Assessment of Diesel exhaust particulate exposure and surface characteristics in association with levels of oxidative stress biomarkers

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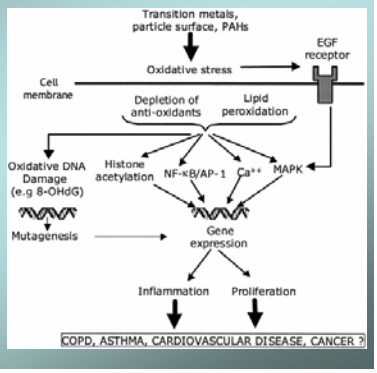
Introduction

➢ Particulate matter (PM) exposure is associated with a range of adverse health effects. **Surface characteristics** (reactivity, area) are of prime importance to understand the mechanisms which lead to harmful effects.

➢ A central hypothetical mechanism to explain these adverse health effects is the ability of some components (organics, metal ions) adsorbed on these particles to induce **oxidative stress** [1].

➢ **8-hydroxy-2'-deoxyguanosine** and **several aldehydes** may be considered as **oxidative stress biomarkers**.



Objective of the research

➢ The aim of this research project is to test whether there is an association between the exposure to Diesel exhaust particulate (DEP) and the oxidative stress status. For that purpose, a survey is conducted in a real occupational situation where workers are exposed to DEP and possibly to other ambient aerosols (bus depots) :

- Selection of a homogeneous group of DEP exposed workers ;
- Urine and serum sampling during two consecutive days of exposure ;
- Quantification of several oxidative stress biomarkers in urine or serum of volunteers ;
- Assessment of the exposure to DEP through stationary and personal sampling.

Materials and methods

➢ Particles have been sampled in a bus depot (maintenance yard) by means of a **High-Volume Sampler** on silanized quartz fiber filters.

➢ **Exposure variables :**

- Particulate number, size distribution and surface (**Scanning Mobility Particle Sizer**).
- Particulate mass – PM_4 (**gravimetry**).
- Elemental and organic carbon (**coulometry**).
- Surface functional groups present on particles (**Knudsen Flow Reactor**).
- Total adsorbed heavy metals (**atomic absorption**).
- NO_x and ozone concentrations (**direct reading instruments**).

➢ **Oxidative stress biomarkers :**

- **8-hydroxy-2'-deoxyguanosine** in urine (clean-up by **SPE**, analysis by **LC/MS-MS**).
- **Several aldehydes** in serum (clean-up by **SPE**, analysis by **GC/MS**).

Fig. 1 : Pictures of the apparatus used during the sampling in a bus depot (maintenance workshop).

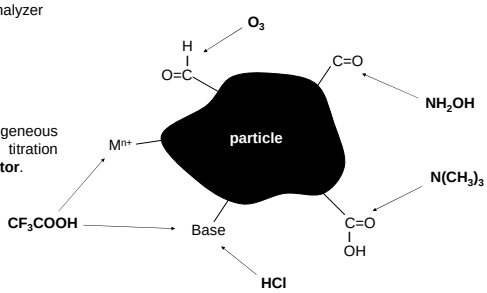


Fig. 2 : Schematic drawing of the heterogeneous chemical reactions used during the titration experiments in the **Knudsen Flow Reactor**.

Reference

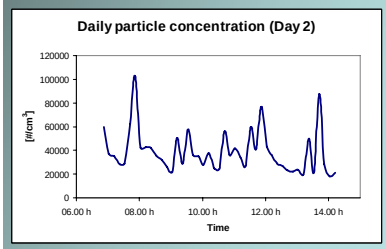
[1] K. Donaldson et al., *Free Radical Biol Med*, 34, 1369-1382, **2003**.

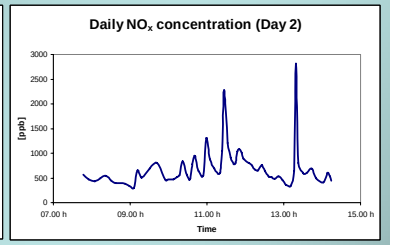
Results

➢ **Up to now, three different occupational situations have been surveyed. The following results refer to one of them.**

➢ **Exposure characterization (stationary sampling) :**

	Day 1	Day 2
PM_4 (mean ± std dev)	92 ± 10 [μg/m^3]	58 ± 4 [μg/m^3]
Elemental Carbon (mean ± std uncertainty)	17 ± 1 [μg/m^3]	12 ± 1 [μg/m^3]
Organic Carbon (mean ± std uncertainty)	27 ± 3 [μg/m^3]	23 ± 3 [μg/m^3]
Daily NO_x (mean ± std dev)	574 ± 219 [ppb]	697 ± 401 [ppb]
Daily ozone (mean ± std dev)	4.1 ± 2.2 [ppb]	2.6 ± 0.5 [ppb]
Particulate Fe	1.4 [μg/m^3]	1.16 [μg/m^3]
Particulate Cu	0.14 [μg/m^3]	0.07 [μg/m^3]
Particulate Mn	0.011 [μg/m^3]	0.007 [μg/m^3]





➢ **Exposure characterization (personal sampling) :**

	Day 1	Day 2	Worker
PM_4	120 [μg/m^3]	99 [μg/m^3]	Worker 1
	96 [μg/m^3]	44 [μg/m^3]	Worker 2
Elemental Carbon (mean ± std uncertainty)	10 ± 3 [μg/m^3]	10 ± 3 [μg/m^3]	Worker 1
	14 ± 3 [μg/m^3]	9 ± 2 [μg/m^3]	Worker 2
Organic Carbon (mean ± std uncertainty)	51 ± 9 [μg/m^3]	35 ± 7 [μg/m^3]	Worker 1
	48 ± 8 [μg/m^3]	34 ± 6 [μg/m^3]	Worker 2

➢ **Investigation of the surface functional groups present on particles by means of titration in the Knudsen Flow Reactor** (mean ± std uncertainty) **:**

Gas-phase probe	Functional groups on particles	Day 1 [#/mg]	Day 2 [#/mg]
$N(CH_3)_3$	Acidic sites	not detected	not detected
NH_2OH	Carbonyl functions	$(2.0 \pm 0.3) \cdot 10^{17}$	$(1.4 \pm 0.2) \cdot 10^{17}$
CF_3COOH	High basicity sites / Heavy metals	$(3.0 \pm 0.7) \cdot 10^{15}$	$(4.3 \pm 1.0) \cdot 10^{15}$
HCl	All basic sites	$(1.4 \pm 0.2) \cdot 10^{16}$	$(1.6 \pm 0.3) \cdot 10^{16}$
O_3	Oxidizable sites	$(5.8 \pm 0.1) \cdot 10^{16}$	$(7.3 \pm 0.7) \cdot 10^{16}$

Units : [#/mg] = number of gas-phase probe molecules taken up per mg of particles
Not detected : $< 1.5 \cdot 10^{15}$ [#/mg]

➢ **Quantification of oxidative stress biomarkers** (mean ± std dev) **:**

Worker	Biomarker	Day 1 Before shift [nmol / ml serum]	Day 2 End of shift [nmol / ml serum]
Worker 1 (non-smoker)	Hexanal	0.92 ± 0.3	6.0 ± 2.2
	Nonanal	1.1 ± 0.3	9.8 ± 3.5
	4-hydroxy-nonenal	0.04 ± 0.01	0.09 ± 0.01
Worker 2 (non-smoker)	Hexanal	0.6 ± 0.4	0.5 ± 0.2
	Nonanal	0.6 ± 0.2	0.6 ± 0.2
	4-hydroxy-nonenal	0.04 ± 0.01	0.04 ± 0.01

Discussion

Occupational exposure

➢ Occupational exposure to particulate is low.
➢ Workers are exposed to rather high NO_x levels, while ozone concentrations are negligible.
➢ Surface of sampled particles are characterized by high carbonyl and low acidic site content.

Biological effects

➢ Validation of the analytical method for 8-hydroxy-2'-deoxyguanosine will be soon ready.
➢ Determination of aldehydes in urine and serum is in progress.

Conclusion

When all results of biomarkers will be available, correlations between exposure parameters and biomarker levels will be explored.

Acknowledgements

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