SAMAP 2019

EXPOSURE TO DIESEL EXHAUST EMISSIONS: IRRITANTS

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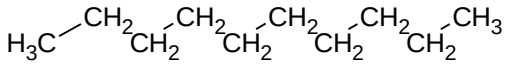
AUSTRALIA

Dedicated to the memory of Peter Hanhela (1950 – 2019) former team member and friend.

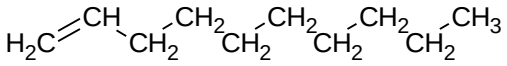
DIESEL FUEL CHEMICAL COMPOSITION: HYDROCARBONS

STRAIGHT CHAIN ALKANES (Paraffins)



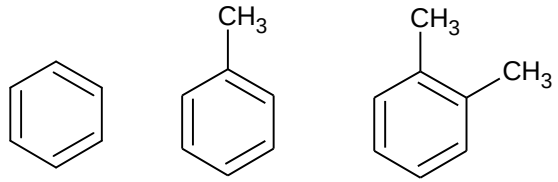
n-Decane $C_{10}H_{22}$

STRAIGHT CHAIN ALKENES



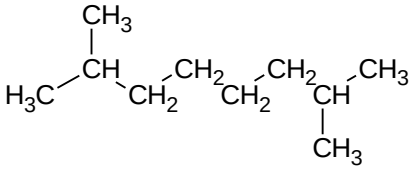
1-Decene $C_{10}H_{20}$

AROMATIC HYDROCARBONS



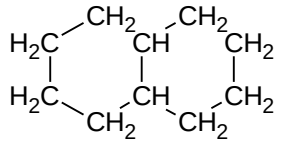
BENZENE TOLUENE XYLENE

BRANCHED CHAIN ALKANES(Iso-Paraffins)



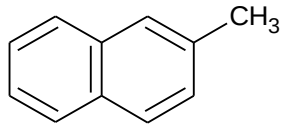
2,7-Dimethyloctane $C_{10}H_{22}$

CYCLIC HYDROCARBONS



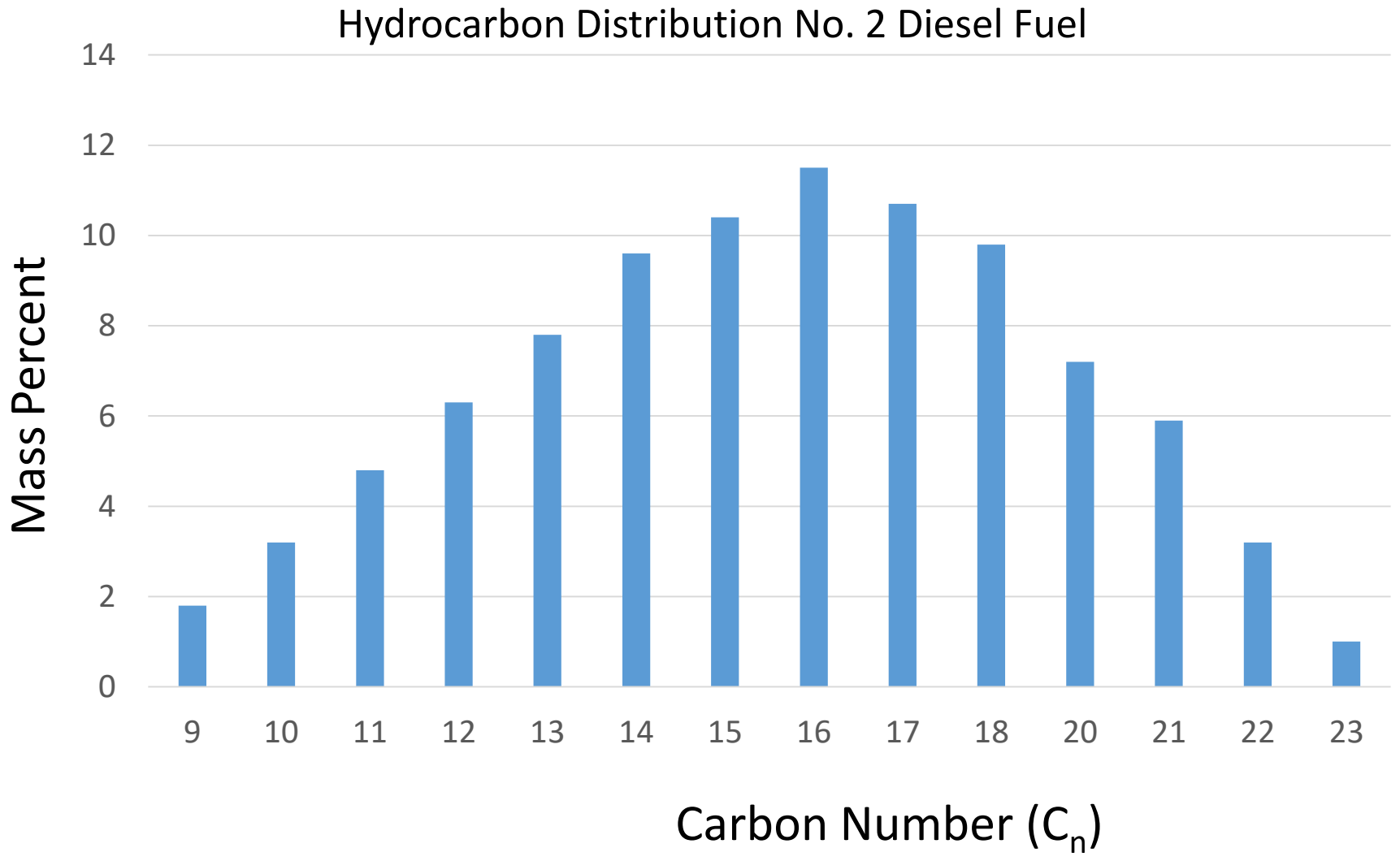
Decalin $C_{10}H_{18}$

POLYCYCLIC AROMATIC HYDROCARBONS



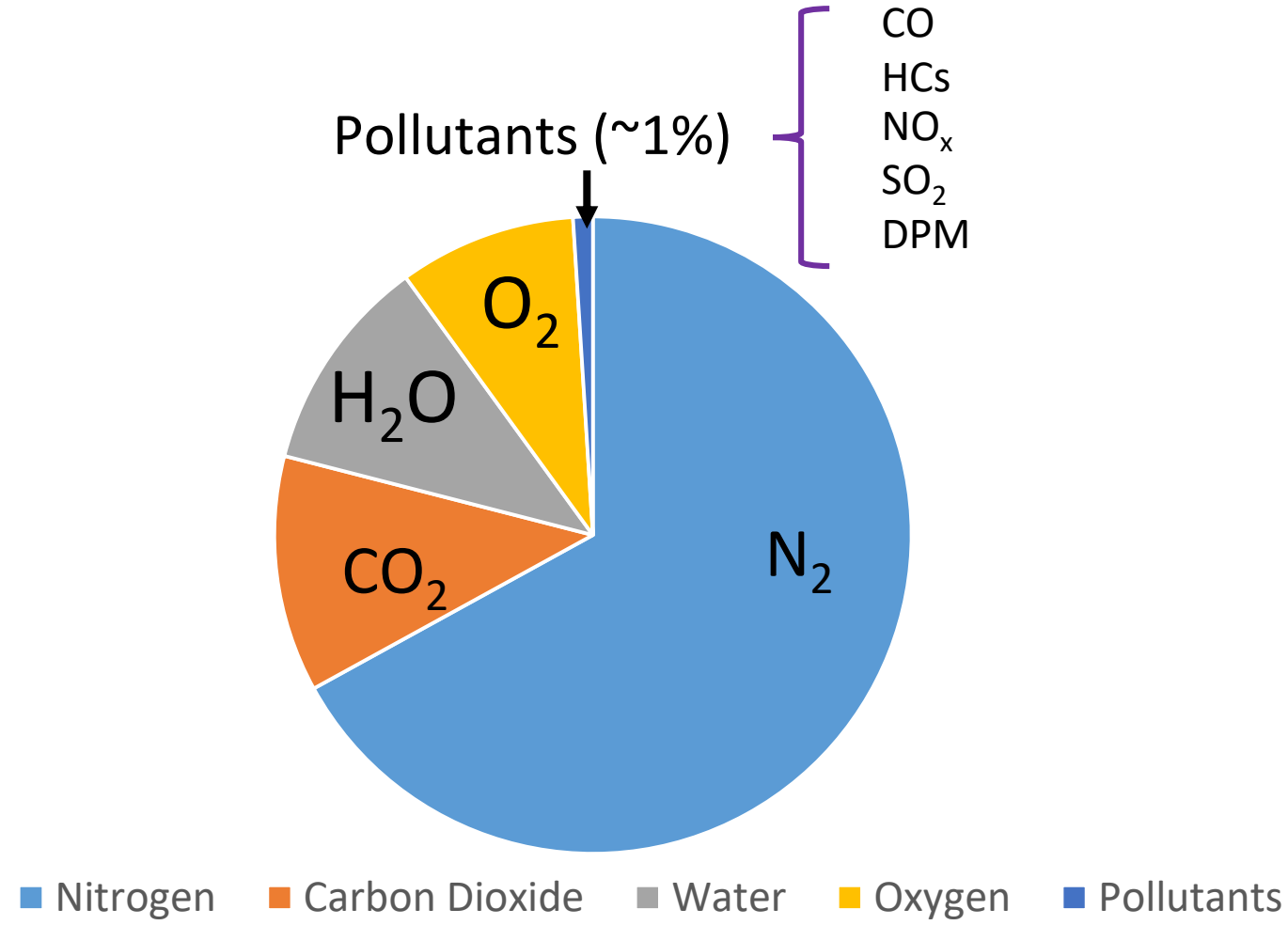
2-Methylnaphthalene

DIESEL FUEL FRACTION



Chevron, 2007, “Diesel Fuels Technical Review” www.chevron.com/products/prodserv/fuels/bulletin/diesel

DIESEL ENGINE EXHAUST EMISSIONS



Uniqueness of Military Diesel Engine Applications

- Length of service (age)
- Designer engines (submarines)
- Exhaust configurations (armoured vehicles, submarines)
- Absence of emission controls

EXPOSURE TO ENGINE EXHAUST IN MILITARY PLATFORMS

- Tanks and Armoured vehicles
- Helicopters
- Submarines

ACUTE HEALTH EFFECTS OF DIESEL EXHAUST EXPOSURE:

- irritation of the nose and eyes,
- lung function changes,
- respiratory changes,
- headache,
- fatigue and nausea

A. Sydbom, A. Blomberg, S. Parnia, N. Stenfors, T. Sandström, S-E. Dahlén, Health effects of diesel exhaust emissions European Respiratory Journal 2001 17: 733-746

CHRONIC HEALTH EFFECTS OF DIESEL EXHAUST EXPOSURE

- Largely focused on particulates (followed by NO_x , CO, HCs)

Thomas W. Hesterberg, Christopher M. Long, William B. Bunn, Charles A. Lapin, Roger O. McClellan and Peter A. Valberg, Health effects research and regulation of diesel exhaust: an historical overview focused on lung cancer risk, Inhalation Toxicology, 2012; 24(S1): 1–45

EU emission standards for passenger cars (Category M_1*)

Stage	Date	CO	HC	HC+NOx	NOx	PM	PN
		g/km					#/km
Positive Ignition (Gasoline)							
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	-	-
Euro 2	1996.01	2.2	-	0.5	-	-	-
Euro 3	2000.01	2.30	0.20	-	0.15	-	-
Euro 4	2005.01	1.0	0.10	-	0.08	-	-
Euro 5	2009.09[b]	1.0	0.10[d]	-	0.06	0.005[e,f]	-
Euro 6	2014.09	1.0	0.10[d]	-	0.06	0.005[e,f]	6.0×10^{11} [e,g]
Compression Ignition (Diesel)							
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	0.14 (0.18)	-
Euro 2, IDI	1996.01	1.0	-	0.7	-	0.08	-
Euro 2, DI	1996.01[a]	1.0	-	0.9	-	0.10	-
Euro 3	2000.01	0.64	-	0.56	0.50	0.05	-
Euro 4	2005.01	0.50	-	0.30	0.25	0.025	-
Euro 5a	2009.09[b]	0.50	-	0.23	0.18	0.005[f]	-
Euro 5b	2011.09[c]	0.50	-	0.23	0.18	0.005[f]	6.0×10^{11}
Euro 6	2014.09	0.50	-	0.17	0.08	0.005[f]	6.0×10^{11}

* At the Euro 1..4 stages, passenger vehicles > 2,500 kg were type approved as Category N_1 vehicles
† Values in brackets are conformity of production (COP) limits
a. until 1999.09.30 (after that date DI engines must meet the IDI limits)
b. 2011.01 for all models
c. 2013.01 for all models
d. and NMHC = 0.068 g/km
e. applicable only to vehicles using DI engines
f. 0.0045 g/km using the PMP measurement procedure
g. 6.0×10^{12} 1/km within first three years from Euro 6 effective dates

PN = Particle Number PM= Particle Mass HC = hydrocarbons

REF. DieselNet https://www.dieselnet.com Accessed 15 Jul., 2019

EU DIESEL EMISSION REGULATIONS

EU Stage V emission standards for LOCOMOTIVE engines						
Category	Net Power	Date	CO	HC[a]	NOx	PM
	kW		g/kWh			
RLL-v/c-1 (Locomotives)	P > 0	2021	3.50	4.00[b]		0.025

[a] A = 6.00 for gas engines
[b] HC + NOx

Nitrogen oxides - respiratory tract irritants, lung diseases and lung cancer (

Ibrahim Aslan Resitoglu, Kemal Altinisik, Ali Keskin; The pollutant emissions from diesel-engine vehicles and exhaust after-treatment systems , Clean Techn Environ Policy (2015) 17:15–27)

DieselNet https://www.dieselnet.com Accessed 15 Jul., 2019

DIESEL ENGINE EXHAUST EMISSIONS: OXYGENATED CPDS

- Nitrogen dioxide
- Sulfur dioxide
- Formaldehyde
- Acetaldehyde
- Acrolein

CARBONYLS

Cernansky, N. P. 1983. Diesel exhaust odor and irritants: a review. J. Air Pollut. Cont. Assoc. 33:97–104.

JULIA A. NIGHTINGALE, RICHARD MAGGS, PAUL CULLINAN, LOUISE E. DONNELLY, DUNCAN F. ROGERS, ROBERT KINNERSLEY, K. FAN CHUNG, PETER J. BARNES, MICHAEL ASHMORE, and ANTHONY NEWMAN-TAYLOR , Airway Inflammation after Controlled Exposure to Diesel Exhaust Particulates, AMERICAN JOURNAL OF RESPIRATORY AND CRITICAL CARE MEDICINE VOL 162 2000 p161-166.

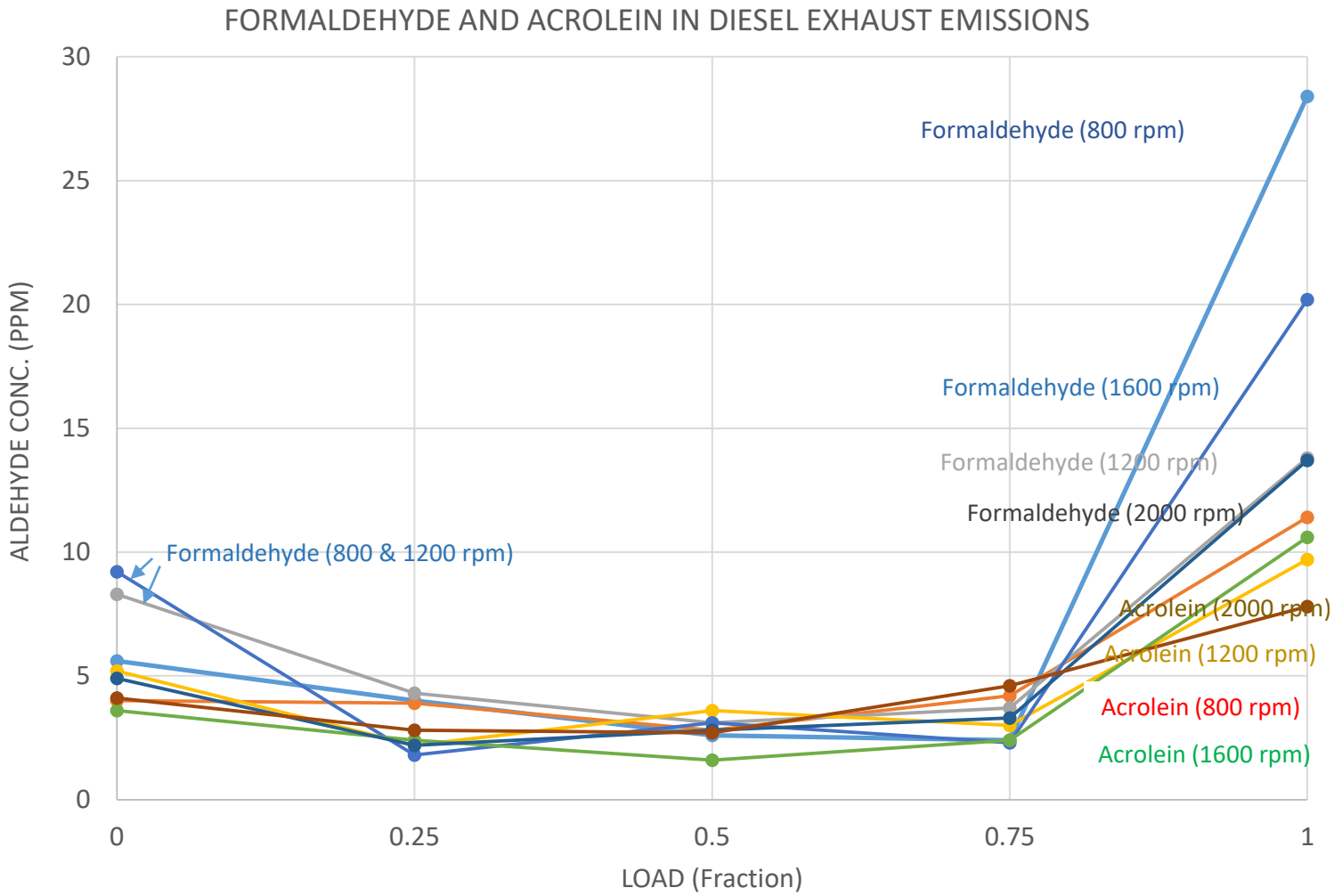
CARBONYLS in DIESEL EXHAUST

- FORMALDEHYDE
- ACETALDEHYDE
- ACROLEIN

} ~80% of Carbonyls

- ACETONE
- PROPIONALDEHYDE
- CROTONALDEHYDE
- METHYL ETHYL KETONE
- N-BUTYRALDEHYDE
- METHACROLEIN
- VALERALDEHYDE

Source: Central Pollution Control Board (2010) Study of the Exhaust Gases from different fuel based vehicles for Carbonyls and Methane Emissions, Ministry of Environment, Forest and Climate Change, Govt. of India.



Diesel engine: 7 L, 6 Cyl, (1962)

R. H. Linnell, W. E. Scott, (1962) Diesel exhaust composition and odor studies, Journal of the Air Pollution Control Association, 12, (1 1), 510-515

DIESEL EXHAUST ALDEHYDES (1962)

	Engine Speed	
Compound	500 rpm (0 Load)	1600 rpm (Full Load)
Formaldehyde	5±0.5 ppm	15±4 ppm
Acrolein	5±0.7 ppm	8±1 ppm

Acrolein was determined by the 4-hexyl-resorcinol method and formaldehyde by the chromotropic acid method. In both methods we collect diesel exhaust directly into the reagent in a fritted glass bubbler

Diesel engine: 7 L, 6 Cyl, (1962)

R. H. Linnell, W. E. Scott, (1962) Diesel exhaust composition and odor studies, Journal of the Air Pollution Control Association, 12, (1 1), 510-515

DIESEL ENGINE EXHAUST EMISSIONS: ALDEHYDES (1983, 2014)

	Diesel Exhaust	Health Effects
FORMALDEHYDE	0.40 mg m^{-3} (0.33 ppm) (2014)[1]	0.16 – 0.54 mg m^{-3} (0.13 – 0.44 ppm) eye irritation[1]
		TLV-TWA = 0.12 mg.m^{-3} (0.1 ppm) ACGIH (2017)[4]
		STEL = 0.36 mg.m^{-3} (0.3 ppm) ACGIH "
"	4 mg m^{-3} (3 ppm) (1983)[2]	
ACETALDEHYDE	0.20 mg m^{-3} (0.1 ppm) (2014)[1]	TLV - Ceiling = 45 mg.m^{-3} (25 ppm) ACGIH (2014)[5]
ACROLEIN	0.23 mg m^{-3} (0.1 ppm) (1983)[2]	TLV – Ceiling = 0.23 mg.m^3 (0.1 ppm) ACGIH (2001)

[1]Aneta Wierzbicka ,*, Patrik T. Nilsson , Jenny Rissler , Gerd Sallsten , Yiyi Xu , Joakim H. Pagels , Maria Albin , Kai Österberg , Bo Strandberg , Axel Erikssone , Mats Bohgard , Kerstin Bergemalm-Rynell , Anders Gudmundsson, Atmospheric Environment 86 (2014) 212 – 219 (The diesel exhaust was generated by an idling (900 rpm) Volkswagen Passat TDI)

[2] Cernansky, N. P. 1983. Diesel exhaust odor and irritants: a review. J. Air Pollut. Cont. Assoc. 33:97–104. (engine operating conditions not stated)

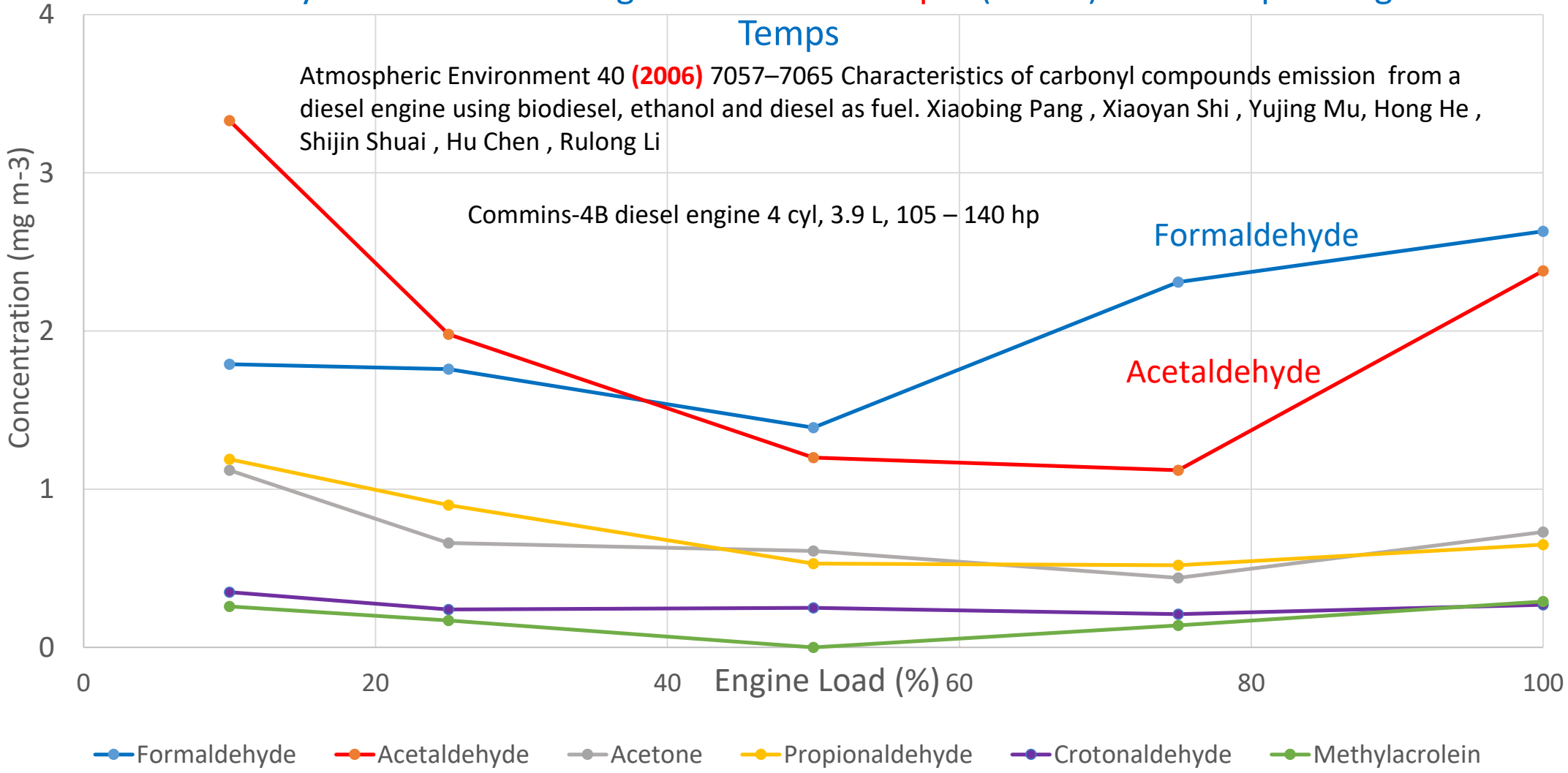
[3]JULIA A. NIGHTINGALE, RICHARD MAGGS, PAUL CULLINAN, LOUISE E. DONNELLY, DUNCAN F. ROGERS, ROBERT KINNERSLEY, K. FAN CHUNG, PETER J. BARNES, MICHAEL ASHMORE, and ANTHONY NEWMAN-TAYLOR , Airway Inflammation after Controlled Exposure to Diesel Exhaust Particulates, AMERICAN JOURNAL OF RESPIRATORY AND CRITICAL CARE MEDICINE VOL 162 2000 p161-166.

[4]TLV -TWA Threshold Limit Values – Time – weighted Average for 8 h exposure, American Conference of Governmental Industrial Hygienists (ACGIH)

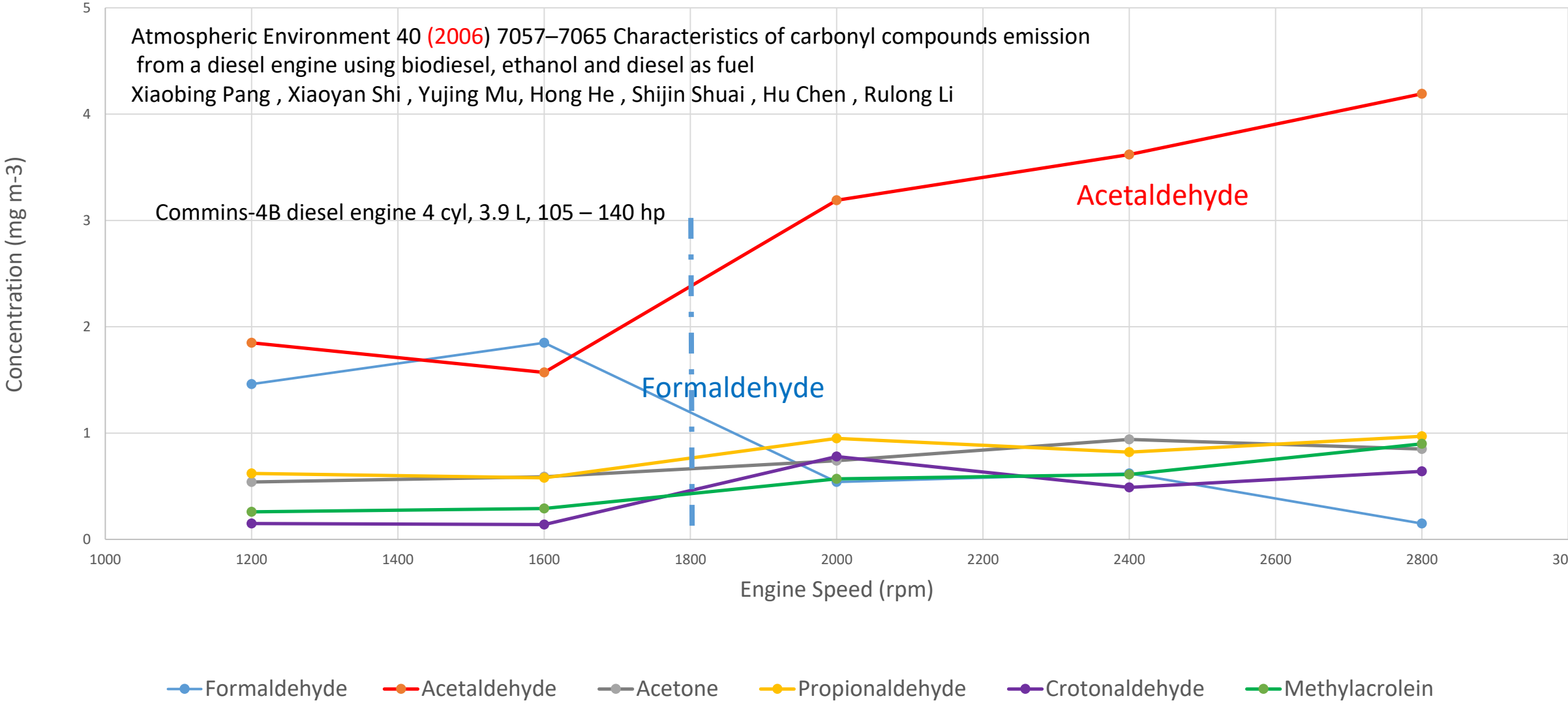
[5] The concentration in air that should not be exceeded during any part of the working exposure.

2006

Carbonyl Emissions with Engine Load at 1800 rpm (Diesel) Normal Operating Temps



Carbonyl Emissions with Engine Speed (Diesel) Normal Operating Temps



2011

Average emissions from US 2004 compliant (corresponding to EU 1998–2000) and US 2007 compliant (corresponding to EU 2013) heavy-duty diesel engines .

Compound	US 2004 (EU 1998–2000) compliant engines (average ± SD, mg/h)	US 2007 (EU 2013) compliant engines (average ± SD, mg/h)	Reduction of emissions (%)
Carbonyls (including aldehydes)	12,500 ± 3,536	255 ± 95	98

Khalek IA, Bougher TL, Merritt PM, Zielinska B. Regulated and unregulated emissions from highway heavy-duty diesel engines complying with US Environmental Protection Agency 2007 emissions standards. *J Air Waste Manage* 2011;61:427-442.

Medium-duty diesel truck emissions

(dynamometer study on the Federal Test Procedure urban driving cycle with hot start)

Emission Rates of Gas-Phase

Alkanes	15.8 mg/km (as an example)
Formaldehyde	22.3 mg/km
Acetaldehyde	41.8 mg/km

Alan C. Lloyd and Thomas A. Cackette (2001) Diesel Engines: Environmental Impact and Control, Journal of the Air and Waste Management Association, 51:6, 809-847

ALDEHYDES: SAMPLING AND ANALYSIS

1. 10 Litres Diesel Exhaust sample collected in a sampling bag (eg Tedlar)
2. 20 mL 2,4 Dinitrodiphenyl hydrazine (DMPH) soln. added.
3. 10 µL sample injected into HPLC chromatographed with 1:1 acetonitrile/water

Direct Injection Diesel Engine, 7L (2007)

(sampling at operating temp., 700 rpm)

Formaldehyde: 9-12 ppm

Acetaldehyde: 2.5 – 2.75 ppm

- *M.M. Roy,* HPLC Analysis of Aldehydes in Automobile Exhaust Gas: Comparison of Exhaust Odor and Irritation in Different Types of Gasoline and Diesel Engines, *International Energy Journal 8 (2007) 199-206*

DNPH Cartridge Sampling and Analysis of Aldehydes from Engine Exhaust

Exhaust Sampling:

The carbonyl samples are collected by flowing dilute exhaust (approximately 1.0 liter/min. flow rate) through cartridges (Tejada, 1986). The samples are then brought to the laboratory for analysis.

Extraction and Analysis:

Each cartridge contains an absorbing compound 2,4 Dinitrophenyl Hydrazine (2,4-DNPH) which complexes with the carbonyl compounds to form their dinitrophenylhydrazone derivatives .The cartridges are then extracted with 5.0 mL acetonitrile and analyzed (Tejada, 1986).

Separation and analysis is performed using a High Performance Liquid Chromatograph (HPLC) with an ultraviolet (UV/VIS) detector.

Central Pollution Control Board (Ministry of Environment & Forests) India, (2010) Study of the Exhaust Gases from different fuel based vehicles for Carbonyls and Methane Emissions