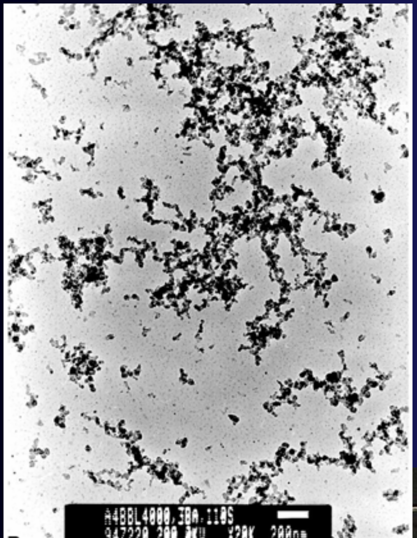
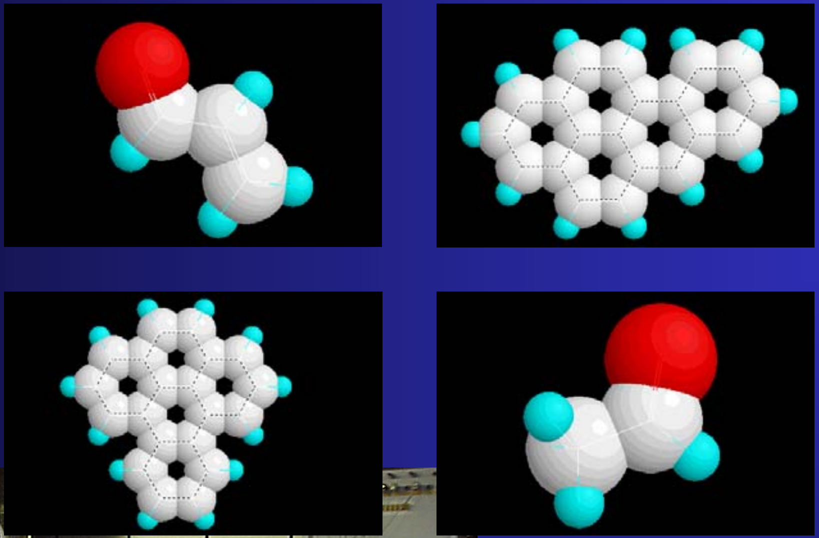
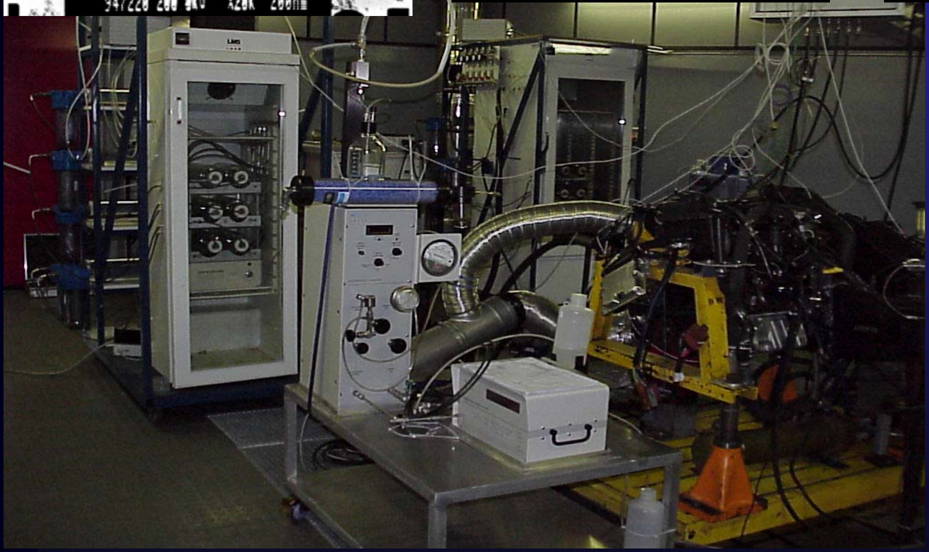
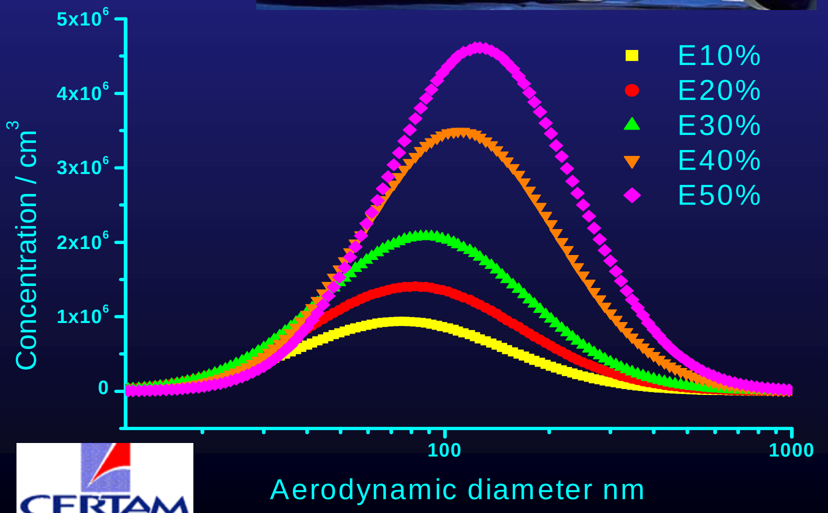
Pro-Oxidant Impacts of Diesel Engine Emissions according to Fuel and After-treatment Strategies









9th ETH Conference on Combustion Generated Nanoparticles

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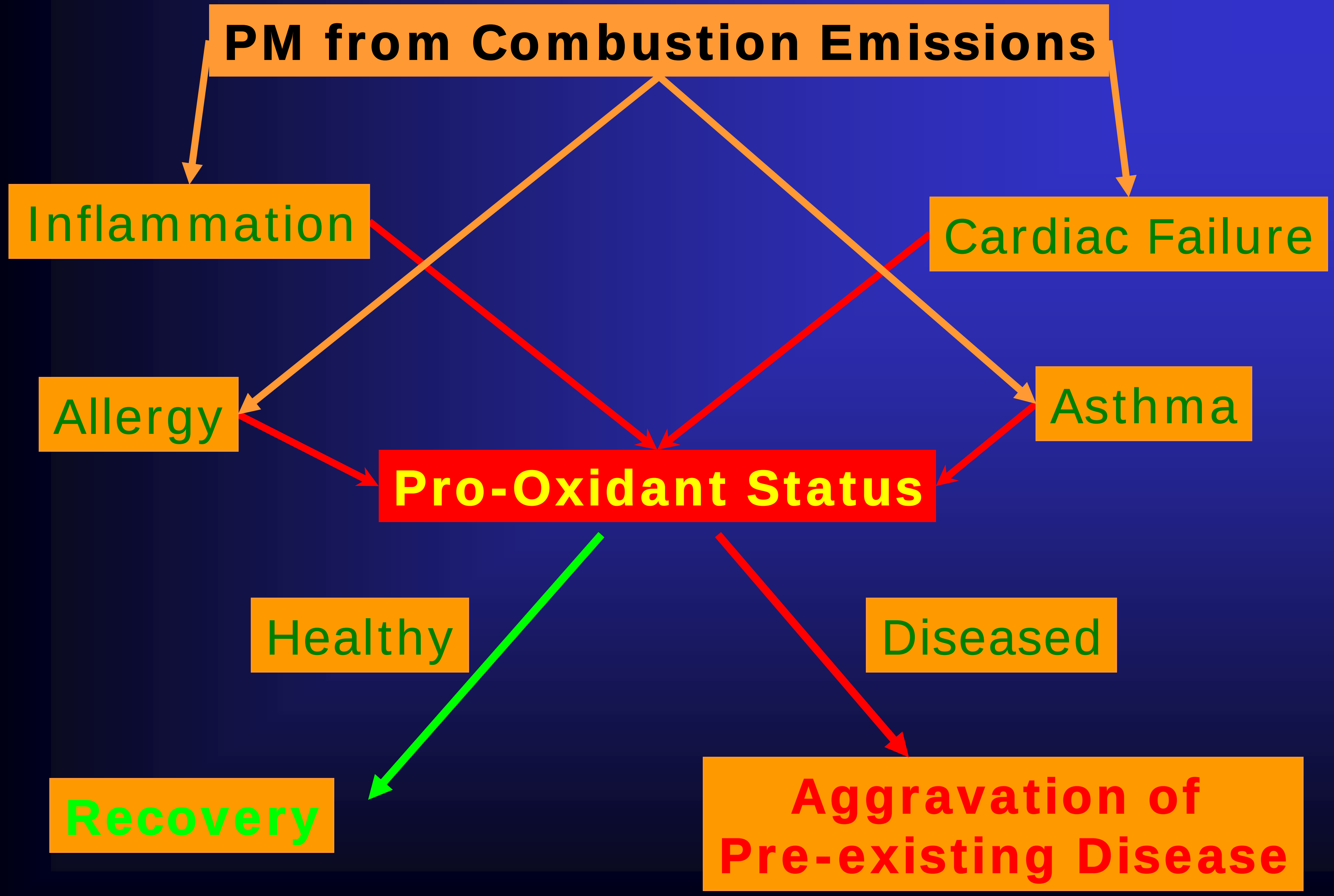

PM from Combustion Emissions

Inflammation

Cardiac Failure

Allergy

Asthma

Pro-Oxidant Status

Healthy

Diseased

Recovery

Aggravation of Pre-existing Disease

Choice of Exposure Strategy

in vivo Inhalation / *in vivo* Instillation

Bi-phasic models
Air / Liquid *in vitro*

/

PM resuspended in
aqueous solutions *in vitro*

Global Approach

Partial Approach

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OPTIMISED and STANDARDISED Combustion Aerosol Sampling Dilution Systems *In vitro* and *in vivo* Exposure Designs

*** Interactions Aerosol/Biological sample mimicking the in vivo situation (low flow velocity at biological interface)**

*** No alteration of both gazeous phase and PM physicochemical properties**

*** No Alteration of pollutant Bioavailibility**

*** Global Approach of Exhaust impact : gas + PM**

Toxicity Endpoints

-**Cell viability** :

Intracellular ATP content

- **Oxidative stress and Detoxication** :

Intracellular glutathione content (GSH)

Enzyme activity of SOD, Catalase, GPx, GST

8-hydroxy-2'-deoxyguanosin (histological staining)

- **Inflammatory response** :

TNFα (release in culture medium)

ICAM-1 (histological staining)

-**Apoptosis :**

-Nucleosome Assay

-TUNEL (histological staining)

-DNA Ladders

Modulation of Engine Emissions Quality

2liters 4 Cylinder in line Euro 3 Car engine

Fuel, Engine load, DPF, « Treatment »

Modulation of CO, NOx, HC, PM

Diesel Engine Emissions

⇨ Exhaust Characteristics

Gas Phase	A	B	C	D	E	F	G	H
HC (ppm)	29	29	19	19	10	10	0	0
CO (ppm)	137	137	0	0	0	0	0	0
NOx (ppm)	423	423	406	406	467	467	484	484
NO_2 (ppm)	**24**	**24**	**106**	**106**	**191**	**191**	**260**	**260**
NO (ppm)	399	399	300	300	277	277	224	224
NO_2 / NOx	**0.06**	**0.06**	**0.26**	**0.26**	**0.41**	**0.41**	**0.54**	**0.54**

Oxidant Potential →

Smoke Index	A	B	C	D	E	F	G	H
FSN	1.8	ND	1.8	ND	0.7	ND	0.7	ND
mg/m^3	44	ND	44	ND	12	ND	12	ND

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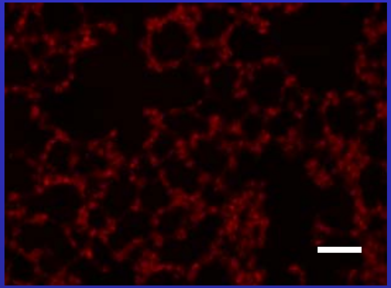
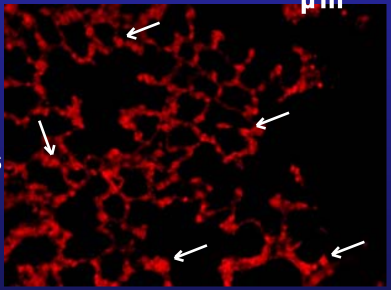
Detoxication Systems, Anti-oxidant Defenses

		A,B	C,D	E,F	G,H
Detoxication Systems	GSH	↘	↘	↘	↘
	GST	↗	↗	=	=
Oxidant Stress	GPx	↗	↗	↗	↗
	Catalase	=	=	↗	↗
	MnSOD	↗	↗	=	=
	8-oxoguanine	+	+	+	+
		Low NO_2/NOx		High NO_2/NOx	



Control



Diesel

- ⇨ **Distinct Profiles According to NO_2 / NOx Ratio**
- ⇨ **Predominant impact of gaseous phase**
- ⇨ **Oxidant stress is main toxic figure in response profile**

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RESULTS OF IN VIVO EXPERIMENTS
Systemic oxidant stress status

ORGAN	DIS50/10W40	DIS0/5W30
	CF	*CF*
HEART	*(12)*	*(12)*
GPx	=	↘
LIVER	*(12)*	*(12)*
Catalase	↗ ↗	=
GST	↗ ↗	↗
GPx	↗	↗
KIDNEY	*(12)*	*(12)*
Catalase	↗	↗
GST	↗ ↗	↗

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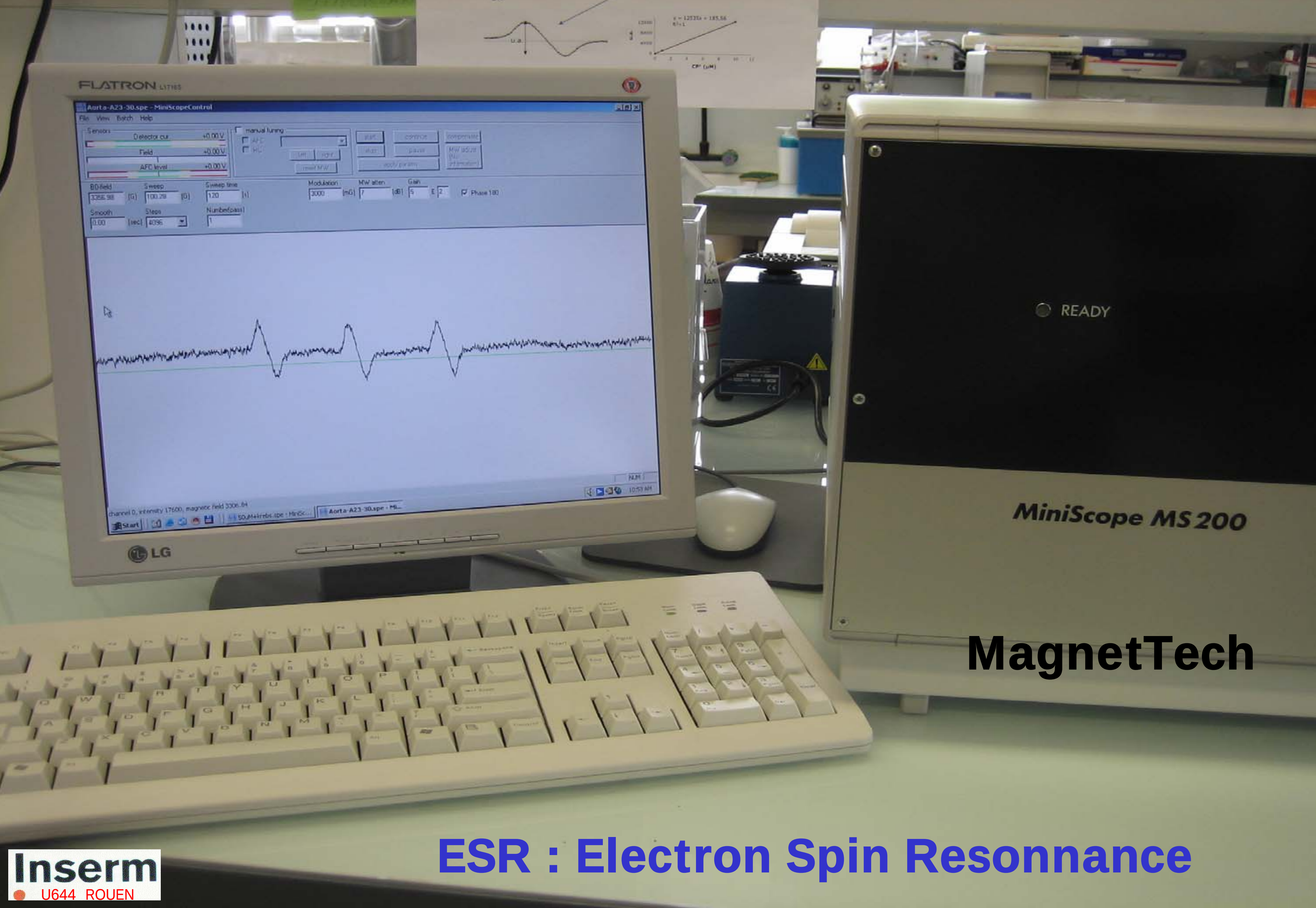
Oxidant stress related to Emission Oxidant Potential based on NO_2/Nox ratio appears to be a **major toxicity trigger from gas Phase**

Reducing fuel sulphur content
Using oxidation catalysis

↗ NO_2/Nox ratio

Hypothesis of Reactive Oxygen Species (ROS) occurrence in combustion aerosols
As candidates for triggering oxidant stress



MagnetTech

ESR : Electron Spin Resonnance

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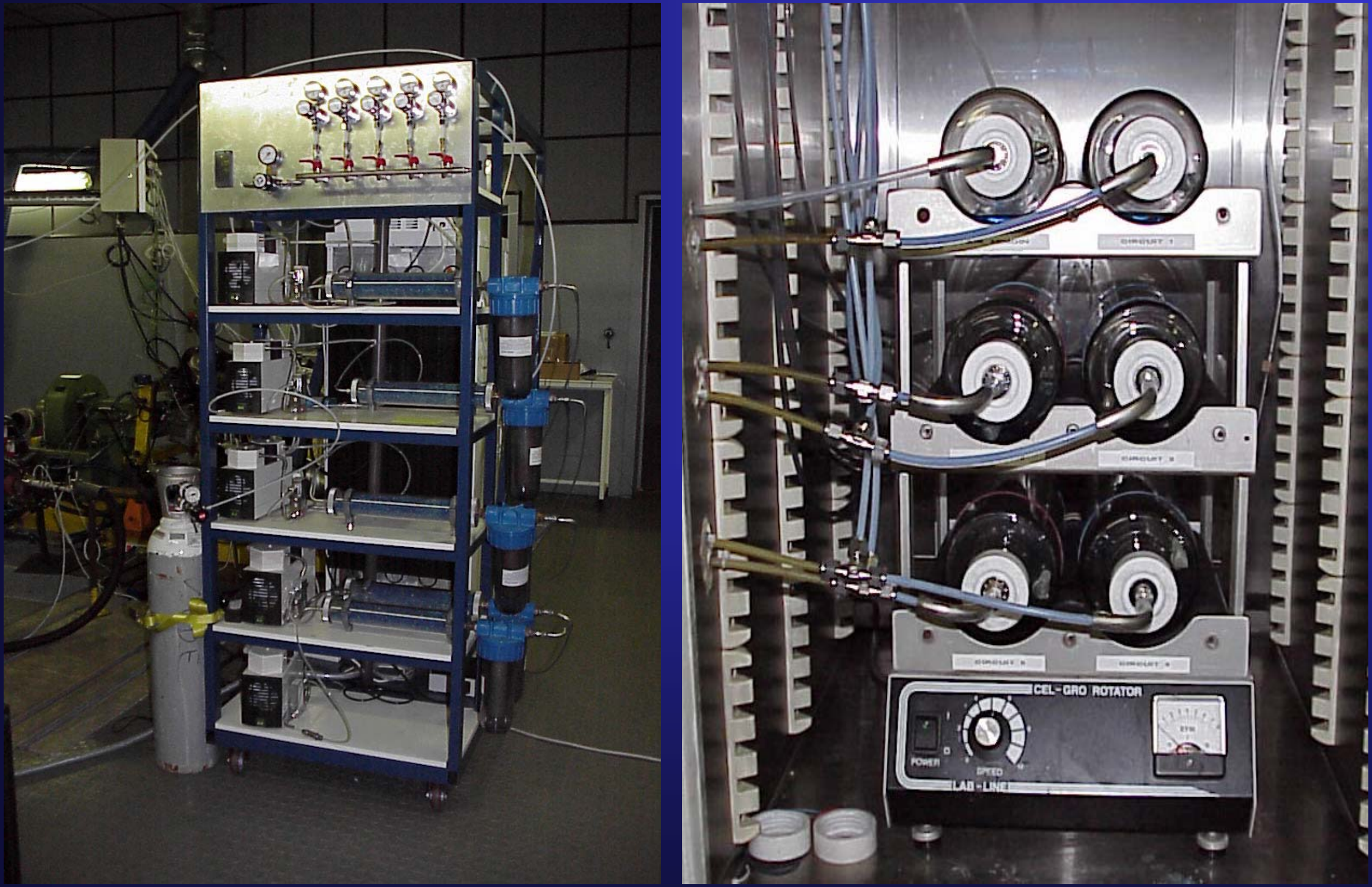
Standardized Dilution and Exposure Systems



Same design as for organotypic cultures
Vials with culture medium + Spin Probe
1 hour duration

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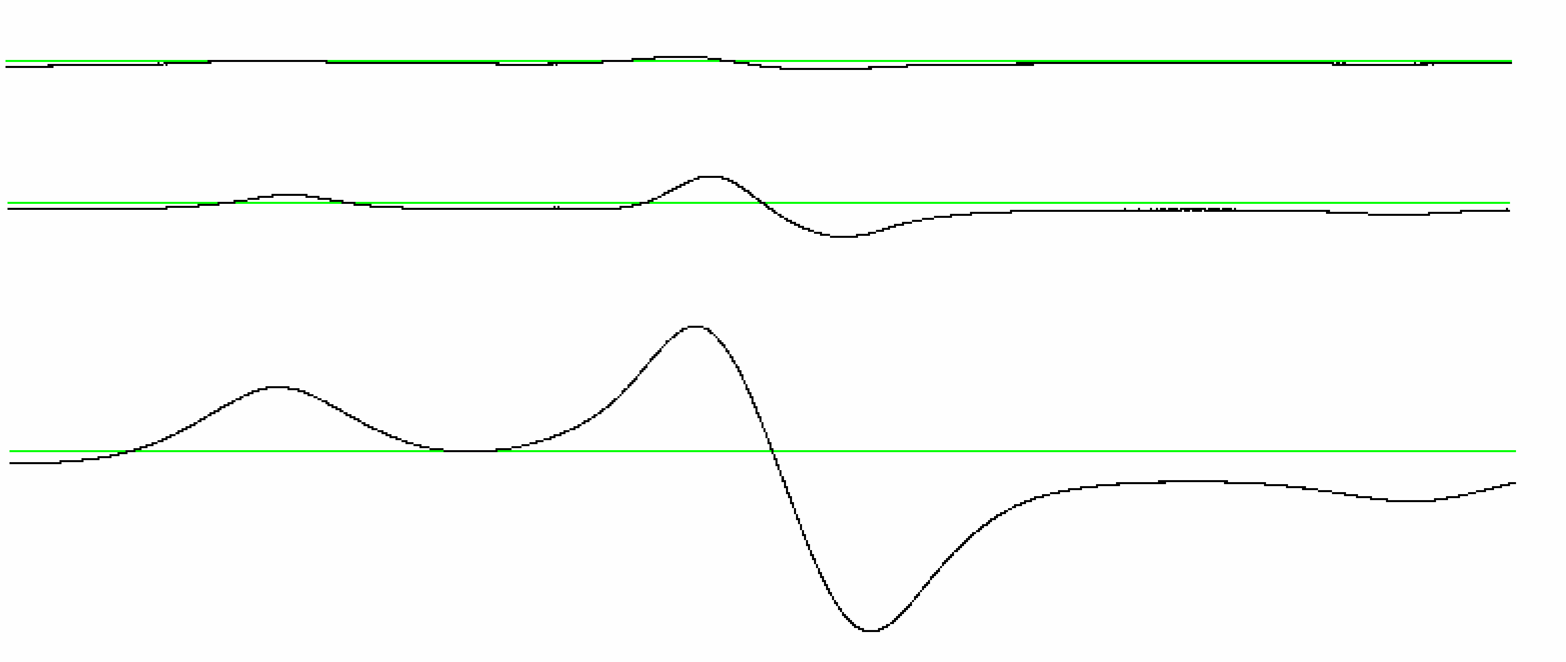
ESR : Electron Spin Resonnance

Use of CPH as a spin probe – Detection of $CP^{\cdot}$



Clean Air

Not treated

Oxicat

Microwave frequency : 9.75 GHz   Microwave power : 1 mW

Bo-field : 3350 G   Field sweep : 100 G   Sweep Time : 120 s   Modulation : 5 G   Gain : 5

Data from MAAPHRI Program

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Fuel sulphur doping mixture for DIS0 Fuel

S 0ppm, PAH <0.5%, Aromatics 13%

Sulfur-mixture A (3 compounds)

	CAS#	MW g/mol	BP °C	Comp. % in mix	Comp. g in mix	Sulfur g in mix	Sulfur % in mix
Dibenzothiophene	132-65-0	184,3	332	50	41,7	7,25	38 %
Benzothiophene	95-15-8	134,2	221	30	25	5,95	31 %
Di-tert-butyl disulfide	110-06-5	178,4	200	20	16,7	5,98	31 %
					83,3 g	19,2 g	100 %

Sulphur as the sole change in Fuel composition

Data from MAAPHRI Program

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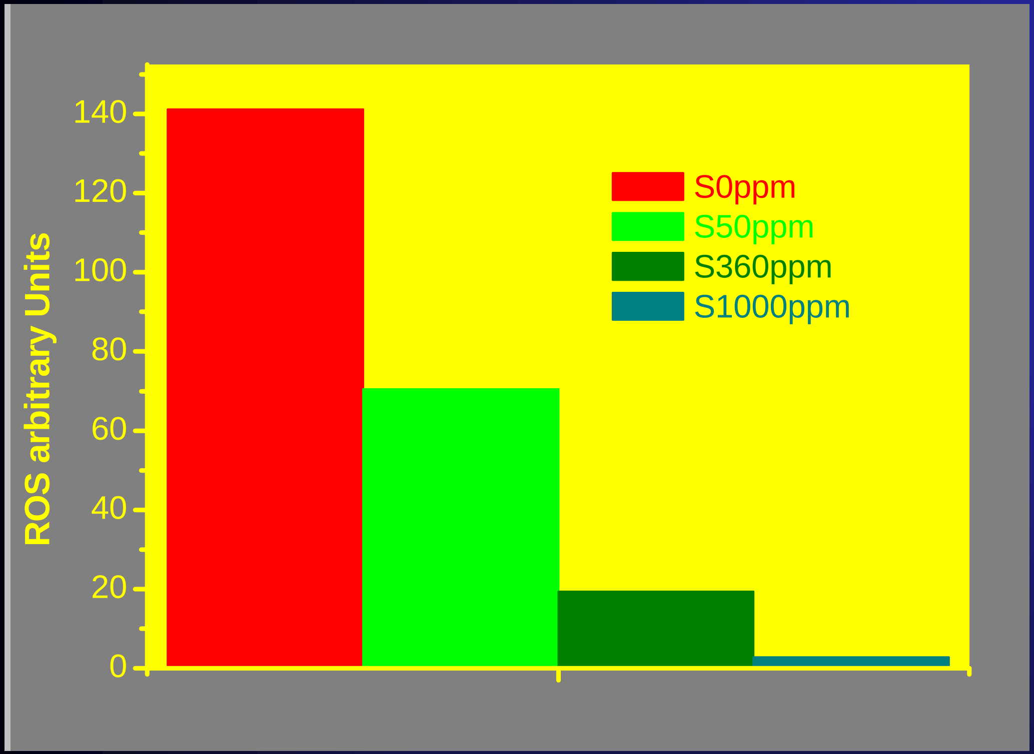
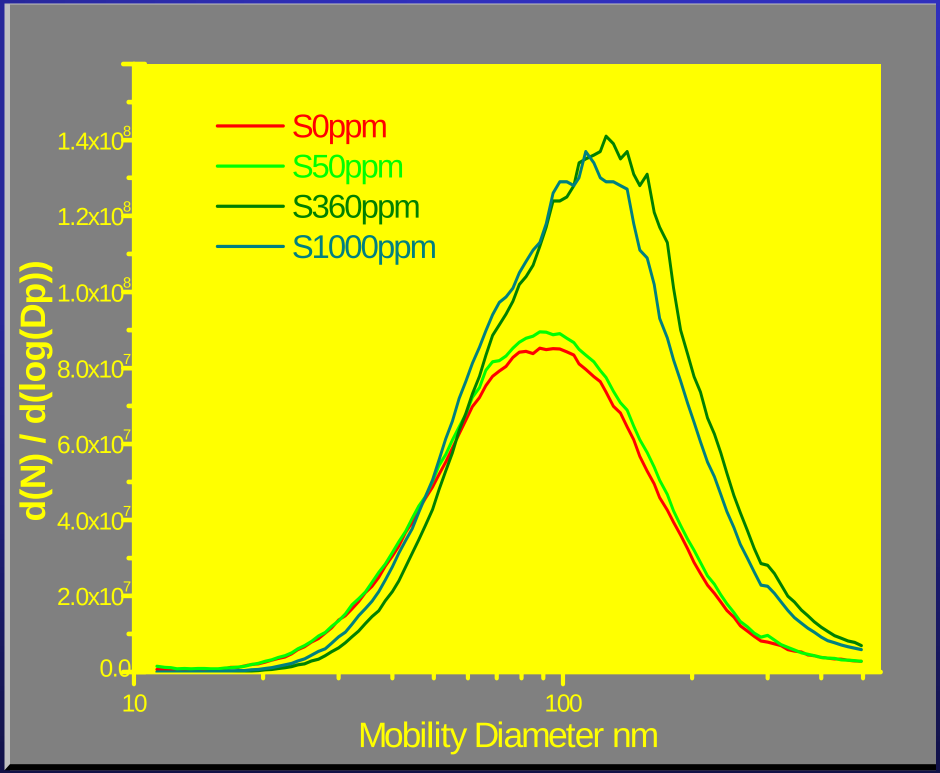
ROS trapping Followed by ESR Measurements
Impact of Sulphur in Fuel (Additivation of Dis0 fuel)





Monocylinder Diesel PowerEngine

Data from MAAPHRI Program

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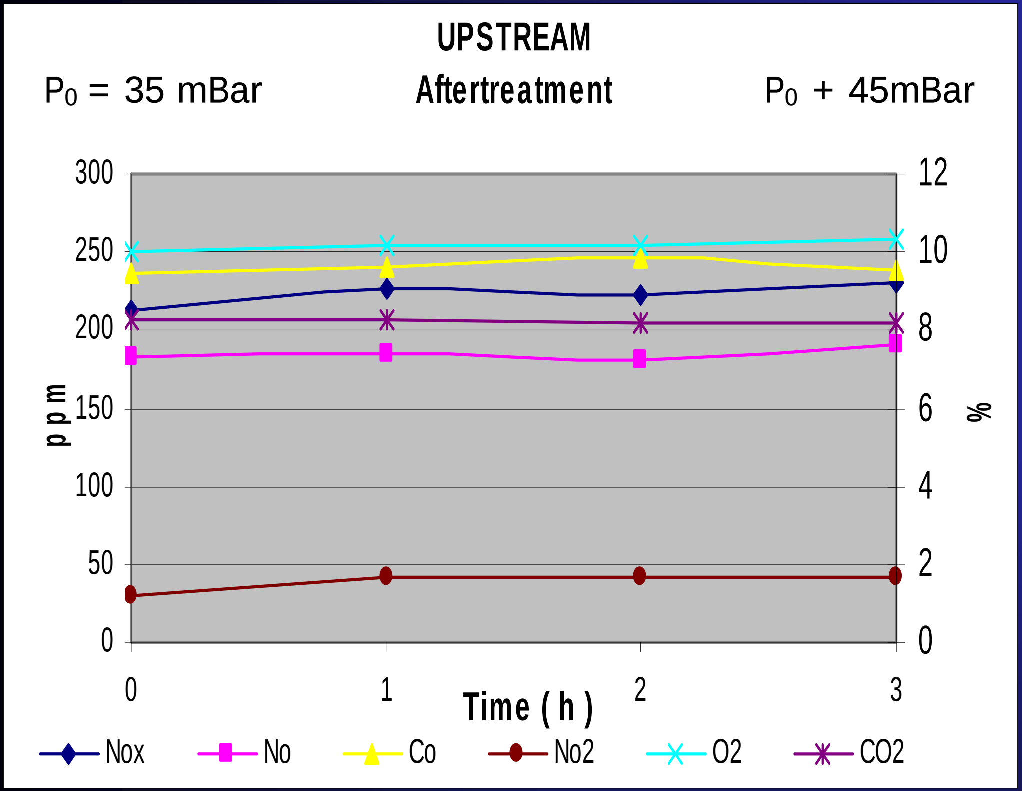
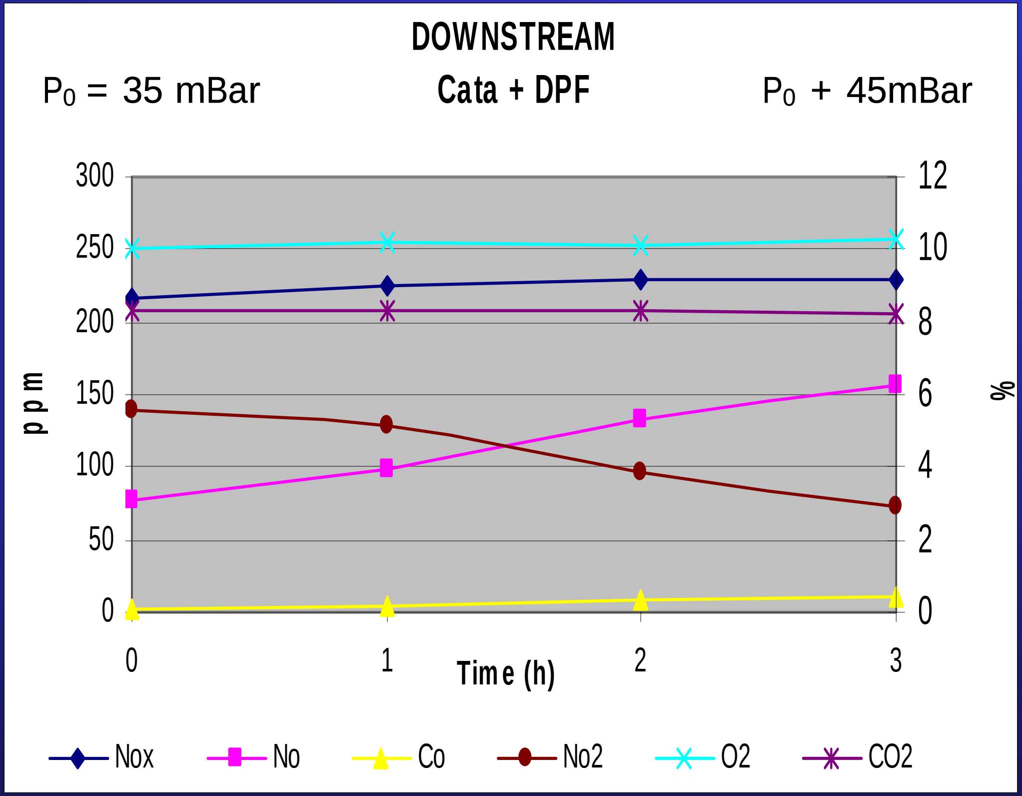
Pollutant Emission Time Evolution





No Change in Total NOx But Changes in NO_2 and NO proportions

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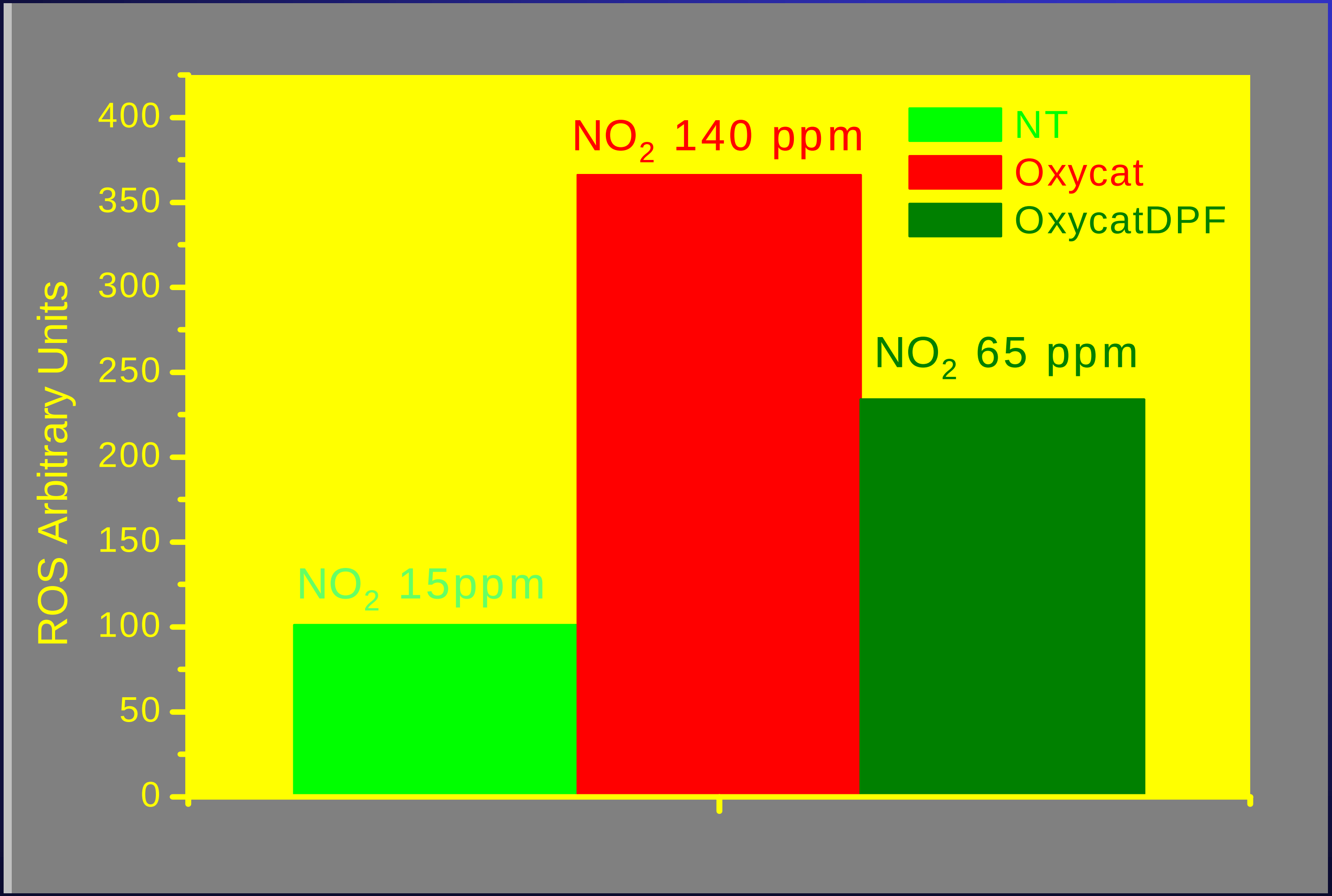
Data from MAAPHRI Program

ROS trapping into liquids and ESR Measurements
Impact of After-Treatment (Dis0-LowSPash)



Euro 3 type 4 cylinder Engine

Data from MAAPHRI Program

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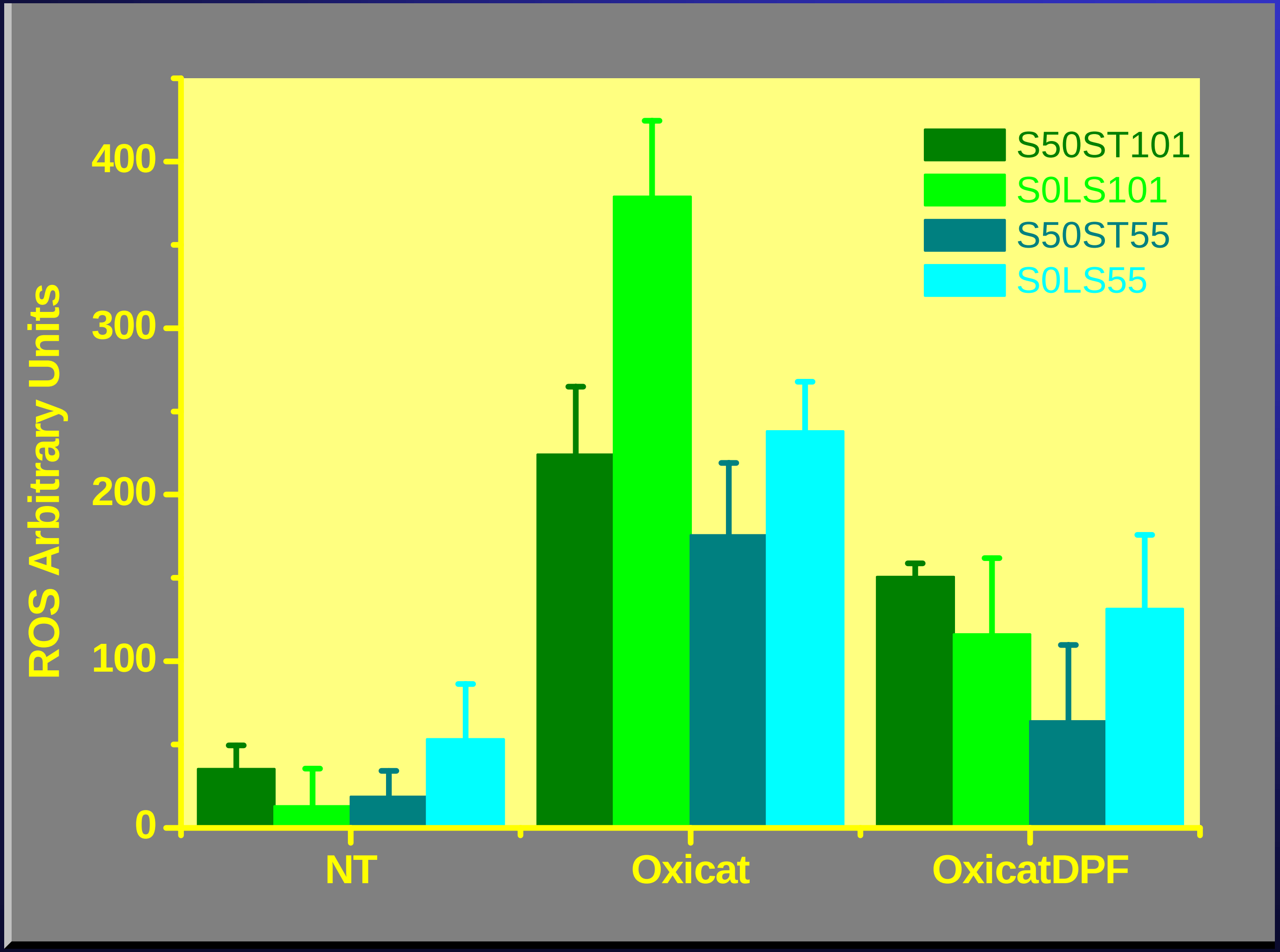
ROS trapping into liquids and ESR Measurements
Impact of Sulphur, Engine load and After-Treatment



Euro 3 type 4 cylinder Engine

Data from MAAPHRI Program

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CONCLUSION

While low ROS were found in Untreated emissions,
Elevated ROS were found after OXICAT

When DPF is combined with OXICAT, ROS reduction occurs
ROS reduction rate varies with DPF load

ROS assay in engine emissions show a good correlation between the presence of ROS in the aerosol and the NO_2 / NOx ratio.

CONCLUSION

Toxicological studies show a very good correlation between tissue oxidative damage and NO_2/NOx ratio in the combustion aerosol. The correlated presence of ROS in the combustion aerosol may trigger these oxidative damage

Further investigations will be conducted to identify the ROS profiles (superoxide anions, peroxinitrites, hydroxyl radicals) in the emissions which could be modulated according to fuel composition and/or after-treatment strategy.

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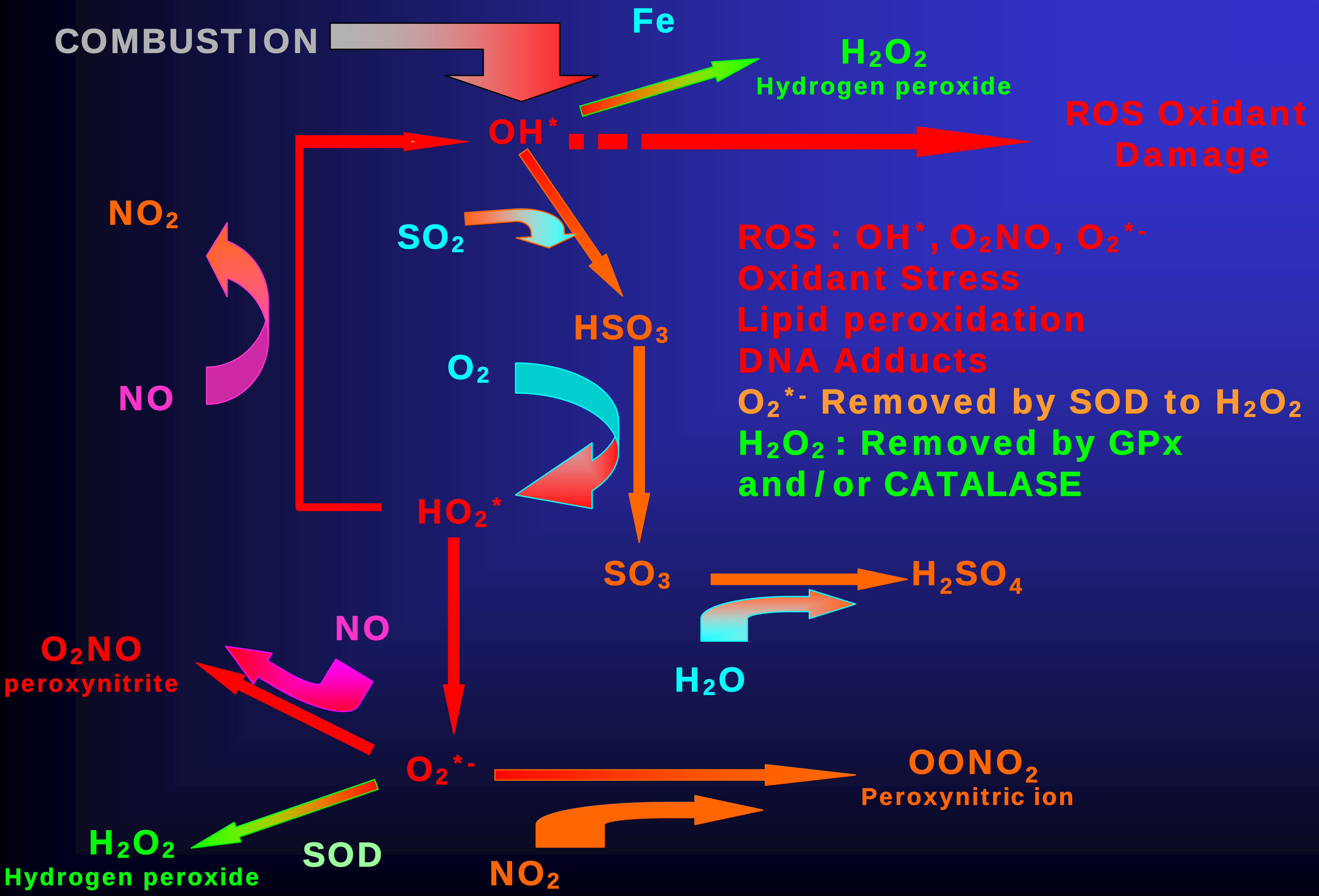


COMBUSTION

Fe

H_2O_2
Hydrogen peroxide

OH^*

ROS Oxidant Damage

NO_2

SO_2

HSO_3

NO

O_2

HO_2^*

SO_3

H_2SO_4

H_2O

NO

O_2NO
peroxynitrite

O_2^{*-}

$OONO_2$
Peroxynitric ion

H_2O_2
Hydrogen peroxide

SOD

NO_2

ROS : OH^*, O_2NO, O_2^{*-}

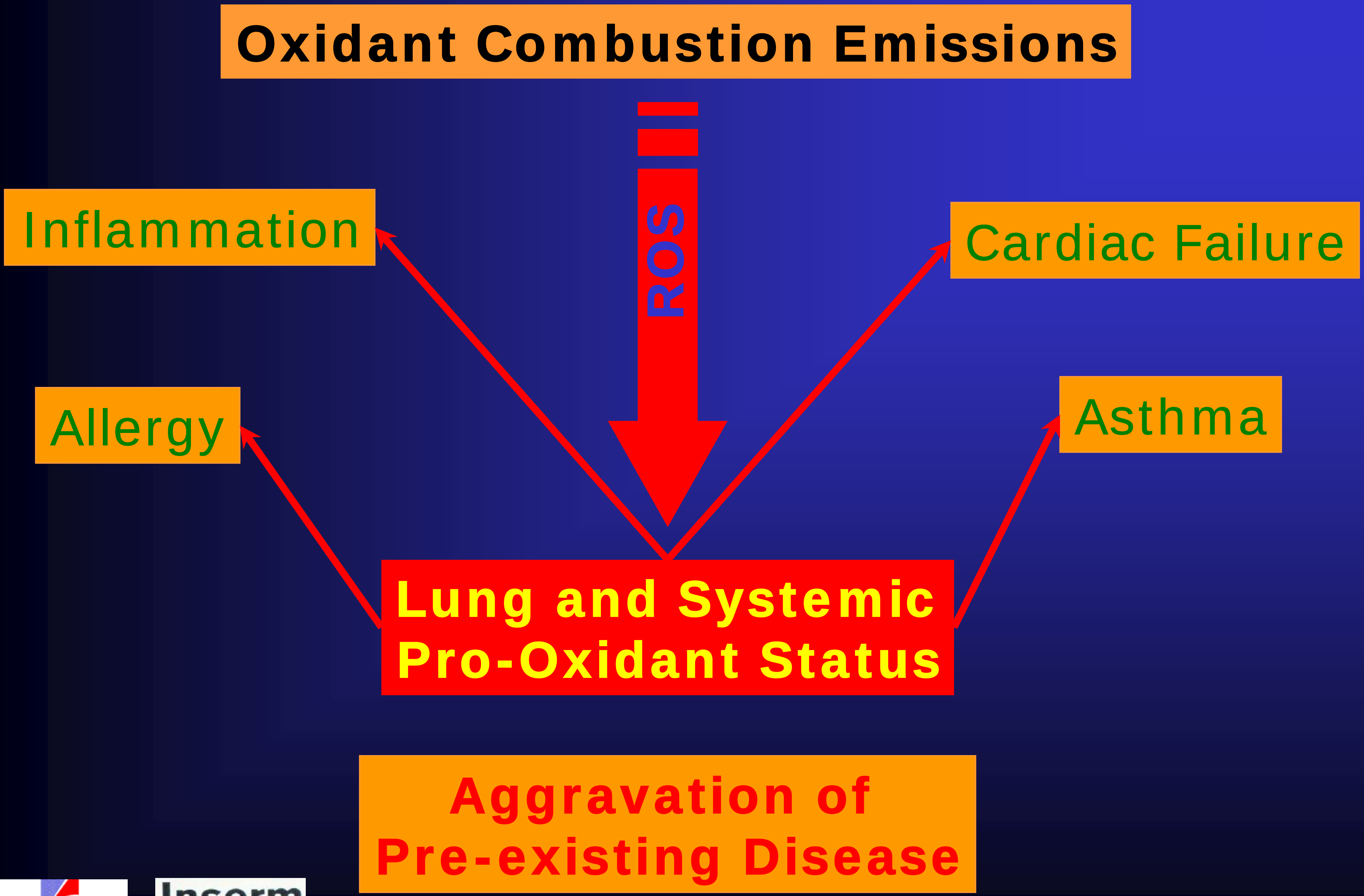
Oxidant Stress

Lipid peroxidation

DNA Adducts

O_2^{*-} Removed by SOD to H_2O_2

H_2O_2 : Removed by GPx and / or CATALASE



Oxidant Combustion Emissions

ROS

Inflammation

Cardiac Failure

Allergy

Asthma

Lung and Systemic Pro-Oxidant Status

Aggravation of Pre-existing Disease

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Several Strategies for After Treating Diesel Engine Emissions rely on increasing the Oxidant Potential of the Gas phase through fuel sulphur reduction and oxidation catalysis.

Health Concerns may Arise from these Strategies

**Beside Total Nox measurements,
NO_2 and NO proportions should be monitored
as a potential pertinent marker of
Diesel Engine Emission
Oxidant potential and « Health Safety »**

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