



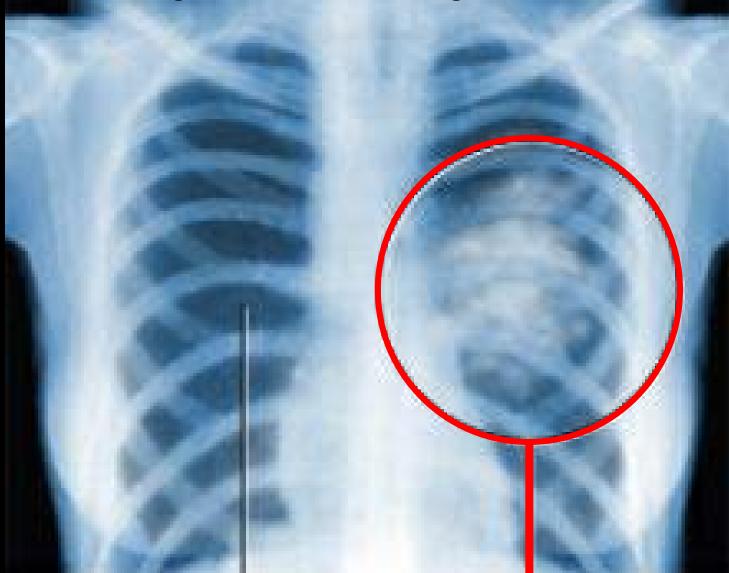
Catalysis, a key property of particle filters to lower genotoxicity of diesel exhaust



18th ETH Conference on Combustion Generated Nanoparticles Zürich, June 22nd – 25th, 2014

World Health Organization, IARC Diesel engine exhaust: A group 1 carcinogen

Diesel engine exhausts cause lung cancer in humans



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Diesel engine exhausts cause lung cancer in humans

International Agency for Research on Cancer



PRESS RELEASE N° 213



IARC: DIESEL ENGINE EXHAUST CARCINOGENIC

Lyon, France, June 12, 2012 -- After a week-long meeting of international experts, the International Agency for Research on Cancer (IARC), which is part of the World Health Organization (WHO), today classified diesel engine exhaust as **carcinogenic to humans (Group 1)**, based on sufficient evidence that exposure is associated with an increased risk for lung canceled.

Group 1

Background

In 1988, IARC classified diesel exhaust as *probably carcinogenic to humans (Group 2A)*. An Advisory Group which reviews and recommends future priorities for the IARC Monographs Program had recommended diesel exhaust as a high priority for re-evaluation since 1998.

There has been mounting concern about the cancer-causing potential of diesel exhaust, particularly based on findings in epidemiological studies of workers exposed in various settings. This was re-emphasizeing cancer the publication in March 2012 of the results of a large US National Cancer Institute/National Institute for Occupational Safety and Health study of occupational exposure to such emissions in underground miners, which showed an increased risk of death from lung cancer in exceed workers (1).

World Health Organization, IARC **Diesel engine exhaust: a group 1 carcinogen**

Diesel engine exhaust cause cancer in humans

The Diesel Exhaust in Miners Study: A Nested Case-Control Study of Lung Cancer and Diesel Exhaust

Debra T. Silverman, Claudine M. Samanic, Jay H. Lubin, Aaron E. Blair, Patricia A. Stewart, Roel Vermeulen, Joseph B. Coble, Nathaniel Rothman, Patricia L. Schleiff, William D. Travis, Regina G. Ziegler, Sholom Wacholder, Michael D. Attfield

Manuscript received February 16, 2011; revised June 3, 2011; accepted October 21, 2011.

Correspondence to: Debra T, Silverman, ScD, Occupational and Environmental Epidemiology Branch, Division of Cancer Epidemiology and Genetics. National Cancer Institute, Rm 8108, 6120 Executive Blvd, Bethesda, MD 20816 (e-mail: silvermd@mail.nih.gov).

- Background Most studies of the association between diesel exhaust exposure and lung cancer suggest a modest, but consistent, increased risk. However, to our knowledge, no study to date has had quantitative data on historical diesel exposure coupled with adequate sample size to evaluate the exposure-response relationship between diesel exhaust and lung cancer. Our purpose was to evaluate the relationship between 23 to mates of Orkers, 8 mines exposure to diesel exhaust and lung cancer mortality after adjustment for small 23 to mates of Orkers, 8 mines confounders.
- We conducted a nested case-control study in a cohort of 12315 workers in eight no 98 initiations cancer death which included 198 lung cancer deaths and 562 incidence density-sampled control subjects. For such case Methods subject, we selected up to sontrol subjects, individually matched on mining facility, sex, race/ethnicity, birth year (within 5 years), from an workers who were alive before the day the case subject died. We estimate 6 in 1000) diesel exhaust exposure, represented by respirable elemental carbon (REC), by job and year, for each sul based on an extensive retrospective exposure assessment at each mining facility. We conducted both categorical and continuous regression analyses adjusted for cigarette smoking and other potential confounding variables (eg, history of employment in high-risk occupations for lung cancer and a history of respiratory disease) to estimate odds ratios (ORs) and 95% confidence intervals (Cls). Analyses were both unlagged and lagged to exclude recent exposure such as that occurring in the 15 years directly before the date of death (case subjects)/ reference date (control subjects). All statistical tests were two-sided.
- We observed statistically significant increasing trends in lung cancer risk with increasing cumulative REC and Results average REC intensity. Cumulative REC, lagged 15 years, yielded a statistically significant positive gradient in lung cancer risk overall ($P_{treat} = .001$); among heavily exposed workers (ie, above the median of the top quartile $[\text{REC} \ge 1005 \ \mu\text{g/m}^3\text{-y}])$, risk was approximately three times greater (OR = 3.20, 95% Cl = 1.33 to 7.69) than that among workers in the lowest quartile of exposure. Among never smokers, odd ratios were 1.0, 1.47 (95% Cl = 0.29 to 7.50), and 7.30 (95% Cl = 1.46 to 36.57) for workers with 15-year lagged cumulative REC tertiles of less than 8, 8 to less than 304, and 304 µg/m³-v or more, respectively. We also observed an interaction between smoking and 15-year lagged cumulative REC (P_{interaction}, .086) such that the effect of each of these exposures was attenuated in the presence of high levels of the other content of the exposure such as a strength of the sector of the exposure such as a strength of the sector of the exposure such as a strength of the exposure su

Our findings provide further evidence that die a exhaust exposure may cause lung ca Conclusion

represent a potential public health burden. J Natl Cancer Inst 2012;104:1-14







a potential public health burden

Swiss occupational health legislation

Grenzwerte am Arbeitsplatz 2009



	MAK	-Wert	Kurzzeitgrenzwerte		HSB	С	М	R _F	RE	SS	Messmethoden/	
Stoff [CAS-Nummer]	ml/m³ (ppm)	mg/m ³	ml/m³ (ppm)		Zeitl. Begren- zung (Häufig- keit x Dauer in min./Schicht)							besondere Bemerkungen
1,3-Dichlorpropen (cis und trans) [542-75-6]	0,11	0,5				HS	2	3				
2,2-Dichlorpropionsäure [75-99-0] und ihr Natriumsalz [127-20-8]	1	6	1	6	15 min							
1,2-Dichlor-1,1,2,2-tetrafluorethan (R 114) [76-14-2]	1000	7000										DFG, NIOSH
Dicyclopentadienyleisen [102-54-5]		10 e										
Dieldrin (HEOD)		0,25 e				н	3					NIOSH
Dieselmotor-Emissionen (gemessen als elementarer Kohlenstoff)		0,1 a					2					BG

"Für Dieselmotoremissionen beträgt der Arbeitsplatzgrenzwert 100 µg/m³ mit dem Zusatz des Minimierungsgebotes, da Dieselmotoremissionen als krebserzeugend eingestuft sind. Generell sind Massnahmen die zu einer Verringerung der Dieselmotoremissionen führen damit sinnvoll."



Ordinance on Air Pollution Control (OAPC): List of carcinogenic substances

Luftreinhalte-Verordnung (LRV)

83 Tabelle von krebserzeugenden Stoffen

Stoff	Summenformel	Klasse
Benzo(a)pyren	C ₂₀ H ₁₂	1
Benzol	C_6H_6	3
Dibenz(a, h)anthracen	$C_{22}H_{14}$	1
1,2-Dibromethan	$C_2H_4Br_2$	3
1,4 Dichlorbenzol	$C_6H_4Cl_2$	3
1,2-Dichlorethan	$C_2H_4Cl_2$	3
Dieselruss		3
Diethylsulfat	$C_4H_{10}O_4S$	2



What does asbestos has in common with diesel exhaust?

814.318.142.1

Ordinance on Air Pollution Control (OAPC): List of carcinogenic substances

Luftreinhalte-Verordnung (LRV)

83 Tabelle von krebserzeugenden Stoffen Summenformel Stoff Klasse Benzo(a)pyren $C_{20}H_{12}$ 1 Benzol C_6H_6 3 Dibenz(a, h)anthracen $C_{22}H_{14}$ 1 1,2-Dibromethan $C_2H_4Br_2$ 3 1,4 Dichlorbenzol $C_6H_4Cl_2$ 3 1,2-Dichlorethan $C_2H_4Cl_2$ Dieselruss Diethylsulfat $C_4H_{10}O_4S$



Both are group 1 carcinogens and cause cancer in humans

814.318.142.1



Retrofitting of Euro-III to Euro-V heavy duty vehicles – an option for Switzerland?

CH national council rejected (12.3832



NATIONALRAT

Abstimmungsprotokoll

Geschäft / Objet

Mo. Vischer Dan el. Nachrüstung von Dieselfahrzeugen mit Partikelfiltern 12.3832 Mo. Vischer Dan Equiper les véhicules diesel de filtres à particules

Germanier

Cilli

Giezendanner

Ref. 10185

CONSEIL NATIONAL

Retrofitting of HDVs?

Procès-verbal de vote

Gegenstand / Objet du vote:

Abstimmung vom Vote du: 06.05.2014 17.06:49

Aebi Andreas	-	V	BE	
Aebischer Matthias	+	S	BE	ĺ
Aeschi Thomas	-	V	ZG	
Allemann	+	S	BE	
Amarelle	+	S	VD	
Amaudruz	-	V	GE	
Amherd	-	CE	VS	
Amstutz	-	V	BE	
Aubert	+	S	VD	
Baader Caspar	-	V	BL	
Badran Jacqueline	+	S	ZH	
Barazzone	-	CE	GE	
Bäumle	+	GL	ZH	
Bernasconi	+	S	GE	
Bertschy	+	GL	BE	
Rindor		V	7Ц	

Fischer Roland	+	GL	LU		Keller Peter	-	V	NW	
Flach	+	GL	AG		Kessler	+	GL	SG	
Flückiger Sylvia	-	V	AG		Kiener Nellen	0	S	BE	
Fluri	-	RL	SO		Killer Hans	-	V	AG	
Français	0	RL	VD		Knecht	-	V	AG	
Frehner	-	V	BS		Landolt	-	BD	GL	
Freysinger	-	V	VS		Lehmann	-	CE	BS	
Fridez	0	S	JU		Leuenberger-Genève	+	G	GE	
Friedl	+	S	SG		Leuteneaaer Filippo	-	RL	ZH	
Galladé	_			_		_			
Gasche Ree	Ci				th 64 yes	C	11		E
Gasser	T	OL	ON		Lusoner	-		UL	
Geissbühler	-	V	BE	1	Lustenberger	Ρ	CE	LU	

0

RL

V

0

VS

AG

20

Keller Peter	-	V	NW
Kessler	+	GL	SG
Kiener Nellen	0	S	BE
Killer Hans	-	V	AG
Knecht	-	V	AG
Landolt	-	BD	GL
Lehmann	-	CE	BS
Leuenberger-Genève	+	G	GE
Leuteneager Filippo	-	RL	ZH

G

GL

C

GE

ΖH

NIE

Cohillinor

Maier Thomas

Maira Jaaguaa Andrá

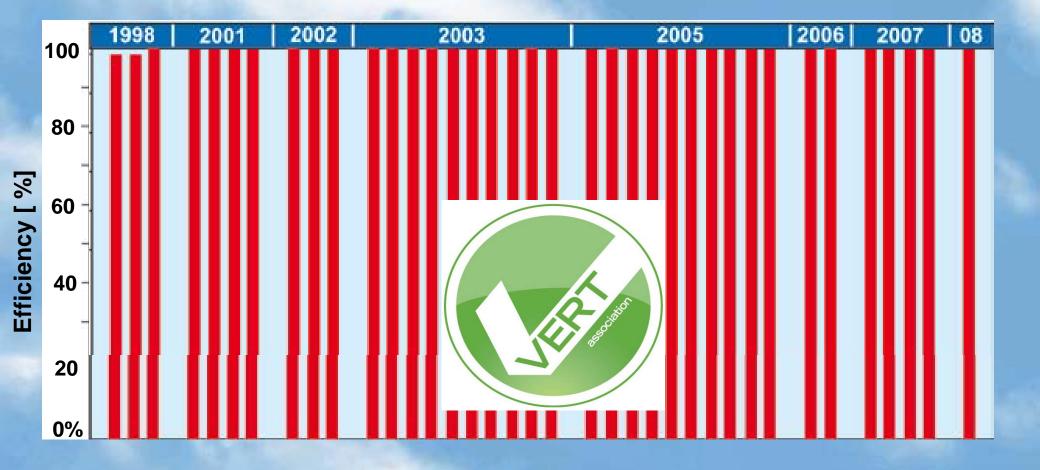
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	Reimann Maximilian	-	V	AG
	Reynard	+	S	VS
	Rickli Natalie	-	V	ZH
	Riklin Kathy	=	CE	ZH
	Rime	-	V	FR
	Ritter	-	CE	SG
	Romano	-	CE	TI
	Rossini	+	S	VS
	Rösti	-	V	BE
			V	TI
5	t 102 no's	5	V	ZH
	Nytz Negula	т	G	BE
	Schelbert	+	G	LU
	Schenker Silvia	+	S	BS
	Schibli	-	V	ZH

DL

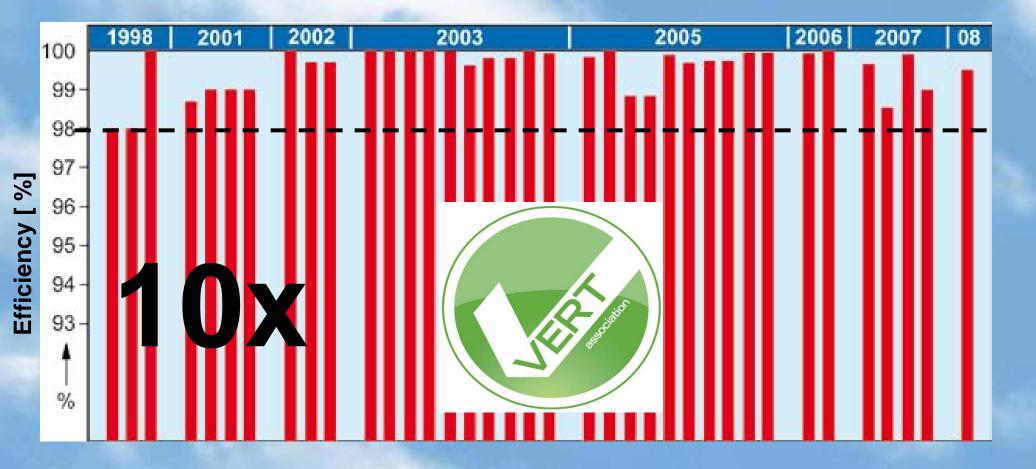
1.111

More than 40 VERT-tested DPFs. All approved systems are excellent particle filters



Mayer et al. MTZ, 2009, 70, 72-79

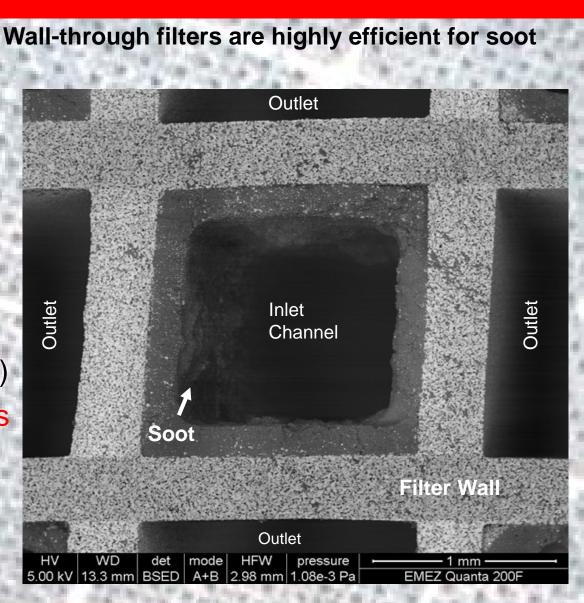
You have to zoom in to see differences among filters



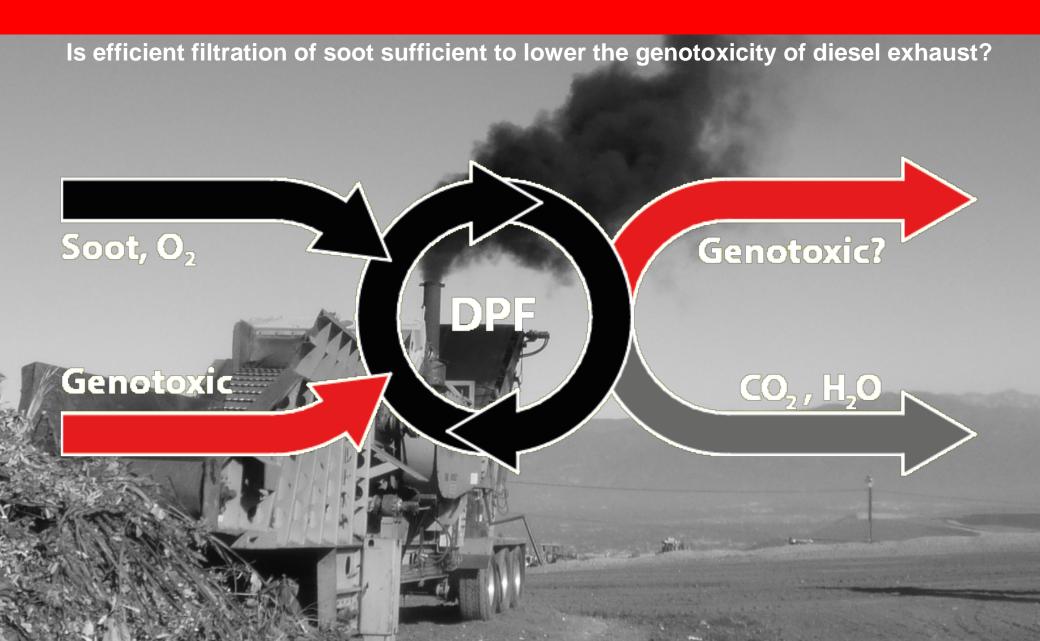


VERT-approved DPFs:

Reduce PN-emissions (>98%)
Reduce genotoxic compounds (a.m.a.p.)
Low risks of toxic secondary emissions

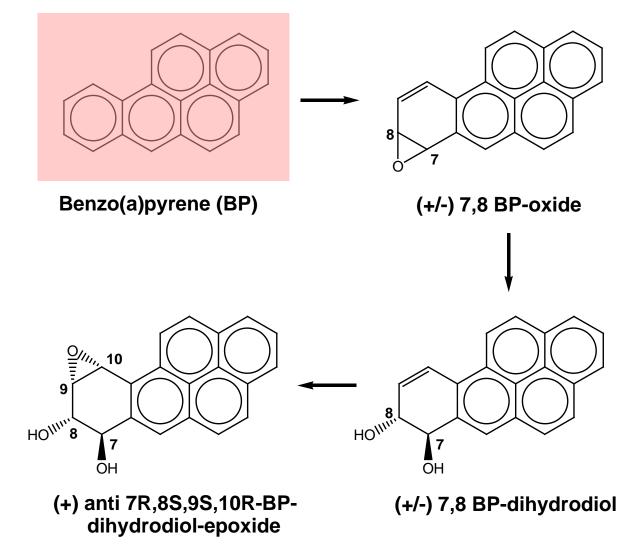


Impact of DPFs on genotoxicity

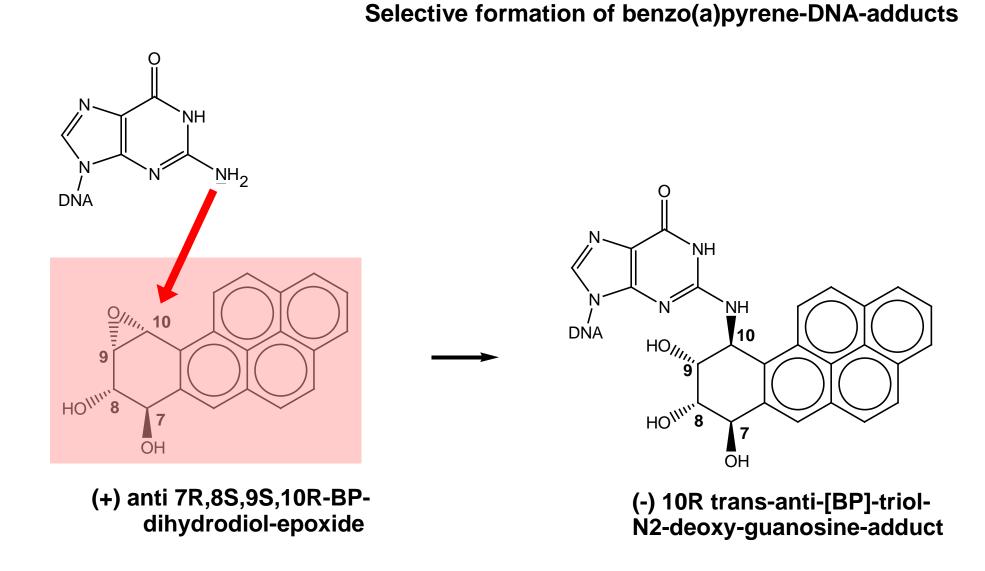


Carcinogenesis from benzo(a)pyrene

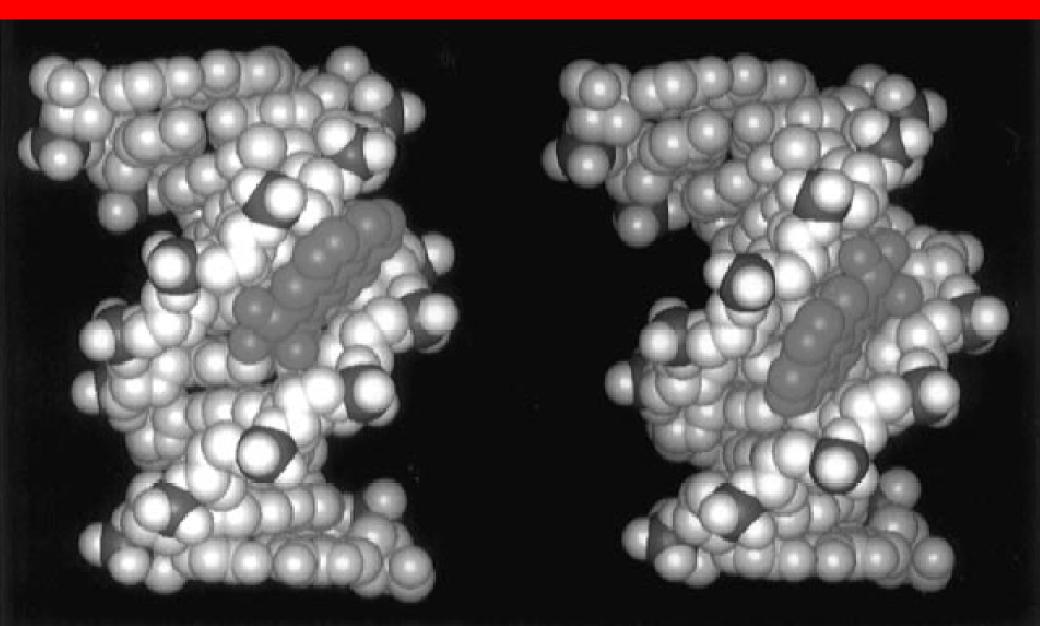
Oxidative metabolic activation of benzo(a)pyrene by cytochrome P450 enzymes



Carcinogenesis from benzo(a)pyrene

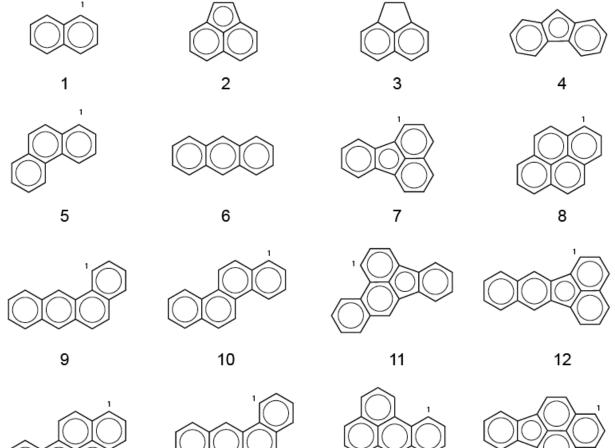


Carcinogenesis from benzo(a)pyrene



PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs



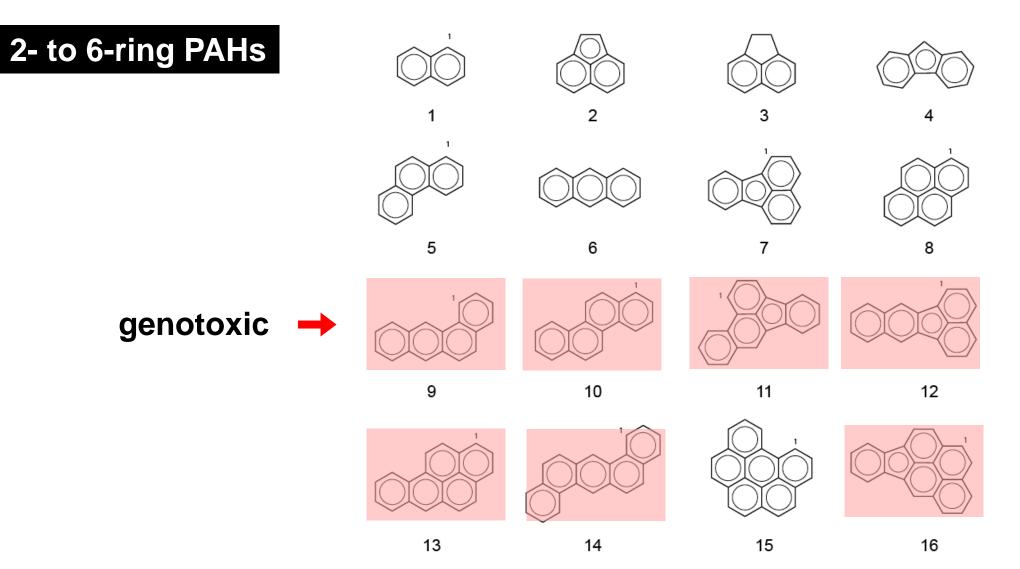


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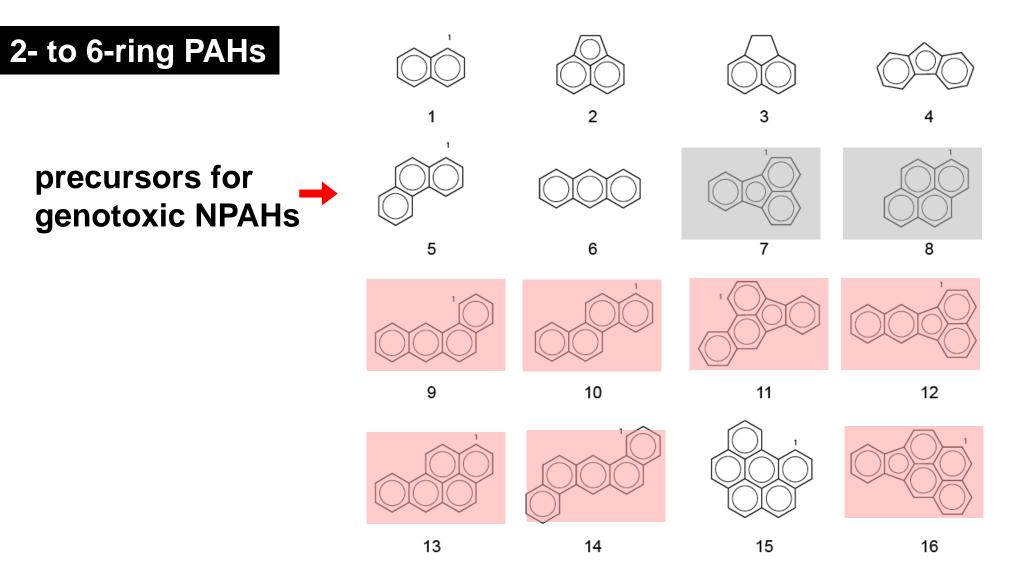


16

PAHs - a diverse class of compounds with variable physicochemical properties



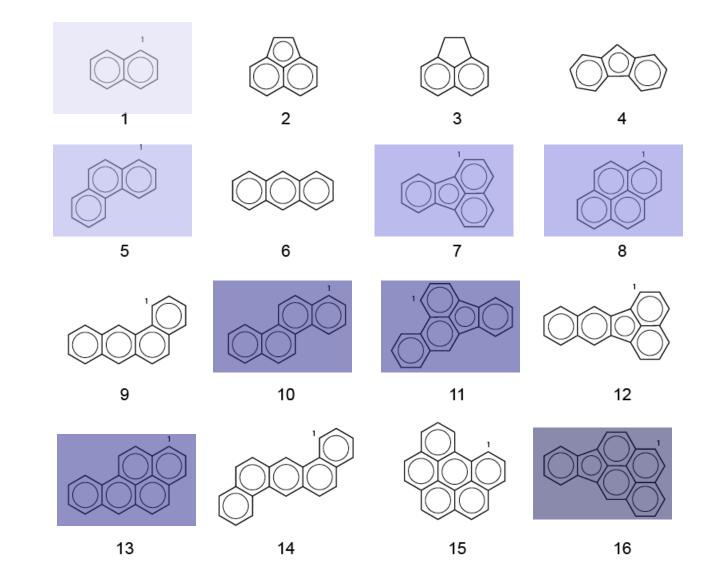
PAHs - a diverse class of compounds with variable physicochemical properties



PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

differ in mass, size & volatility

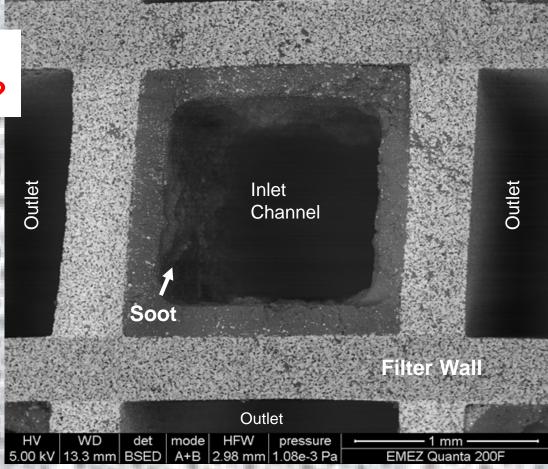


Non-catalyzed filters are as efficient for soot. How about genotoxic compounds?

What do you expect, can PAHs penetrate DPFs?

Non-catalyzed DPFs:

- Accumulate soot (>98%)
- Do they reduce genotoxic compounds a.m.a.p?
 Do they have toxic secondary emissions?



Outlet

Non-catalyzed filter operated <200 °C accumulate soot. How about hydrocarbons?

Do PAHs penetrate non-catalyzed DPFs if operated below 200 °C? 600 ົວ engine-out 450 Temperature 300 before DPF 150 after DPF 0

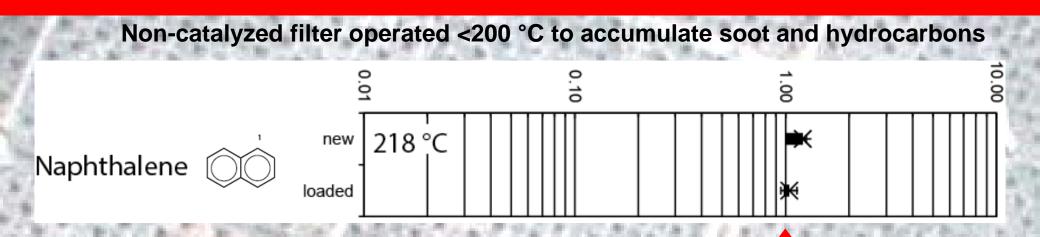
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40

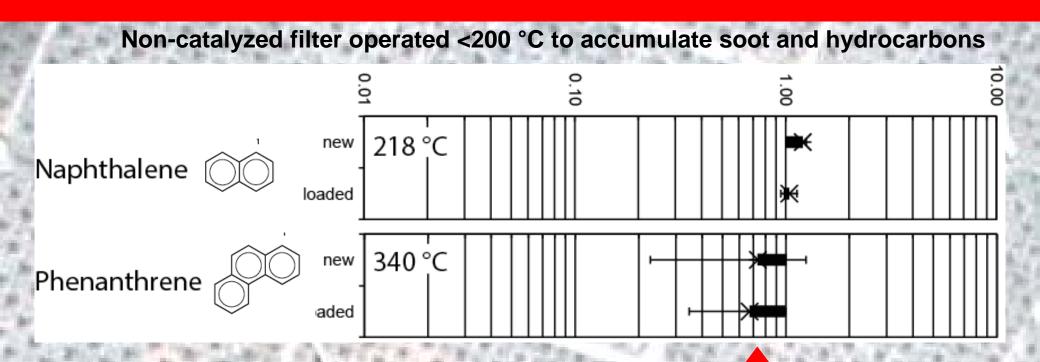
60

80

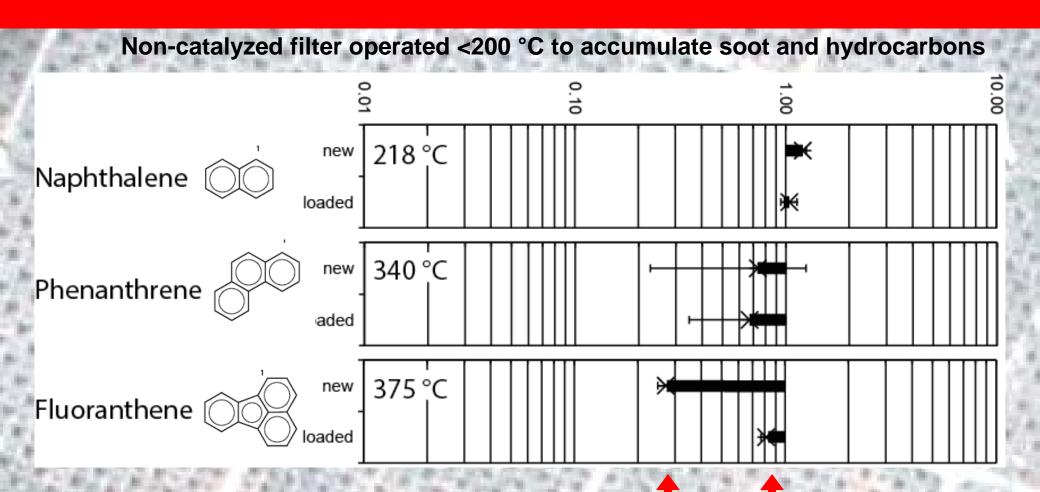
Time [min]



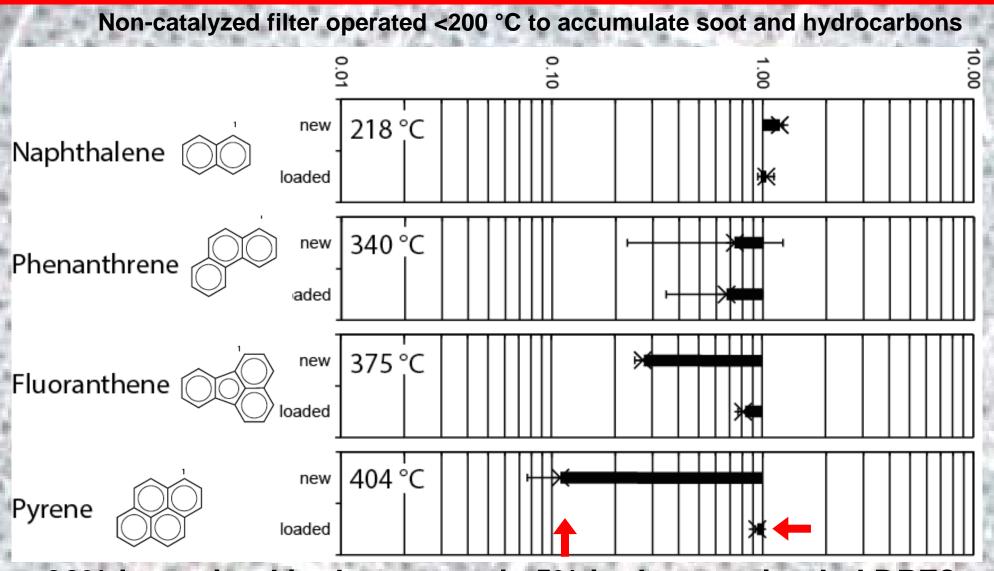
- No retention of naphthalene in a new and a soot-loaded DPF
- Naphthalene is too volatile, it even escapes from a cold filter (<200 °C)



About 30% retention, both in a new and a soot-loaded DPF
 Phenanthrene is partly stored in a cold filter (<200 °C)



- 70% is retained in the new, only 15% in the soot-loaded DPF?

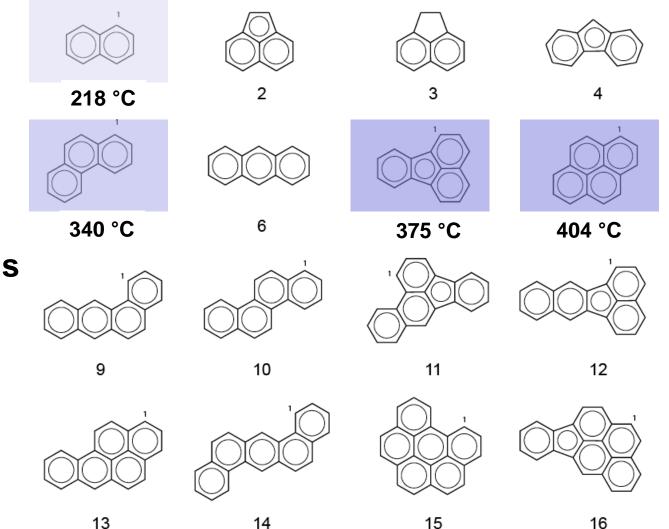


- 90% is retained in the new, only 5% in the soot-loaded DPF?

PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

High penetration of volatile 2-4-ring PAHs

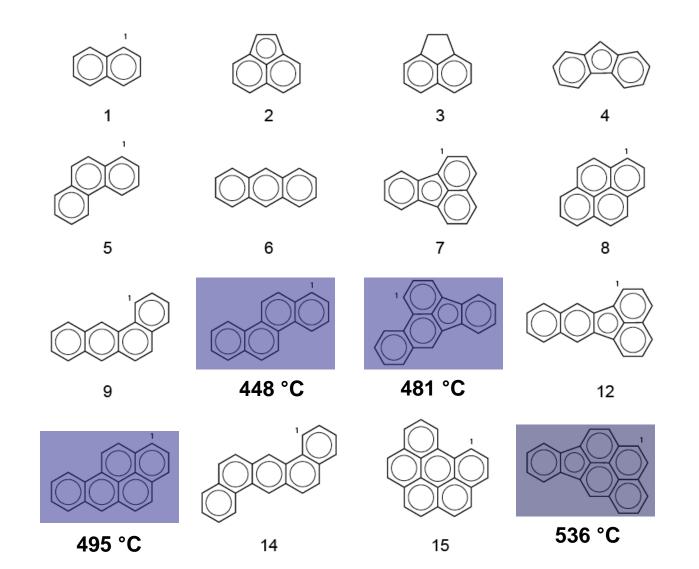


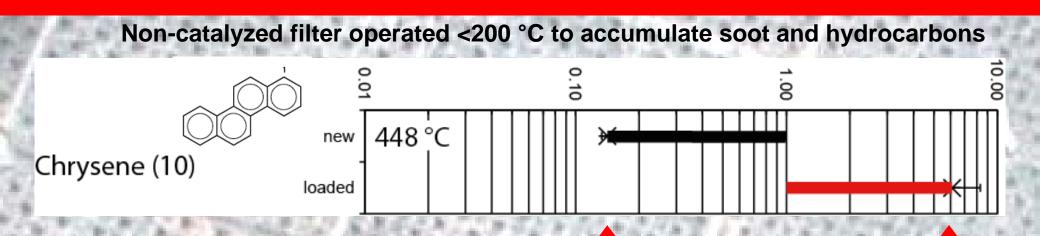
14

PAHs - a diverse class of compounds with variable physico-chemical properties

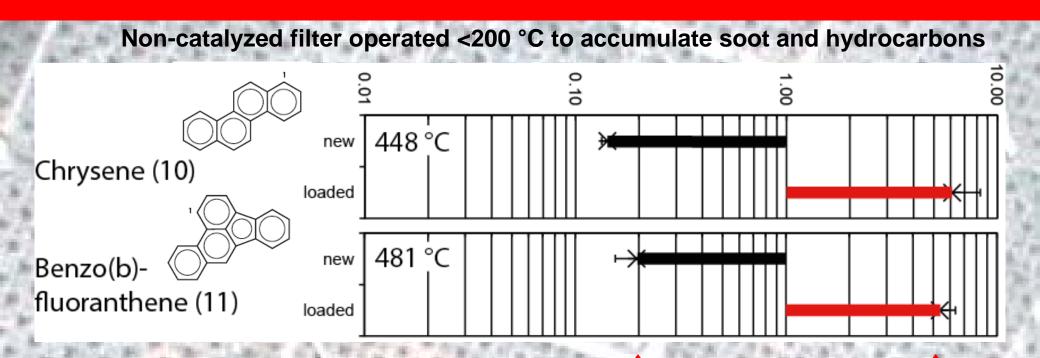
2- to 6-ring PAHs

What do we expect for less volatile PAHs?

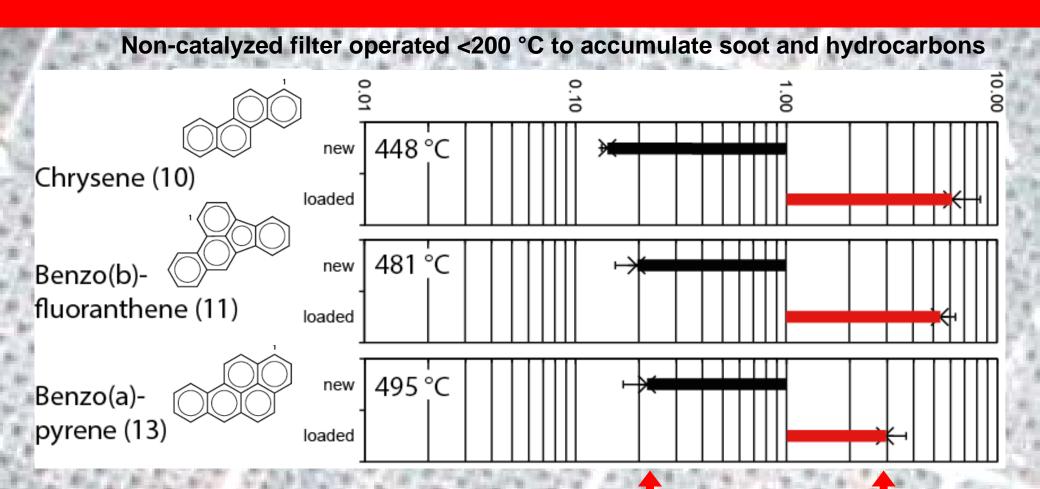




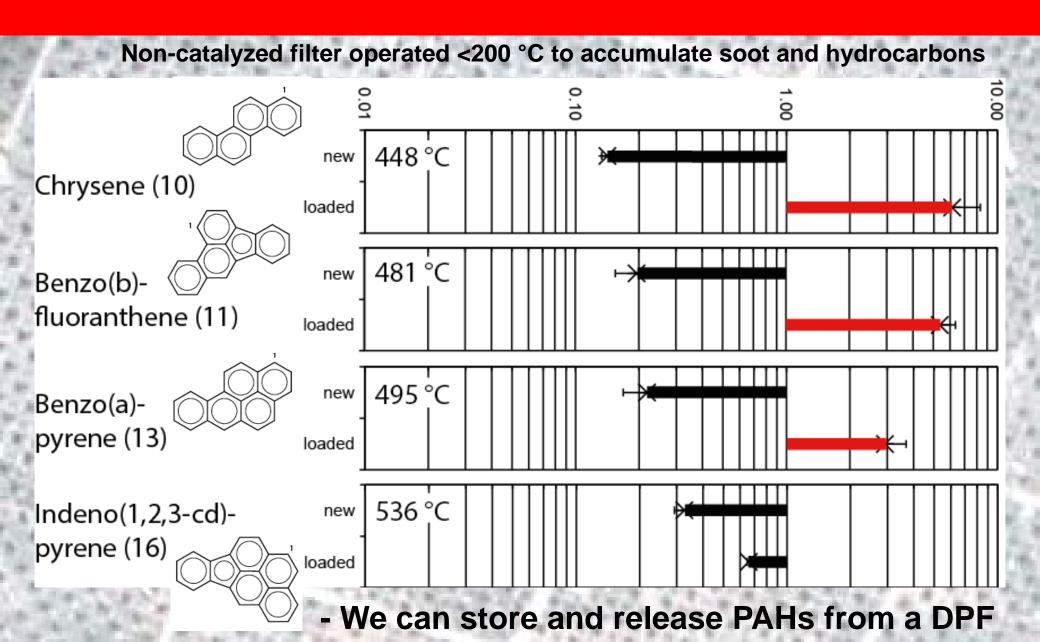
- 85% retention in the new DPF
- 6x higher emissions from the soot-loaded DPF



- 80% retention in the new DPF
- 5x higher emissions from the soot-loaded DPF



- 80% retention in the new DPF
- 3x higher emissions from the soot-loaded DPF



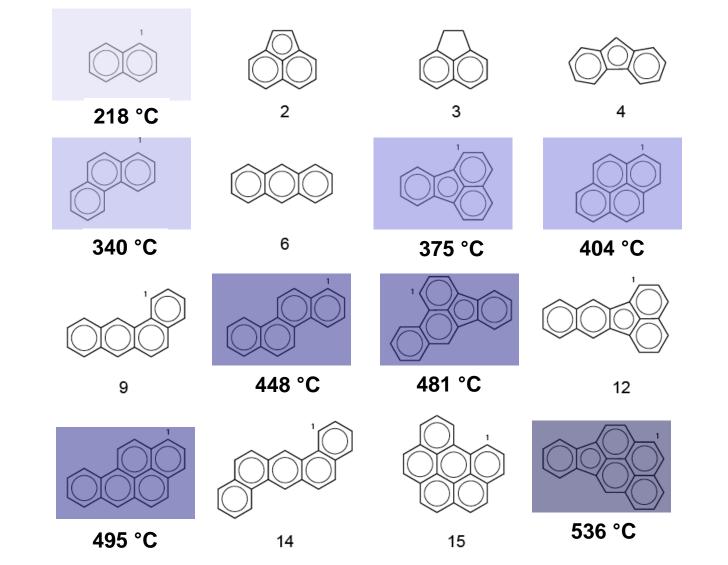
PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

- Volatile PAHs penetrate DPFs

- Semi-volatile PAHs are stored, but can be released again

- Non-volatile PAHs are stored like soot



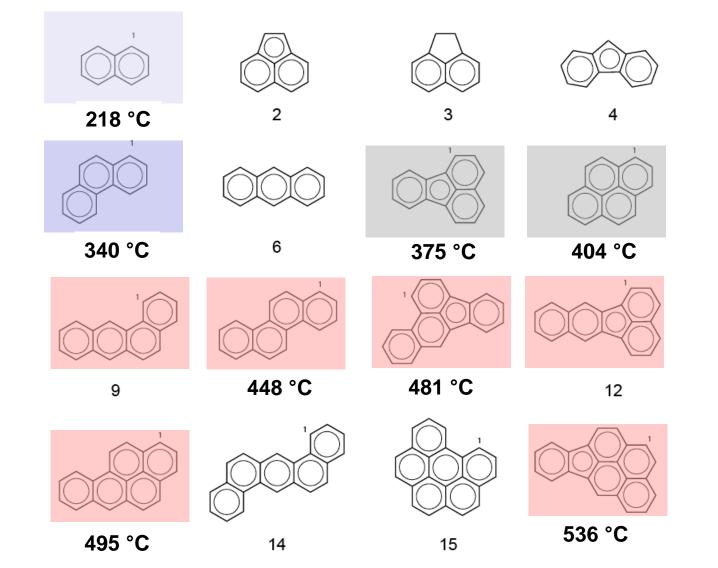
Many of the semi-volatile PAHs are genotoxic or precursors of genotoxic compounds

2- to 6-ring PAHs

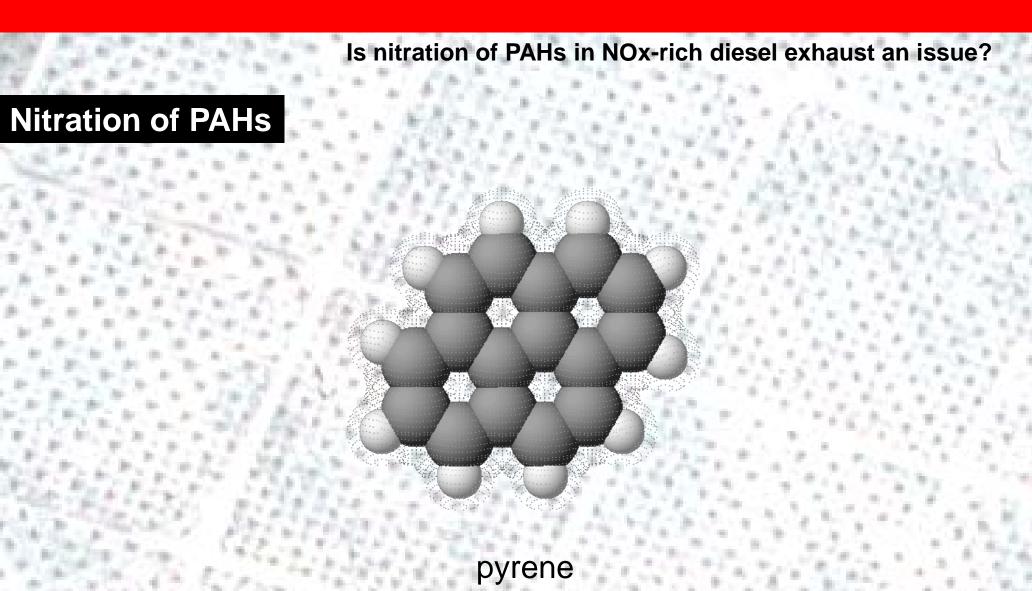
- Volatile PAHs penetrate DPFs

- Semi-volatile PAHs are stored, but can be released again

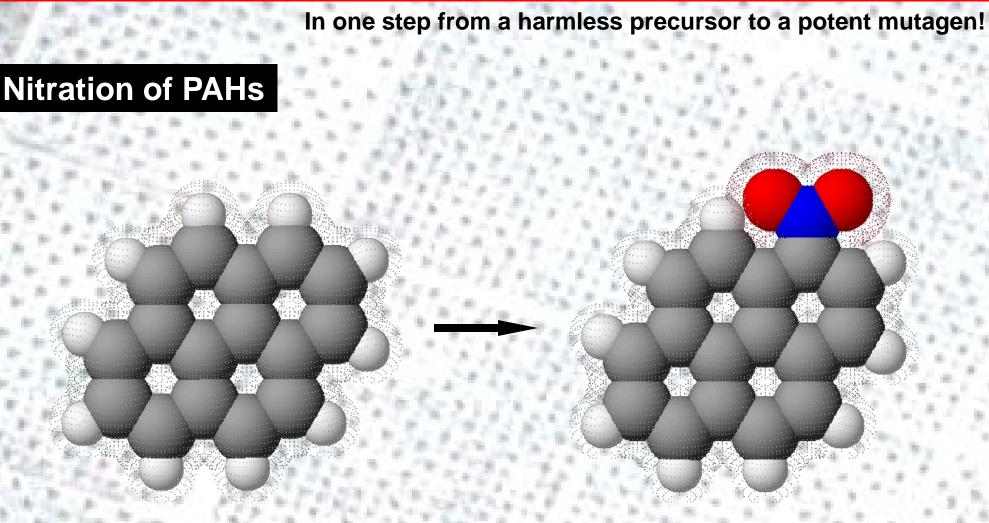
- Non-volatile PAHs are stored like soot



The DPF – a chemical reactor



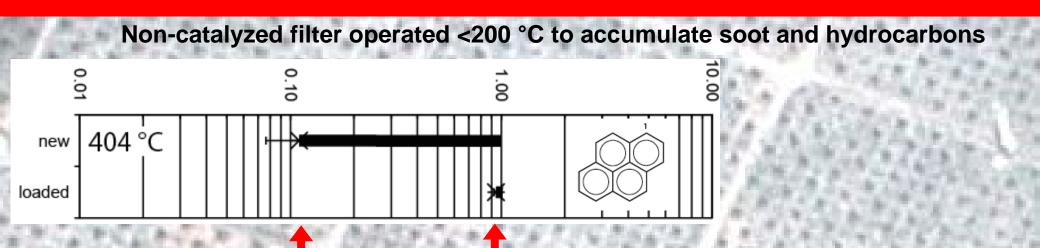
The DPF – a chemical reactor



pyrene

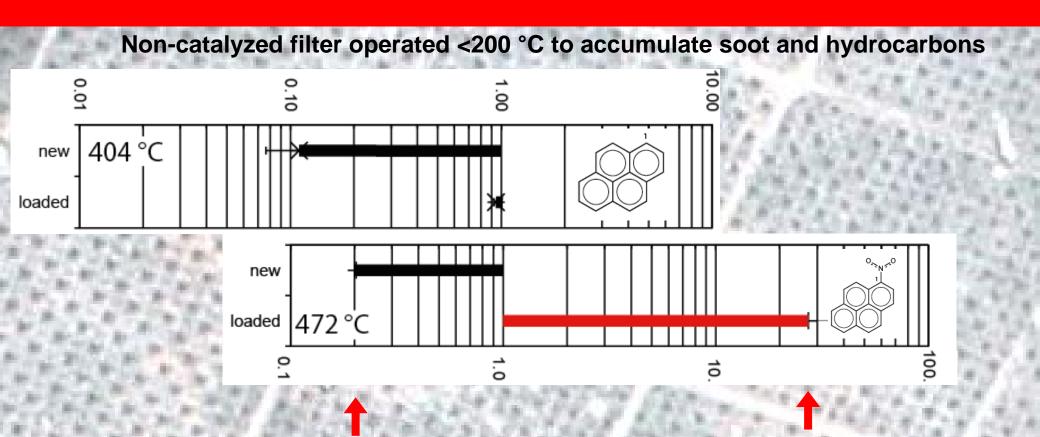
1-nitro pyrene

Nitro-PAHs in non-catalyzed DPF



- Pyrene is stored in a new, but released from a soot-loaded DPF

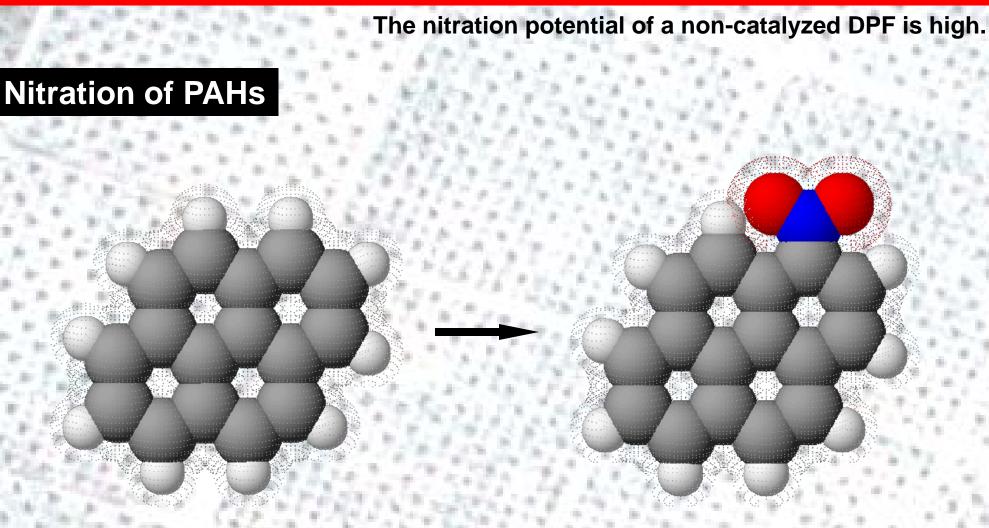
NPAHs in non-catalyzed DPF



Pyrene is stored in a new, but released from a soot-loaded DPF

 1-Nitro pyrene is stored in a new, but formed and released from a soot-loaded DPF (30x)

Even a non-catalyzed DPF is a chemical reactor



pyrene

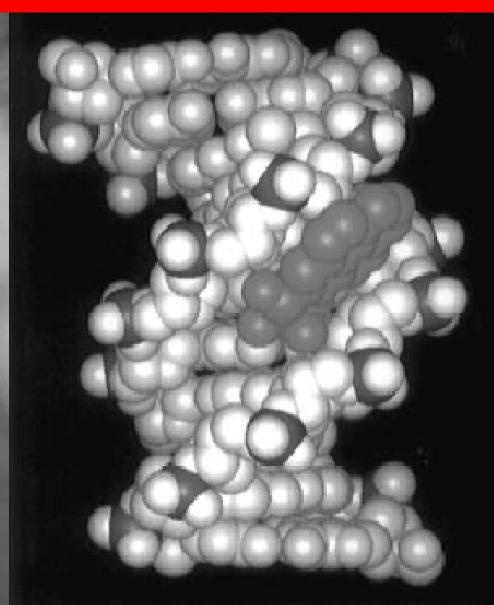
1-nitro pyrene

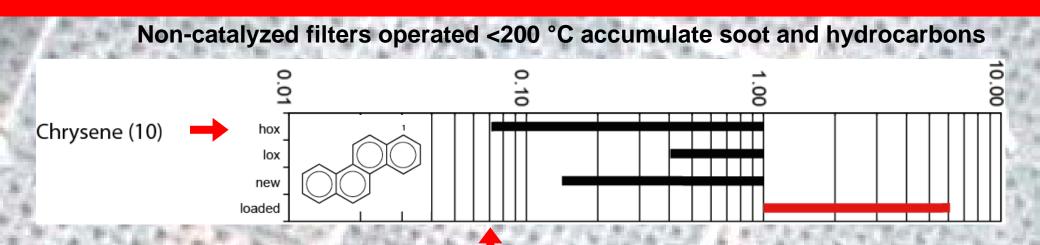
Adverse health effects of diesel exhaust

Problem: Genotoxicity

- Unfiltered diesel exhaust is genotoxic
- Filtration as such is not sufficient to remove all genotoxic compounds
- Efficient catalysts are needed to convert genotoxic compounds

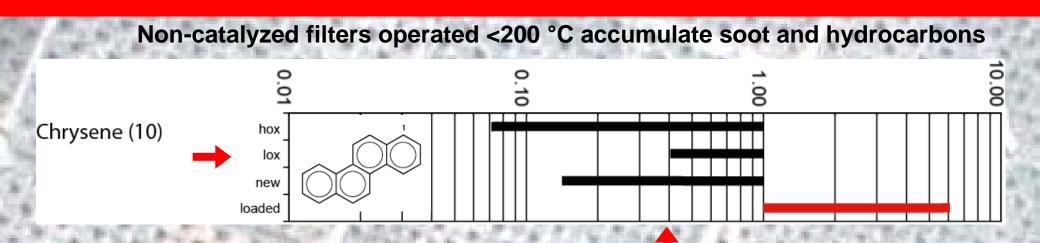
We need catalyzed DPFs!





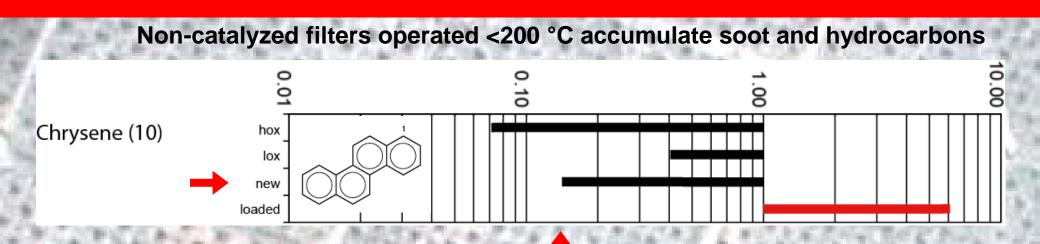
- Hox-DPF convert >90% chrysene

Heeb et al. ES&T, 2010, 42, 3773-3779

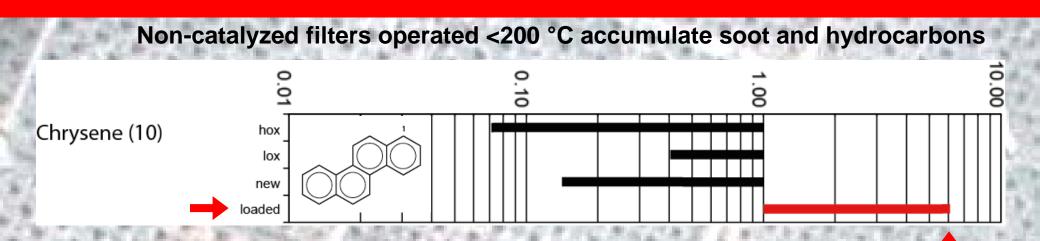


- Hox-DPF convert >90% chrysene
 - Lox-DPF convert >60% chrysene

Heeb et al. ES&T, 2010, 42, 3773-3779

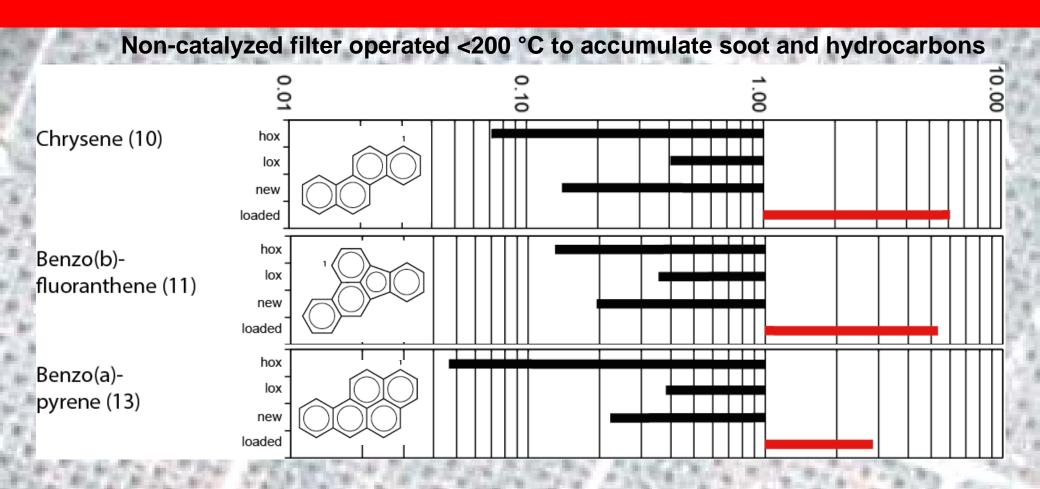


- Hox-DPF convert >94% chrysene
 - Lox-DPF convert >60% chrysene
 - A new non-catalyzed DPF stores chrysene
 - (at low temperatures even better than a lox-DPF)



- Hox-DPF convert >94% chrysene
 - Lox-DPF convert >60% chrysene
 - A new non-catalyzed DPF stores chrysene (at low temperatures even better than a lox-DPF)
 A loaded non-catalyzed DPF can release chrysene (at higher temperatures)

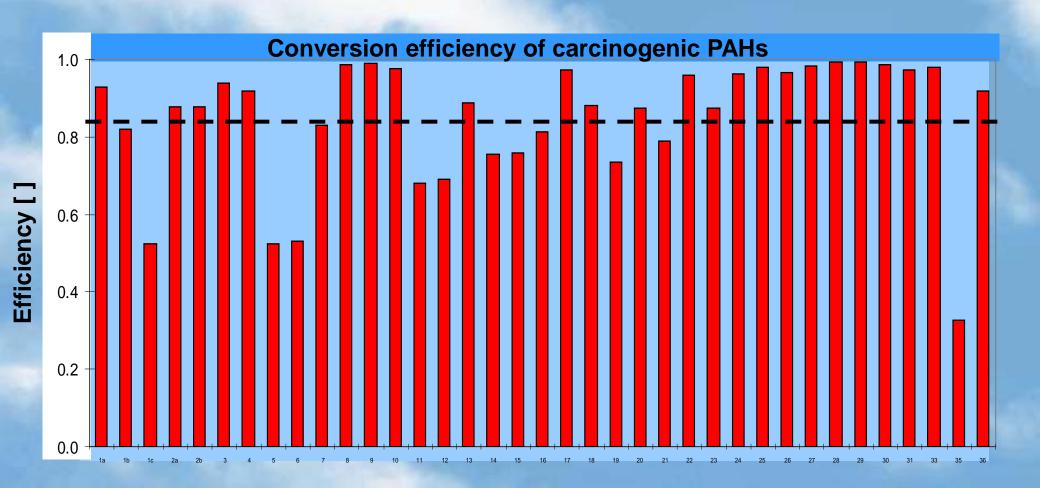
Heeb et al. ES&T, 2010, 42, 3773-3779



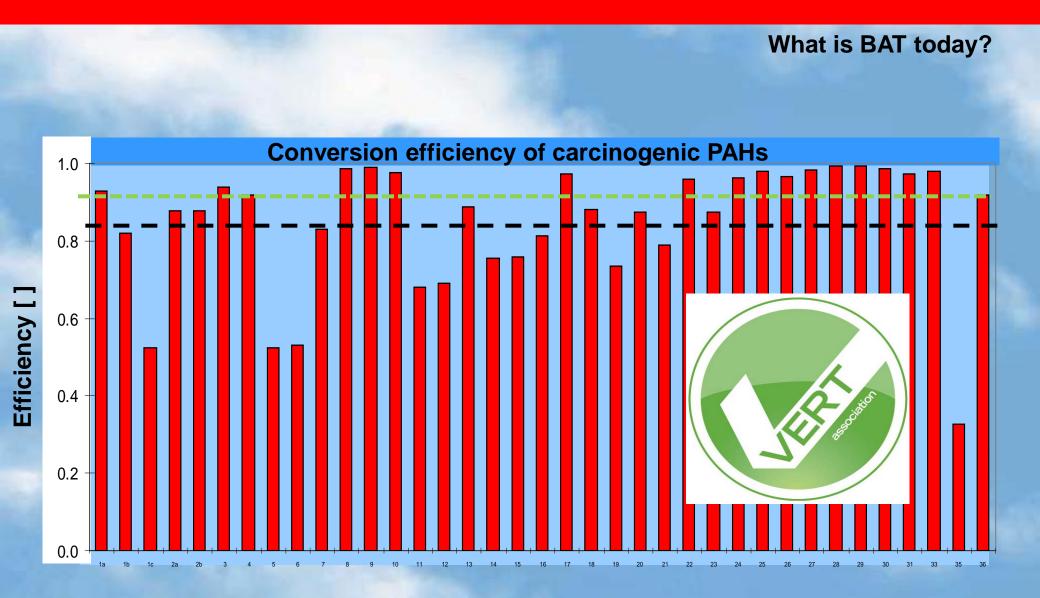
This is the general trend for many genotoxic PAHs

Adverse health effects of diesel exhaust

VERT-tested catalytic DPFs convert carcinogenic PAHs (on average 85%)



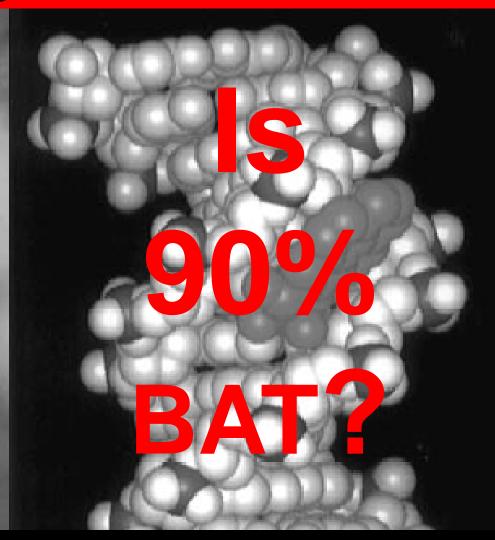
Adverse health effects of diesel exhaust



Catalysis, a key property of particle filters to lower genotoxicity of diesel exhaust

Problem: Genotoxicity

- Non-filtered diesel exhaust is genotoxic
- Filtration as such is not sufficient to remove genotoxic compounds
- Efficient catalysts are needed to convert genotoxic compounds



Catalytic DPFs are BAT to lower the genotoxicity of diesel exhaust, but some are considerably better than others!

Catalysis, a key property of particle filters to lower genotoxicity of diesel exhaust

A combined effort with many important contributions

Thanks:

- VERT team: Andreas Mayer, TTM, Niederrohrdorf Jan Czerwinski, Sandro Napoli, Tobias Neubert, Thomas Hilfiker, Samuel Bürki, Jean-Luc Petermann, Yan Zimmerli, Hervé Nauroy Uni. Appl. Sci., Biel. Markus Kasper, Adrian Hess, Thomas Mosimann, Matter Aerosols, Wohlen Hans Jaeckle, Urs Debrunner, Oliver Schumm, Intertek Caleb Brett, Schlieren.
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- Filter- & catalyst manufacturers: >40 different diesel particulate filter systems



Materials Science & Technology

Ø	SCHWEIZ, CHEMISCHE GESELLSCHAFT, SCG
	SOCIETE SUISSE DE CHIMIE 🛛 🖉 🗁 SSC
	SWISS CHEMICAL SOCIETY SCS

Traugott Sandmeyer (1854-1922)





If you see smokers like this, you urgently ask for catalyzed DPFs

Depression

