Secondary Effects of Catalytic Diesel Particulate Filters:

Reduced Emissions of Potential Endocrine Disruptors

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Emissions of diesel engines are a relevant source of potential endocrine disruptors in the air.

- Aryl hydrocarbon receptor (AhR) agonists

- Estrogen receptor (ER) agonists

Catalytic diesel particulate filters reduce emissions of potential endocrine disruptors with AhR- or ER-mediated activity.

- A favourable secondary effect of diesel particulate filters

- Promising technology to detoxify diesel exhaust

The Endocrine System

Hormones: endogenous chemical messengers

- Produced in the glands

- Transported by the blood system

- Recognized by **receptors** in the target cells ➔ induction of specific cellular responses

- Regulate biological processes (reproduction, development, behaviour, …)
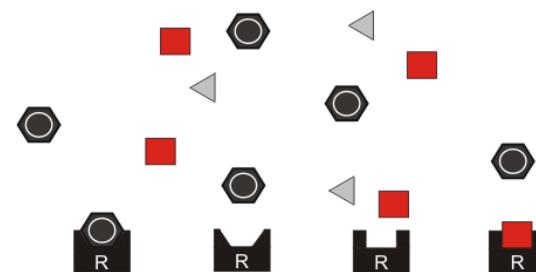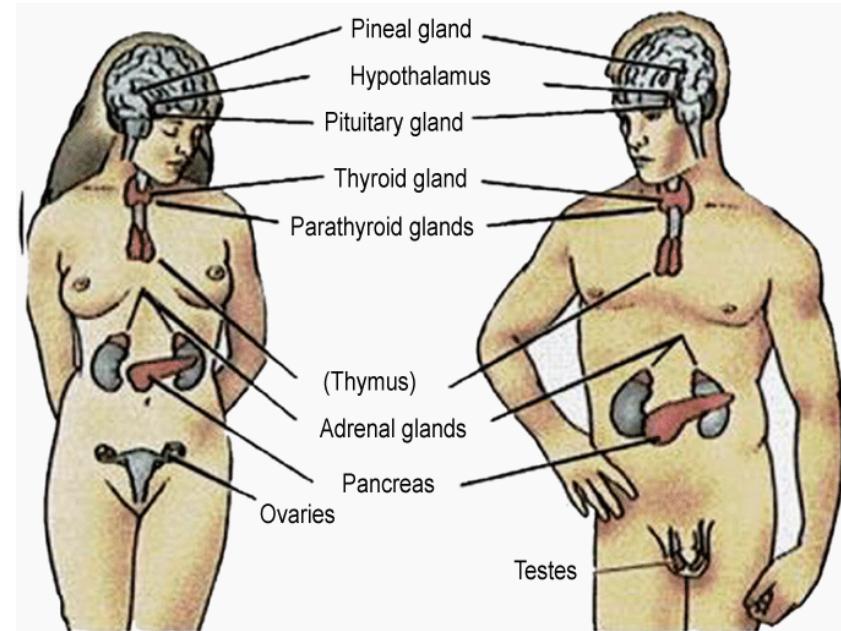
Endocrine Disruptors

Endocrine disruptors:

natural or man-made exogenous compounds

- Interfere with the normal functioning of human and wildlife endocrine systems ➔ adverse health effects

- Act at multiple sites

- Exhibit multiple mechanisms of action, for example, interaction with receptor systems
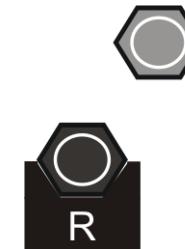
**Receptor agonists**: activate receptors

Receptor antagonists: block receptors

Inhalation

Alveolus

Blood capillary
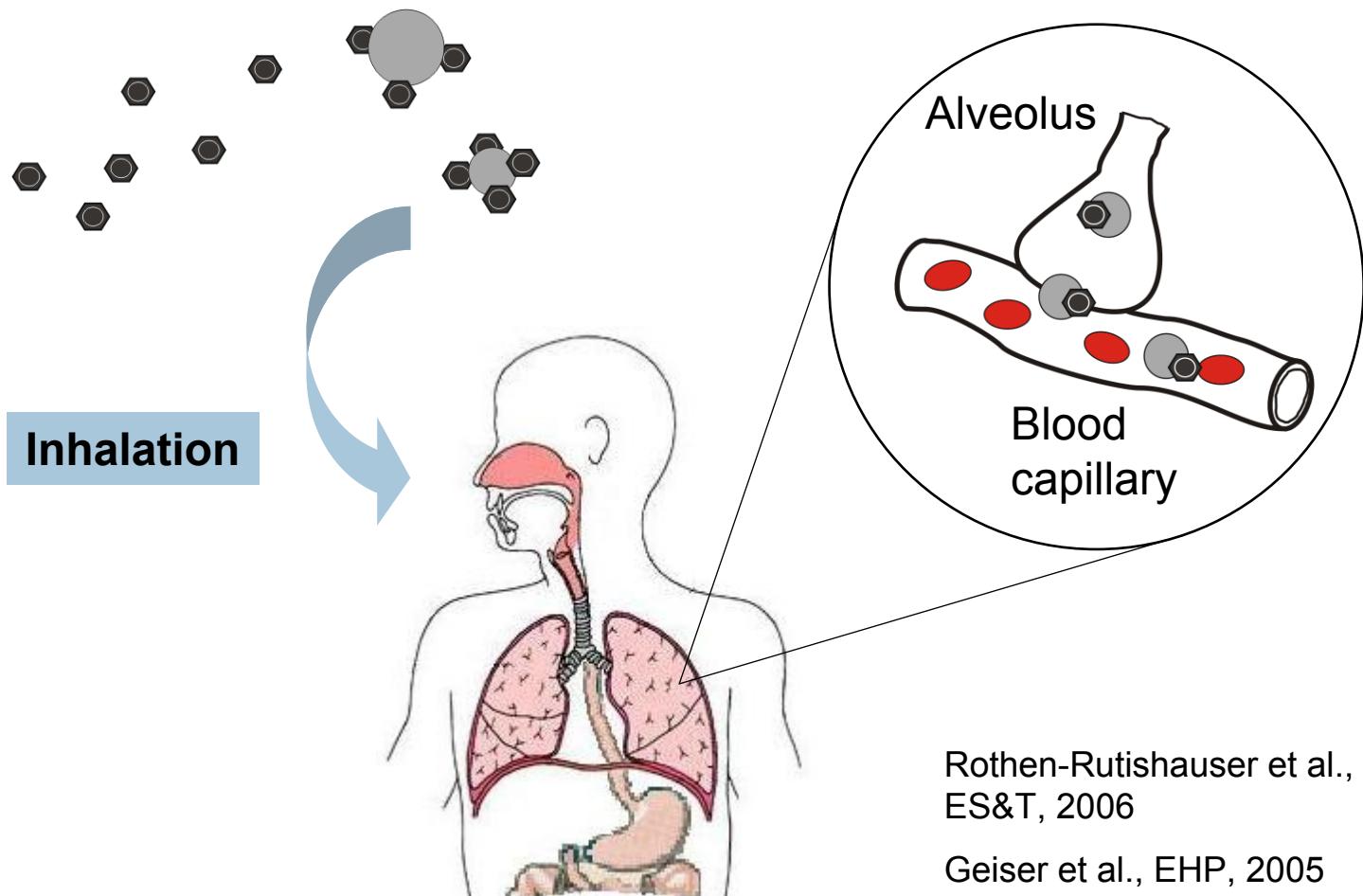
Rothen-Rutishauser et al., ES&T, 2006

Geiser et al., EHP, 2005

Diesel Exhaust: Endocrine Disruptors?

Endocrine disruptors?

Source

Exhaust treatment by diesel particulate filter

Exposure

Effect on endocrine disruptors?
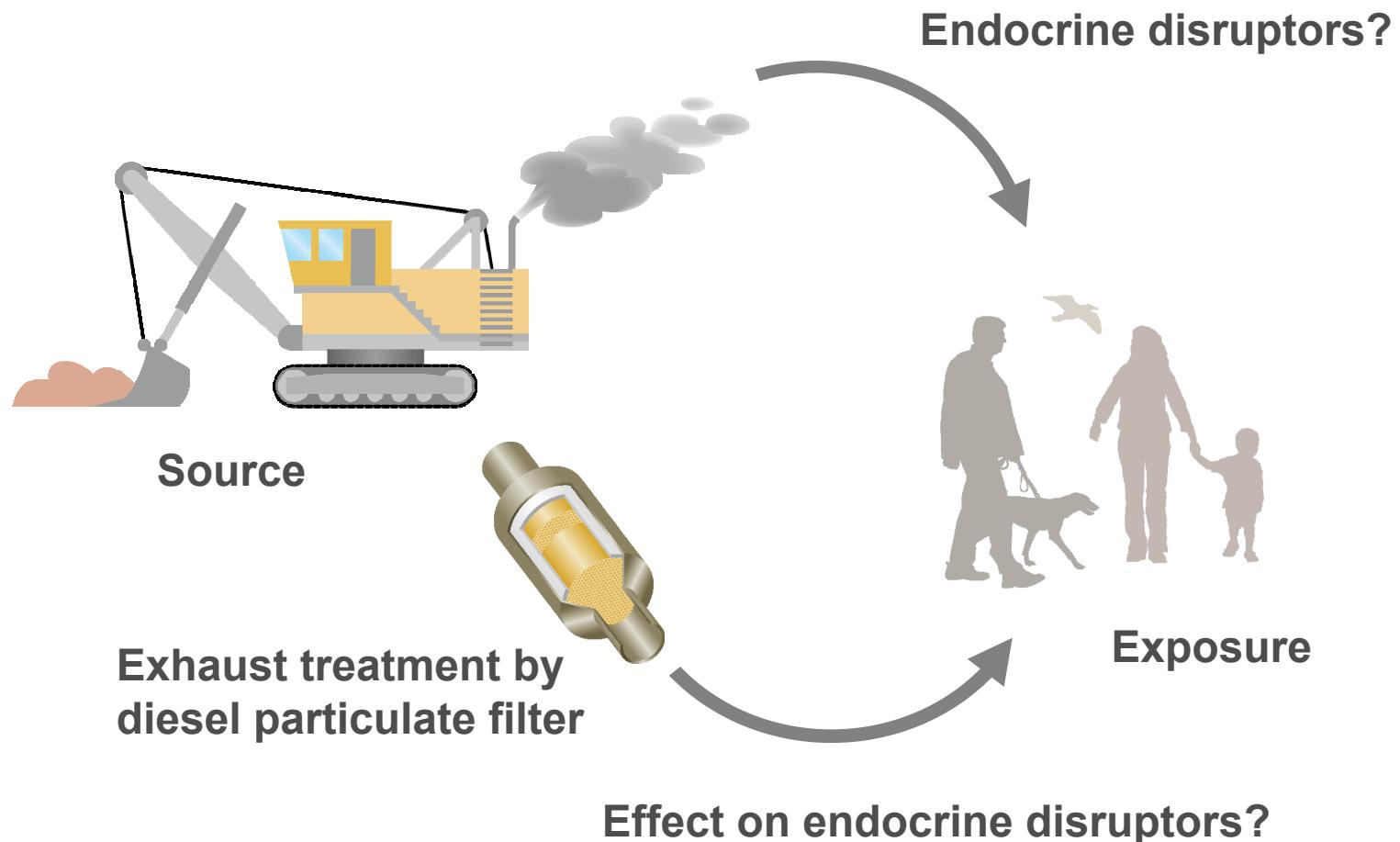
Diesel Exhaust: Endocrine Disruptors?

Collection of diesel exhaust samples

- Heavy-duty diesel engine (Liebherr)
- ISO 8178/4 C1 test cycle
- All-glass sampling devices: quartz fiber filter, condensate separator, adsorbens
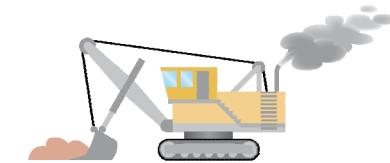
With or without exhaust treatment by DPF

DPFs: uncoated, cordierite-based, monolithic, wall-flow (Greentop)

- Iron-based fuel additive (catalyst)
- Copper/iron-based fuel additive
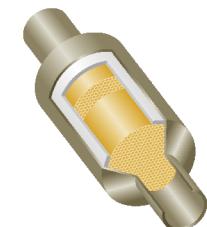
Analysis of exposure: CALUX assays + GC/HRMS

Bioassays:

- Aryl hydrocarbon receptor (AhR) agonists
- Estrogen receptor (ER) agonists

Generation of Diesel Exhaust

Heavy-duty diesel engine (Liebherr, type D914T, 6.11 L, 4 cylinders, 105 kW, Bulle, Switzerland), **ISO 8178/4 C1 test cycle**:
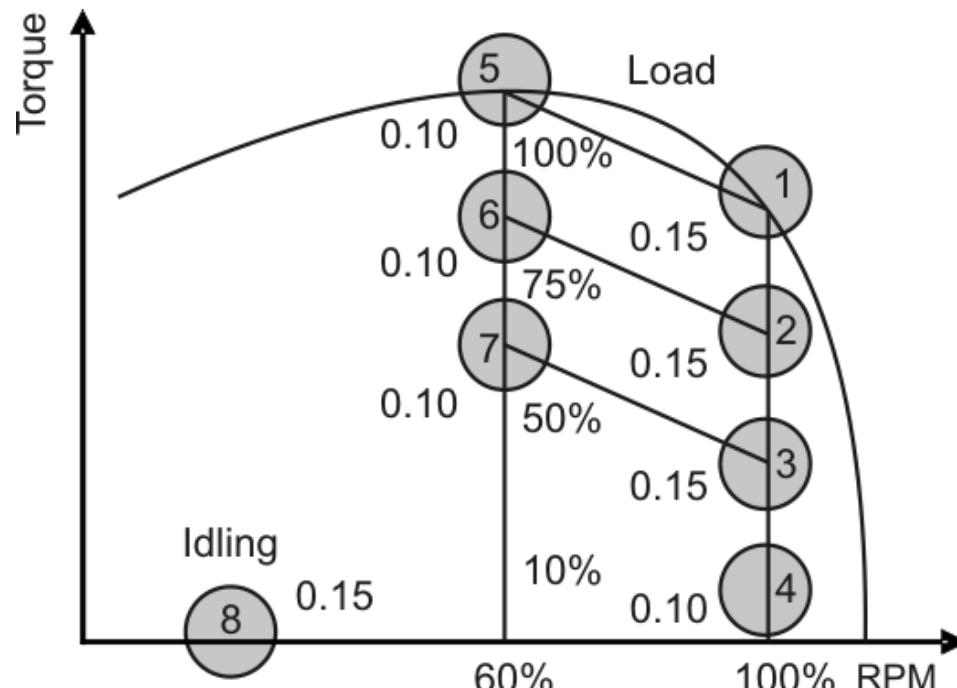
- 8 load-stages

- Total cycle time: 100 min

- 2 consecutive runs for each sample (200 min)

- Mass flow proportional aliquots of undiluted exhaust gas were taken at each load-stage (per sample: 4-7 m^3 exhaust).

Exhaust sampling: Fachhochschule Biel, Empa Dübendorf

Collection of Samples and Extraction

All-glass sampling device

Quarz fiber filter

Cooler

Adsorber unit, XAD-2 (< 4°C)

Ice bath

Unfiltered or filtered exhaust gas

Condensate separator
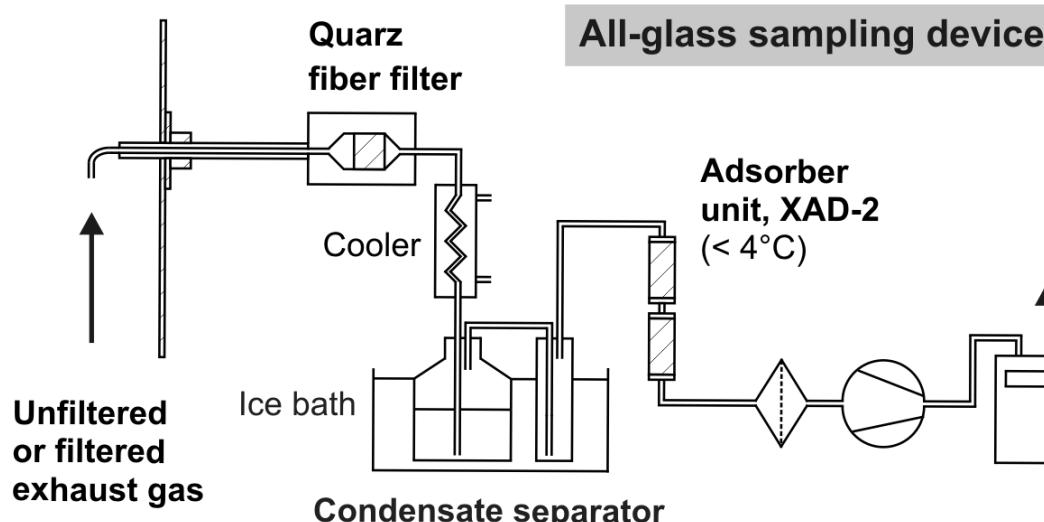
Exhaust treatment by diesel particulate filter (DPF)

DPFs: uncoated, cordierite-based, monolithic, wall-flow (100 CPI, 22.8 L, Greentop, Grävenwiesbach, Germany)

- Iron-based fuel additive (catalyst)
- Copper/iron-based fuel additive

Transfer to DMSO for **assay analysis**

Clean-up for **GC/HRMS**
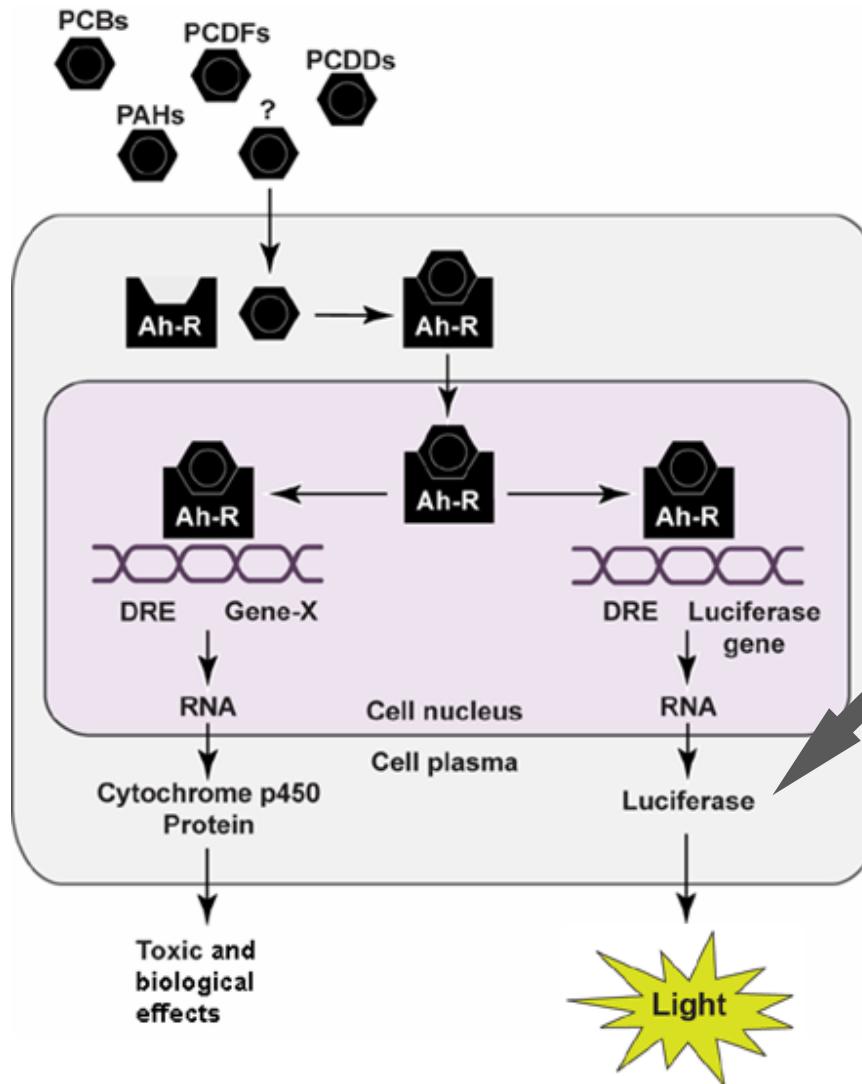
Chemically Activated
LUciferase gene eXpression
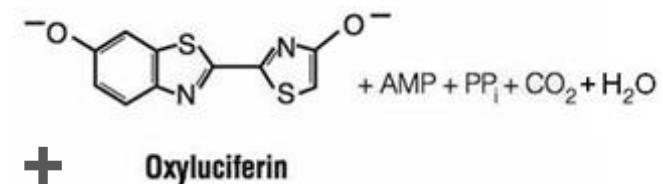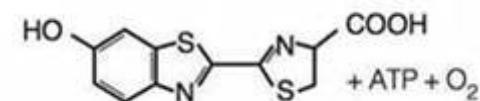
Human adenocarcinoma cells (T47D)
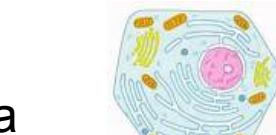
Rat hepatoma cells (H4IIE)

Seeding
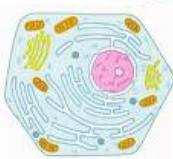
CALUX cells

Extracts of diesel exhaust in DMSO

Dilution series: E2 or 2,3,7,8-TCDD

24 h exposure

Calibration curve
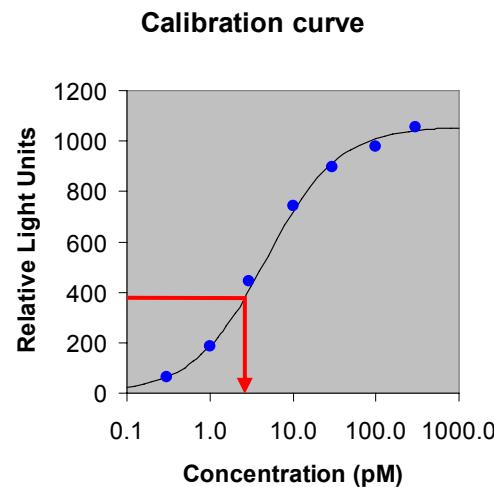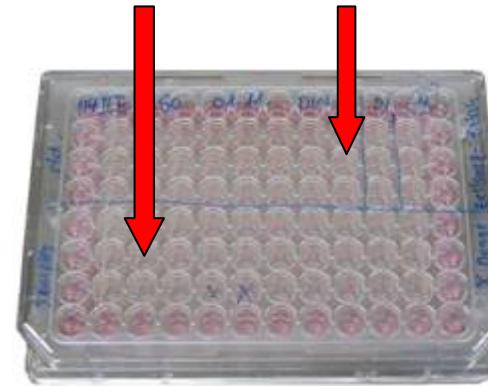
Toxicological information

Luminometer: Measurement of luciferase activity as light units

Samples: conversion of light units into 2,3,7,8-TCDD or E2 equivalents

Aryl Hydrocarbon Receptor (AhR) Agonists

AhR agonists induce a wide spectrum of biological effects**:**

Adaptive effect

- AhR-mediated degradation of toxic compounds (e.g., xenobiotics)

Adverse effects

- AhR-mediated biotransformation: mutagenic/carcinogenic metabolites (e.g., benzo[*a*]pyrene)

- Long-time activation of the AhR: dioxin-like toxicity of AhR agonists (e.g., loss of weight, chloracne)

- **Endocrine-disrupting effects** (e.g., antiestrogenic effects, antiandrogenic effects)

Quantification of AhR Agonists

2,3,7,8-TCDD concentration [pM]

Legend:
- 2,3,7,8-TCDD
- Unfiltered exhaust
- Filtered exhaust

Y-axis: **Luciferase induction [% 2,3,7,8-TCDD 300 pM]**

X-axis: **Diesel exhaust [m³]**
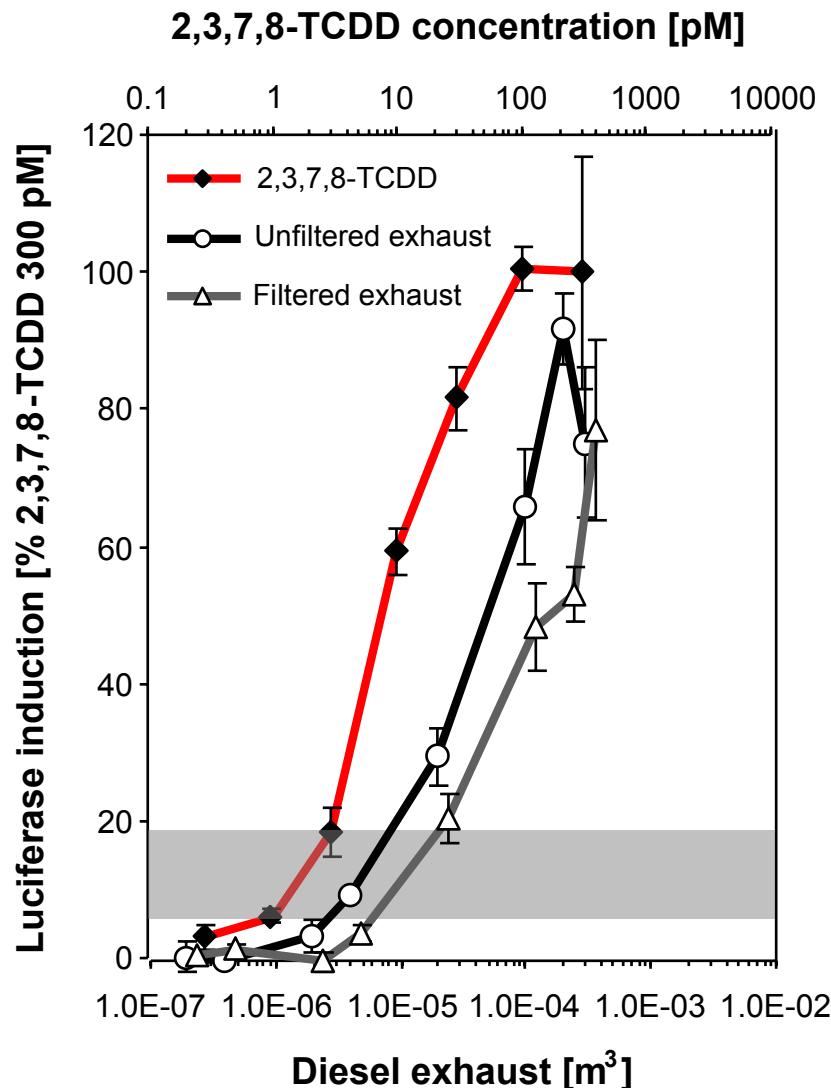
Aryl hydrocarbon receptor (AhR) agonists in diesel exhaust:

- Dose-dependent luciferase induction

- Dose-dependent response is similar to 2,3,7,8-TCDD

2,3,7,8-tetrachloro dibenzo-*p*-dioxin
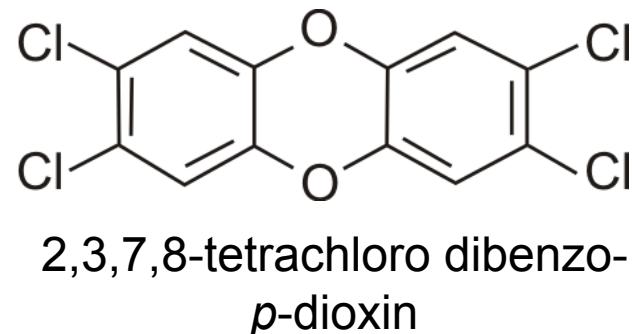
AhR Agonists in Diesel Exhaust
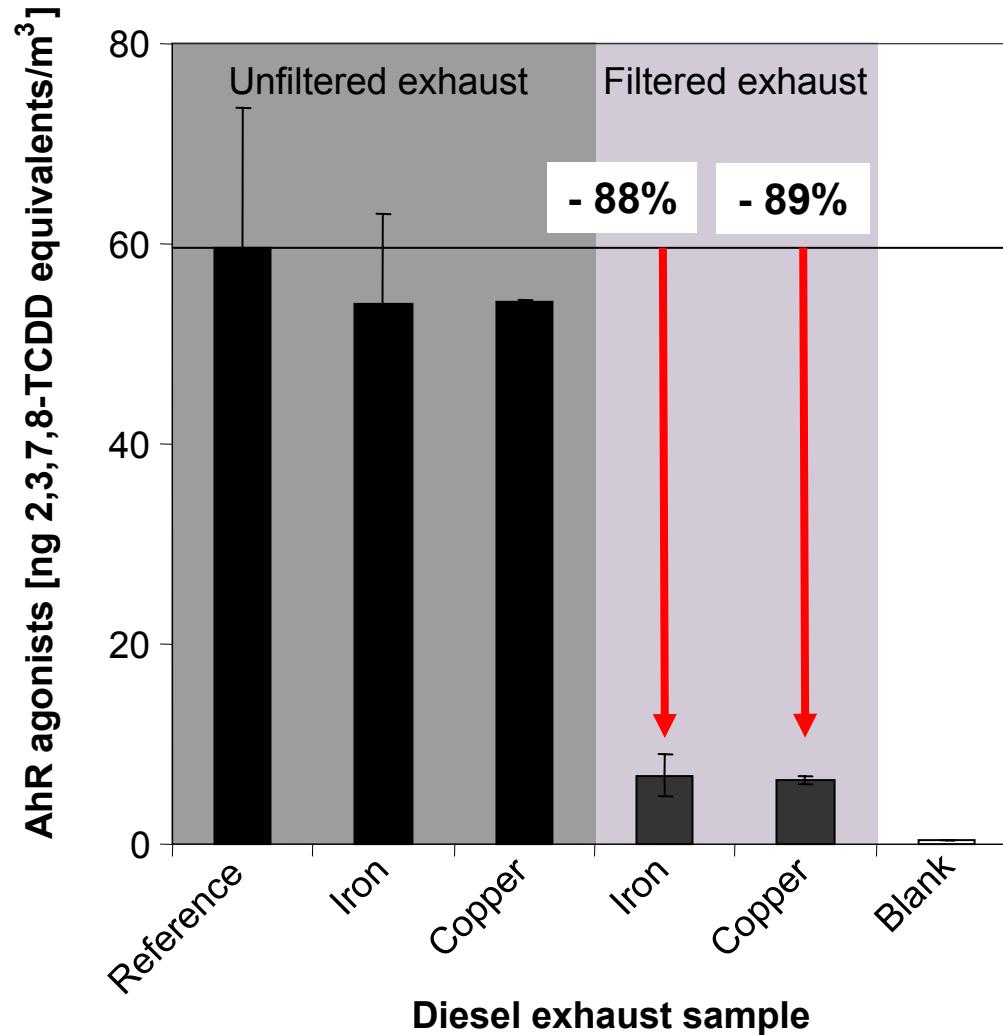
Air particulate matter (PM$_{10}$, Berne): 0.02 ng 2,3,7,8-TCDD equivalents/m^3 air

Diesel engines: a **relevant emission source** for AhR agonists in the air

Beneficial secondary effect of catalytic diesel particulate filters

Known AhR Agonists (GC/HRMS)
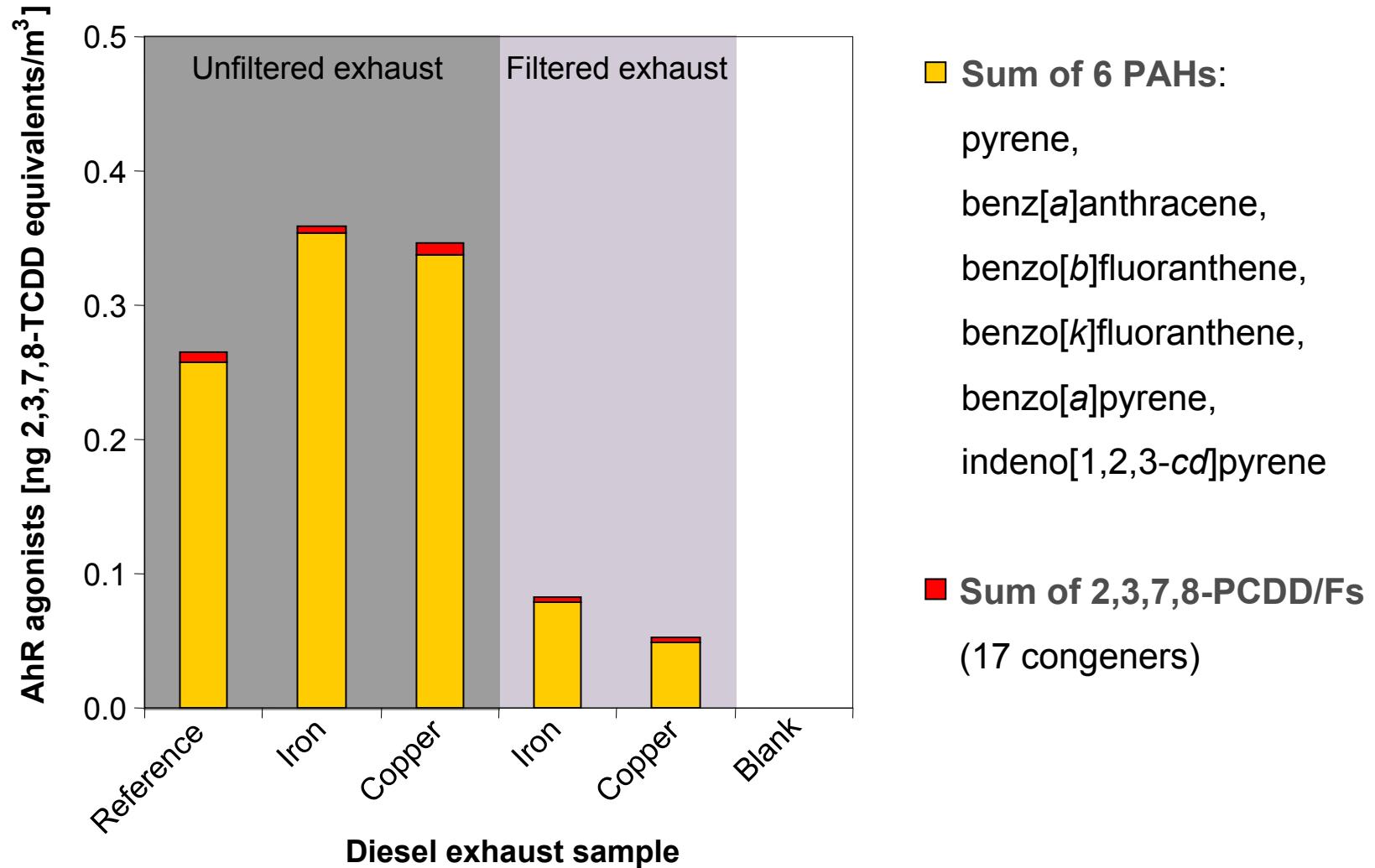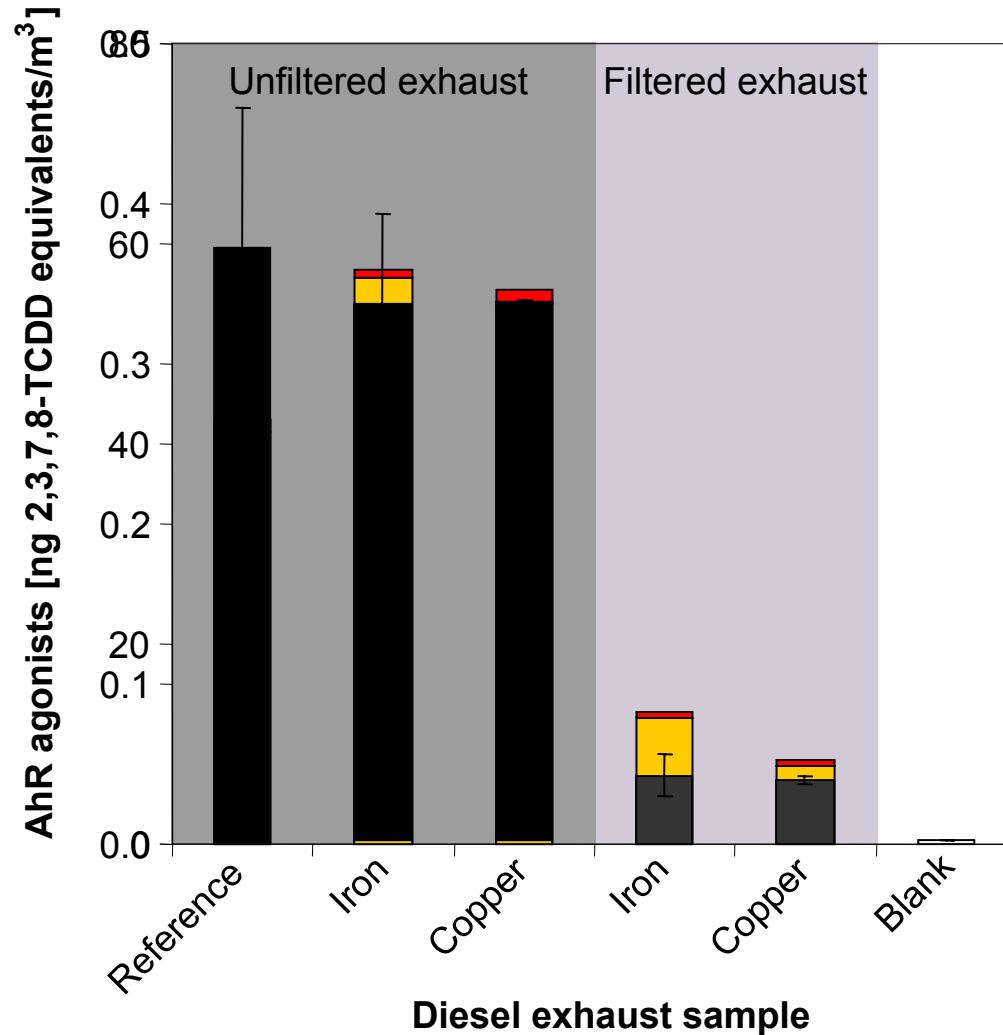
99% of the 2,3,7,8-TCDD equivalent concentration in unfiltered as well as in filtered exhaust is not explained

Estrogen Receptor (ER) Agonists

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Endogenous ER agonists (estrogens, female sex hormones)

- Function: promote the development of female secondary sex characteristics, regulate functions of the reproductive system in females and males

Exogenous ER agonists (xeno-estrogens)

- Disruption of female and male hormone systems (e.g., impaired reproduction)

Quantification of ER Agonists

E2 concentration [pM]

Legend:
- E2
- Unfiltered exhaust
- Filtered exhaust

Y-axis: **Luciferase induction [% E2 60 pM]**
X-axis: **Diesel exhaust [m^3]**
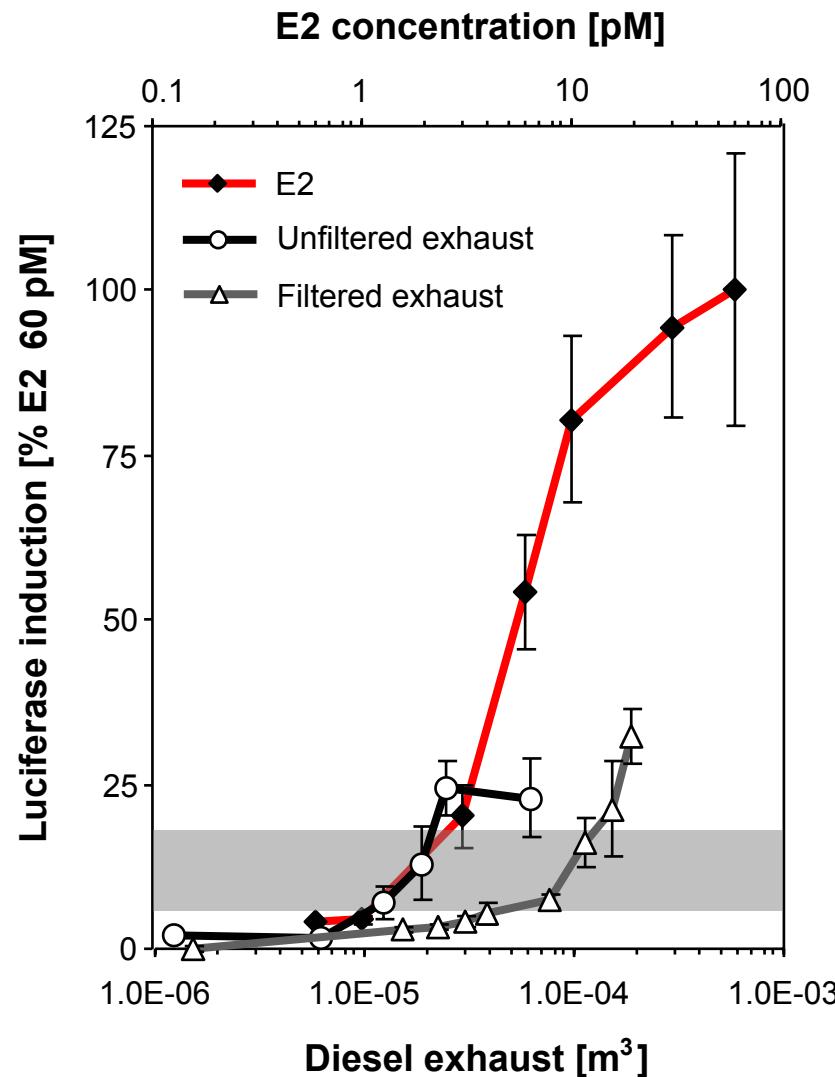
Estrogen receptor (ER) agonists in diesel exhaust:

- Dose-dependent luciferase induction

- Dose-dependent response is similar to E2

17β-estradiol (E2)
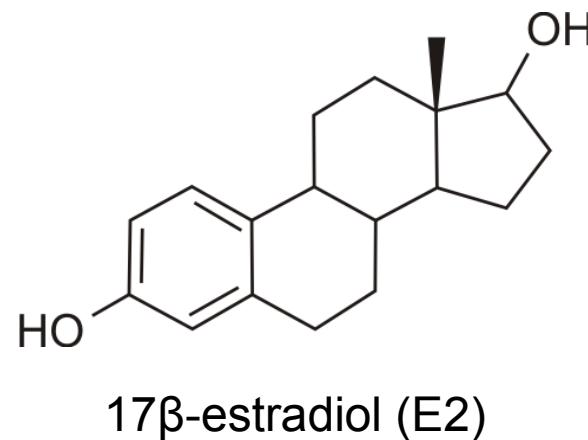
ER Agonists in Diesel Exhaust
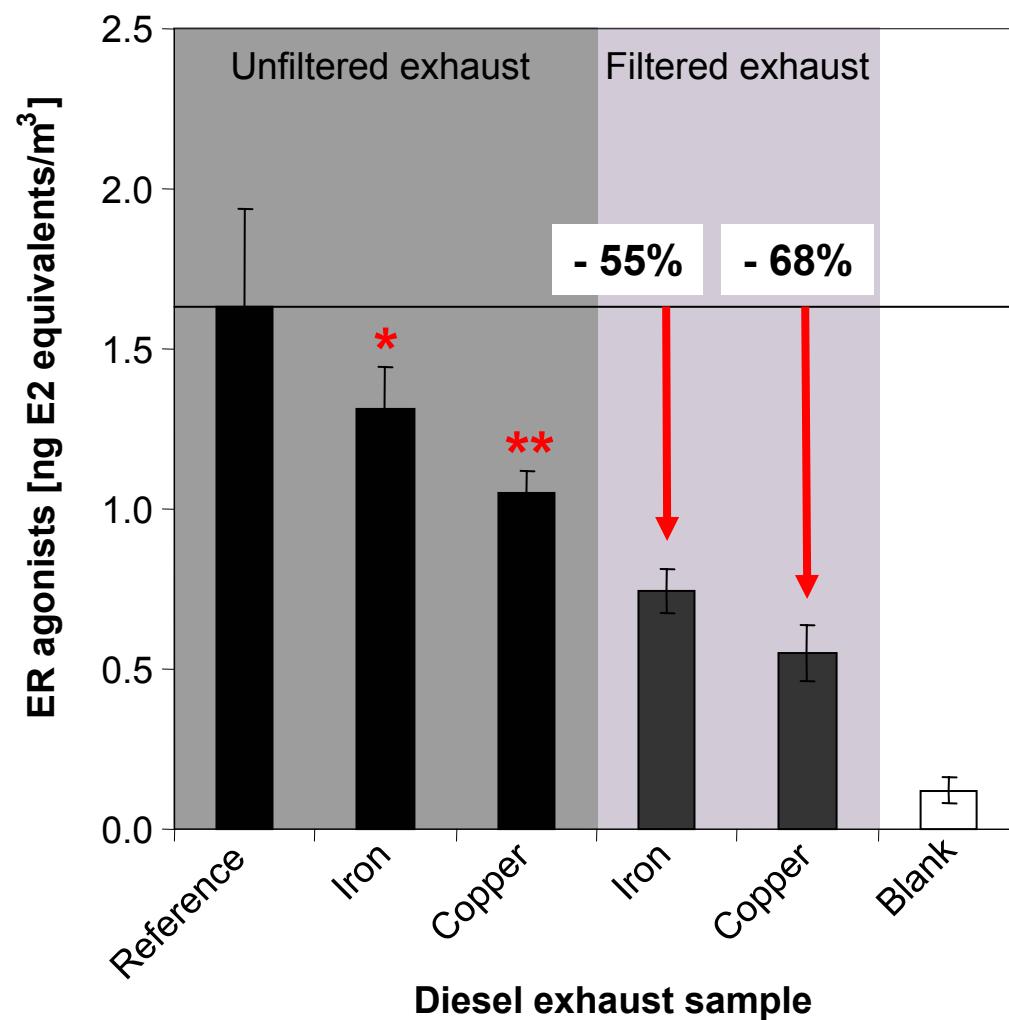
Air particulate matter (PM$_{10}$, Berne): 5×10^{-7} ng E2 equivalents/m^3 air

Diesel engines: a **relevant emission source** for ER agonists in the air

Beneficial secondary effect of catalytic diesel particulate filters

Summary and Conclusions

Emissions of diesel engines

- Relevant source of potential endocrine disruptors in the air

Secondary effects of catalytic diesel particulate filters

- Reduced emissions of AhR agonists
  by almost 90%

- Reduced emissions of ER agonists by
  55-70%

- Promising technology to detoxify diesel exhaust in
  respect to pollutants with AhR- or ER-mediated activity
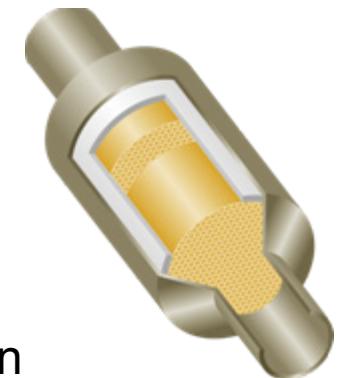
Wenger et al., submitted, 2007

THANK YOU FOR YOUR ATTENTION
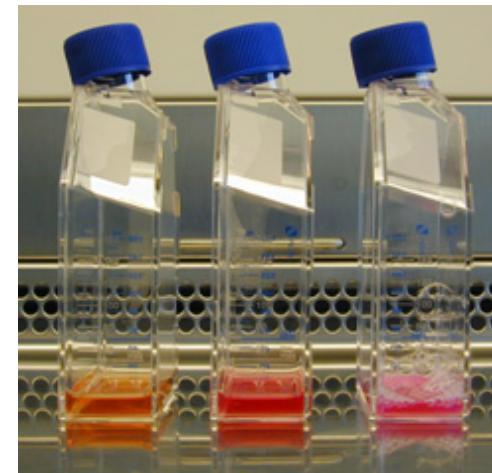
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