transfer line thus possibly preventing the analysis of high molecular weight compounds.

(ii) The comparison study between the developed sampler and the Partisol sampler demonstrated that the thermal desorption method was much more efficient to quantify low molecular weight compounds. However, the demonstration study carried out in a more contaminated environment revealed that the cold trapping conditions were not sufficiently strong to retain those compounds. This prevents the quantification of naphthalene, which may contribute significantly to the carcinogenicity of a PAH mixture. This compound was recently classified as probably carcinogenic by the international agency for research on cancer (IARC). One possible solution to suppress breakthrough during cold trapping is the use a liner with a stronger adsorbent. Further investigation is required to evaluate the desorption of compounds with high boiling points from this type of liner.

(iii) The present method was validated for PAHs up to benzo(a)pyrene. The level of agreement with certified ambient air particles (SRM1649a, NIST) and the concentrations of indoor filters determined by a well-validated solvent extraction procedure was approximately 20%. For heavier PAHs, the uncertainty was higher due to their incomplete thermal extraction.

(iv) The developed procedure was not validated for the entire chemical class. The quantification of some alkylphenols and pesticides is subject to a great level of uncertainty because the response for these compounds was quadratic. The quantification of a broad range of chemicals present in indoor air that may induce health effects is probably impossible using this thermal desorption based method.

Overall, the developed method is very attractive, but still needs some improvements and validation. The method can also be applied to quantify organic esters of plasticizers such as phthalates and organophosphorous compounds, although a comparative study with a solvent extraction method would be required to fully validate the method. However, the quantification of all the chemical classes investigated (PAHs, OPAHs, phthalates, organophosphate esters, alkylphenols and pesticides) from the same sample is complicated because the expected concentrations of those compounds vary from the sub ng/m^3 to the µg/m^3 levels. In addition, polar and low volatile compounds are difficult to quantify by thermal extraction method due to adsorption through the sample flow path and poor desorption recovery.

An alternative or complementary method to overcome these problems is the use of a solvent extraction method coupled with large volume injection gas chromatography mass spectrometry. Recent advances in sample preparation instrumentation, such as accelerated solvent extraction (ASE), greatly reduce the drawbacks of solvent extraction procedures. This method greatly reduces extraction times and consumes much less solvent than traditional solvent extraction techniques such as soxhlet or sonication. In addition, this technique is fully automated and requires very little sample handling. The solvent evaporation step of solvent extraction procedure is also greatly facilitated with automated solvent drying systems.

Solvent extraction based methods combined with GC analysis using a conventional split/splitless injector are not sufficiently sensitive to quantify compounds present in the low ng/m^3 from low volume sampling because only a fraction of the extract is injected in the analytical system (only 2 µL of the extract can be injected). On the contrary, as much as 500 µL of the extract can be injected using a large volume injector with typical injection volume ranging from 50 µL to 150 µL. A number of studies have demonstrated its applicability for the quantification of PAHs , nitro-PAHs and organophosphate esters from low volume air samples (Crimmins *et al.*, 2006, Ericsson *et al.*, 2003, Kirschmer *et al.*, 2005, Leon *et al.*, 2003, Norlock *et al.*, 2002, Sanchez *et al.*, 2003, Vecera *et al.*, 2005, Vecera *et al.*, 2005).

Although recent advances in sample preparation techniques have led to reduced preparation time for solvent extraction procedures, the developed thermal desorption method is without doubt more attractive on this aspect since the sample preparation step is limited to the introduction of filter strips in thermal desorption tubes. The developed TD procedure is also certainly the method of choice for the characterisation of low molecular weight compounds although the method should be optimised for characterising compounds from heavily contaminated samples. On the other hand, the thermal desorption of high molecular weight compounds should be further investigated and the use of a solvent extraction method coupled with large volume injection gas chromatography/mass spectrometry is probably a good alternative.

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Appendices

Appendix 1: Poster, 19th International Symposium on PAC, Amsterdam, The Netherlands

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Development of a vapour generation system for PAH and other related semivolatile organic compounds (SVOC)

Abstract

The generation of semivolatile organic vapours under controlled parameters (temperature, humidity and concentrations) representative of atmospheric conditions has been reported only on a few occasions [1,2]. The purpose of this work is to present preliminarily results on the development of a vapour generation system (VGS) based on the diffusion method intended for breakthrough measurements on adsorbents compatible with thermal desorption procedures and to estimate sampling artefacts of a *personal air sampler for 24 hours collection of PAH and other related SVOC*.

This primarily experiment has shown that the developed generator was effective to produce vapours for a broad range of SVOC. It was also found that experimental and theoretical values were closely related for some compounds.

Methodology

Vapour generation: The vapour generation developed in this study (Figure 1) is based on the diffusion method. This method works on the principle that a liquid contained in a reservoir evaporates at a constant rate and the vapours diffuses slowly through the capillary tube into a flowing gas stream. Vapours were generate for 6 compounds including at least one compounds from 4 chemical family (PAH, alkylphenols, organophosphate esters and phthalate esters).

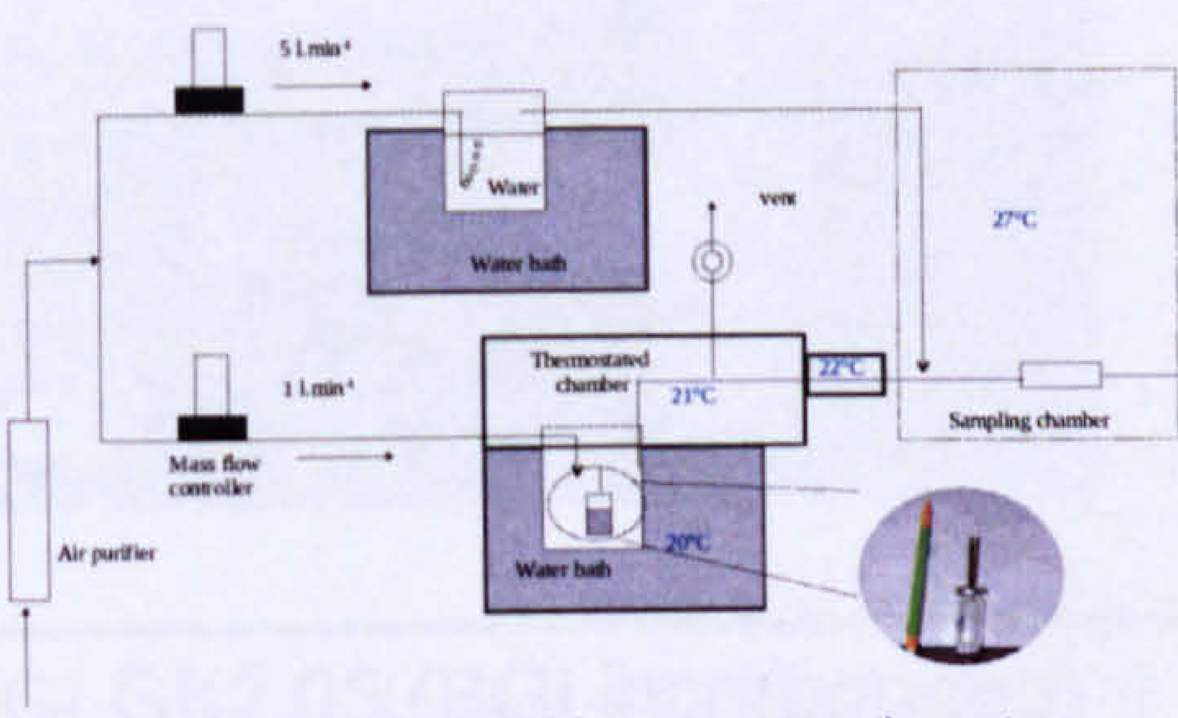

Figure 1 : Schematic diagram of the vapour generation system

The generated concentrations are influenced by the temperature, dilution rates and size of the diffusion cells. Diffusion cell dimensions for a given concentration were estimated using the equation describing the diffusion of a vapour through a capillary tube (Equation 1).

Equation 1

$$r = DMPS \ln[P/(P-p)]\,(RTL)^{-1}$$

r : Diffusion rate (g/s)
M : Molecular mass (g/mol)
T : Temperature of the diffusion cell (K)
S : Cross sectional area of the cell (cm^2)
p : Partial pressure of the diffusion vapour at the absolute temperature (KPa)
D : Coefficient of molecular diffusion
P : Total pressure in the diffusion cell (KPa)
R : Gas constant ([ml Kpa]/[mol K])
L : Length of the capillary (cm)

Diffusion rates were estimated using the equation described by fuller et al (1966) (Equation 2).

Equation 2

$$D_{ij} = (10^{-3} T^{1.75} (1/M_i + 1/M_j)^{1/2}) / (p(V_i^{1/3} + V_j^{1/3})^2)$$

T : Temperature (K)
p : Pressure (atm)
D : Diffusion coefficient of a compound i in the medium j (air)
M : Molecular weight (g/mol)
V : Molecular volume

Determination of the concentration of the vapours generated: Concentrations were determined by pumping the generated atmosphere through Tenax TA sample tubes and subsequent analysis were performed by TD-GC-FID.

Results

Vapours was generated successfully for 3 out of the 6 compounds (Table 1). In the light of figure 2, it can be noticed that stable concentrations are reached after a period of 3-4 days. Variation of the concentrations from day to day and over the one month experiment is roughly less than 15% for the 3 compounds generated.

The non-detection of Tributyl phosphate (TBP) and bis (2-ethylhexyl)phthalate (DEHP) is suspected to arise from their strong adsorption onto the wall of the generator (compounds recognised as 'sticky'). Inadequate dimension of the phenanthrene diffusion cell (erroneous vapour pressure) and hence generation of vapours at concentrations below the detection limit is likely for phenanthrene.

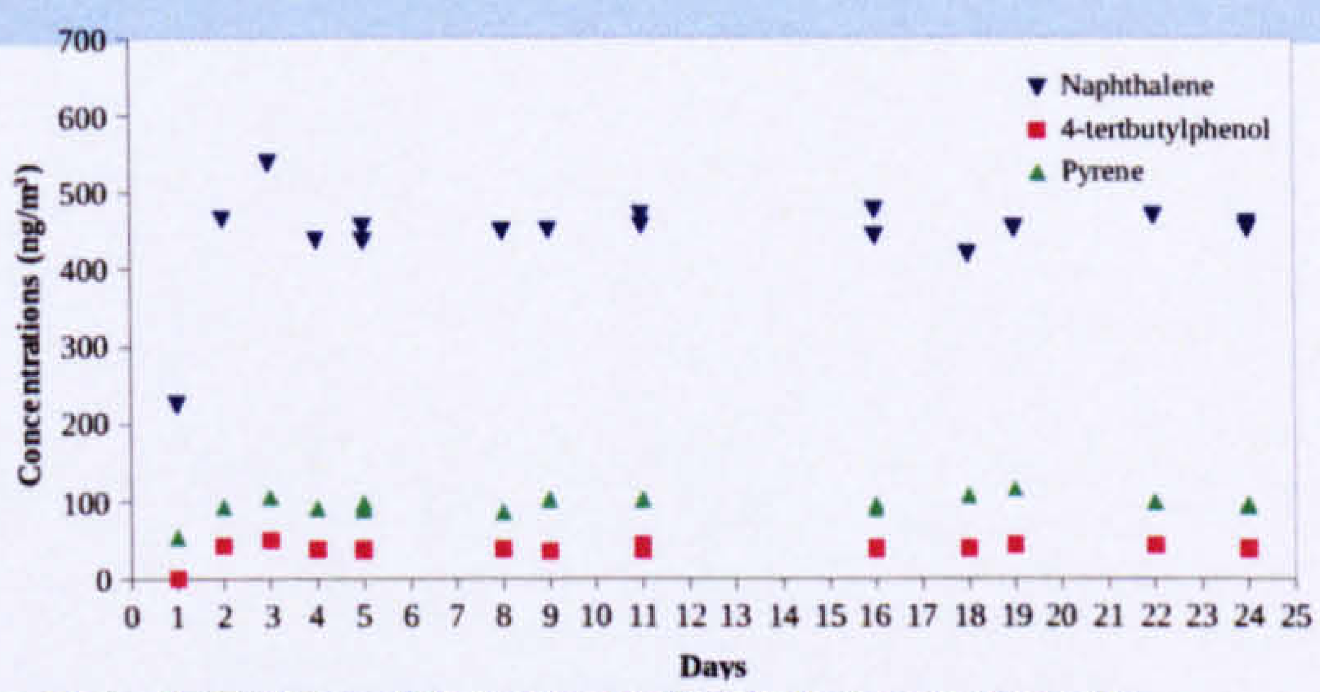

Figure 2 : Evolution of the concentrations in the vapour generator

Finally, it can be observed that experimental and theoretical concentrations are closely related for naphthalene and in good agreement for the compound 4-tertbutylphenol (Table 1). A plug in the 4-tertbutylphenol diffusion tube is probably the reason for its generation at lower concentrations than those expected.

Table 1 : Comparison of the theoretical and experimental concentrations

Compounds	Vapour pressure (kPa)	Capillary tube dimensions (length x Ø in cm)	Expected concentrations (ng/m^3)	Experimental concentrations (ng/m^3)
Naphthalene	0.0104	5 x 1	580	450
4-tertbutylphenol	0.005	6 x 0.8	130	40
TBP	0.009	4.7 x 2	300	<LOD
Phenanthrene	9.07×10^{-5}	1 x 2	127	<LOD
Pyrene	3.33×10^{-7}	Open cell	-	100
DEHP	8.6×10^{-7}	Open cell	-	<LOD

Perspectives

In order to better control the vapour generation more effectively, the same experiment will be repeated by placing each diffusion cell in separate diffusion chambers. Each diffusion chamber will be equipped with a split line. Therefore, diffusion rates for each compounds will be controlled by the temperature, dimensions of the diffusion cells and split ratios.

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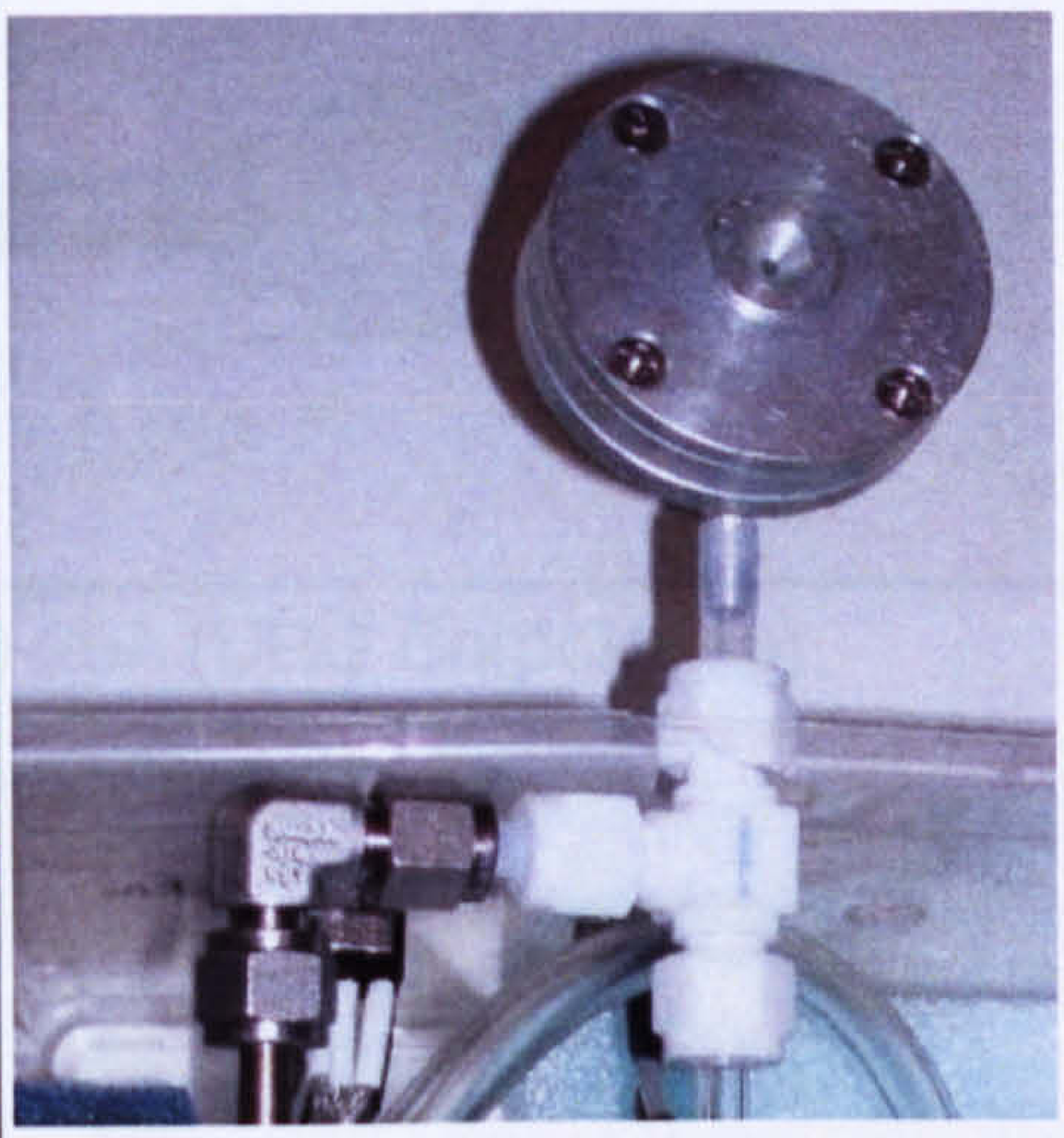
Appendix 2: Description of commercially available $PM_{2.5}$ personal samplers

The $PM_{2.5}$ impactor of a Chempass sampler was used in this study. Its performances have been well characterised and it was easily modified to incorporate a sample tubes downstream of the impactor to collect the gaseous phase. The connection between the sampling head and the sample tube was done using a short 6 mm Teflon tube and a Teflon T connector. Other commercially available lightweight $PM_{2.5}$ sampling heads are also presented in this appendix.

$PM_{2.5}$ Chempass impactor

http://www.thermo.com

Filter diameter: 37 mm



BGI GK2.05 (BGI incorporated)

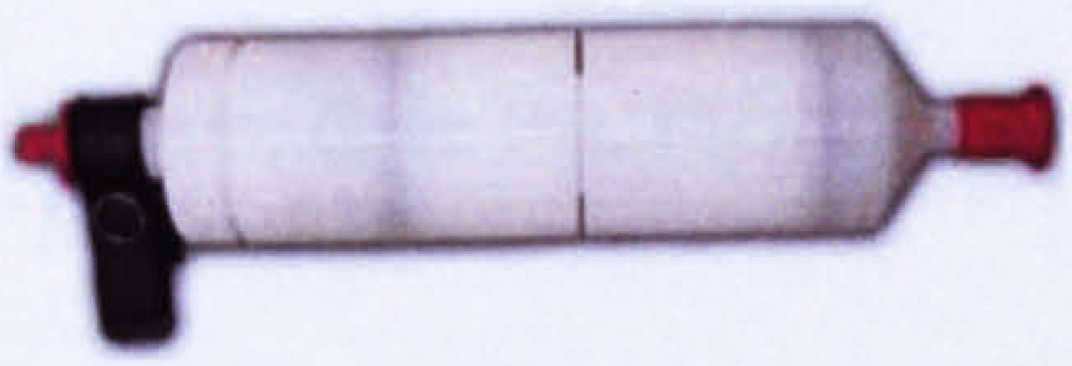
http://www.bgiusa.com/ihi.ktl.htm

Filter diameter: 37 mm

Height: 9.52 cm

Diameter: 4.06 cm

Weight : 112 g

PEM Model 200 (MSP corporations). **Available as PM10, $PM_{2.5}$ a,d PM_1** **http://www.mspcorporation.com/pdf_files/MSP200.pdf** 	Filter diameter: 37 mm
URG-2000-15T (URG Corporation) **http://www.urgcorp.com** 	Filter diameter: 25 mm Height: 20 cm
URG-2000-25A (URG Corporation) http://www.urgcorp.com/ 	Filter diameter: 25 mm Height: 16 cm Weight: 96 g

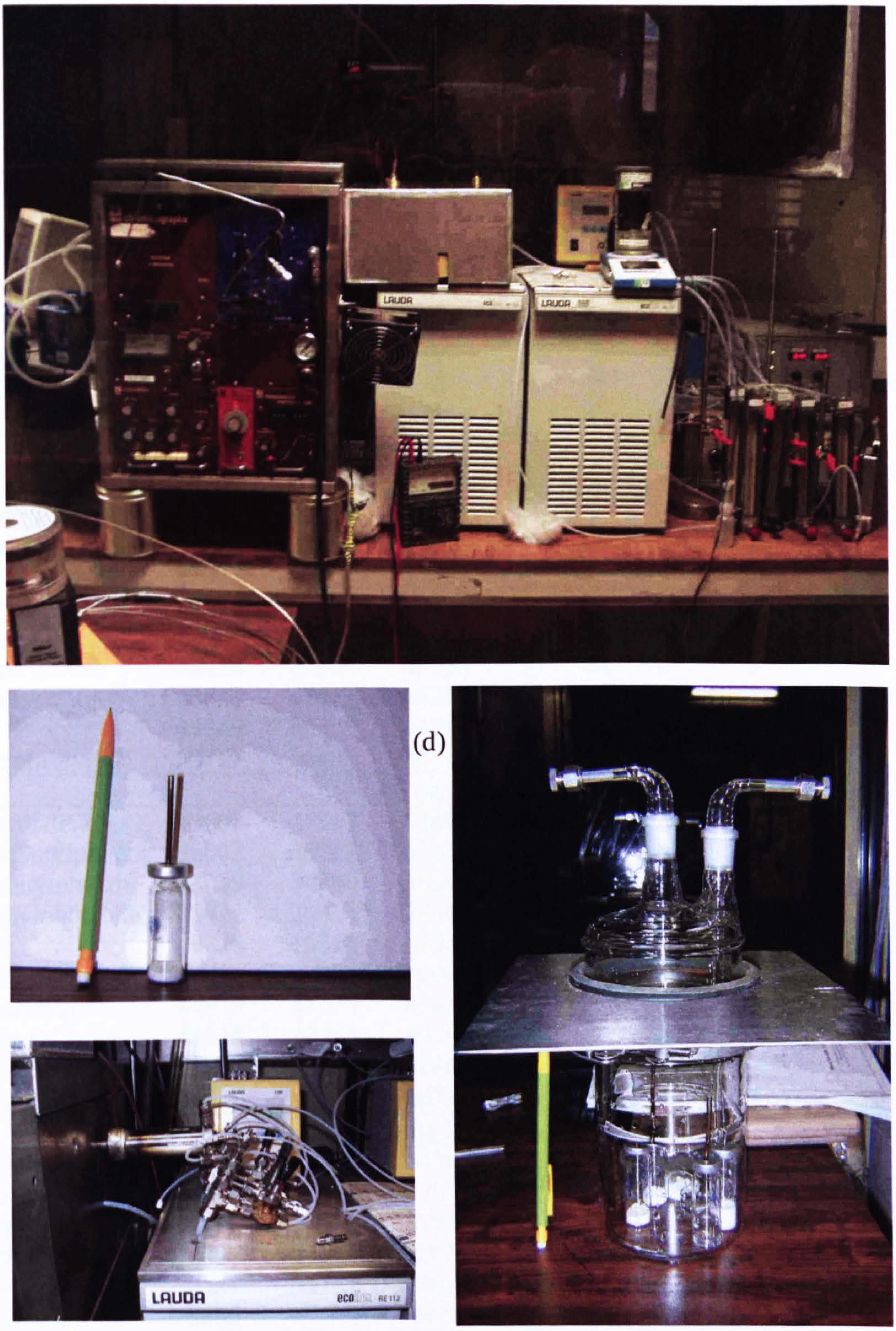
Appendix 3: Calculation of the molecular volume according to Le Bas

Element	Atomic Volume + Bonding Increments
Carbon	14.8
Chlorine	24.6
Bromine	27.0
Iodine	37.0
Sulphur	25.6
Hydrogen	3.7
Oxygen	
- in aldehydes and ketones	7.4
- in methyl esters	9.1
- in methyl ether	9.9
- in long chained esters and ether	11.0
- in acids	12.0
Nitrogen	
- with double or triple bonds	15.6
- in primary amines	10.5
- in secondary amines	12.5
Subtraction for one benzoic ring	-15
Subtraction for two benzoic rings (Naphthalene)	-30

Sources: G. Le Bas, The molecular volumes of liquid chemical compounds, David McKay, New York (1915)

Appendix 4: Vapour generation system

(a) (b) (c) (d)



(a) vapour generation system (b) diffusion cell (c) separate diffusion chambers connected to the modified mixing chamber (d) diffusion chamber for single compound

Appendix 5: Optimisation of desorption time (TD-GC-FID method)

	FID response per ng			RSD (%)			Relative bias between 20 minutes and 30 minutes (%)	Relative bias between 20 minutes and 40 minutes (%)
	20 minutes	30 minutes	40 minutes	20 minutes	30 minutes	40 minutes		
50 ng level								
Naphthalene	40399	40012	41119	3	1	2	-1	2
4-tertbutylphenol	39528	39193	39490	4	1	2	-1	0
2-phenylphenol	37243	37222	37505	5	1	2	0	1
Diethylphthalate	27071	27061	27269	4	2	3	0	1
TBP	22140	21483	22830	5	8	4	-3	3
TCEP	9762	9932	10107	5	8	3	2	4
Phenanthrene	48013	47922	48156	4	1	1	0	0
Pyrene	48815	47171	49312	3	4	1	-3	1
DEHP	43543	42335	44316	3	7	3	-3	2
Benzo(a)pyrene	39777	36492	40213	4	7	3	-8	1
25 ng level								
Naphthalene	40605	41515	43892	5	2	4	2	8
4-tertbutylphenol	36862	38211	35316	5	4	1	4	-4
2-phenylphenol	33029	34842	36641	3	4	1	5	11
Diethylphthalate	25427	26614	26565	4	5	1	5	4
TBP	16126	15548	17340	10	6	12	-4	8
TCEP	6586	6624	10085	9	4	7	1	53
Phenanthrene	44919	47073	45421	3	5	1	5	1
Pyrene	46519	47363	49565	4	2	2	2	7
DEHP	33814	33566	41667	10	6	8	-1	23
Benzo(a)pyrene	34539	35996	38711	7	3	2	4	12
5 ng level								
Naphthalene	40308	42804	44708	1	5	5	6	11
4-tertbutylphenol	39255	39698	41919	2	4	1	1	7
2-phenylphenol	30601	34330	37819	2	8	3	12	24
Diethylphthalate	25439	30154	30558	3	9	5	19	20
TBP	6331	11187	16643	31	17	9	77	163
TCEP	3655	6274	6639	24	18	10	72	82
Phenanthrene	44550	47180	50343	5	3	2	6	13
Pyrene	46711	50122	52667	2	3	1	7	13
DEHP	24031	24714	32495	26	15	9	3	35
Benzo(a)pyrene	31446	37168	41658	8	8	4	18	32

Appendix 6: *SRM1649a concentrations by the TD method using ~ 0.7 mg of the reference material*

Compounds	1	2	3	4	5	6	Mean	sd	RSD (%)
Fl	0.943	0.941	0.962	0.892	1.351	2.837	1.397	0,82	59
Phe	5.623	3.875	4.092	3.489	7.932	5.862	5.050	1.85	36
Ant	0.955	0.900	0.900	0.781	2.129	1.183	1.178	0.55	46
Flu	7.278	4.605	4.824	3.746	10.508	6.514	6.039	2.69	44
Pyr	5.917	3.556	3.762	2.958	7.883	4.738	4.580	1.95	42
BaA	2.117	1.540	1.776	1.337	4.376	1.916	2.189	1.24	56
Chr/TriP	3.326	2.178	2.140	1.927	4.452	2.265	2.592	1.04	40
BbF/BjF	7.918	6.585	6.903	6.034	10.425	7.576	7.504	1.72	22
BkF	1.927	1.505	1.541	1.258	2.549	1.586	1.688	0.49	29
BaP	2.741	1.733	1.929	1.413	4.301	2.056	2.286	1.15	50
DahA	3.721	2.969	2.965	2.554	5.107	3.007	3.321	1.01	30
BghiP	0.431	0.319	0.365	0.263	0.723	0.354	0.405	0.18	44
IP	3.525	2.846	2.893	2.593	4.076	3.019	3.085	0.57	18

Appendix 7: Performance of the HPLC method

✓ *Recovery after the reduction step (n=6)*

A solution of 20 ml of DCM was spike with 10 µL of a PAH solution in acetonitrile (1000 µg/mL). The spiked solution was then concentrated with a zymark evaporator until 0.1 ml and made up to volume with CH3CN in a volumetric flask (1 ml).

Compounds	1	2	3	4	5	6	Mean
Nap	99,5	95,2	99	88,4	101,2	98,1	96,9
AcN	93,7	87,1	92,2	84,3	91,6	90,3	89,9
Fl	99,2	96,6	98,2	88,2	96,8	95,4	95,7
Phe	99,1	97,6	96,7	93,1	95	93,6	95,9
Ant	93,0	92,9	91,9	82,2	89,0	88,6	89,6
Flu	100,1	101	101,1	92,5	100,3	100,6	99,3
Pyr	97,2	92,1	90,2	85,8	88,5	87,0	90,1
BaA	91,7	88,8	91	83,7	86,4	90,0	88,6
Chr	98,4	100,2	99,7	91,5	97,4	94,8	97,0
BbF	102	98,5	101,1	92,6	97,8	96,6	98,1
BkF	97,3	96,1	97,5	89,4	95,9	94,6	95,1
BaP	93	95,1	93,2	83,7	89,5	90	90,8
DahA	95,6	95,1	95,3	88,1	93,4	93	93,4
BghiP	100,6	99,5	97,1	90,4	96,3	94	96,3
IP	96,2	98,8	100,3	97,3	99,9	94,9	97,9
Final volume (ml)	1	1	1	1	1	1	

✓ *Analysis of SRM1649a by solvent extraction/HPLC (n=6)*

Analysis of approximately accurately 20 mg of NIST SRM1649a reference material by HPLC

Compounds	1	2	3	4	5	6	Mean	Theory	Ratio $\frac{\text{Study}}{\text{Theory}}$
Phe	4.5	3.6	5.3	4.3	5.3	4.0	4.50	4.14	1.09
Ant	0.35	0.34	0.42	0.38	0.43	0.31	0.37	0.432	0.86
Flu	7.3	5.6	7.8	6.6	7.7	6.2	6.87	6.45	1.06
Pyr	5.8	4.5	6.0	5.3	6.2	5.0	5.47	5.29	1.03
BaA	2.2	2.3	2.8	2.8	3.1	2.6	2.63	2.21	1.19
Chr	3.9	2.9	3.7	3.5	4.0	3.2	3.53	3.049	1.16
BbF	6.4	4.7	6.0	5.9	6.8	5.2	5.83	6.45	0.90
BkF	1.8	1.4	1.7	1.7	1.9	1.5	1.67	1.913	0.87
BaP	2.6	2.1	2.5	2.4	2.7	2.1	2.40	2.509	0.96
DahA	0.4	0.4	0.4	0.3	0.4	0.3	0.37	0.288	1.27

Appendix 8: Gaseous and Particulate concentrations from a Partisol sampler and two Chempass samplers placed in parallel

DAYS	DAY 1			DAY 2			DAY 3			DAY 4			DAY 5			DAY 6		
Compounds	Partisol	Modified Chempass (Tube freshly packed)	Modified Chempass (Tube already used)	Partisol	Modified Chempass (Tube freshly packed)	Modified Chempass (Tube already used)	Partisol	Modified Chempass (Tube freshly packed)	Modified Chempass (Tube already used)	Partisol	Modified Chempass (Tube freshly packed)	Modified Chempass (Tube already used)	Partisol	Modified Chempass (Tube freshly packed)	Modified Chempass (Tube already used)	Partisol	Modified Chempass (Tube freshly packed)	Modified Chempass (Tube already used)
Nap	<LOD	64.67	59.16	<LOD	47.57	44.01	<LOD	68.45	71.62	<LOD	28.66	31.36	<LOD	22.07	23.32	<LOD	43.36	45.81
AcN	0.71	16.67	16.54	0.50	6.64	6.64	1.37	23.68	21.80	<LOD	10.98	10.04	<LOQ	6.57	6.46	1.11	10.24	10.37
Fl	3.07	11.09	10.67	2.84	7.89	7.81	4.56	20.11	19.34	3.36	7.81	6.90	2.99	5.46	5.20	3.33	10.19	10.16
Phe	10.95	11.95	10.87	11.65	9.36	9.40	16.00	15.36	15.74	7.98	8.18	7.95	<LOQ	5.30	5.57	7.71	7.81	8.27
Ant	<LOD	0.17	0.22	<LOD	0.22	0.21	<LOQ	0.20	0.23	<LOD	0.22	0.26	<LOD	0.19	0.23	<LOQ	0.18	0.22
Flu	<LOQ	1.24	1.05	2.12	1.75	1.55	3.49	3.38	2.81	1.54	1.38	1.33	<LOQ	0.75	0.73	0.90	1.17	1.09
Pyr	<LOQ	0.35	0.31	<LOQ	0.37	0.37	0.94	0.83	0.77	<LOD	0.34	0.37	<LOD	0.21	0.18	<LOD	0.30	0.34

✓ *Concentrations Partisol (ng)*

Compounds	1	2	3	4	5	6	Blank	Blank	Blank	Mean blanks	LOD (Mean blank + 3sd)	LOQ (Mean blank + 10 sd)
Phenanthrene	148	153	210	113	68.4	108	21.7	15	12.9	16.5	30.3	62.5
Fluoranthene	13.1	29	46.3	22.8	8.9	14.8	3.5	4.3	4.6	4.1	5.8	9.8
Pyrene	7.2	9.6	14.2	1.9	1.5	2.1	2.4	2.7	3.4	2.8	4.4	8.0

Appendix 9: Gaseous and particulate concentrations from 6 collocated Chempass samplers

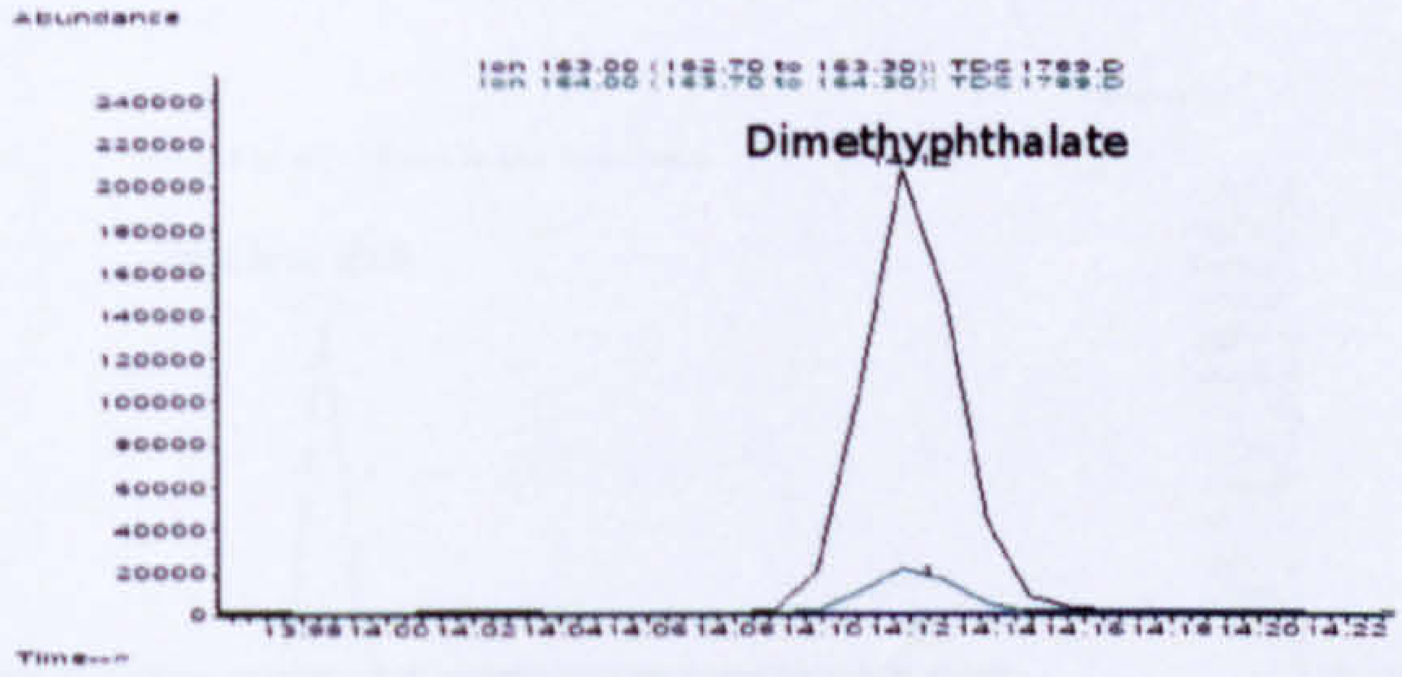
✓ *Gaseous concentrations*

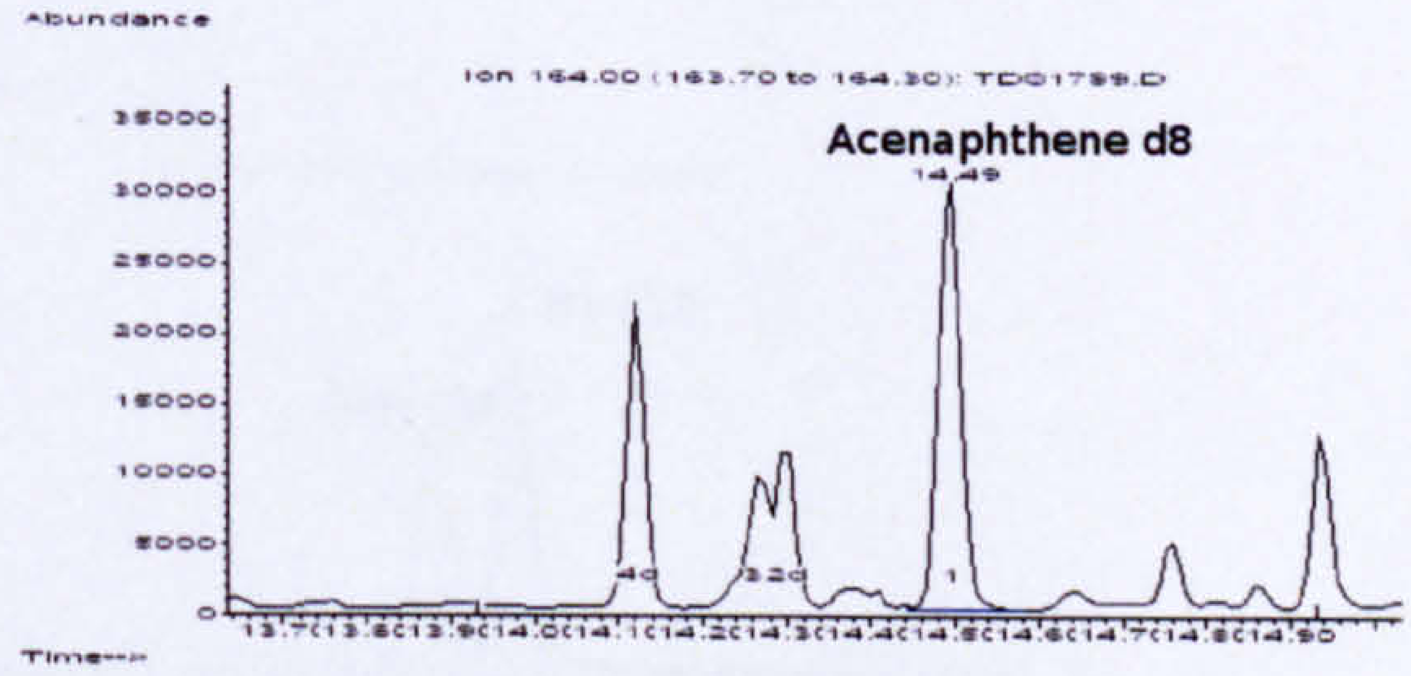
Compounds	1	2	3	4	5	6	Mean	Sd	RSD (%)
Naphthalene	347.9	291.3	304.7	344.8	350.8	342.5	330.3	25.6	7.7
Acenaphthylene	3.0	3.1	3.1	3.0	2.9	2.8	3.0	0.1	3.9
Acenaphthene	0.9	0.8	0.8	1.1	0.8	1.1	0.9	0.1	15.2
Fluorene	7.2	7.2	6.6	6.7	7.6	7.6	7.2	0.4	5.9
Phenanthrene	14.1	14.0	13.2	13.6	15.1	15.6	14.3	0.9	6.3
Anthracene	0.4	0.6	0.5	0.5	0.5	0.6	0.5	0.1	10.8
Fluoranthene	2.3	2.7	2.1	2.3	2.1	2.4	2.3	0.2	8.5
Pyrene	1.1	1.3	1.0	1.1	1.0	1.2	1.1	0.1	9.2
BaA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
Chr/TriP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
BbF/BjF	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
BkF	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
BaP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
IP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
DahA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
BghiP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
9-FlO	5.1	4.8	4.6	4.6	4.7	4.8	4.8	0.2	3.9
9,10-AQ	1.0	0.9	0.8	0.9	0.8	1.1	0.9	0.1	13.2
9-PheC	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
BAO	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
BaA-7,12-O	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
DMP	183.8	176.9	182.9	176.6	160.1	169.2	174.9	9.0	5.1
DEP	170.5	163.9	163.6	207.9	158.1	164.9	171.5	18.3	10.7
DBP	2.3	6.1	2.8	4.4	3.8	9.9	4.9	2.8	57.4
BBP	1.1	2.0	1.4	4.9	2.1	4.9	2.7	1.7	62.0
DEHP	3.7	4.7	3.4	87.4	8.3	81.9	31.6	41.2	130.5
TBP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
TCEP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
4-tertbutylphenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
2-phenylphenol	19.7	17.7	17.3	17.4	19.3	18.7	18.3	1.0	5.7
2-octylphenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
4-octylphenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-

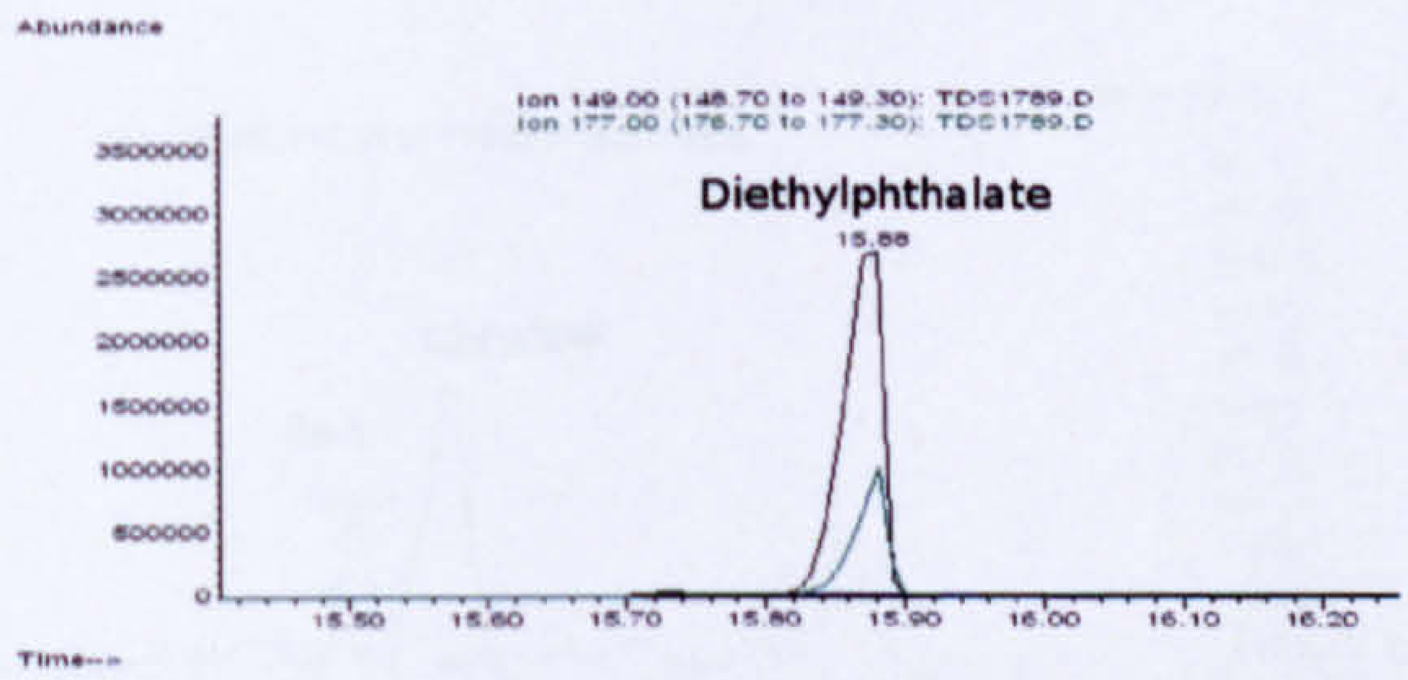
✓ *Particulate concentrations*

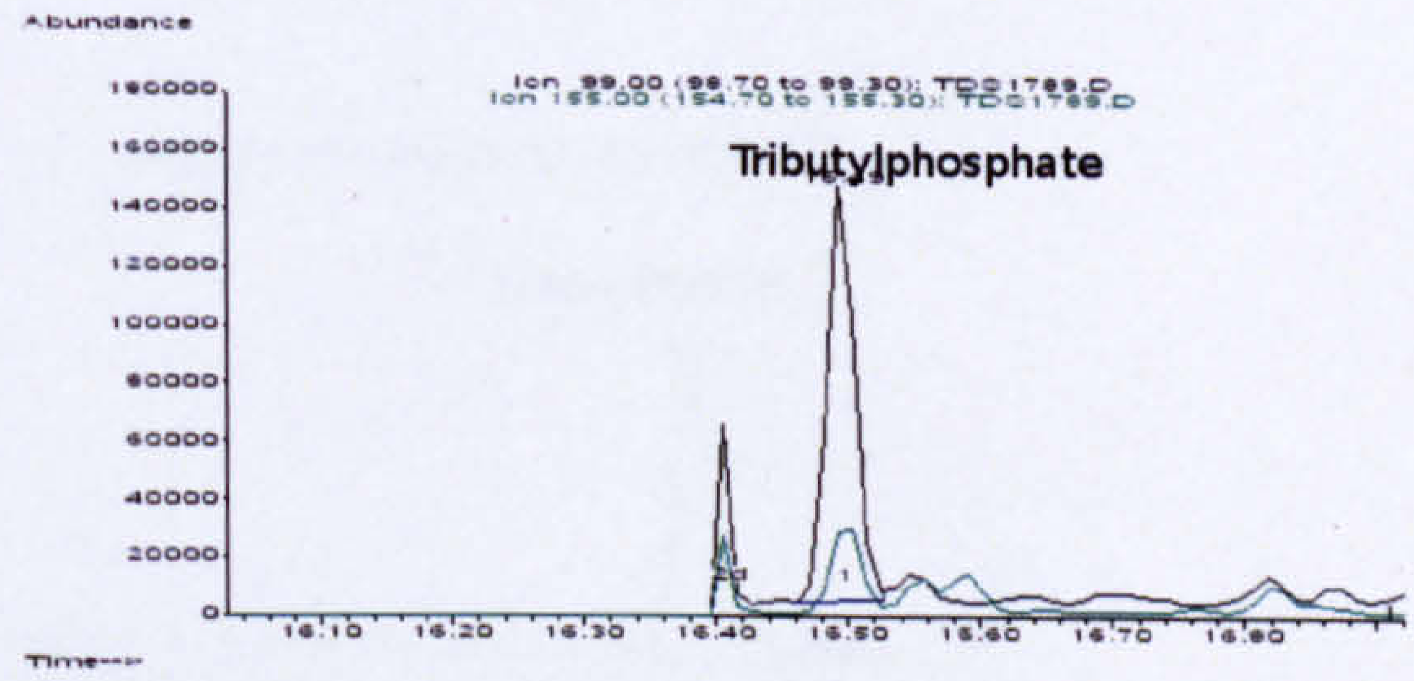
Compounds	1	2	3	4	5	6	Mean	Sd	RSD (%)
Naphthalene	NQ	NQ	NQ	NQ	NQ	NQ	-	-	-
Acenaphthylene	0.13	0.13	0.16	0.14	0.17	0.18	0.15	0.02	14.8
Acenaphthene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
Fluorene	0.07	0.08	0.05	0.04	0.04	0.03	0.05	0.02	29.5
Phenanthrene	0.16	0.18	0.16	0.15	0.15	0.15	0.15	0.01	3.3
Anthracene	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.00	12.7
Fluoranthene	0.27	0.28	0.23	0.27	0.28	0.24	0.26	0.02	7.7
Pyrene	0.19	0.18	0.16	0.20	0.18	0.18	0.18	0.01	6.4
BaA	0.11	0.13	0.12	0.13	0.11	0.11	0.12	0.01	10.2
Chr/TriP	0.23	0.23	0.20	0.22	0.24	0.22	0.22	0.01	4.9
BbF/BjF	0.30	0.30	0.31	0.32	0.35	0.32	0.32	0.02	6.7
BkF	0.12	0.10	0.10	0.12	0.11	0.11	0.11	0.01	6.7
BaP	0.18	0.17	0.17	0.20	0.19	0.20	0.18	0.01	6.6
IP	0.22	0.22	0.21	0.24	0.25	0.24	0.23	0.01	6.3
DahA	0.05	0.05	0.05	0.05	0.05	0.06	0.05	0.00	9.3
BghiP	0.24	0.22	0.22	0.26	0.24	0.25	0.24	0.01	5.6
9-FlO	0.48	0.62	0.52	0.47	0.53	0.48	0.52	0.06	10.8
9,10-AQ	0.78	0.78	0.82	0.88	1.00	0.87	0.85	0.08	9.7
9-PheC	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
BAO	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
BaA-7,12-O	0.24	0.22	0.22	0.26	0.26	0.26	0.24	0.02	7.6
DMP	11.47	13.75	12.11	13.15	12.51	14.82	12.97	1.20	9.3
DEP	78.36	95.01	79.98	74.39	75.42	83.83	81.17	7.58	9.3
DBP	128.8	109.7	124.6	121.8	111.0	104.6	116.80	9.62	8.2
BBP	18.10	16.11	16.50	18.76	20.33	17.16	17.83	1.57	8.8
DEHP	71.66	65.30	69.55	69.80	76.81	69.83	70.49	3.74	5.3
TBP	9.58	8.35	10.37	8.72	9.07	6.58	8.78	1.29	14.7
TCEP	1.99	1.32	1.95	1.79	1.90	1.50	1.74	0.27	15.6
4-tertbutylphenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
2-phenylphenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
2-octylphenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-
4-octylphenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-

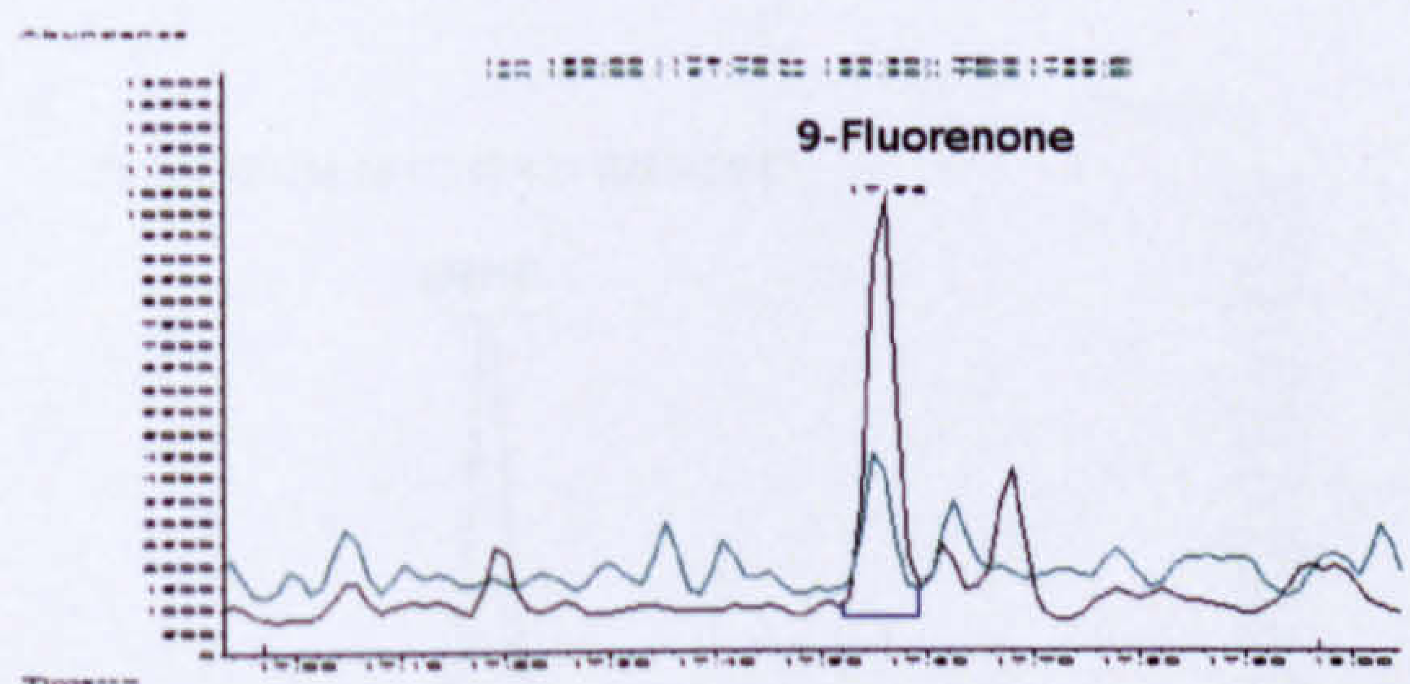
Appendix 10: Extracted ions chromatograms for the target compounds detected in the particulate phase of an indoor air sample

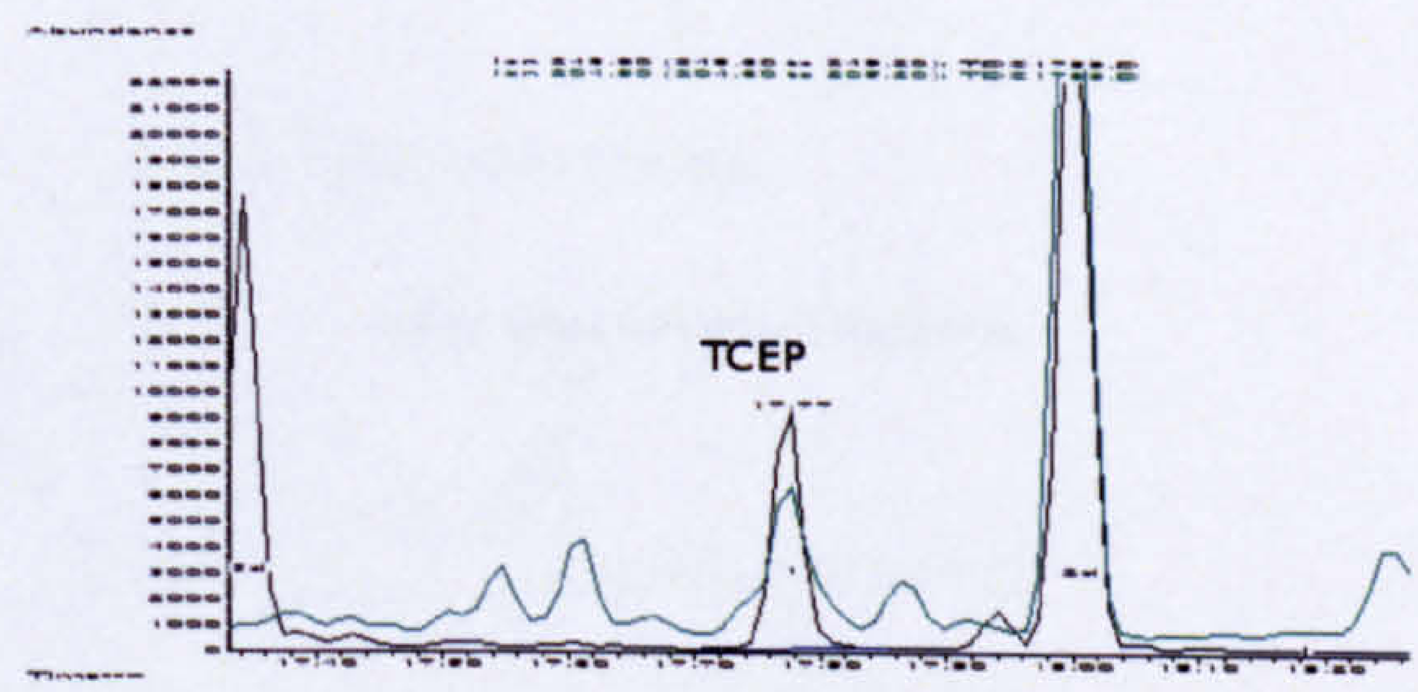


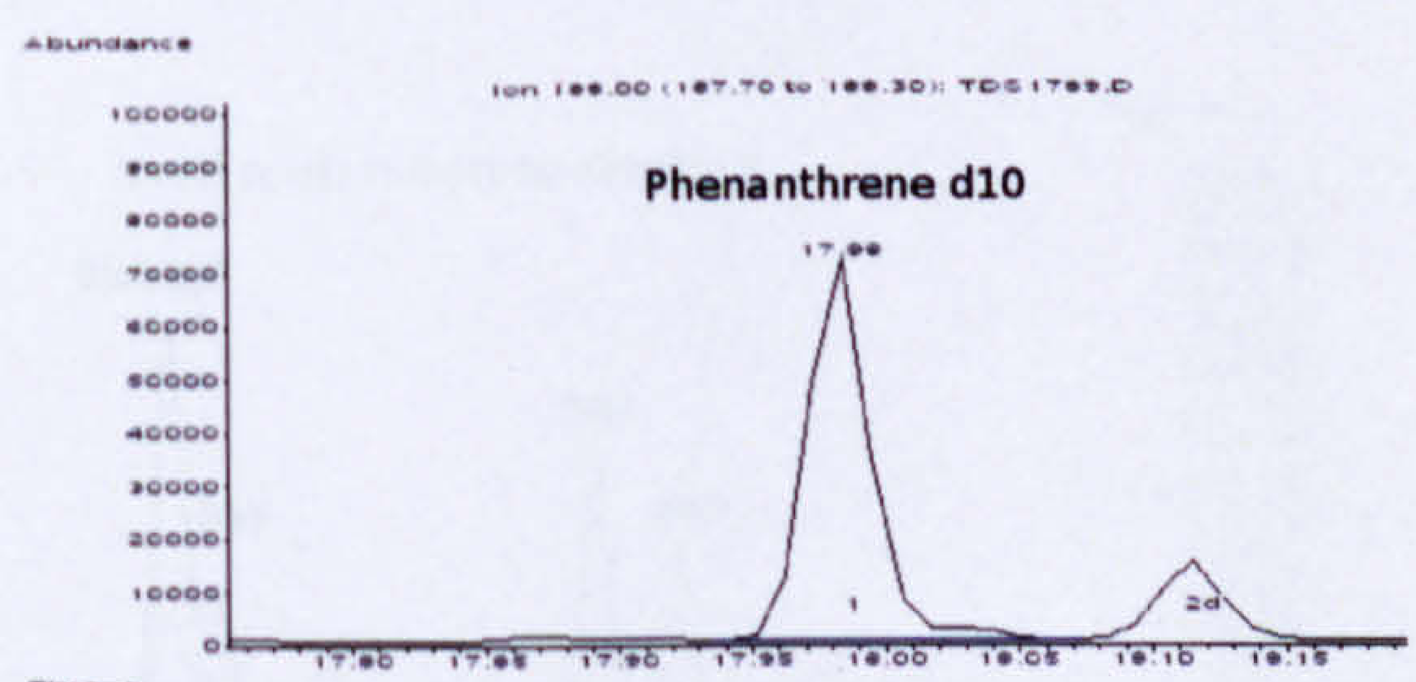


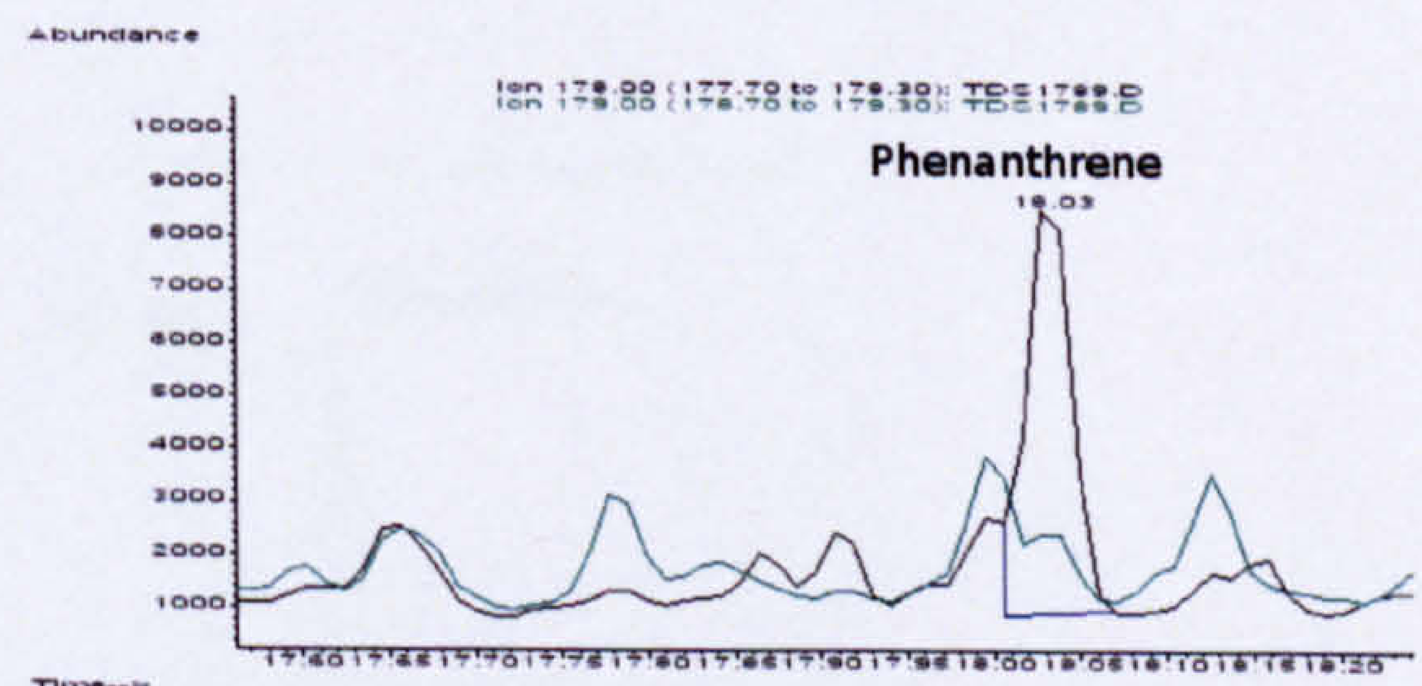


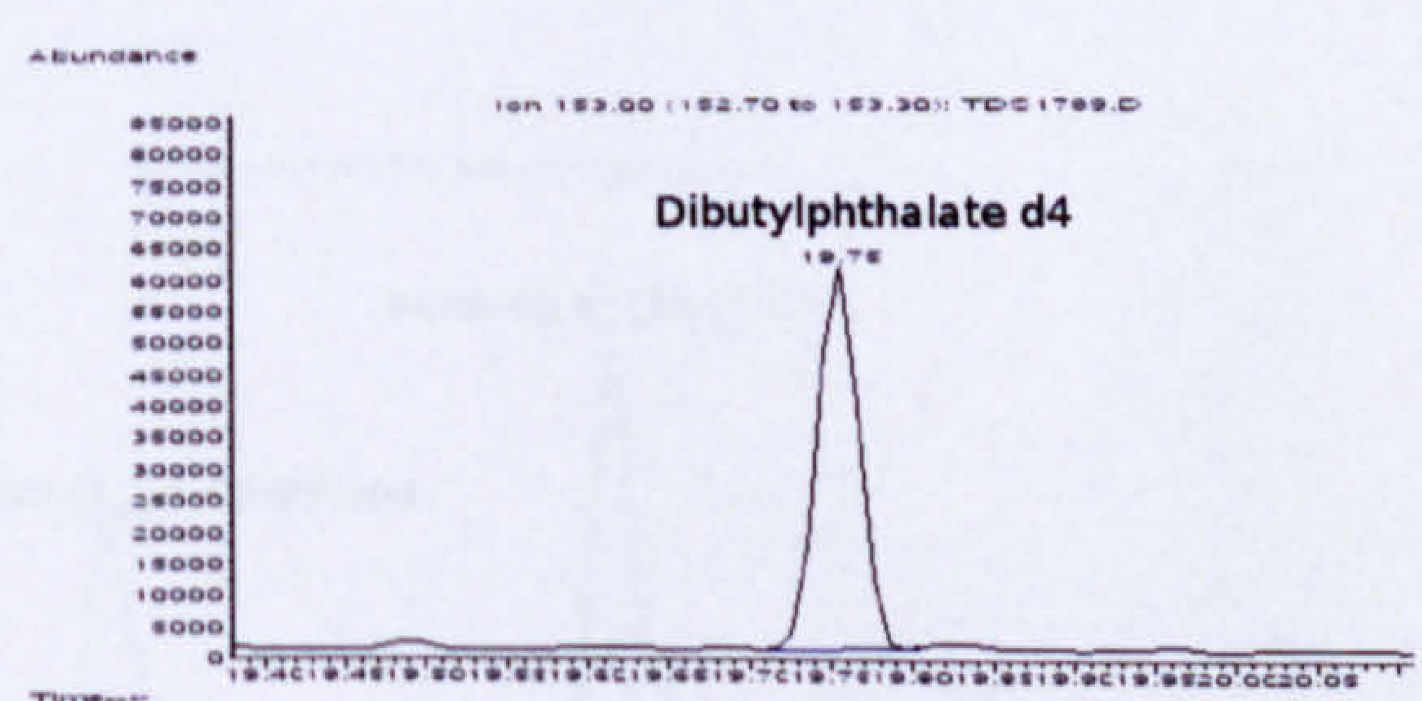


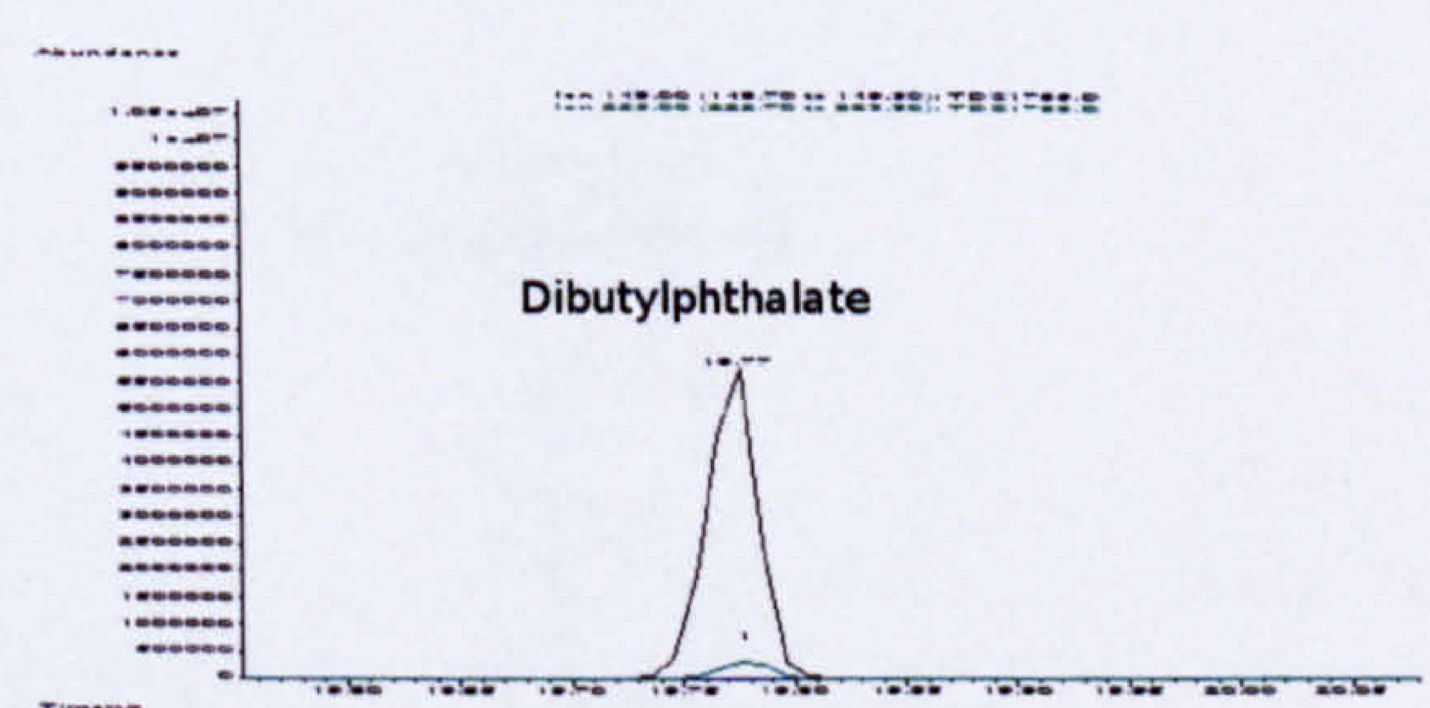


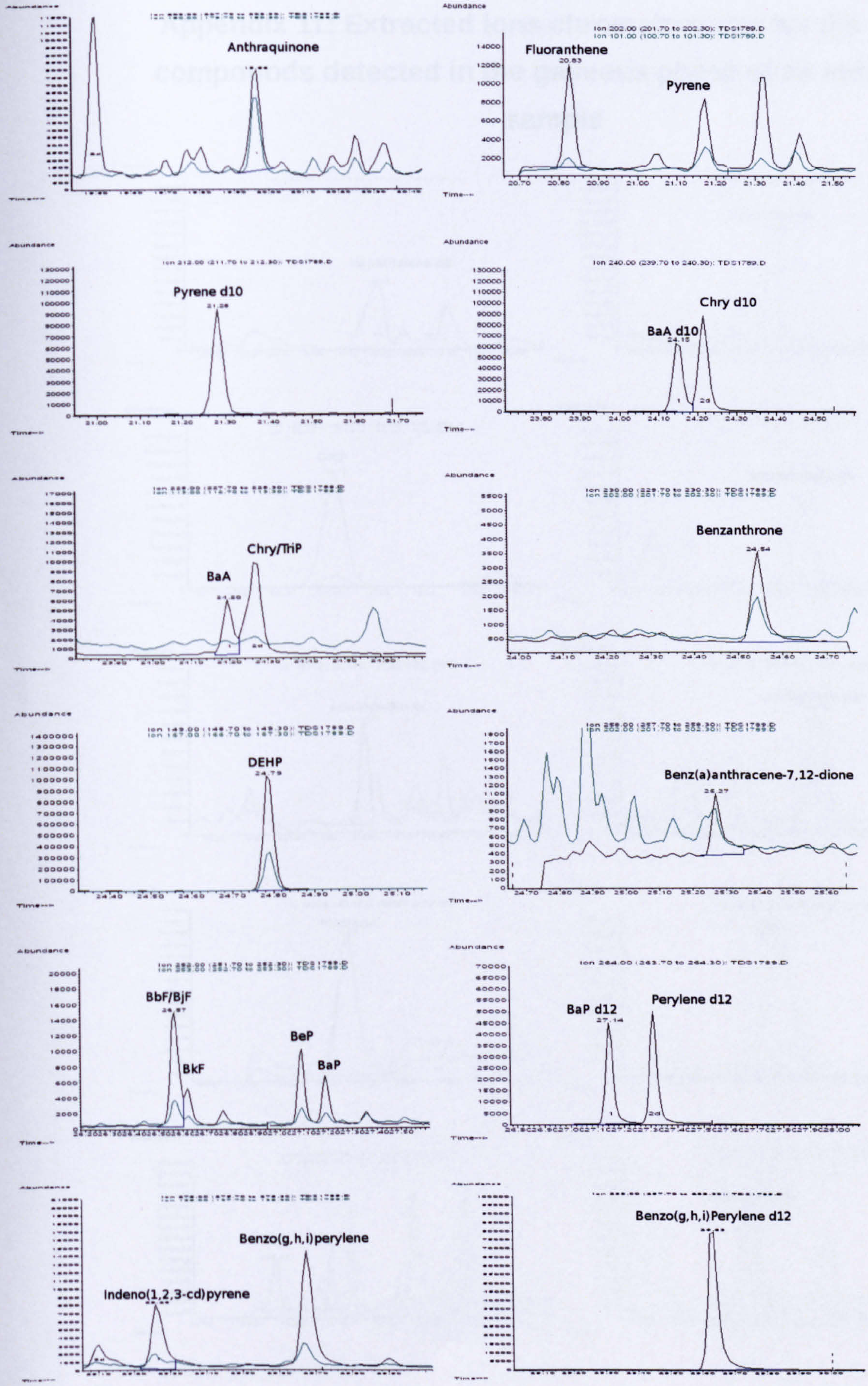




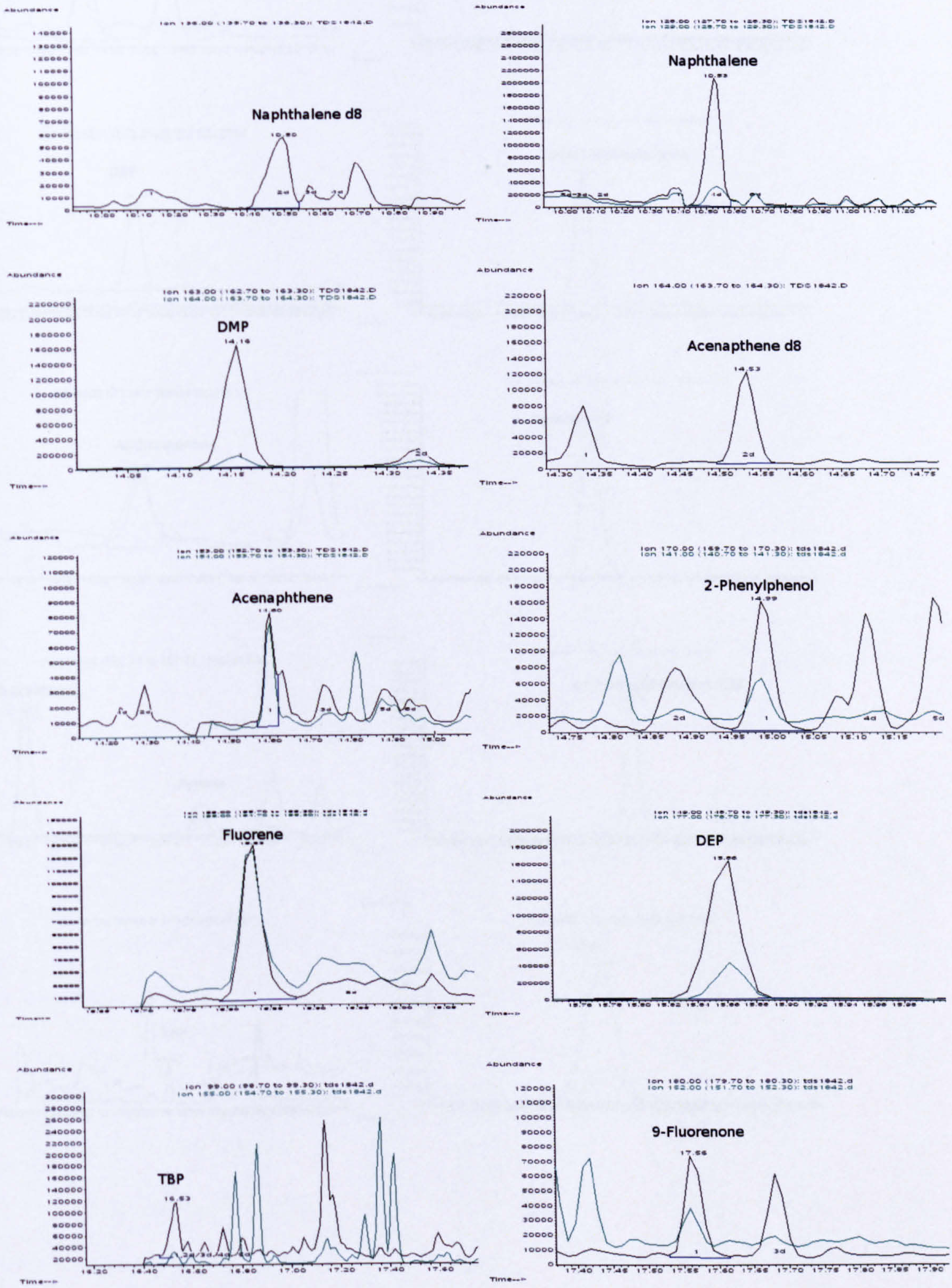


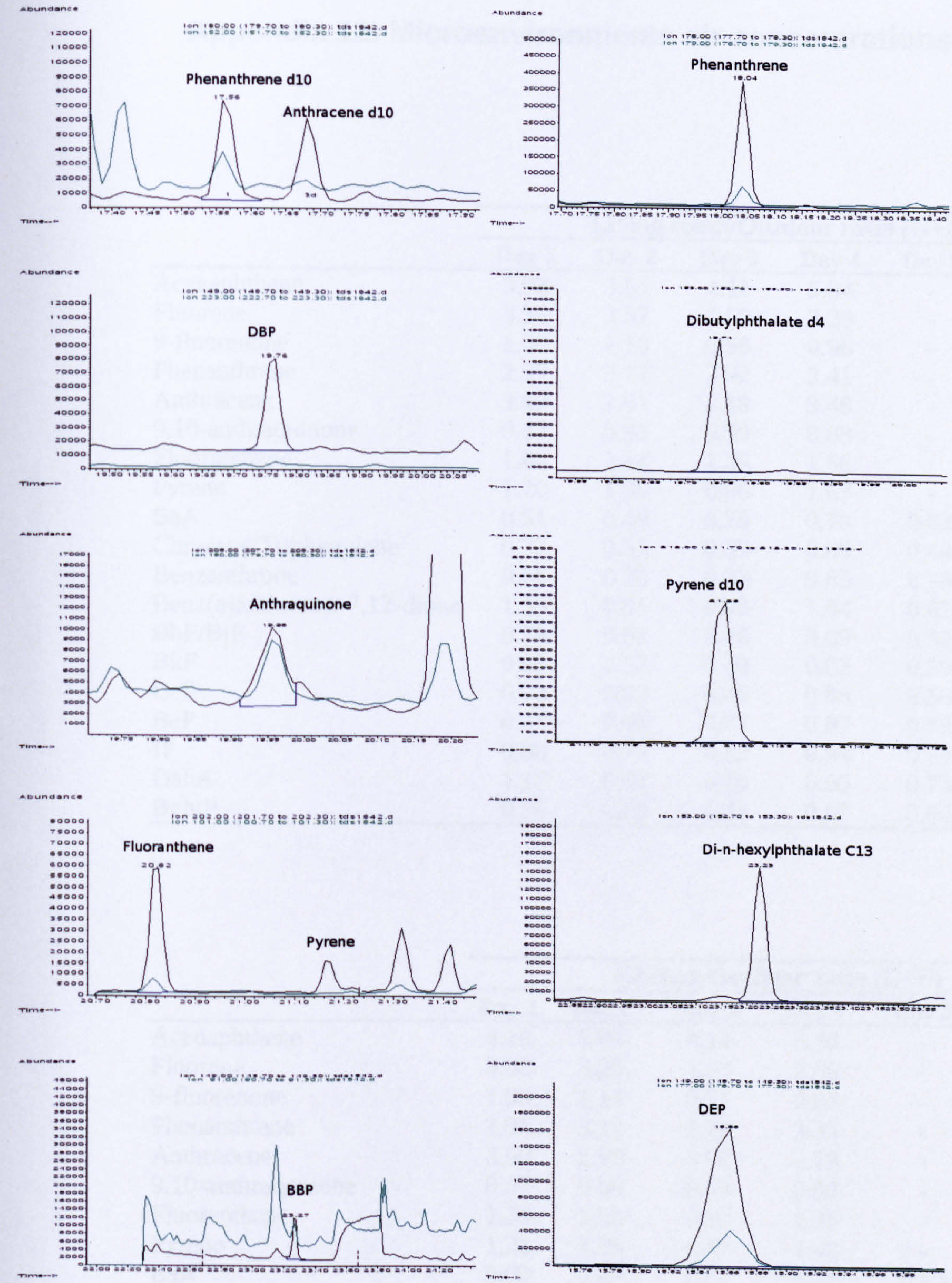





Anthraquinone
Fluoranthene
Pyrene
Pyrene d10
Chry d10
BaA d10
Chry/TriP
BaA
Benzanthrone
DEHP
Benz(a)anthracene-7,12-dione
BbF/BjF
BkF
BeP
BaP
BaP d12
Perylene d12
Benzo(g,h,i)perylene
Indeno(1,2,3-cd)pyrene
Benzo(g,h,i)Perylene d12

Appendix 11: Extracted ions chromatograms for the target compounds detected in the gaseous phase of an indoor air sample




Abundance
Time-->
Phenanthrene d10
Anthracene d10
Phenanthrene
DBP
Dibutylphthalate d4
Anthraquinone
Pyrene d10
Fluoranthene
Pyrene
Di-n-hexylphthalate C13
BBP
DEP

Appendix 12: Microenvironments air concentrations ratios

	Living room/Outdoor ratio (G+P)					
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
Acenaphthene	3.98	3.54	4.11	5.34	-	3.08
Fluorene	3.36	3.57	1.59	3.29	-	1.76
9-fluorenone	1.00	1.19	0.68	0.96	-	0.87
Phenanthrene	2.97	3.72	2.02	3.41	-	3.04
Anthracene	3.69	2.91	2.18	3.48	-	3.87
9,10-anthraquinone	0.87	0.95	0.59	0.88	-	0.94
Fluoranthene	1.66	2.14	1.25	1.66	-	1.58
Pyrene	1.20	1.96	0.96	1.63	-	1.34
BaA	0.51	0.49	0.35	0.78	0.63	0.44
Chrysene/Triphenylene	0.77	0.53	0.32	0.60	0.44	0.55
Benzanthrone	0.56	0.70	0.33	0.85	0.58	0.74
Benz(a)anthracen-7,12-dione	1.35	0.81	0.42	1.04	0.62	0.97
BbF/BjF	0.75	0.62	0.46	0.89	0.52	0.65
BkF	0.69	0.57	0.40	0.82	0.59	0.60
BeP	0.63	0.62	0.45	0.84	0.56	0.65
BaP	0.71	0.86	0.61	0.87	0.79	0.81
IP	0.68	0.74	0.52	0.94	0.71	0.80
DahA	1.17	0.92	0.70	0.90	0.73	0.94
BghiP	0.55	0.68	0.53	0.87	0.66	0.72

	Kitchen/Outdoor ratio (G+P)					
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
Acenaphthene	4.18	3.08	4.14	6.39	-	2.40
Fluorene	3.88	3.25	1.63	2.56	-	1.86
9-fluorenone	1.06	1.14	0.71	0.83	-	0.80
Phenanthrene	2.94	3.19	2.29	3.37	-	2.76
Anthracene	3.90	2.92	3.92	2.79	-	3.30
9,10-anthraquinone	0.87	0.86	0.65	0.82	-	0.94
Fluoranthene	1.34	1.50	0.90	1.30	-	1.29
Pyrene	1.26	1.35	0.87	1.43	-	1.27
BaA	0.60	0.69	0.41	0.61	0.63	0.48
Chrysene/Triphenylene	0.74	0.60	0.35	0.52	0.44	0.55
Benzanthrone	0.76	0.92	0.34	0.68	0.58	0.95
Benz(a)anthracen-7,12-dione	1.12	1.18	0.45	0.89	0.68	1.11
BbF/BjF	0.74	0.75	0.50	0.66	0.52	0.65
BkF	0.75	0.65	0.47	0.71	0.59	0.68
BeP	0.66	0.72	0.50	0.71	0.56	0.72
BaP	0.78	0.83	0.69	0.76	0.79	0.75
IP	0.69	0.88	0.48	0.79	0.71	0.82
DahA	1.23	1.11	0.67	1.29	0.73	1.10
BghiP	0.53	0.75	0.58	0.73	0.66	0.73

	Personal/Outdoor ratio (G+P)					
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
Acenaphthene	3.58	2.67	5.28	5.64	-	-
Fluorene	3.06	3.19	1.86	0.81	-	-
9-fluorenone	0.89	1.16	0.75	0.80	-	-
Phenanthrene	2.10	3.42	1.64	3.14	-	-
Anthracene	1.82	1.84	1.14	2.89	-	-
9,10-anthraquinone	1.05	1.21	0.82	0.80	-	-
Fluoranthene	1.20	2.21	1.13	1.78	-	-
Pyrene	1.00	1.86	1.04	1.73	-	-
BaA	0.81	0.78	0.47	0.57	0.68	0.37
Chrysene/Triphenylene	0.98	0.88	0.44	0.51	0.48	0.47
Benzanthrone	0.94	1.21	0.41	0.65	0.64	0.60
Benz(a)anthracen-7,12-dione	0.86	1.59	0.55	0.99	0.61	0.82
BbF/BjF	0.80	0.95	0.52	0.68	0.53	0.58
BkF	0.67	0.79	0.52	0.65	0.61	0.60
BeP	0.72	0.96	0.59	0.68	0.57	0.53
BaP	0.83	1.06	0.79	0.70	0.72	0.54
IP	0.63	0.96	0.62	0.78	0.66	0.60
DahA	1.16	1.18	0.68	1.19	0.69	0.91
BghiP	0.47	1.01	0.74	0.70	0.61	0.48

	Living room/Kitchen (G+P)							
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Mean	Sd
Naphthalene	1.0	1.3	1.1	1.3	1.0	1.1	**1.14**	0.13
Acenaphthene	1.0	1.1	1.0	0.8	0.9	1.3	**1.01**	0.17
Fluorene	0.9	1.1	1.0	1.3	0.9	0.9	**1.01**	0.16
Phenanthrene	1.0	1.2	0.9	1.0	1.0	1.1	**1.02**	0.1
Anthracene	0.9	1.0	0.6	1.2	1.1	1.2	**1.00**	0.24
Fluoranthene	1.2	1.4	1.4	1.3	1.3	1.2	**1.31**	0.08
Pyrene	0.9	1.5	1.1	1.1	1.2	1.1	**1.14**	0.17
BaA	0.8	0.7	0.8	1.3	1.3	0.9	**0.97**	0.24
Chrysene/Triphenylene	1.0	0.9	0.9	1.1	1.0	1.0	**1.00**	0.09
BbF/BjF	1.0	0.8	0.9	1.4	1.1	1.0	**1.03**	0.18
BkF	0.9	0.9	0.9	1.2	1.0	0.9	**0.96**	0.12
BeP	0.9	0.9	0.9	1.2	1.1	0.9	**0.98**	0.13
BaP	0.9	1.0	0.9	1.1	1.2	1.1	**1.04**	0.12
IP	1.0	0.8	1.1	1.2	1.1	1.0	**1.04**	0.13
DahA	1.0	0.8	1.0	0.7	1.0	0.9	**0.9**	0.13
BghiP	1.0	0.9	0.9	1.2	1.1	1.0	**1.03**	0.11
9-fluorenone	0.9	1.0	1.0	1.2	1.0	1.1	**1.03**	0.08
9,10-anthraquinone	1.0	1.1	0.9	1.1	1.0	1.0	**1.01**	0.07
Benzanthrone	0.7	0.8	1.0	1.3	1.0	0.8	**0.92**	0.2
Benz(a)anthracen-7,12-dione	1.2	0.7	0.9	1.2	0.9	0.9	**0.96**	0.2