Carbonyl compounds in exhaust from alternative fuels used in modern engines and from two stroke mopeds

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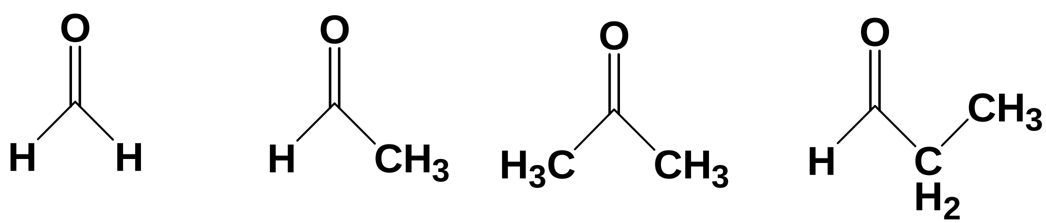
- Carbonyl compounds are major constituents in urban atmospheres

In city areas, they often initiate <u>photochemical smog</u> and keep up reactions <u>leading to ozone formation</u> by an oxidation process involving OH radicals, ozone, and nitrogen oxides in a cyclic mechanism

- In particular formaldehyde, acetaldehyde and acetone, constitutes the most abundant group of <u>oxygenated organic compounds</u> ubiquitously present in the troposphere and some of them are known to be carcinogenic



References: (Hallquist, M. et al,2009);
(U.S. Dep. of Health and Human Services Report on Carcinogens, U.S. 11th Edition. 2005).

- Regardless of the important role of these compounds in the atmospheric processes in Europe and, even if motor vehicle exhaust is one of the main outdoor sources of carbonyls, these compounds are not included in any monitoring protocol at the exhaust stage and their concentration is not measured on a regular basis.

CALIFORNIA EMISSION STANDARDS

	MEDIUM AND HEAVY-DUTY VEHICLES						
Otto Cycle	(g/bhp.h)	**Medium Duty 8.501-14.000 lbs GVW**					
MY	**Emission Category**	**NMHC + Nox**	**NMHC**	**NOx**	**CO**	**HCHO**	**PM**
2004	**ULEV**	2.4 or 2.5 w / 0.5 NMHC	_	_	14.4	**0.5**	_
	SULEV	2	_	_	7.2	**0.25**	_
2005-07	**ULEV**	1	_	_	14.4	**0.5**	_
	SULEV	0.5	_	_	7.2	**0.25**	_
2008 +	**ULEV**	_	0.14	0.2	14.4	**0.01**	0.01
	SULEV	_	0.07	0.1	7.2	**0.005**	0.005
Otto Cycle	(g/bhp.h)	**HD >14.000 lbs GVW**					
MY	**Emission Category**	**NMHC + Nox**	**NMHC**	**NOx**	**CO**	**HCHO**	**PM**
2004	_	2.4 or 2.5 w / 0.5 NMHC	_	_	37.1	**0.05**	_
2005-07	_	1	_	_	37.1	**0.05**	_
2008 +	_	_	0.14	0.2	14.4	**0.01**	0.01

Compression Ignition		**(g/bhp.h)**					
MY	**Emission Category**	**NMHC + Nox**	**NMHC**	**NOx**	**CO**	**HCHO**	**PM**
2004-06	**ULEV Opt B**	2.5 NMHC < = 0.5	_	_	14.4	**0.05**	0.1
	ULEV Opt A	2.4	_	_	14.4	**0.05**	0.1
2007 +	**ULEV**	_	0.14	0.2	15.5	**0.05**	0.01
	SULEV	_	0.07	0.1	7.7	**0.025**	0.005

LEV	*LOW EMISSION VEHICLE (LEV1, LEV2)*
TLEV	*TRANSITIONAL LOW EMISSION VEHICLE*
ULEV	*ULTRA LOW EMISSION VEHICLE (ULEV1, ULEV2*
SULEV	*SUPER ULTRA LOW EMISSION VEHICLE*
ZEV	*ZERO EMISSION VEHICLE*

CALIFORNIA EMISSION STANDARDS

Emission standards for Diesel or dual-fuel URBAN BUS engine (g/bhp.h)

MY	NOx	PM	NMHC	HCHO	CO
2004-06	0.5	0.01	0.05	**0.01**	5
2007 +	0.2	0.01	0,.05	**0.01**	5

CARB source

LDV <= 12 PASSENGERS	LEV 2 EMISSION LIMITS 2004 (onwards)									
g/mi	**NMOG**		**CO**		**NOx**		**PM**		**HCHO**	
Durability	50k	120k	50k	120k	50k	120k	50k	120k	50k	120k
LEV 2	**0.075**	**0.09**	**3.4**	**4.2**	**0.05**	**0.07**	_	**0.01**	**0.015**	**0.018**
ULEV 2	**0.04**	**0.055**	**1.7**	**2.1**	**0.05**	**0.07**	_	**0.01**	**0.008**	**0.011**
SULEV 2	_	**0.01**	_	**1**	_	**0.02**	_	0.01	_	**0.004**
ZEV	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**

NMHC to HMOG: 1.04 certification factor

Tabela 28 – Limites máximos de emissão para veículos leves novos[1]

ANO	CO (g/km)	HC (g/km)	NOx (g/km)	RCHO[2] (g/km)	MP[3] (g/km)	EVAP.[4] (g/teste)	CÁRTER	CO-ML (% vol)
89 - 91	24	2,10	2,0	--	--	6	nula	3
92 - 96[6]	24	2,10	2,0	0,15	--	6	nula	3
92 - 93	12	1,20	1,4	0,15	--	6	nula	2,5
mar/94	12	1,20	1,4	0,15	0,05	6	nula	2,5
jan/97	2	0,30	0,6	0,03	0,05	6	nula	0,5
mai/03	2	0,30	0,6	0,03	0,05	2	nula	0,5
jan/05 (40%)	2	0,16 [5]	0,25 [7]	0,03	0,05	2	nula	0,5 [7]
jan/06 (70%)	2	ou	ou	0,03	0,05	2	nula	0,5 [7]
jan/07 (100%)	2	0,30 [6]	0,60 [3]	0,03	0,05	2	nula	0,5 [7]
jan/09	2	0,05 [5] ou	0,12 [7] ou	0,02	0,05	2	nula	0,5 [7]
jan/09	2	0,30 [6]	0,25 [3]	0,02	0,05	2	nula	0,5 [7]

1 - Medições de acordo com a NBR6601 (US-FTP75), e conforme as Resoluções CONAMA n° 15/95 e n° 315/02.
2 - Apenas para veículos do ciclo Otto. Aldeídos totais de acordo com a NBR 12026.
3 - Apenas para veículos do ciclo Diesel.
4 - Apenas para veículos do ciclo Otto, exceto a GNV.
5 – Hidrocarbonetos não metano (NMHC).
6 – Hidrocarbonetos totais somente para veículos a GNV, que também atendem ao item (5).
7 – Apenas para veículos do ciclo Otto, inclusive a GNV.

In conformity with Brazilian Resolution CONAMA no. 15/95 & no. 315/02

Tabela 37 – Fatores médios de emissão de veículos leves novos[1]

ANO MODELO	COMBUSTÍVEL	CO (g/km)	HC (g/km)	NOx (g/km)	RCHO (g/km)	CO2[2] (g/km)	AUTONOMIA[3] (km/L)	EMISSÃO EVAPORATIVA DE COMBUSTÍVEL (g/teste)
PRÉ - 1980	Gasolina	54,0	4,7	1,2	0,05	nd	nd	nd
1980 -1983	Gasolina C	33,0	3,0	1,4	0,05	nd	nd	nd
	Álcool	18,0	1,6	1,0	0,16	nd	nd	nd
1984 -1985	Gasolina C	28,0	2,4	1,6	0,05	nd	nd	23
	Álcool	16,9	1,6	1,2	0,18	nd	nd	10
1986 - 1987	Gasolina C	22,0	2,0	1,9	0,04	nd	nd	23
	Álcool	16,0	1,6	1,8	0,11	nd	nd	10
1988	Gasolina C	18,5	1,7	1,8	0,04	nd	nd	23
	Álcool	13,3	1,7	1,4	0,11	nd	nd	10
1989	Gasolina C	15,2 (-46%)	1,6 (-33%)	1,6 (0%)	0,040 (-20%)	nd	nd	23,0 (0%)
	Álcool	12,8 (-24%)	1,6 (0%)	1,1 (-8%)	0,110 (-39%)	nd	nd	10,0 (0%)
1990	Gasolina C	13,3 (-53%)	1,4 (-42%)	1,4 (-13%)	0,040 (-20%)	nd	nd	2,7 (-88%)
	Álcool	10,8 (-36%)	1,3 (-19%)	1,2 (0%)	0,110 (-39%)	nd	nd	1,8 (-82%)
1991	Gasolina C	11,5 (-59%)	1,3 (-46%)	1,3 (-19%)	0,040 (-20%)	nd	nd	2,7 (-88%)
	Álcool	8,4 (-50%)	1,1 (-31%)	1,0 (-17%)	0,110 (-39%)	nd	nd	1,8 (-82%)
1992	Gasolina C	6,2 (-78%)	0,6 (-75%)	0,6 (-63%)	0,013 (-74%)	nd	nd	2,0 (-91%)
	Álcool	3,6 (-79%)	0,6 (-63%)	0,5 (-58%)	0,035 (-81%)	nd	nd	0,9 (-91%)
1993	Gasolina C	6,3 (-77%)	0,6 (-75%)	0,8 (-50%)	0,022 (-56%)	nd	nd	1,7 (-93%)
	Álcool	4,2 (-75%)	0,7 (-56%)	0,6 (-50%)	0,040 (-78%)	nd	nd	1,1 (-89%)
1994	Gasolina C	6,0 (-79%)	0,6 (-75%)	0,7 (-56%)	0,036 (-28%)	nd	nd	1,6 (-93%)
	Álcool	4,6 (-73%)	0,7 (-56%)	0,7 (-42%)	0,042 (-77%)	nd	nd	0,9 (-91%)
1995	Gasolina C	4,7 (-83%)	0,6 (-75%)	0,6 (-62%)	0,025 (-50%)	nd	nd	1,6 (-93%)
	Álcool	4,6 (-73%)	0,7 (-56%)	0,7 (-42%)	0,042 (-77%)	nd	nd	0,9 (-91%)
1996	Gasolina C	3,8 (-86%)	0,4 (-83%)	0,5 (-69%)	0,019 (-62%)	nd	nd	1,2 (-95%)
	Álcool	3,9 (-77%)	0,6 (-63%)	0,7 (-42%)	0,040 (-78%)	nd	nd	0,8 (-92%)
1997	Gasolina C	1,2 (-96%)	0,2 (-92%)	0,3 (-81%)	0,007 (-86%)	nd	nd	1,0 (-96%)
	Álcool	0,9 (-95%)	0,3 (-84%)	0,3 (-75%)	0,012 (-93%)	nd	nd	1,1 (-82%)
1998	Gasolina C	0,79 (-97%)	0,14 (-94%)	0,23 (-86%)	0,004 (-92%)	nd	nd	0,81 (-96%)
	Álcool	0,67 (-96%)	0,19 (-88%)	0,24 (-80%)	0,014 (-92%)	nd	nd	1,33 (-87%)
1999	Gasolina C	0,74 (-97%)	0,14 (-94%)	0,23 (-86%)	0,004 (-92%)	nd	nd	0,79 (-96%)
	Álcool	0,60 (-96%)	0,17 (-88%)	0,22 (-80%)	0,013 (-92%)	nd	nd	1,64 (-84%)
2000	Gasolina C	0,73 (-97%)	0,13 (-95%)	0,21 (-87%)	0,004 (-92%)	nd	nd	0,73 (-97%)
	Álcool	0,63 (-96%)	0,18 (-89%)	0,21 (-83%)	0,014 (-92%)	nd	nd	1,35 (-87%)
2001	Gasolina C	0,48 (-98%)	0,11 (-95%)	0,14 (-91%)	0,004 (-92%)	nd	nd	0,68 (-97%)
	Álcool	0,66 (-96%)	0,15 (-91%)	0,08 (-93%)	0,017 (-91%)	nd	nd	1,31 (-87%)
2002[4]	Gasolina C	0,43(-98%)	0,11(-95%)	0,12(-95%)	0,004(-92%)	198	10,9	0,61 (-97%)
	Álcool	0,74(-96%)	0,16(-90%)	0,08(-93%)	0,017(-91%)	191	7,2	nd

1 - Médias ponderadas de cada ano-modelo pelo seu volume da produção.
2 - Com a inclusão do dióxido de carbono, à partir de 2002.
3 - Obtida por balanço de carbono, conforme a NBR 7024, para o ciclo de condução urbana.
4 - Para os modelos a gasolina predominam motores de 1.0L; para os a álcool, de 1.5 à 1.9L.
nd - Não disponível
(%) - Refere-se à variação verificada em relação aos veículos 1985, antes da atuação do PROCONVE.
Gasolina C: 78% gasolina + 22% álcool anidro (v/v).

Emissions tests Facility VELA

Climatic Chambers:

Emissions analyzers for HC, CO, CO2 & NOx

-7°C/30°C (controlled humidity)
4 x 4 chassis Dynamometer for: Passenger cars 2WD / 4WD, Small Trucks, Minivans, Tractors

-30°C to 50°C (controlled humidity)
HD vehicles (Trucks & Buses)

[SESAM FT IR]

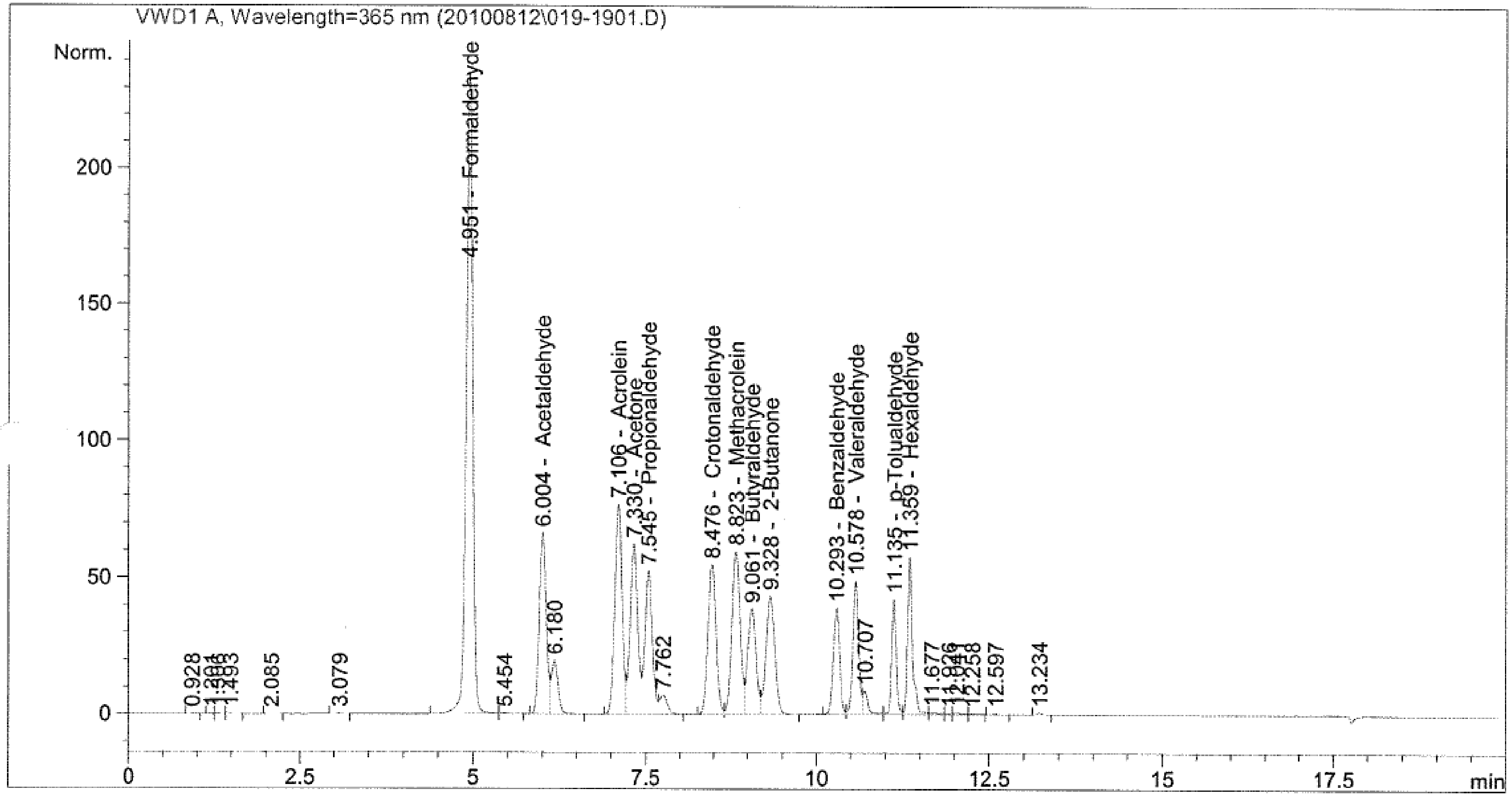
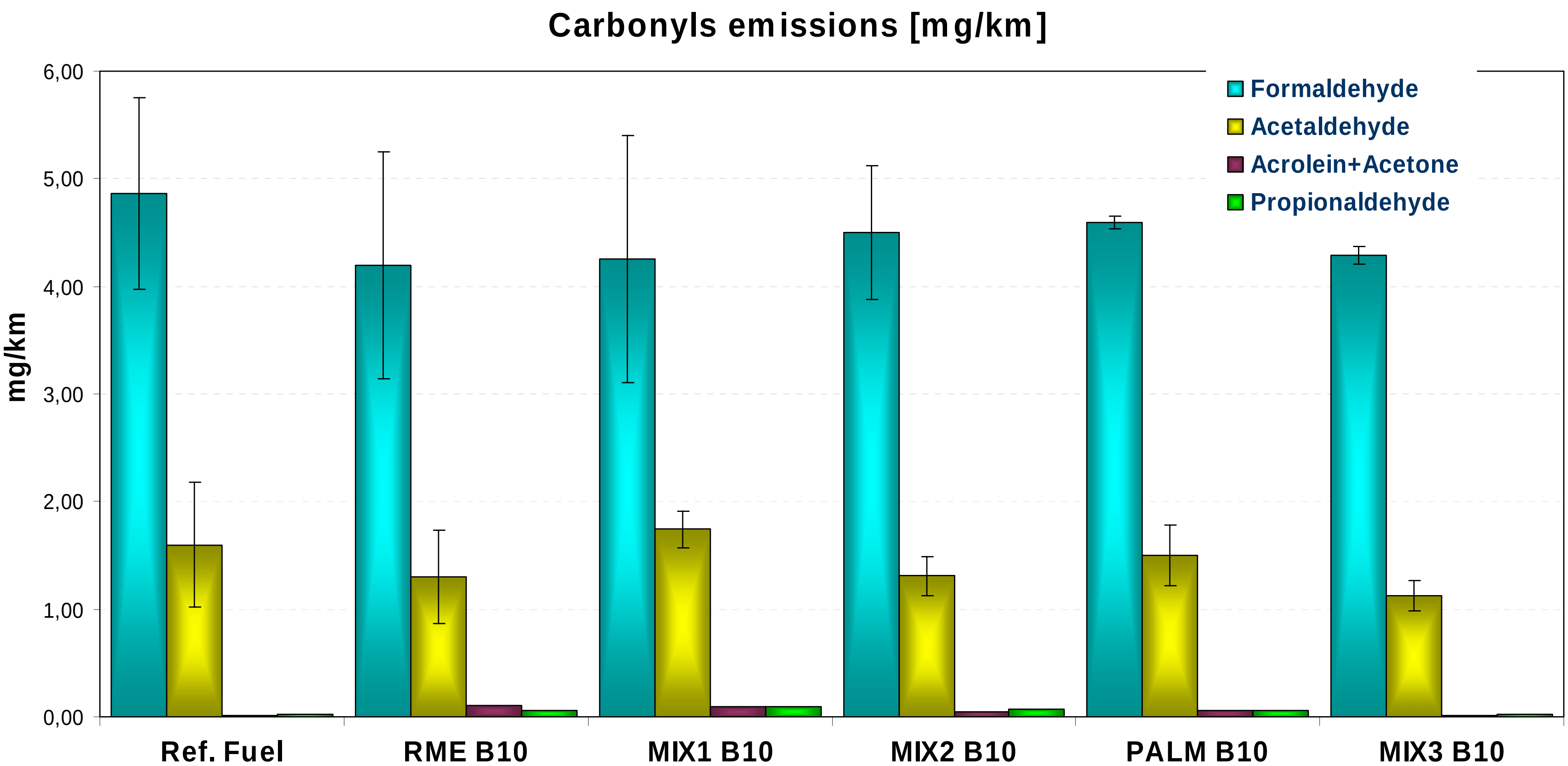
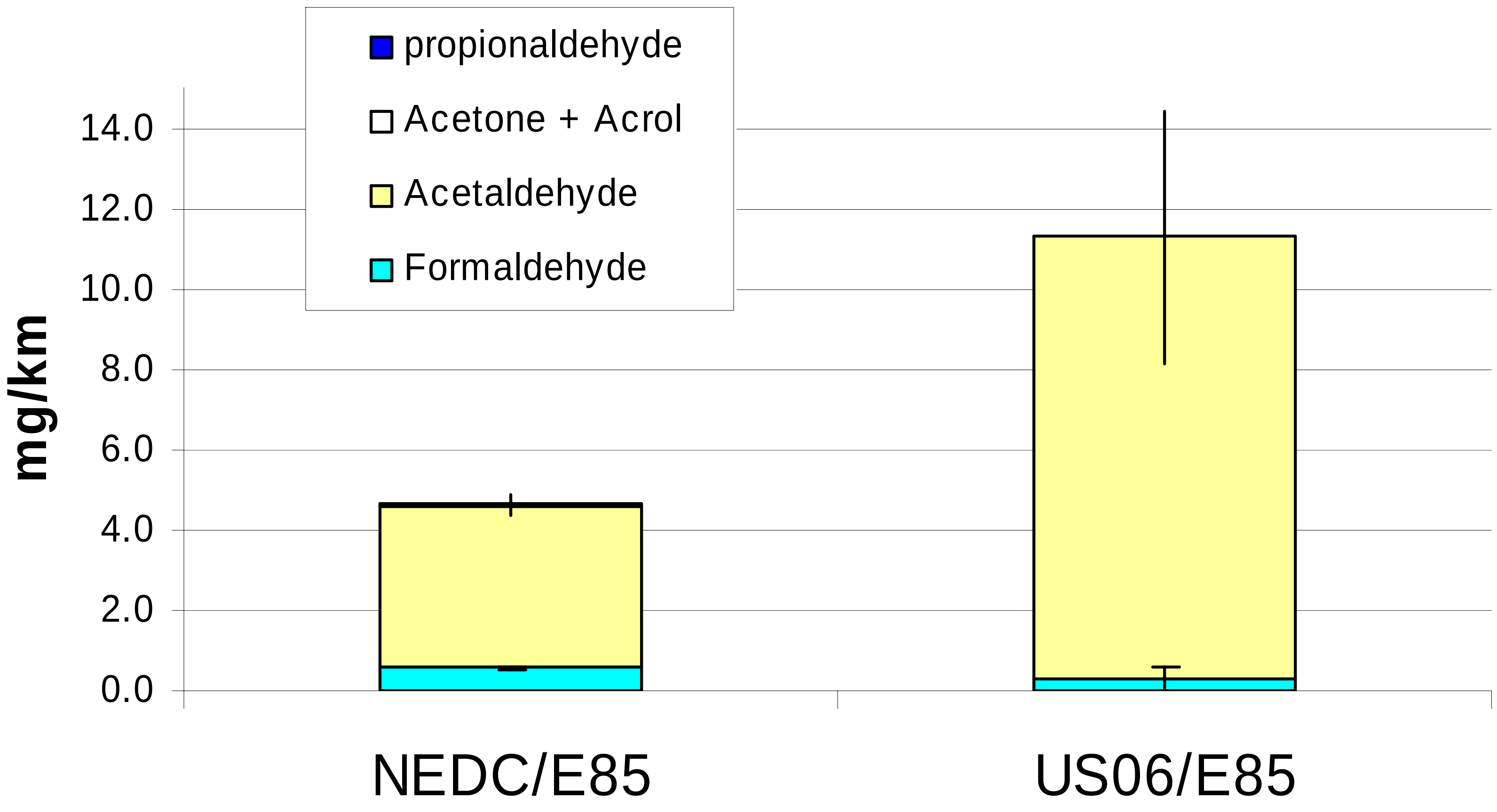


Figure: Standard chromatogram, all compounds at 0.6mg/L except formaldehyde (1.2mg/L)

Carbonyl compounds in Biodiesel emissions



Flexi Fuel vehicle (E85)

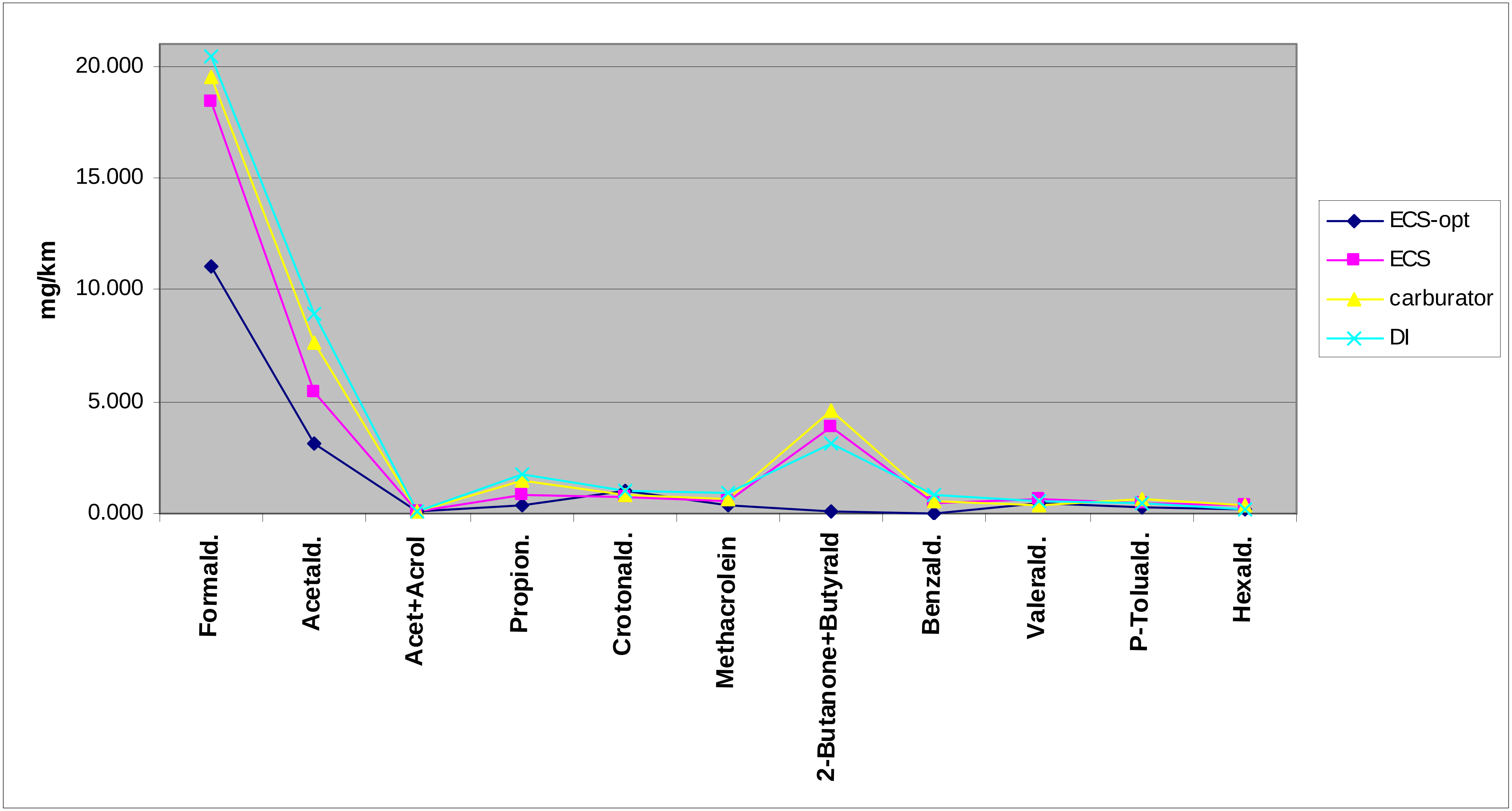


Two stroke Euro 2 mopeds program:
Best available technology

- With the entry into force of the latest LD and HD emission standards (Euro 5/6 and Euro VI respectively) the contribution of two wheelers to overall road transport emissions and therefore to air pollution must be taken into account and the share of this vehicle type is expected to be increasing in the next few years.

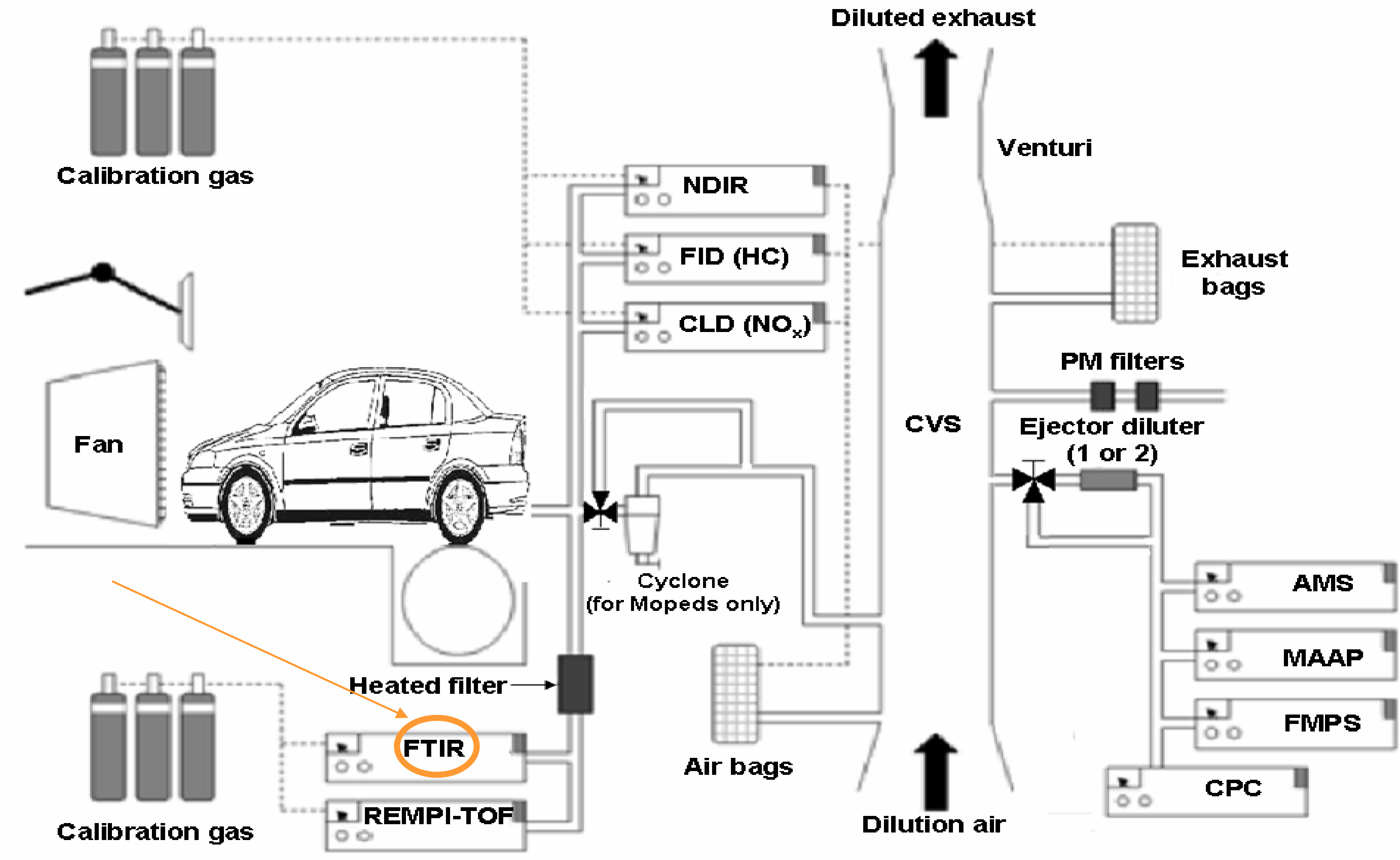
- Test fleet consisted of three EURO-2 new mopeds from different manufacturers with two-stroke engines (different engine technologies, displacements of 50 cm^3, and oxidation catalysts)

Two stroke mopeds program:
Euro 2 best available technology



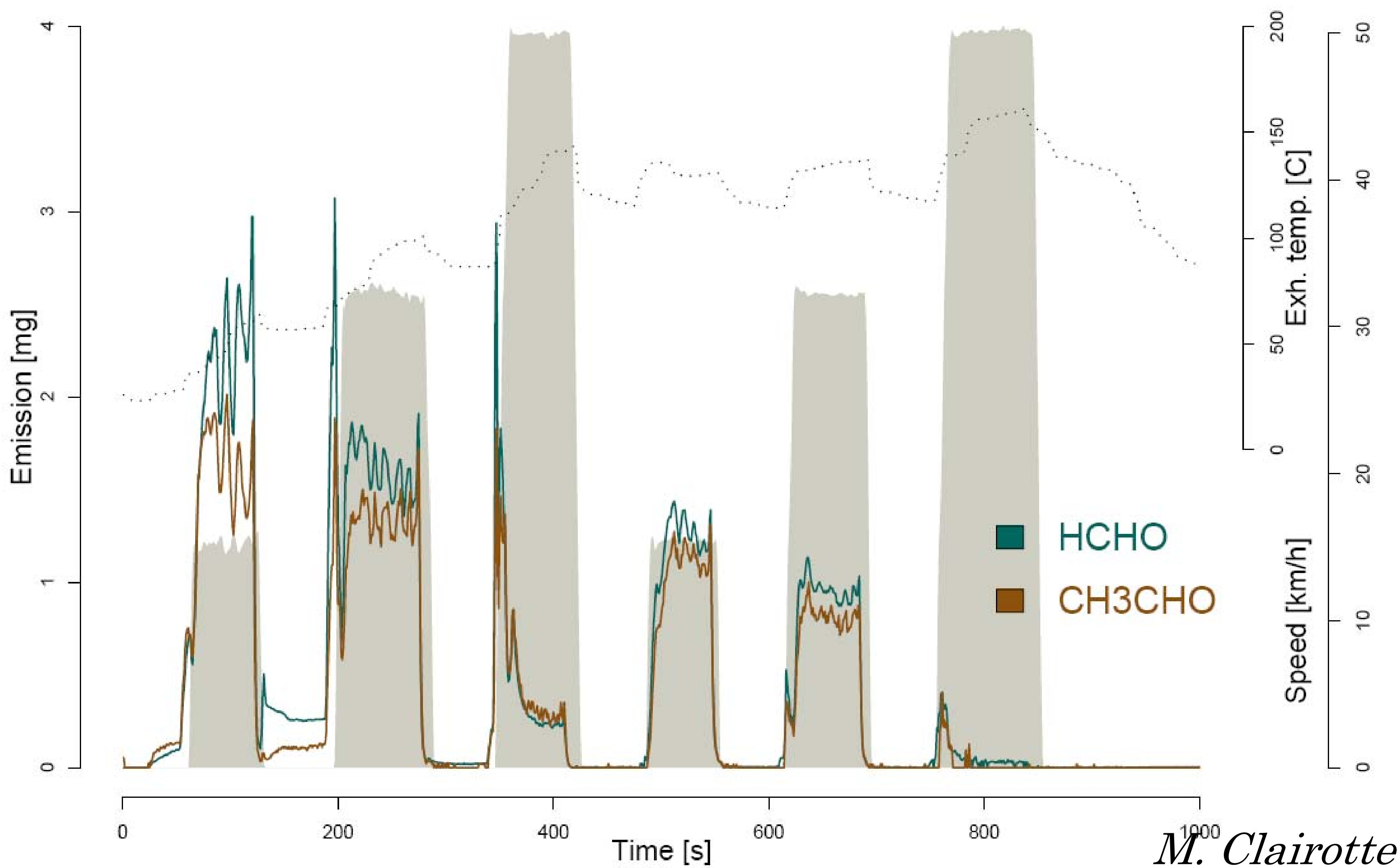
- On line measurements, FT IR.

- Taking advantage of new online real time measurements we may be able to asses more accurately sources and origin of this class of compounds. Formaldehyde and Acetaldehyde have been monitored by a High Resolution Fourier Transforms Infrared spectrometer (HR-FTIR - Multigas analyzer).



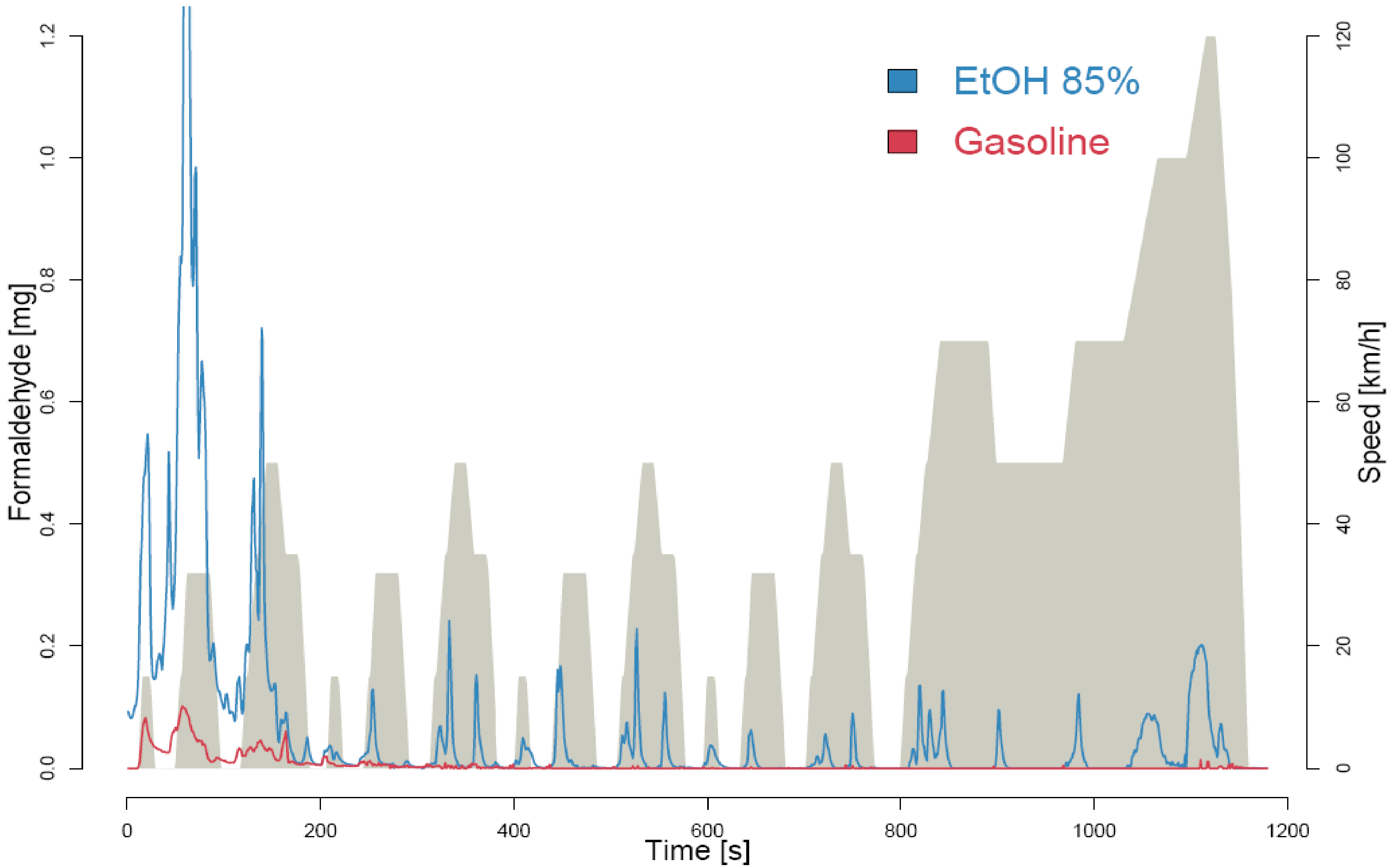
Source: M. Clairotte 2010

Formaldehyde and Acetaldehyde emission from MD E3 vehicle – Intense Traffic cycle – BIO30%



M. Clairotte 2010

Formaldehyde emission from FLEXI EURO4



Mean of 3 tests

M. Clairotte 2010

- Before any alternative fuel will be available in the market or technologies improvement is set up, it is necessary to know if the emissions from such fuels, specially the toxic pollutants, will be lower, or at least same as the fuels before its implementation
- Formaldehyde was the most abundant carbonyl derivative in the exhaust from biodiesel blends, LPG fuelled vehicles and mopeds while there is a clear effect of the increasing fuel content of ethanol on the emissions of acetaldehyde, which is statistically significant and considerably high when E85 is used.
- By having a better knowledge of the potential emitters for ozone precursors we are trying to prevent the formation of smog episodes and to extend the availability of data to be used in the chemical models in order to strength their capability to thereby anticipate the smog episodes.