

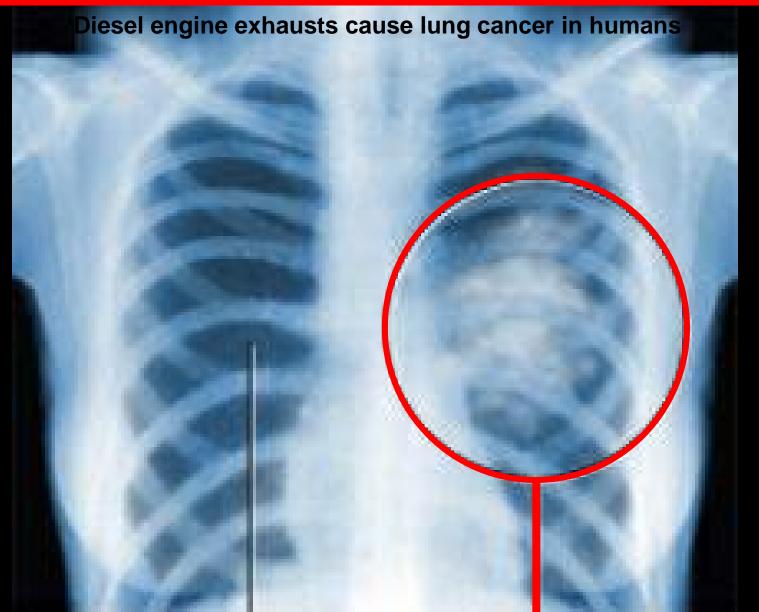


Catalysis, a key property of particle filters to lower genotoxicity of diesel exhaust



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

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



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

Diesel engine exhausts cause lung cancer in humans

International Agency for Research on Cancer



PRESS RELEASE N° 213

12 June 2012

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 cancer 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-emphasize in grant 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 extend 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 15 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 23 15 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 23 15 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 23 15 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 23 15 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 23 15 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 23 15 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 25 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 25 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 25 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 25 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 25 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 25 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 25 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 25 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 25 cm at exposure to diesel exhaust and lung cancer mortality after adjustment for small 25 cm at exhaust and lung cancer mortality after adjustment for small 25 cm at exhaust and lung cancer mortality after adjustment for small 25 cm at exhaust and lung cancer mortality after adjustment for small 25 cm at exhaust and lung cancer mortality after adjustment for small 25 cm at exhaust and lung cancer mortality after adjustment for small 25 cm at exhaust and lung cancer mortality after adjustment for small 25 cm at exhaust and lung cancer mortality after adjustment for small 25 cm at exhaust and lung

Methods

We conducted a nested case-control study in a cohort of 12315 workers in eight no 98 initiating cancer death which included 198 lung cancer deaths and 562 incidence density-sampled control subjects. For each case subject, we selected up to sontrol subjects, individually matched on mining facility, sex, race/ethnicity, birth year (within 5 years), from all 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.

Results

We observed statistically significant increasing trends in lung cancer risk with increasing cumulative REC and average REC intensity. Cumulative REC, lagged 15 years, yielded a statistically significant positive gradient in lung cancer risk overall (P_{trent} = .001); among heavily exposed workers (ie, above the median of the top quartile [REC ≥ 1005 µg/m³-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% CI = 0.29 to 7.50), and 7.30 (95% CI = 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-y or more, respectively. We also observed an interaction between smoking and 15-year lagged cumulative REC (Pinteraction attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of high levels of the other attenuated in the presence of the other attenuated in the other attenu

Conclusion

Our findings provide further evidence that digreen exhaust exposure may cause lung of a potential public health burden represent a potential public health burden. J Natl Cancer Inst 2012;104:1-14

Swiss occupational health legislation

Grenzwerte am Arbeitsplatz 2009



	MAK	-Wert	Kurz	zeitgrenzw	erte	HSB	С	M	R _F	RE	SS	Messmethoden/
Stoff [CAS-Nummer]	ml/m³ (ppm)	mg/m³	ml/m³ (ppm)	mg/m³	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)		0,25e				Н	3					NIOSH
Dieselmotor-Emissionen (gemessen als elementarer Kohlenstoff)		0,1a					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)

814.318.142.1

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



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

Luftreinhalte-Verordnung (LRV)

814.318.142.1

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	$C_2H_4Cl_2$	
Dieselruss		1
Diethylsulfat	$C_4H_{10}O_4S$	





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

Retrofitting of HDVs?

CH national council rejected (

12.3832

Ref. 10185

CONSEIL NATIONAL

Procès-verbal de vote

A₁ NATIONALRAT □ Abstimmungsprotokoll

Geschäft / Objet

12.3832 Mo. Vischer Daniel. Nachrüstung von Dieselfahrzeugen mit Partikelfiltern

Mo. Vischer Dani L. Equiper les véhicules diesel de filtres à particules

Gegenstand / Objet du vote:

Abstimmung vom Vote du: 06.05.2014 17.06:49

Aebi Andreas BE BE Aebischer Matthias Aeschi Thomas ZG BF Allemann S VD Amarelle GE Amaudruz VS Amherd CE BE Amstutz VD Aubert S BL Baader Caspar ZΗ S Badran Jacqueline CE GE Barazzone ZΗ Bäumle GL S Bernasconi BF Bertschv 711 Dindor

Fischer Roland	+	GL	LU
Flach	+	GL	AG
Flückiger Sylvia	-	V	AG
Fluri	-	RL	SO
Français	0	RL	VD
Frehner	-	V	BS
Freysinger	-	V	VS
Fridez	0	S	JU
Friedl	+	S	SG
Galladé			

Keller Peter	-	٧	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

Reimann Maximilian	-	٧	AG
Reynard	+	S	VS
Rickli Natalie	1	٧	ZH
Riklin Kathy	=	CE	ZH
Rime	-	٧	FR
Ritter	-	CE	SG
Romano	-	CE	TI
Rossini	+	S	VS
Rösti	-	V	BE
		1.7	Τ.

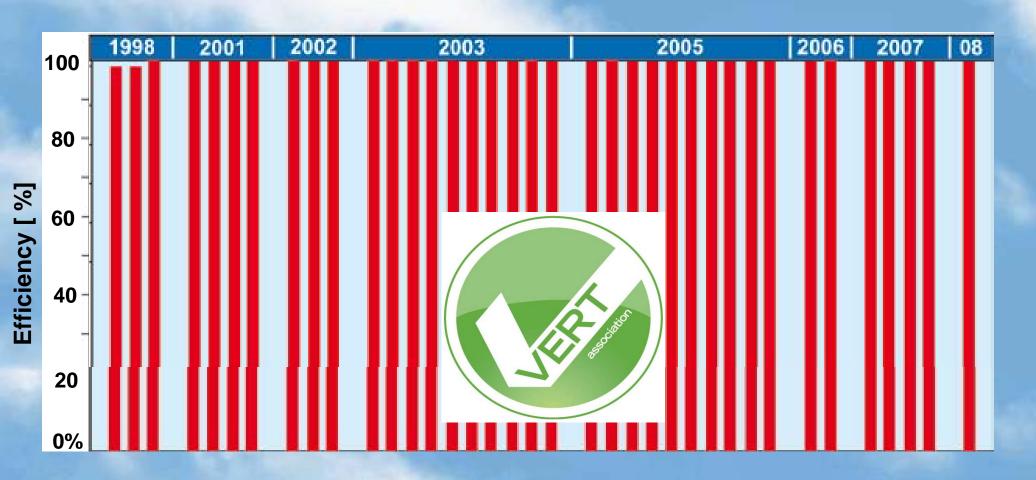
Rejected with 64 yes against 102 no's

Gasser	4	OL.	OIL
Geissbühler	-	V	BE
Germanier	0	RL	VS
Giezendanner	-	V	AG
Gilli	0	G	90

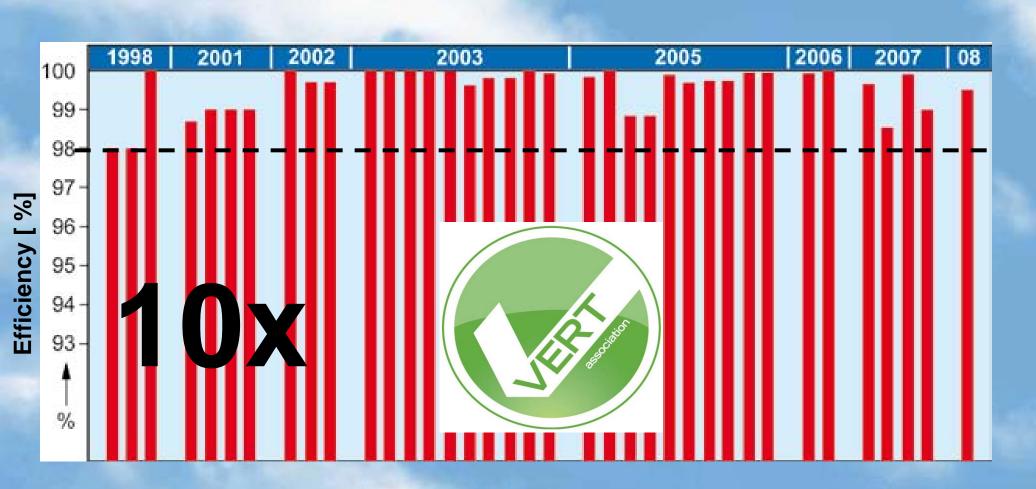
Lusonei	_	IXL	9
₋ustenberger	Р	CE	LU
Mahrer	+	G	GE
Maier Thomas	+	GL	ZH
A 1 /		_	N.I.E.

tytz rtegula	-	G	BE
Schelbert	+	G	LU
Schenker Silvia	+	S	BS
Schibli	-	V	ZH
N = 1= 1111 = 1 = 1		DI	1.11

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



You have to zoom in to see differences among filters

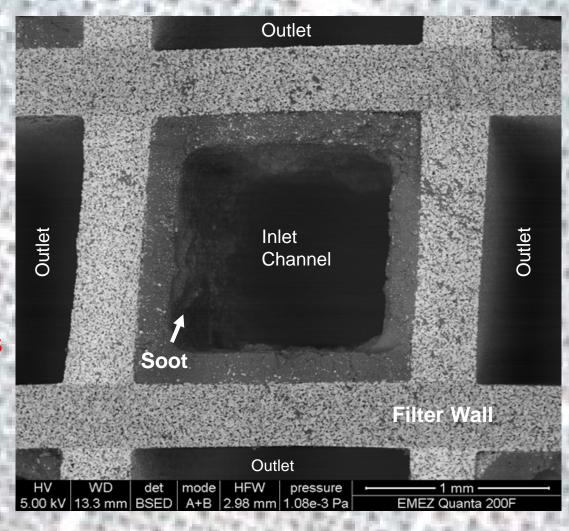




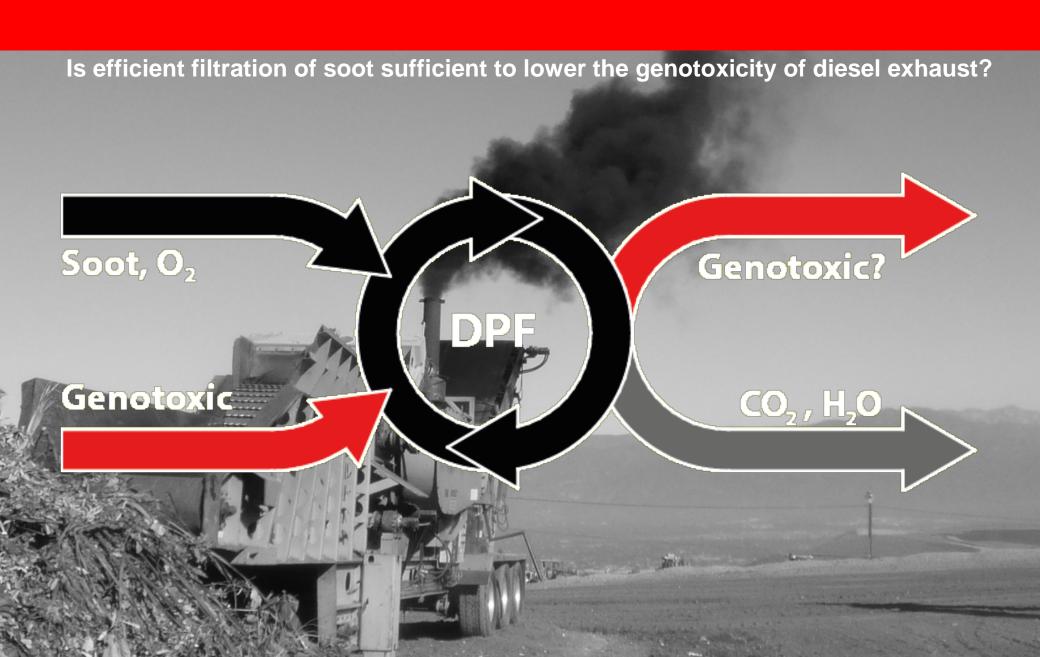
VERT-approved DPFs:

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

Wall-through filters are highly efficient for soot

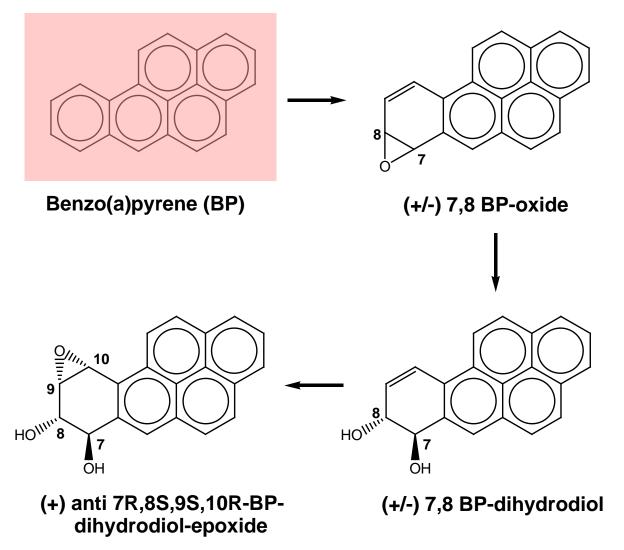


Impact of DPFs on genotoxicity



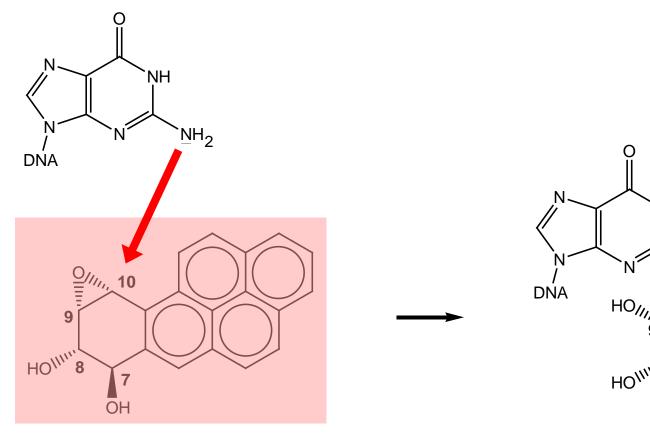
Carcinogenesis from benzo(a)pyrene

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



Carcinogenesis from benzo(a)pyrene

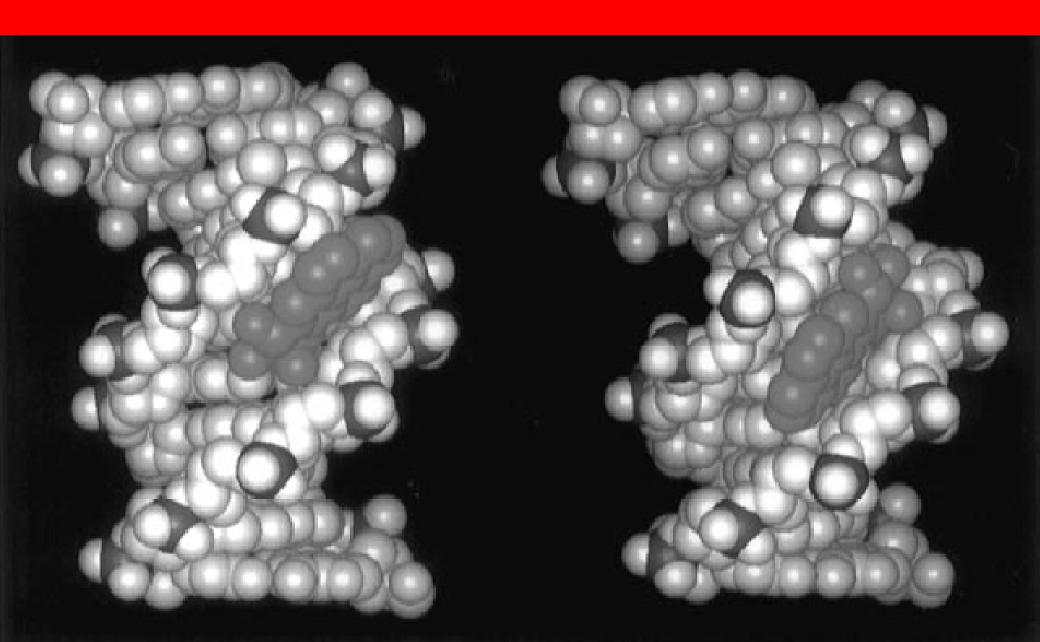
Selective formation of benzo(a)pyrene-DNA-adducts



(+) anti 7R,8S,9S,10R-BP-dihydrodiol-epoxide

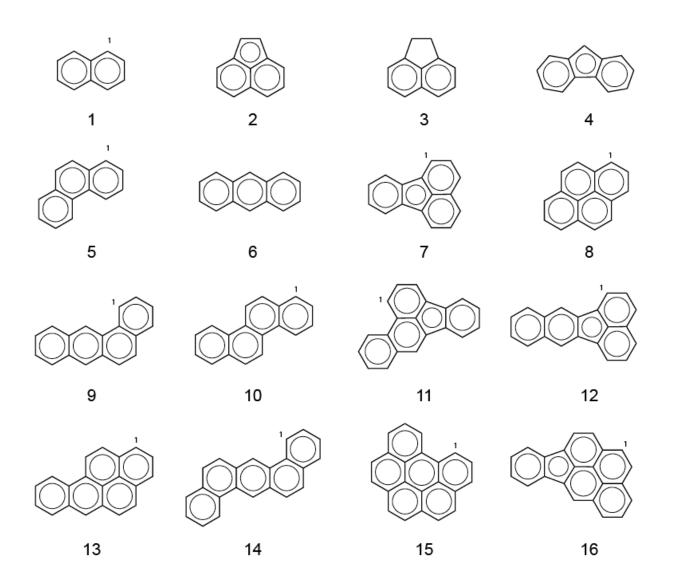
(-) 10R trans-anti-[BP]-triol-N2-deoxy-guanosine-adduct

Carcinogenesis from benzo(a)pyrene

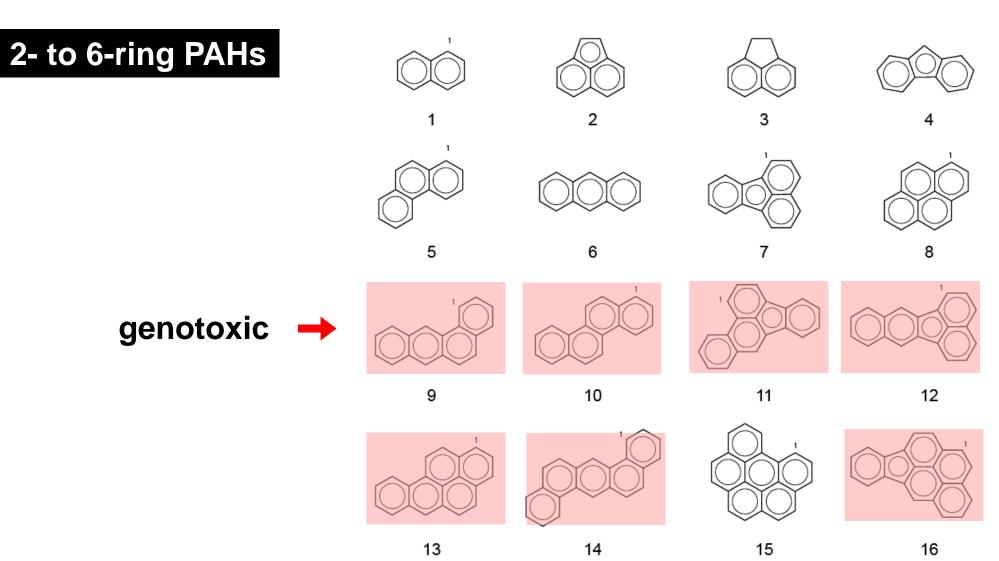


PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs



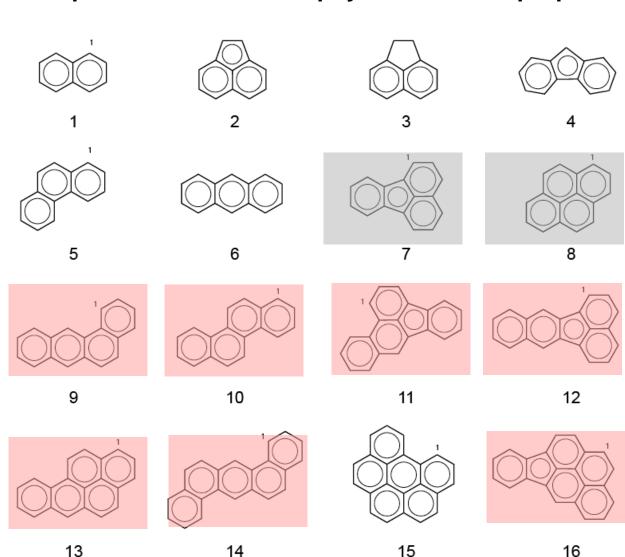
PAHs - a diverse class of compounds with variable physicochemical properties



PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

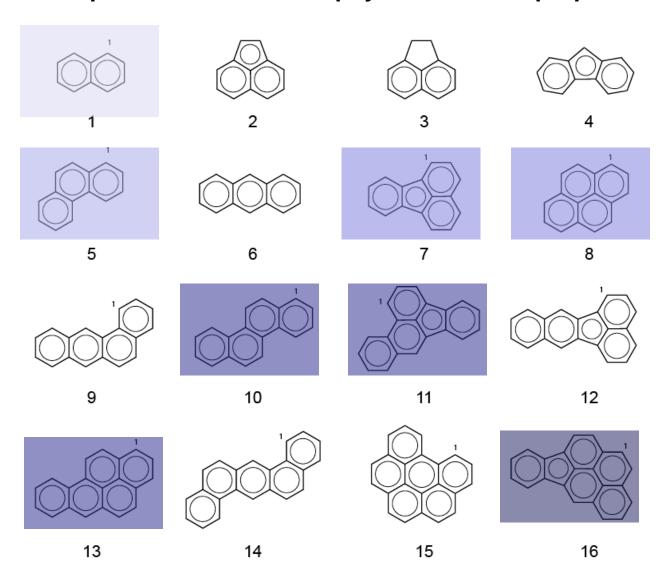




PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

differ in mass, size & volatility

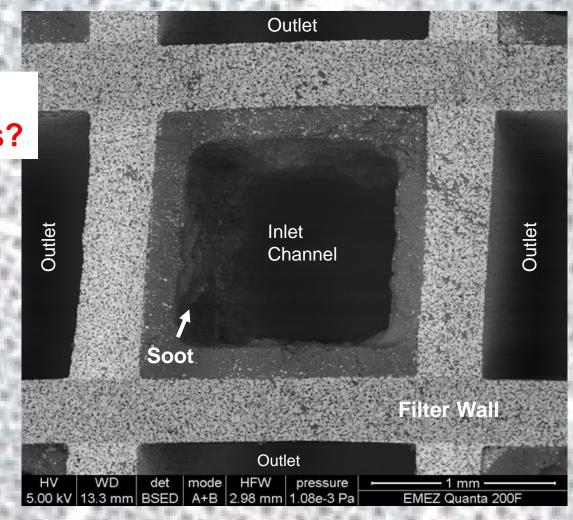


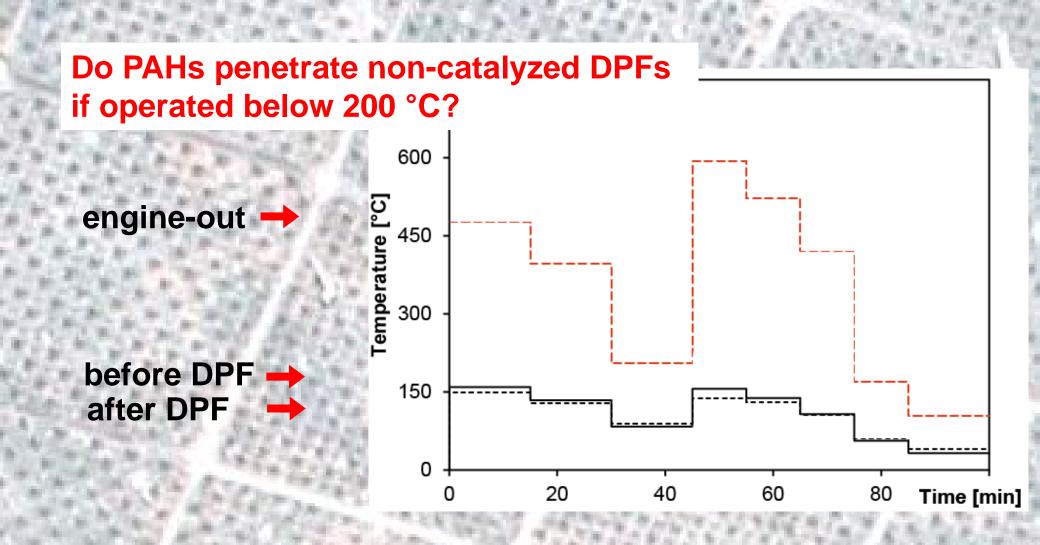
Non-catalyzed filters are as efficient for soot. How about genotoxic compounds?

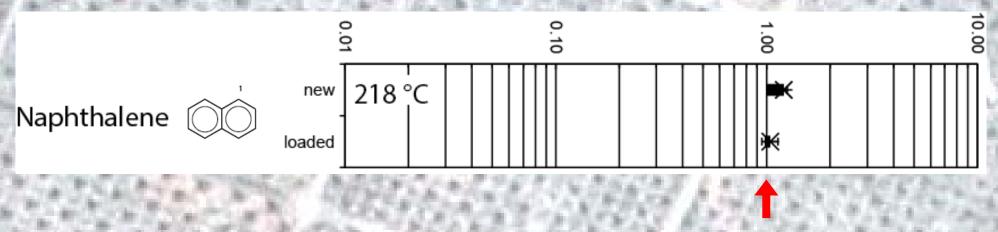
What do you expect, can PAHs penetrate DPFs?

Non-catalyzed DPFs:

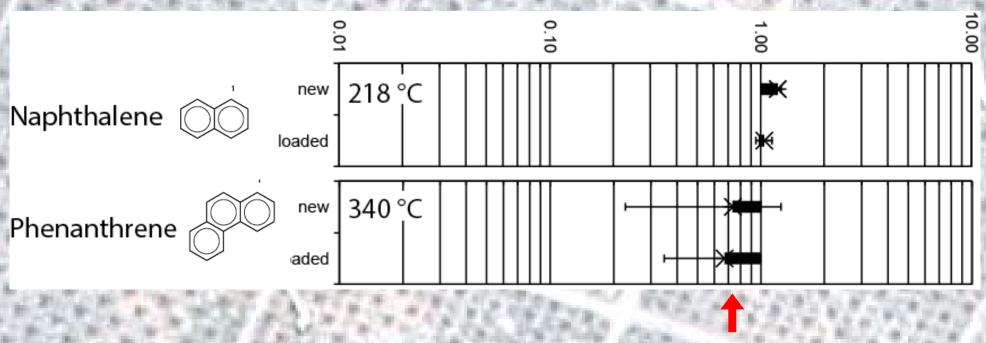
- Accumulate soot (>98%)
- → Do they reduce genotoxic compounds a.m.a.p?
- Do they have toxic secondary emissions?





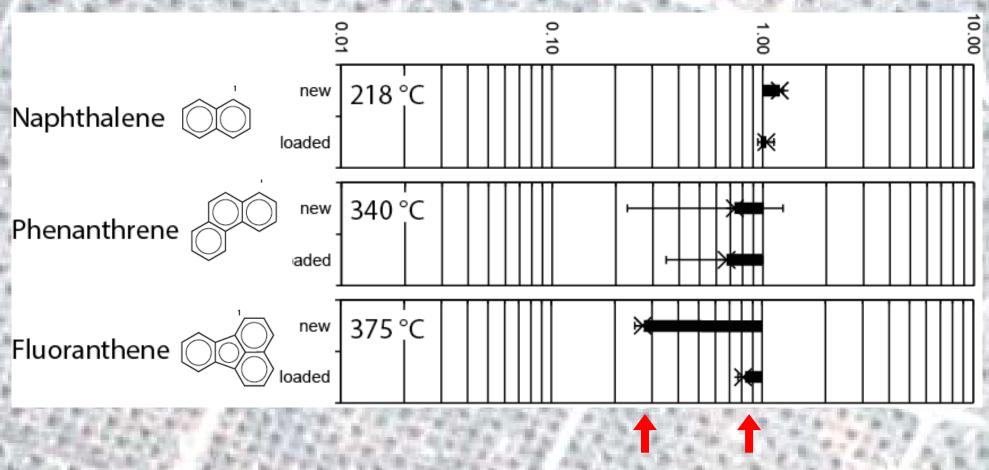


- No retention of naphthalene in a new and a soot-loaded DPF
- Naphthalene is too volatile, it even escapes from a cold filter (<200 °C)



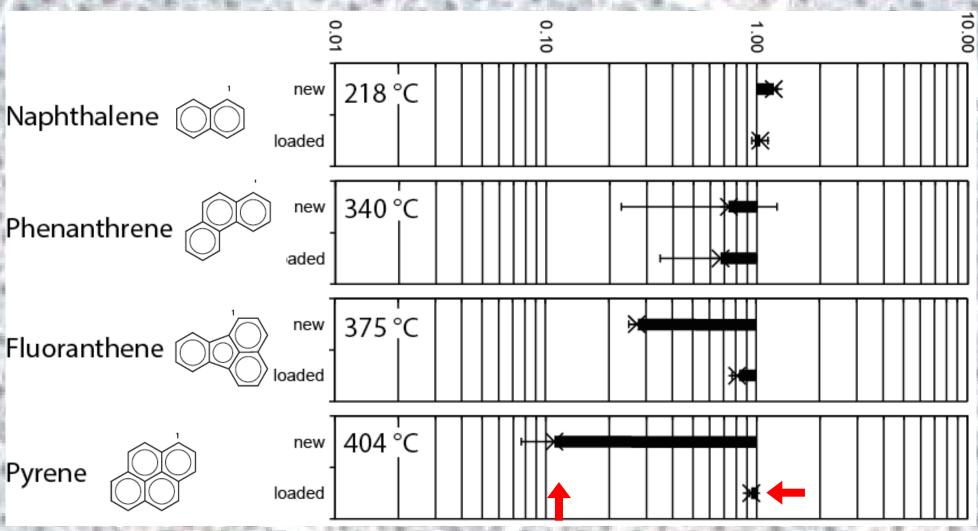
- About 30% retention, both in a new and a soot-loaded DPF
- Phenanthrene is partly stored in a cold filter (<200 °C)

Non-catalyzed filter operated <200 °C to accumulate soot and hydrocarbons



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

Non-catalyzed filter operated <200 °C to accumulate soot and hydrocarbons

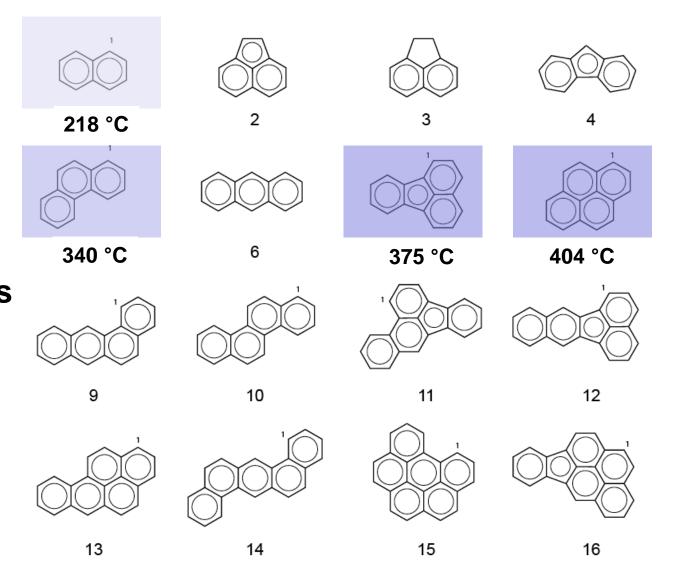


- 90% is retained in the new, only 5% in the soot-loaded DPF?

PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

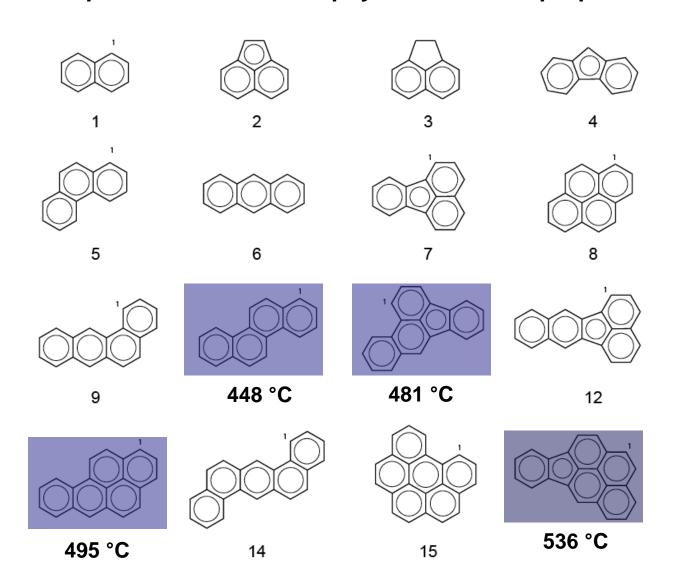
High penetration of volatile 2-4-ring PAHs

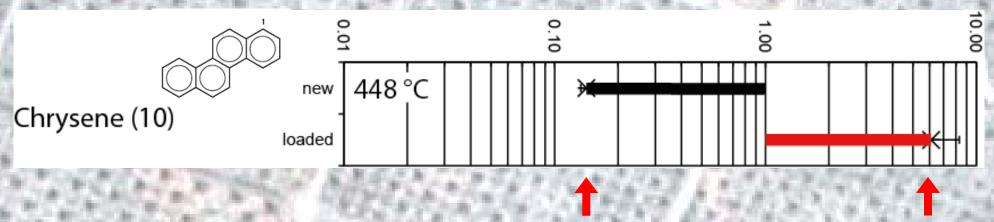


PAHs - a diverse class of compounds with variable physico-chemical properties

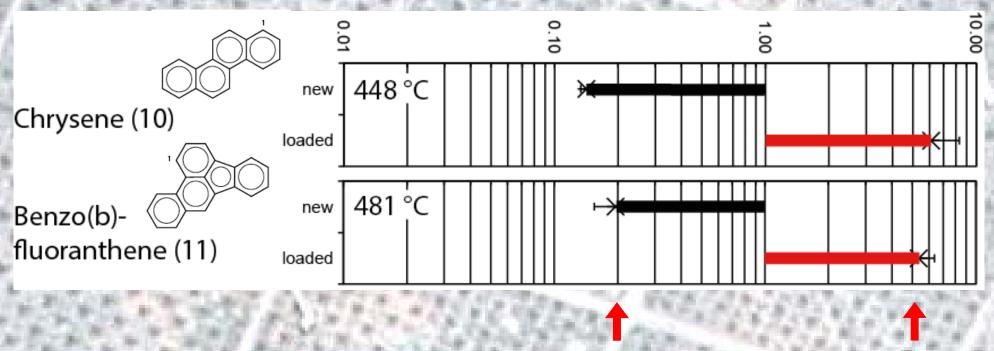
2- to 6-ring PAHs

What do we expect for less volatile PAHs?

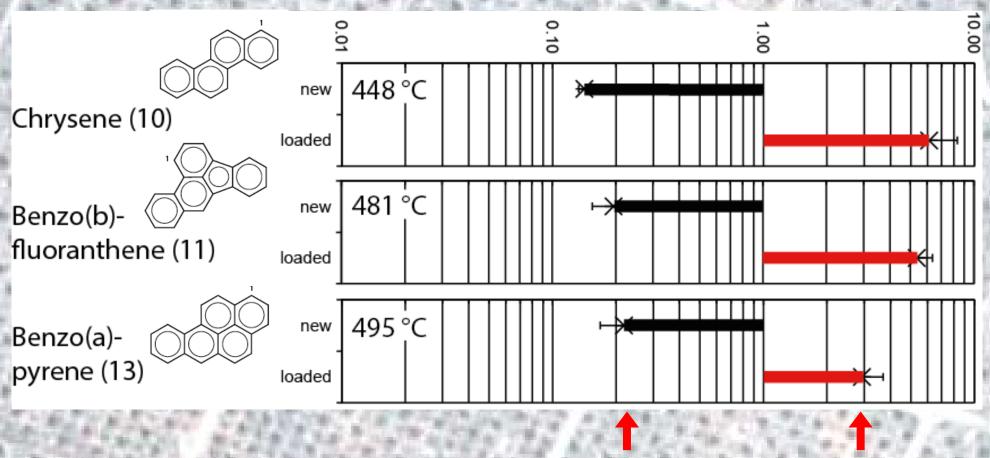




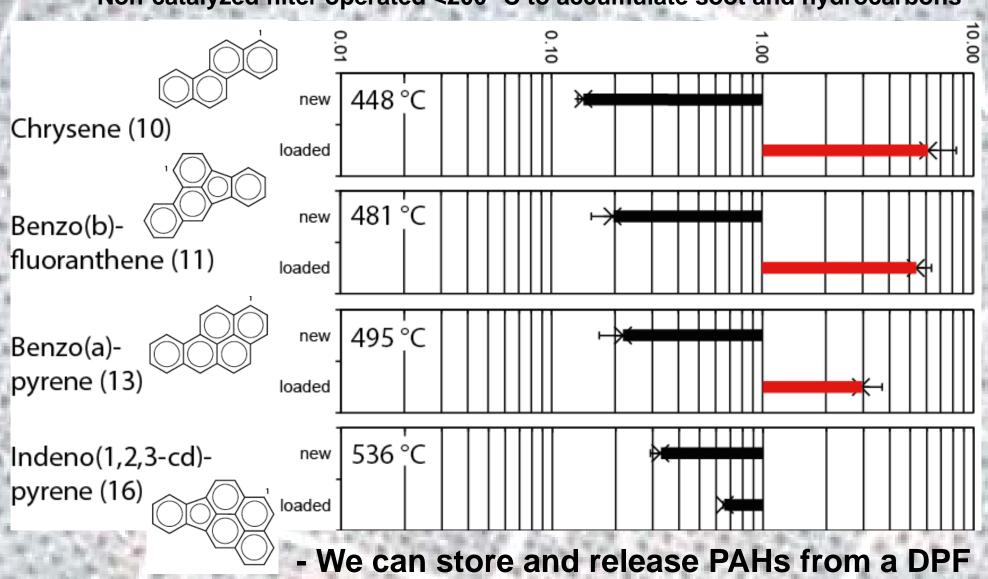
- 85% retention in the new DPF
- 6x higher emissions from the soot-loaded DPF



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



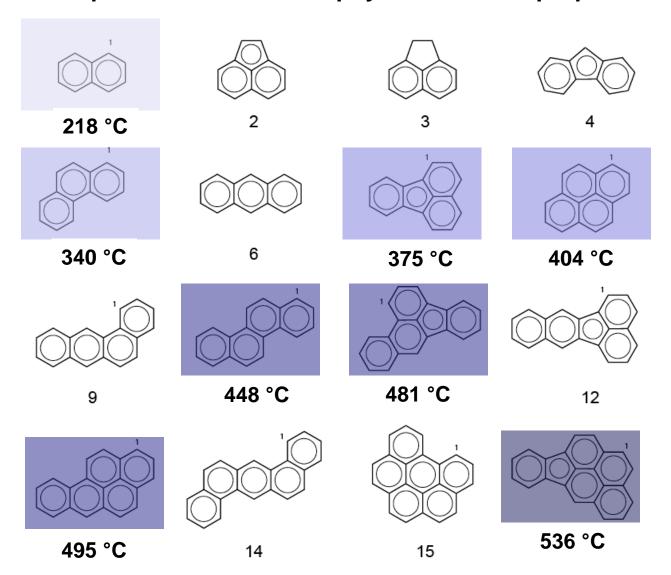
- 80% retention in the new DPF
- 3x higher emissions from the soot-loaded DPF



PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

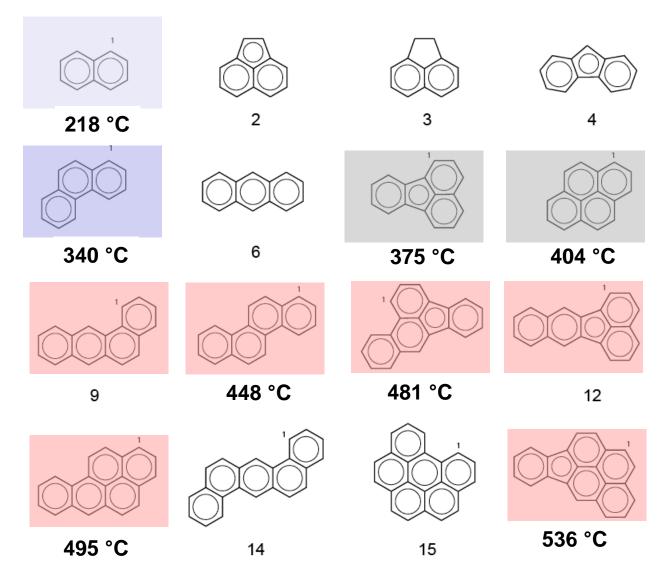
- Volatile PAHs penetrate DPFs
- Semi-volatile PAHs are stored, but can be released again
- Non-volatile PAHs are stored like soot



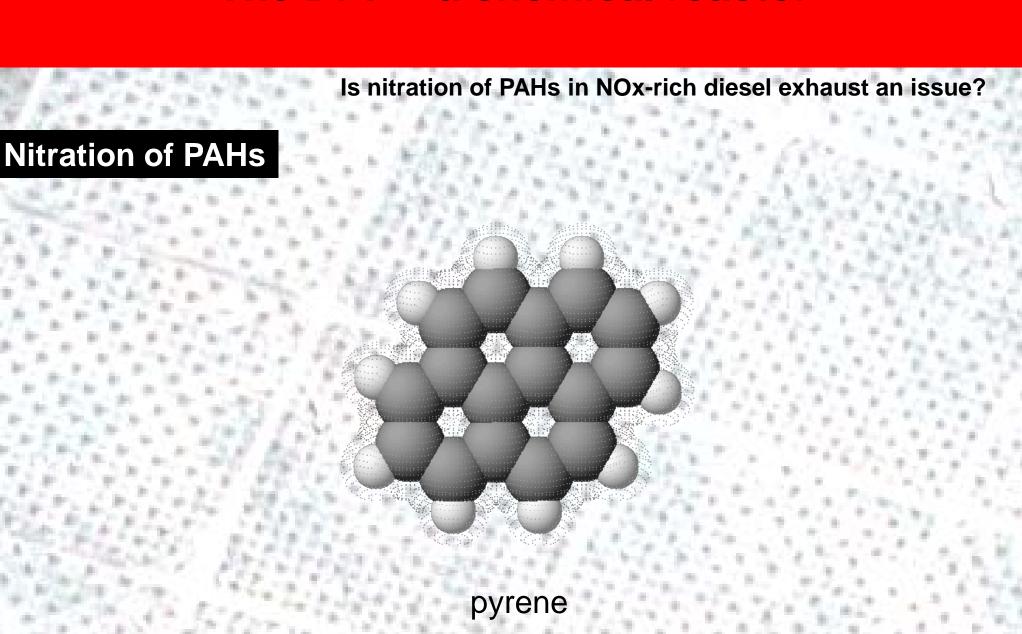
Many of the semi-volatile PAHs are genotoxic or precursors of genotoxic compounds

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



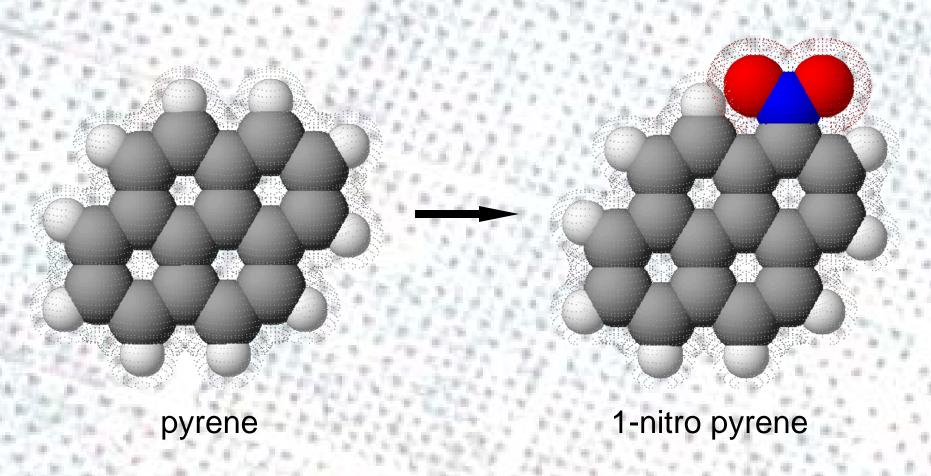
The DPF – a chemical reactor



The DPF – a chemical reactor

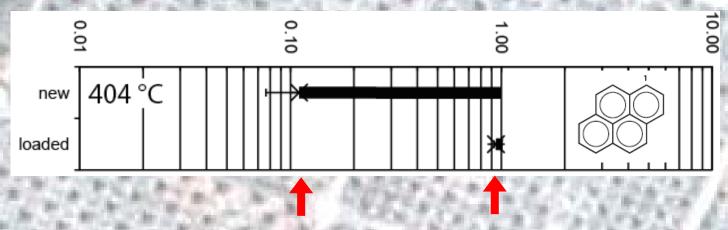
In one step from a harmless precursor to a potent mutagen!

Nitration of PAHs



Nitro-PAHs in non-catalyzed DPF

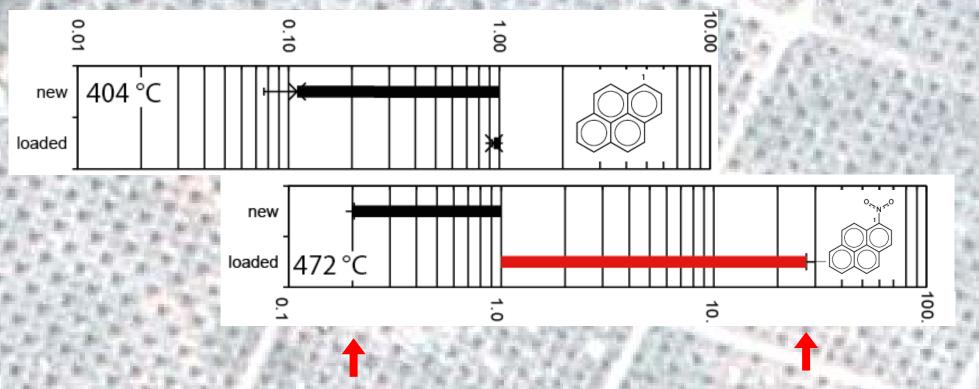
Non-catalyzed filter operated <200 °C to accumulate soot and hydrocarbons



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

NPAHs in non-catalyzed DPF

Non-catalyzed filter operated <200 °C to accumulate soot and hydrocarbons

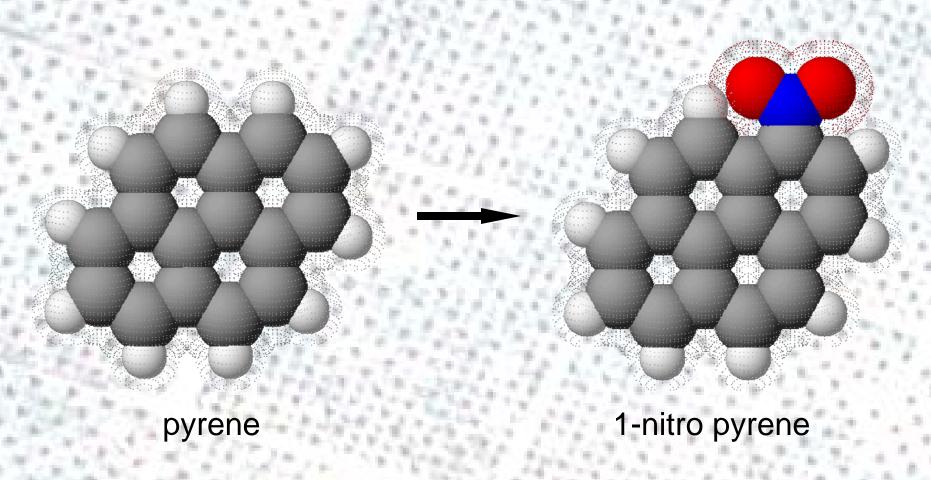


- Pyrene is stored in a new, but released from a soot-loaded DPF
- 1-Nitro pyrene is stored in a new, but formed and released from a soot-loaded DPF (30x)

Even a non-catalyzed DPF is a chemical reactor

The nitration potential of a non-catalyzed DPF is high.

Nitration of PAHs



Adverse health effects of diesel exhaust

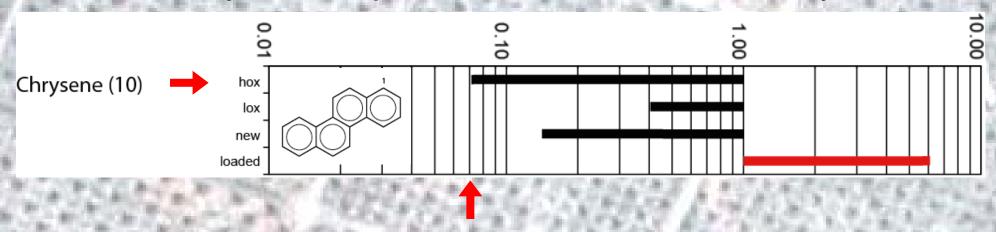
Problem: Genotoxicity

- 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!



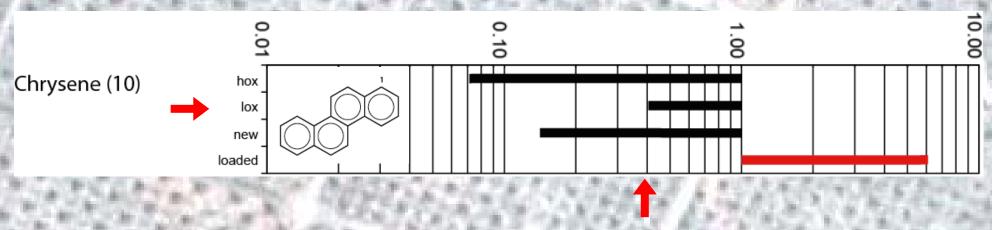
Non-catalyzed filters operated <200 °C accumulate soot and hydrocarbons



- Hox-DPF convert >90% chrysene

Outle

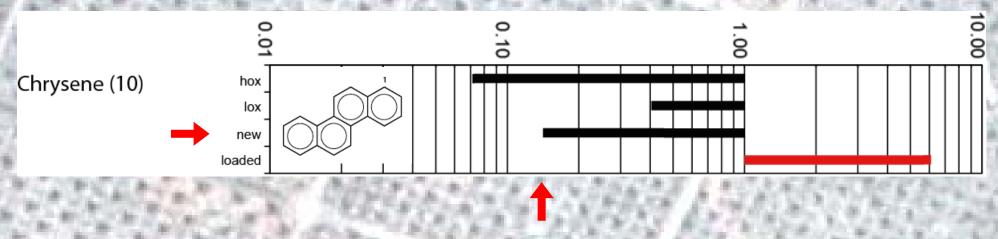
Non-catalyzed filters operated <200 °C accumulate soot and hydrocarbons



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

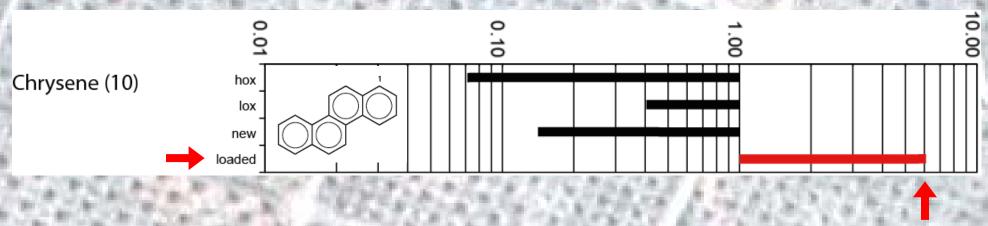
Outle

Non-catalyzed filters operated <200 °C accumulate soot and hydrocarbons



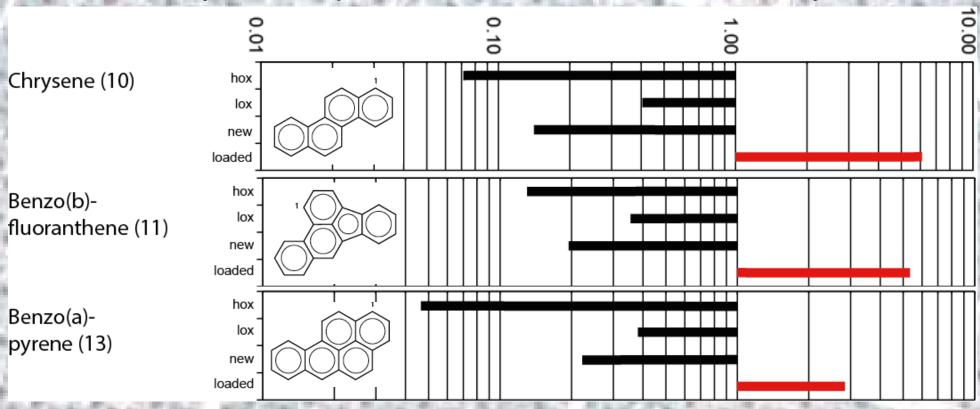
- Hox-DPF convert >94% chrysene
- Lox-DPF convert >60% chrysene
- A new non-catalyzed DPF stores chrysene (at low temperatures even better than a lox-DPF)

Non-catalyzed filters operated <200 °C accumulate soot and hydrocarbons



- 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)

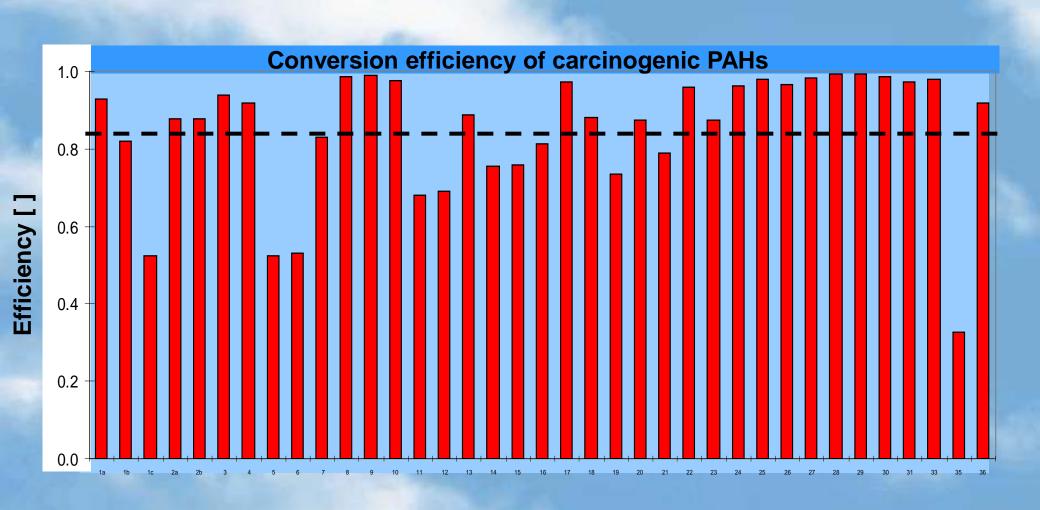
Non-catalyzed filter operated <200 °C to accumulate soot and hydrocarbons



This is the general trend for many genotoxic PAHs

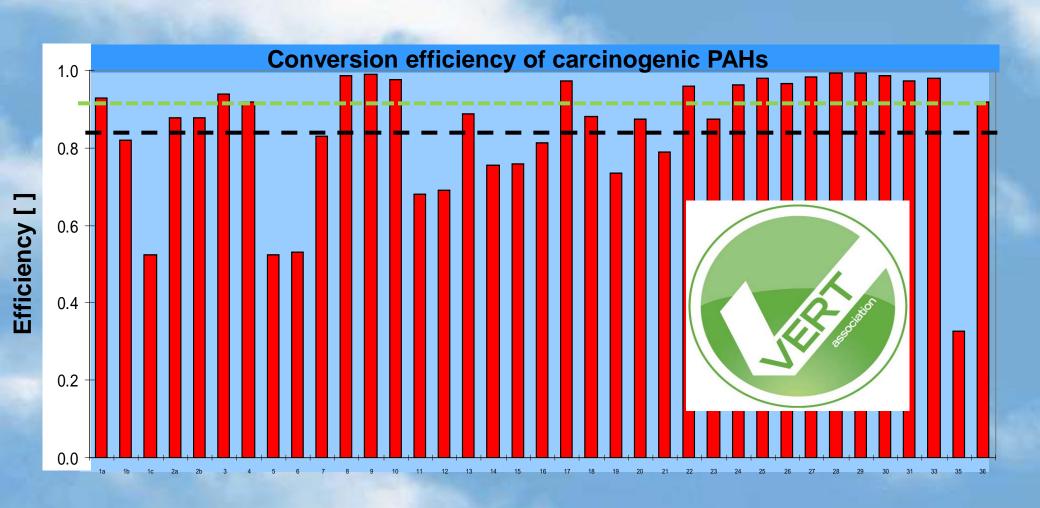
Adverse health effects of diesel exhaust

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



Adverse health effects of diesel exhaust

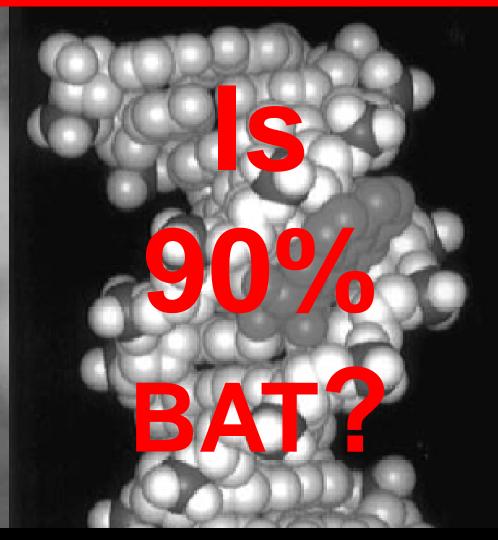
What is BAT today?



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:

- Empa colleagues: Brigitte Buchmann, Thomas Bührer, Lukas Emmenegger, Anna-Maria Forss,
 Urs Gfeller, Maria Guecheva, Peter Graf, Roland Graf, Erika Guyer, Regula Haag, Peter Honnegger, Judith Kobler, Martin Kohler, Peter Lienemann, Alfred Mack, Peter Mattrel,
 Martin Mohr, Joachim Mohn, Christof Moor, Andreas Paul, Peter Schmid, Cornelia Seiler,
 Andrea Ulrich, Heinz Vonmont, Thomas Walter, Max Wolfensberger, Daniela Wenger,
 Adrian Wichser, Markus Zennegg, Kerstin Zeyer.
- Governement: Philipp Hallauer, Giovanni D'Urbano, Felix Reutimann, Max Wyser, Gerhard Leutert, Martin Schiess, Swiss Fed. Office for Environment, Bern Thomas Gasser, Heinz Berger, Gerhard Stucki, Swiss Federal Road Office
- Filter- & catalyst manufacturers: >40 different diesel particulate filter systems





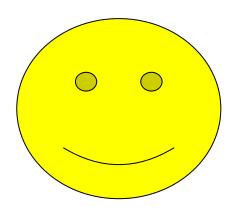




If you see smokers like this, you urgently ask for catalyzed DPFs



Index



Contents

