Secondary Effects of Catalytic Diesel Particulate Filters:

Reduced Emissions of Potential Endocrine Disruptors

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What will be shown?

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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

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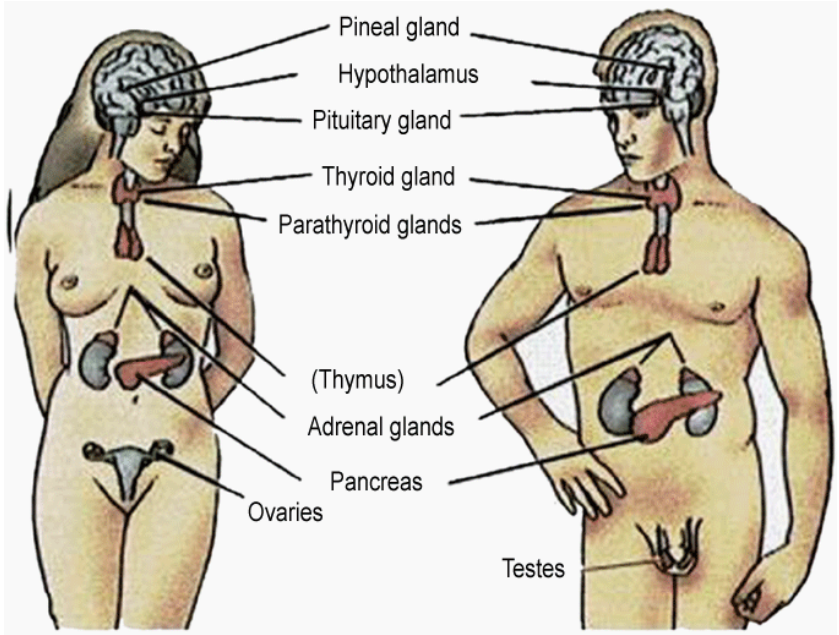
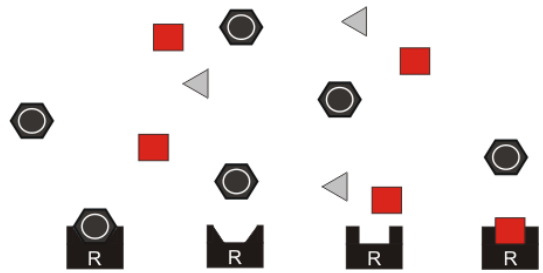
Hormones: endogenous chemical messengers

- 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

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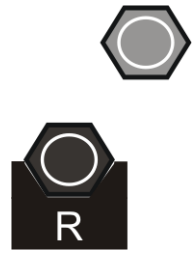
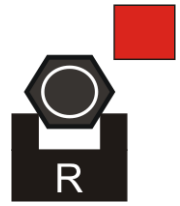
Endocrine disruptors:
natural or man-made exogenous compounds

- 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: A Pathway for Exposure to EDs

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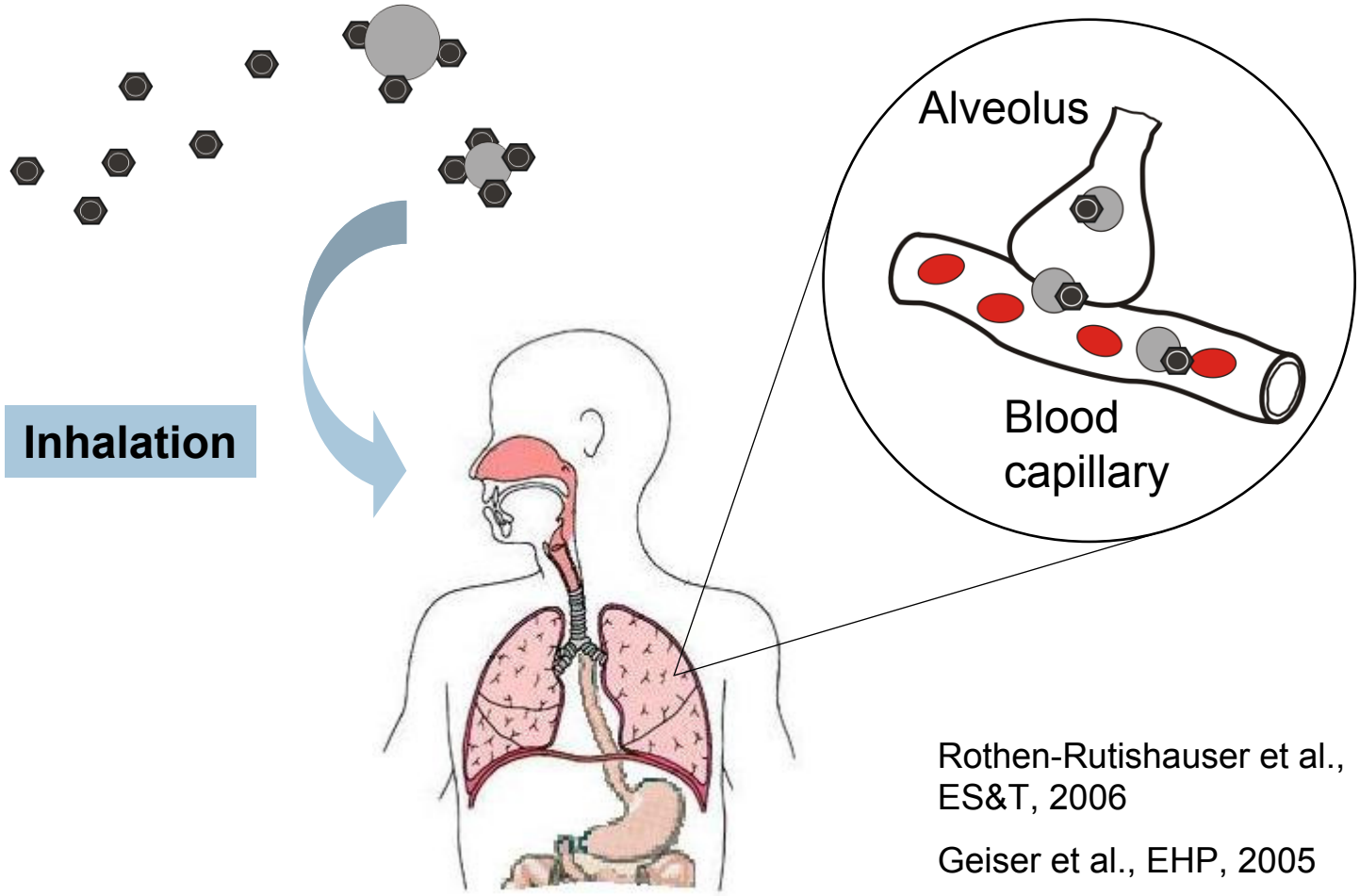

Rothen-Rutishauser et al., ES&T, 2006

Geiser et al., EHP, 2005

Diesel Exhaust: Endocrine Disruptors?

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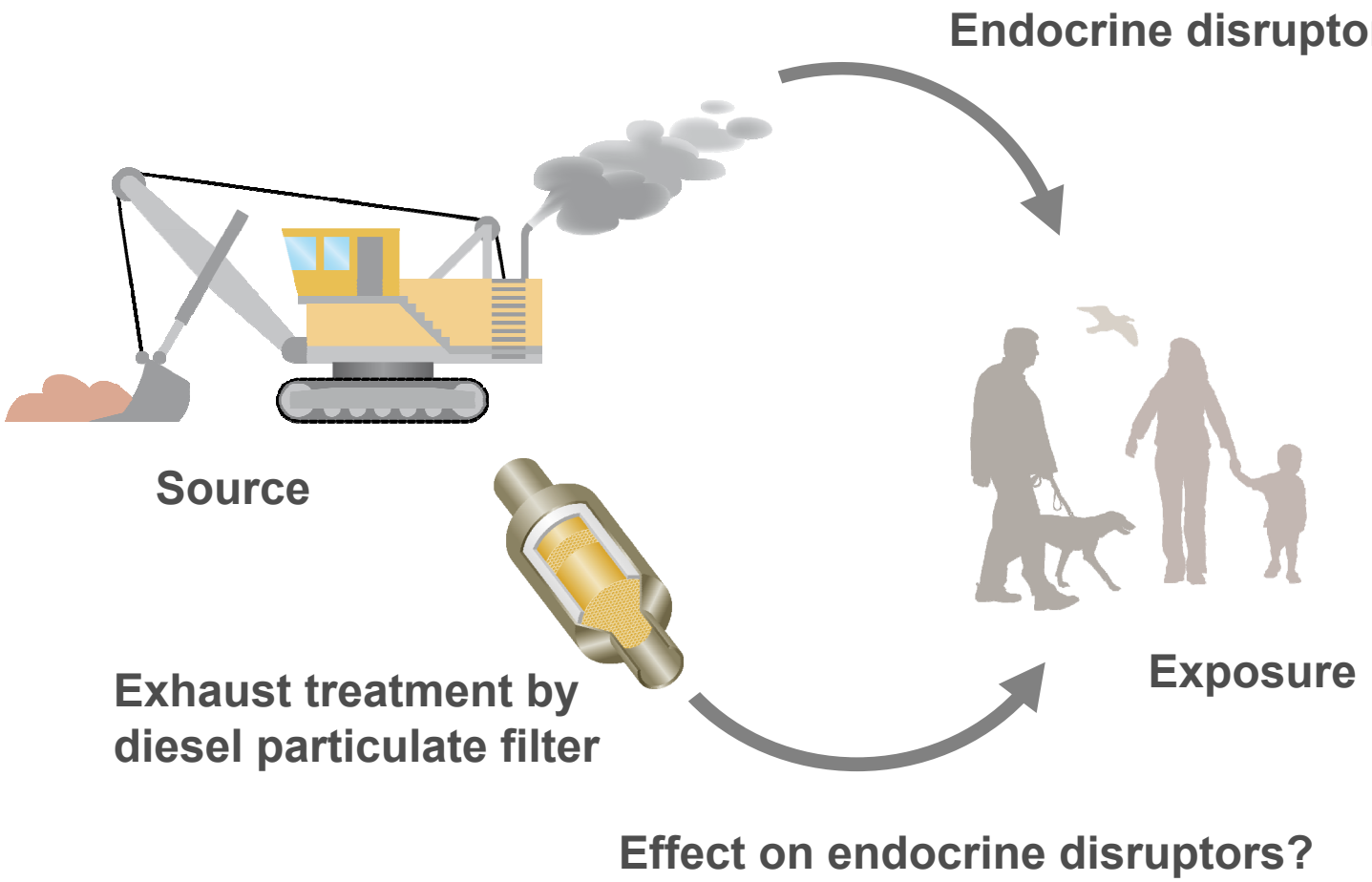

Diesel Exhaust: Endocrine Disruptors?

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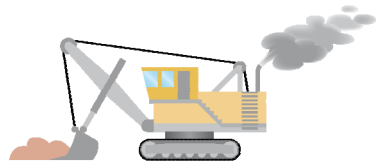
Collection of diesel exhaust samples

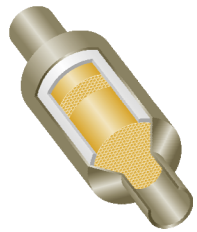
- Heavy-duty diesel engine (Liebherr)
- ISO 8178/4 C1 test cycle
- All-glass sampling devices: quartz fiber filter, condensate separator, adsorbens



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



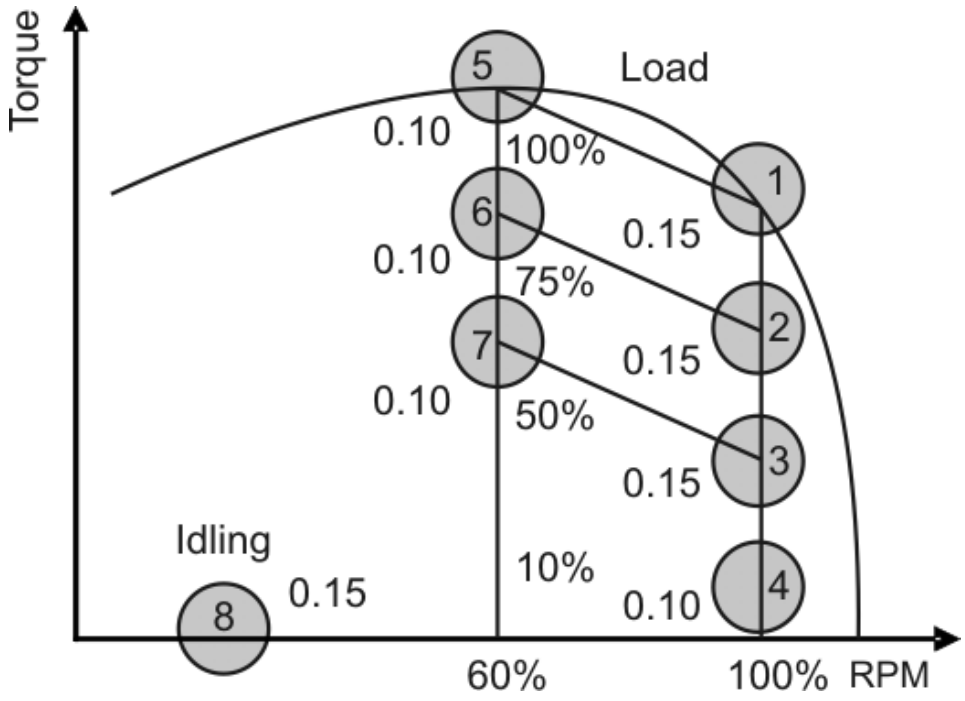
Analysis of exposure: CALUX assays + GC/HRMS

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

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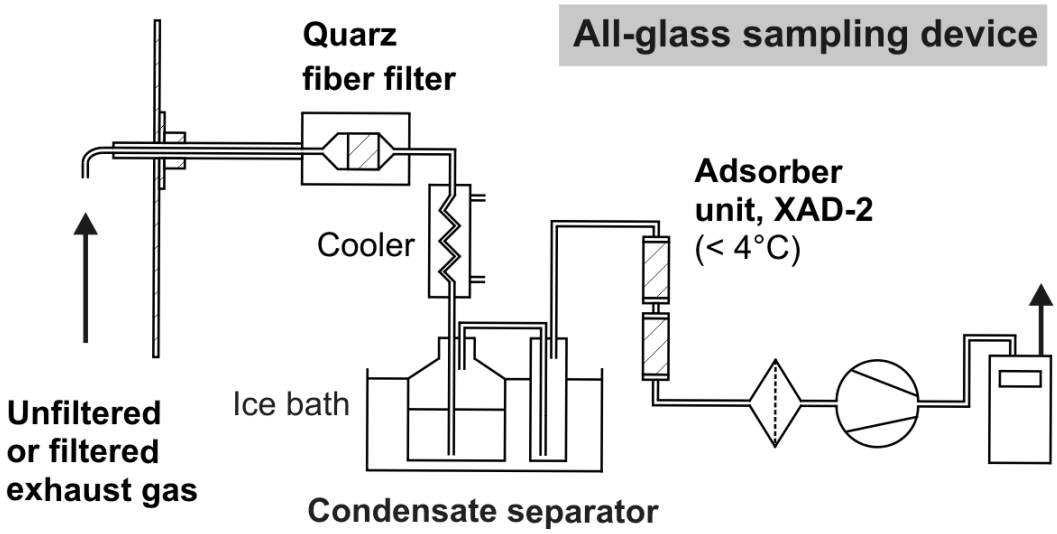
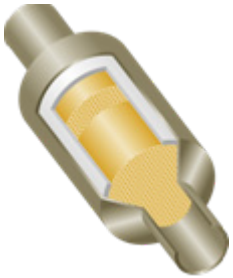


Transfer to DMSO for **assay analysis**

Clean-up for **GC/HRMS**

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

Reporter Gene Assays – CALUX Assays

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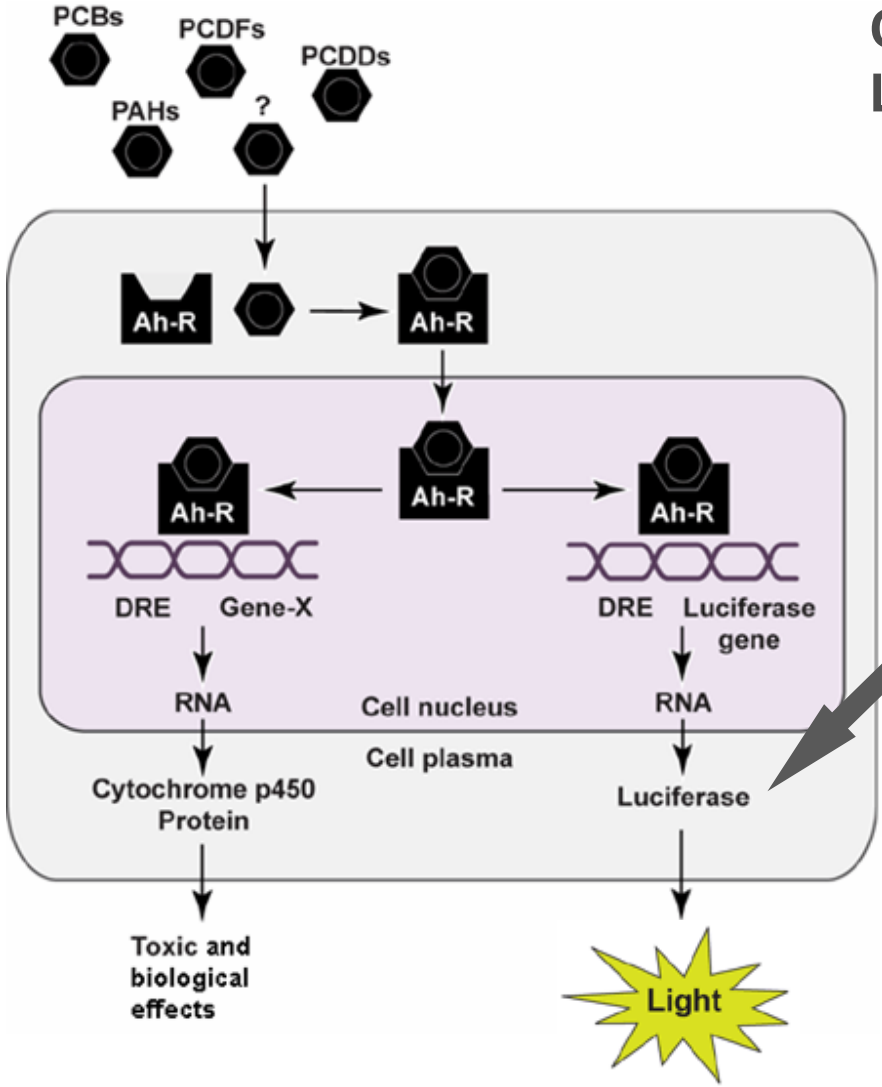
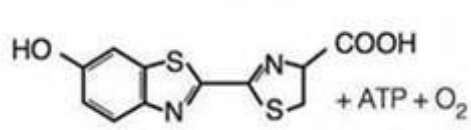
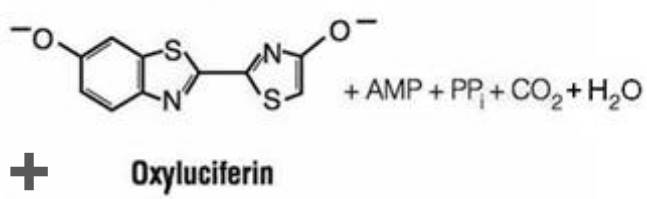
Chemically **A**ctivated
LUciferase gene e**X**pression







Assay Analysis of Exhaust Samples

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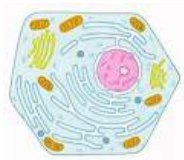
Human adenocarcinoma cells (T47D)

Rat hepatoma cells (H4IIE)

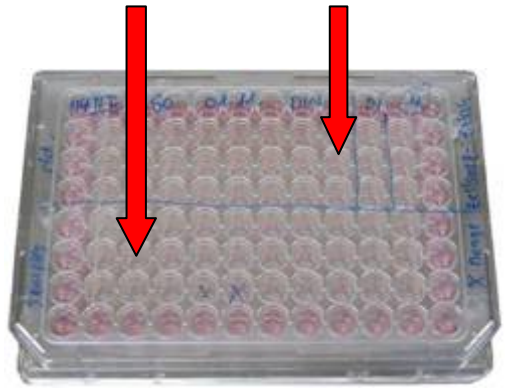


Seeding

CALUX cells

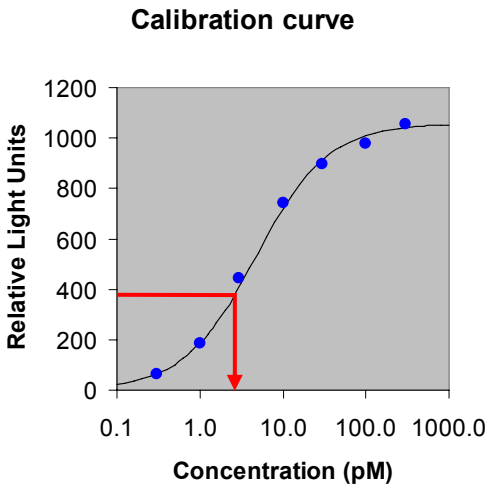
Extracts of diesel exhaust in DMSO

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



24 h exposure

Toxicological information



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

Luminometer: Measurement of luciferase activity as light units

Aryl Hydrocarbon Receptor (AhR) Agonists

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AhR agonists induce a wide spectrum of biological effects:

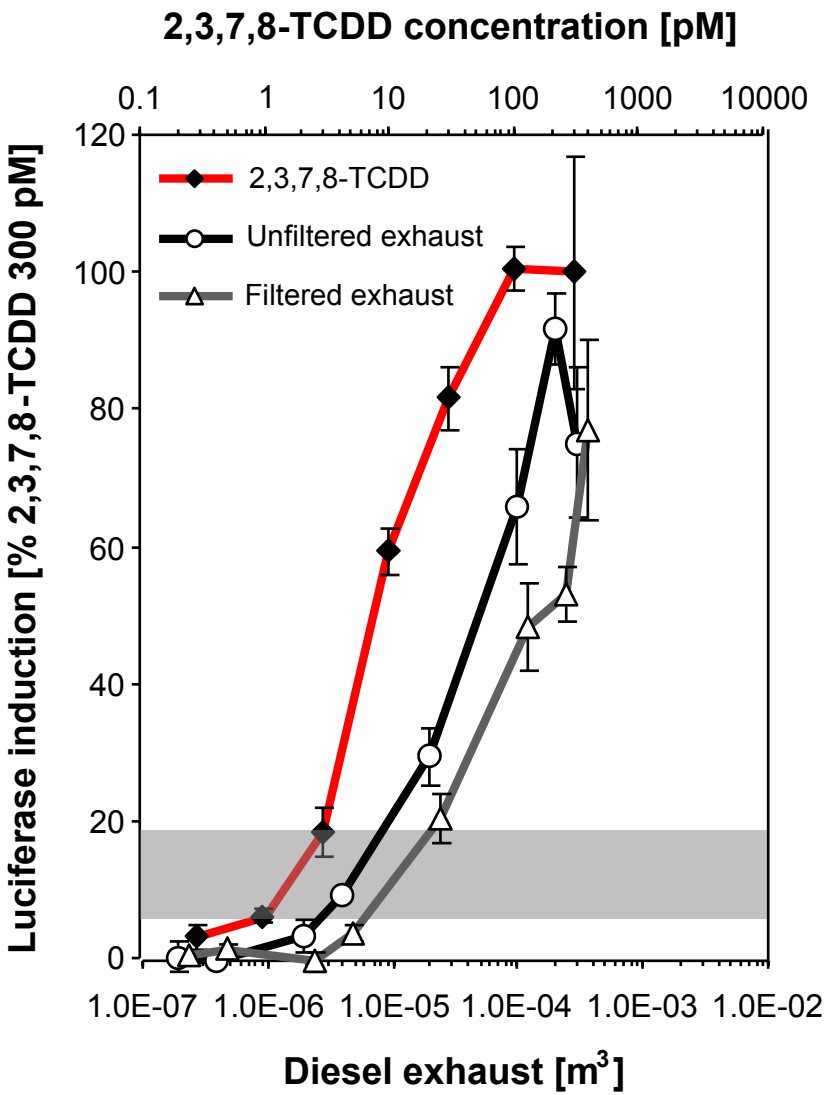
Adaptive effect

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

Adverse effects

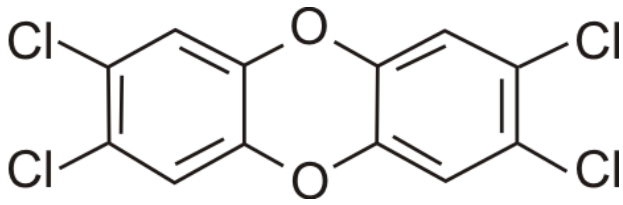
- AhR-mediated biotransformation: mutagenic/carcinogenic metabolites (e.g., benzo[*a*]pyrene)
- Long-time activation of the AhR: dioxin-like toxicity of AhR agonists (e.g., loss of weight, chloracne)
- **Endocrine-disrupting effects** (e.g., antiestrogenic effects, antiandrogenic effects)

Quantification of AhR Agonists



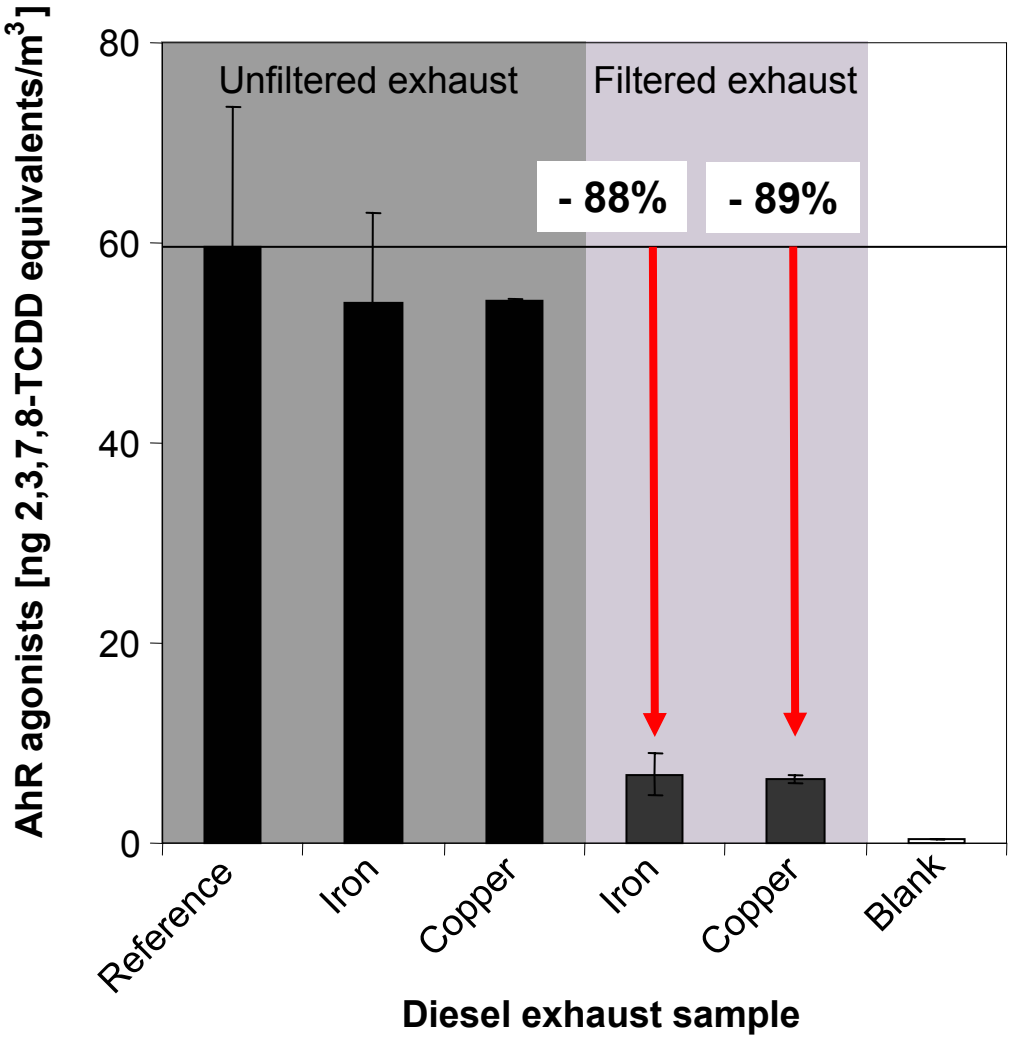
Aryl hydrocarbon receptor (AhR) agonists in diesel exhaust:

- 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

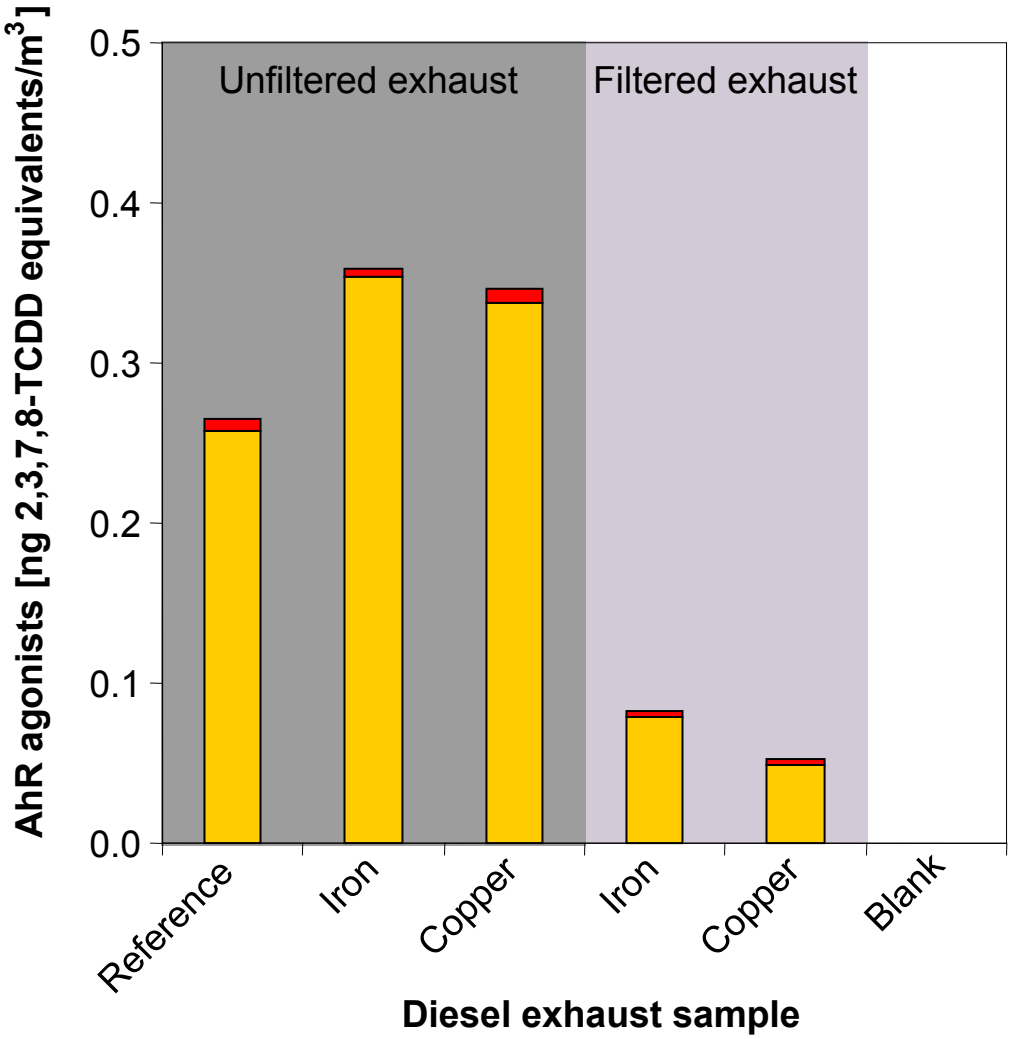


Air particulate matter (PM_{10}, Berne): 0.02 ng 2,3,7,8-TCDD equivalents/m^3 air

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

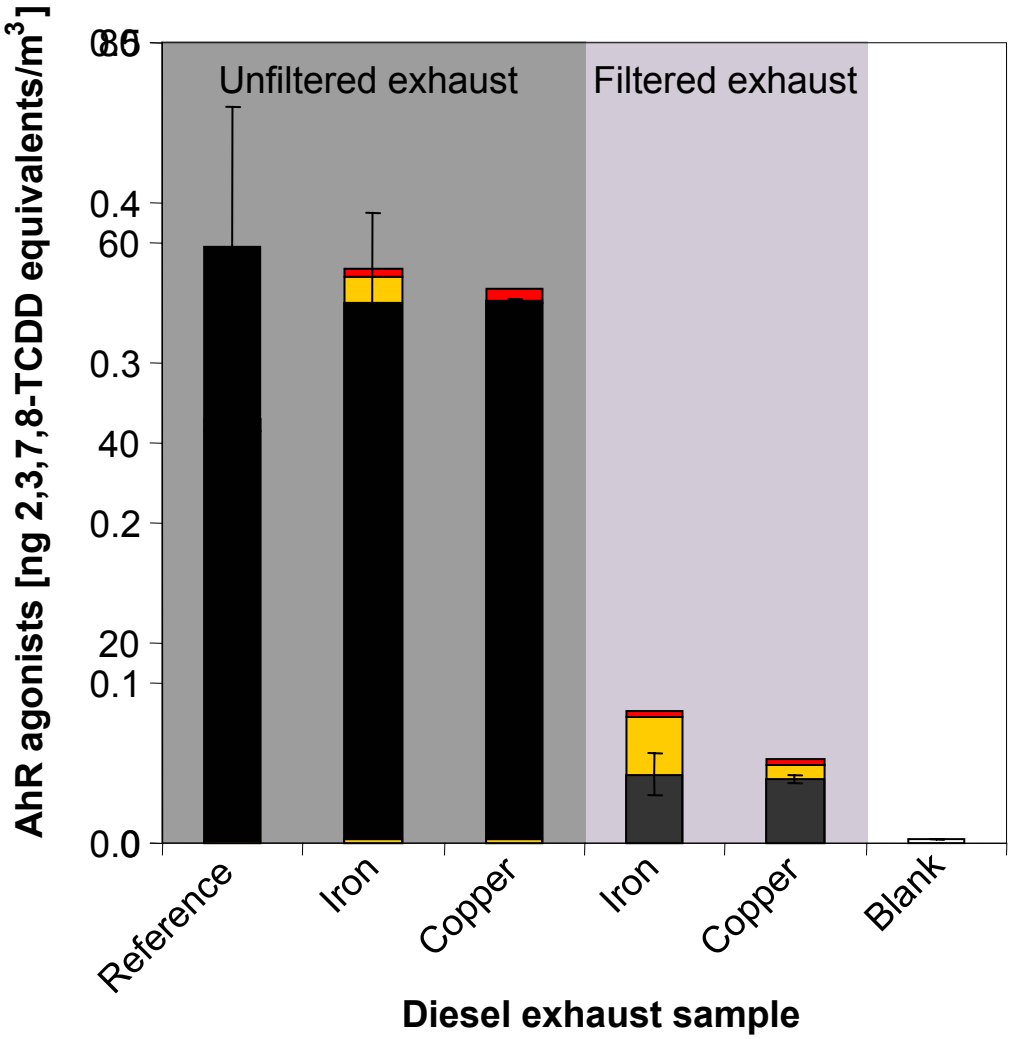
Beneficial secondary effect of catalytic diesel particulate filters

Known AhR Agonists (GC/HRMS)



- **Sum of 6 PAHs**:
  pyrene,
  benz[*a*]anthracene,
  benzo[*b*]fluoranthene,
  benzo[*k*]fluoranthene,
  benzo[*a*]pyrene,
  indeno[1,2,3-*cd*]pyrene
- **Sum of 2,3,7,8-PCDD/Fs**
  (17 congeners)

Contribution of 6 PAHs and 12 PCDD/Fs



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

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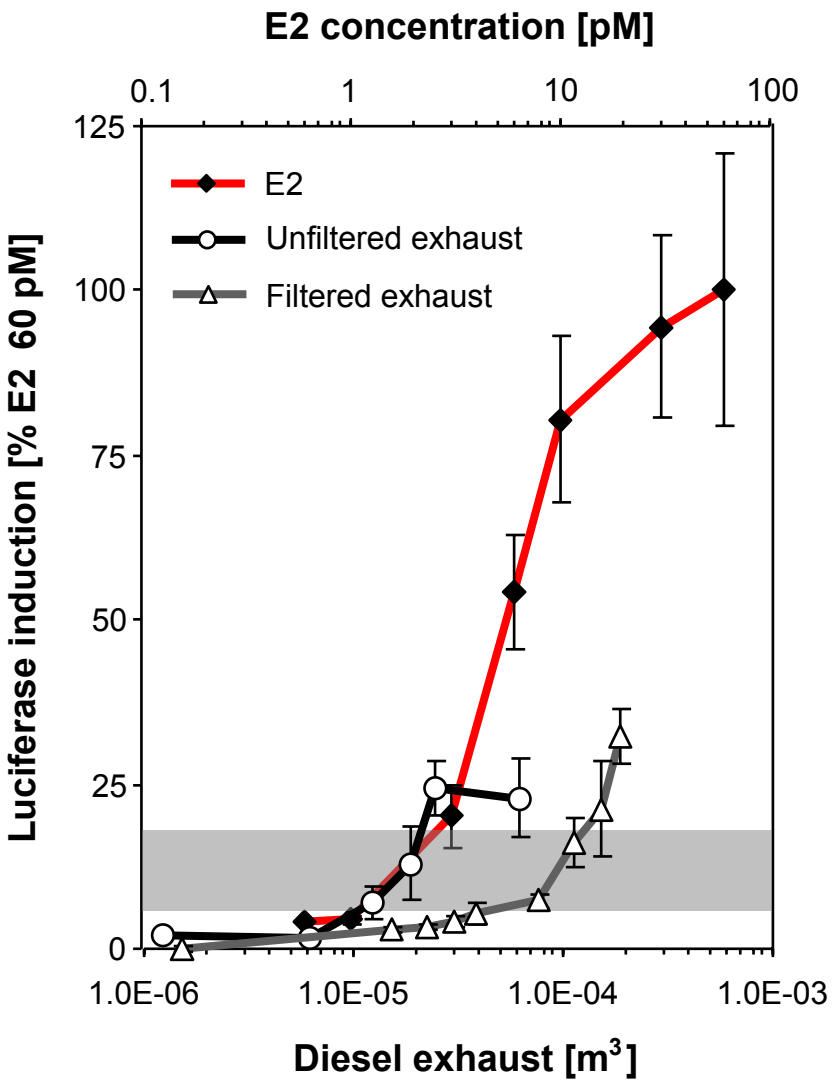
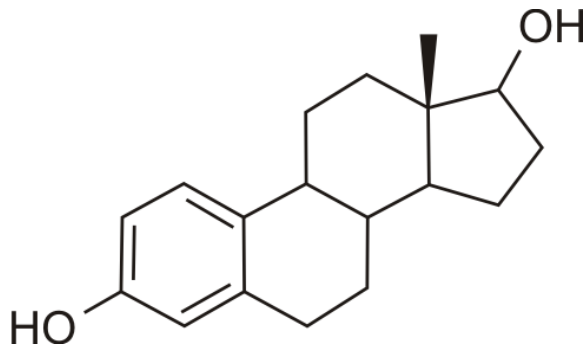


Estrogen receptor (ER) agonists in diesel exhaust:

- Dose-dependent luciferase induction
- Dose-dependent response is similar to E2



17β-estradiol (E2)

ER Agonists in Diesel Exhaust

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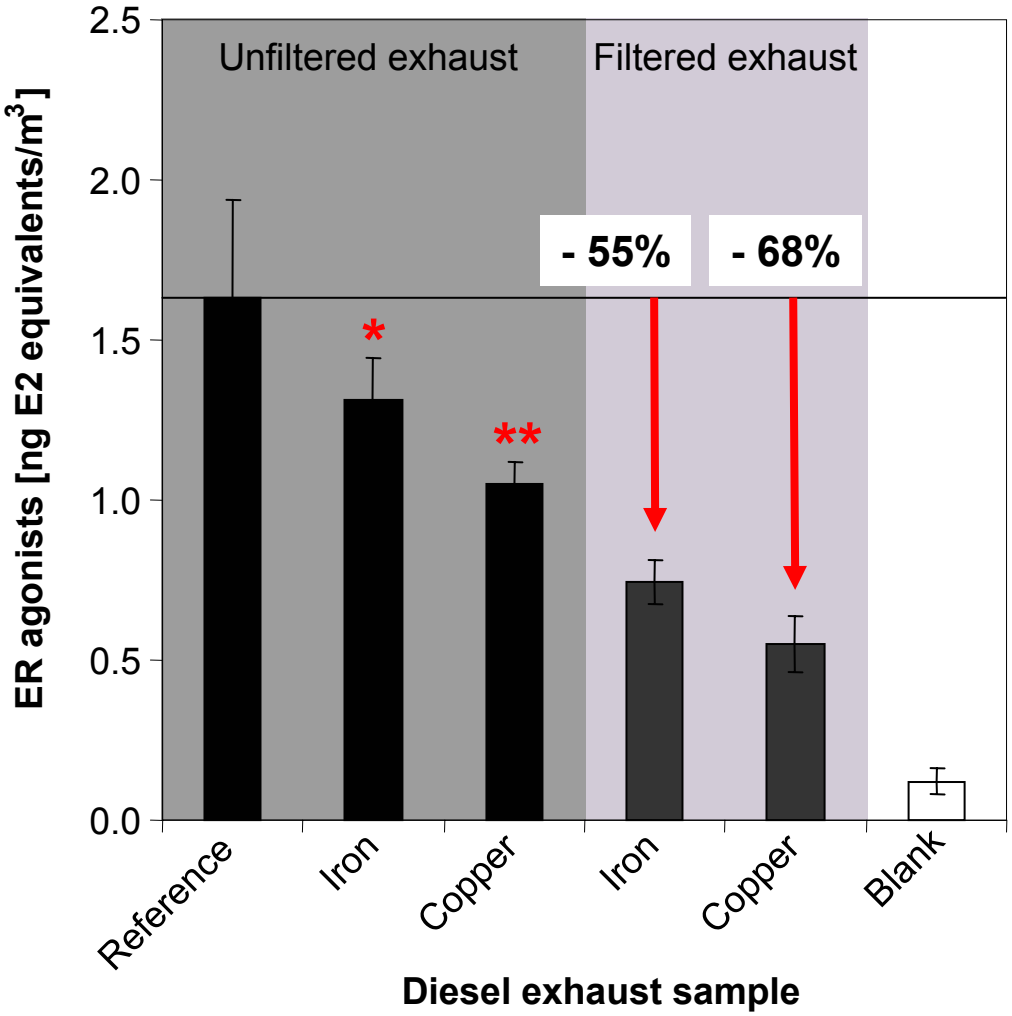

Air particulate matter (PM_{10}, Berne): $5*10^{-7}$ ng E2 equivalents/m^3 air

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

Beneficial secondary effect of catalytic diesel particulate filters

Summary and Conclusions

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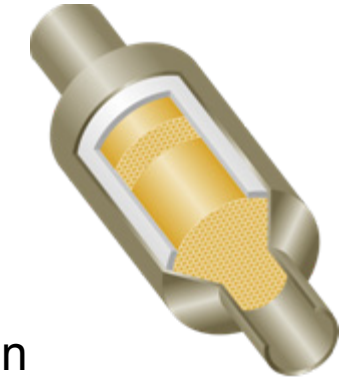
Emissions of diesel engines

- 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

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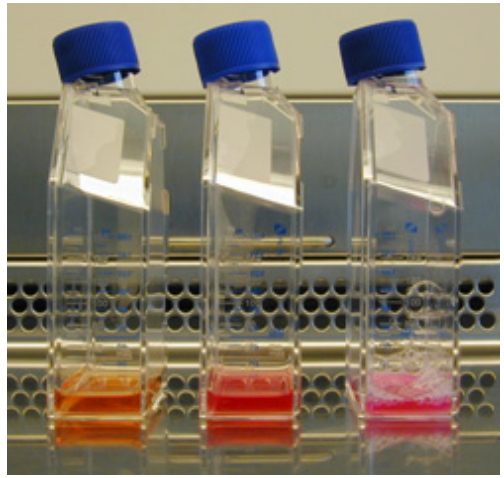
THANK YOU FOR YOUR ATTENTION



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back to index