Emission of aldehydes from light duty diesel vehicles

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Keywords
Hazardous substances. Aldehydes. Acetaldehyde. Formaldehyde. Vehicle emissions. Air pollution.

Abstract

Objective
To characterize acetaldehyde and formaldehyde emissions, which are harmful gases to human health and not yet regulated for diesel engines.
Methods
Standardized tests were performed in four diesel light duty commercial vehicles, using a frame dynamometer and test procedure FTP-75. The pollutants were analyzed by high performance liquid chromatography.
Results
Results have shown acetaldehyde emission ranged from 5.9 to 45.4 mg/km, and formaldehyde emission from 16.5 to 115.2 mg/km. The average emission for aldehyde sum was 58.7 mg/km, ranging from 22.4 to 160.6 mg/km. The proportion between the two substances remained constant, close to 74% for formaldehydes and 26% for acetaldehydes.
Conclusions
The emission of diesel vehicle aldehydes was significant when compared with actual spark ignition vehicle emissions, or with the foresee limit for Otto cycle vehicles in Brazilian legislation. Establishing emission limits for these substances also in diesel vehicles is imperative in the light of the vehicle fleet growth, toxicity of these compounds, and their contribution as precursors in ozone gas formation reactions in low troposphere.

INTRODUCTION

In the metropolitan region of São Paulo (MRSP) fleet of automotive vehicles, 5.9% were powered by diesel fuel in 2002. However, its relative share in mobile source emission was 83% of nitrogen oxides (NOx), 53% of sulphur oxides (SOx), and 77% of particulate matter (PM), not considering the share due to tyre wear emissions and 18.4% of total hydrocarbon rate.[5]

Depending on the increase of van use in public, school, and small delivery service transport, among others, MRSP diesel-powered light commercial vehicle fleet has had an expressive growth of 5.7% per year, a rate much higher than the last ten-year growth average of the world's vehicle fleet, of 2.6% per year.[4]

The emission of some diesel vehicle pollutants (total hydrocarbons, nitrogen oxides, sulphur oxides, particulate matter, among others) has already been regulated in Brazil. Despite that, this high growth rate, associated with epidemiological study results, causes new concerns with respect to the population's health due to aldehyde exposure. This is because the law limits the emission of these pollutants only for spark-ignition vehicles, i.e., gasoline, alcohol, or gas-powered vehicles).[7]

Aldehydes cause irritation of eyes and airways and may cause headaches, general discomfort and irritability. There are reports of asthma caused by respira-

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Table 1 - Characteristics of vehicles tested.

Vehicle	Type	Year	Accumulated distance (km)	Volumetric displacement (L)	Mass (kg)	Power (kW)
A	Pick-up	1995	31182	2.8	1758	64
B	Microbus	1995	101646 / 2831*	2.7	2041	55
C	Microbus	1997	22888	3.1	2020	85
D	Microbus	1998	43697	3.1	1990	85

*After the engine was rectified

tory tract irritation due to formaldehyde exposure.

Additionally they can cause potential harm to flora, including potherbs, and fauna, especially unicellular organisms that are relatively sensitive to formaldehydes.[12,13]

Aldehydes can be involved in chemical reactions in the atmosphere, generating other compounds. Among them the photochemical smog formation that mostly produces oxidizing gases, especially gas ozone. Besides causing respiratory conditions to human beings, oxidizing gases can also damage materials, mainly rubbers.[12]

High gas ozone concentrations have been a reason for warning in many urban centers, especially MRSP, which has presented frequent violations to the air quality standard for this pollutant, as detected in many measuring stations.[5]

Sporadic measurements of the atmosphere in the municipality of Sao Paulo by the Environmental Cleaning Technology Company (Cetesb) in 1997 have showed maximum levels of 40 parts per billion (ppb) of acetaldehyde and 77 ppb of formaldehyde.[5] These levels are not very different from those obtained by Montero et al[8] who in 1999 found maximum levels of 56.6 ppb of acetaldehyde and 46.6 ppb of formaldehyde. The World Health Organization (WHO)[14] recommends a limit level of 86.5 ppb of formaldehyde for 30 minutes as maximum exposure time for the population.

The purpose of the present study was to identify and quantify two of the main aldehydes discharged by diesel cycle light commercial vehicles. In addition, to compare their results with average Otto cycle vehicle discharges and with the limits established in the Brazilian legislation for spark-ignition vehicles.

The present study is intended to provide input for aldehyde emission regulation and public health protection in Brazil.

METHODS

Four diesel cycle light commercial vehicles, three vans and one pick-up were submitted to standardized tests using a Clayton frame dynamometer, model ECE-50, in Cetesb's Vehicle Emission Laboratory. This dynamometer has the capability of simulating vehicle use conditions on the road. Table 1 displays the main characteristics of vehicles used in the study.

Each vehicle was submitted to two tests. All vehicles were tested in accordance with the Brazilian Standard ABNT/NBR 6601/01 which driving cycle is identical to the American test procedure USEPA FTP-75.[11] This standardized test procedure simulates urban driving conditions. It is divided into three phases: cold, stabilization, and hot phase. Vehicle fuel consumption was also measured, in accordance with Standard ABNT/NBR 7024.[3]

Vehicle adjustment and fuel consumption are two variables that can interfere with the results of a vehicle test; that is why test standards specify the use of a standardized fuel in order to reduce dispersion. This is mainly attained in vehicle homologation tests, when the aim is an exclusive assessment of the vehicle, which requires fuel repeatability.

It was sought to know the actual pollutant amount discharged by vehicles in use, including all the variability that a non-standardized fuel or non-previously adjusted vehicles could generate. For that, commercial diesel fuel was used in the study instead of standardized diesel fuel. All vehicles were tested with no previous adjustment in order to assess the effective aldehyde amount emitted into the atmosphere.

Figure 1 shows the sampling apparatus. After being mixed and homogenized with ambient air, samples were collected in accordance with CFR 40 method directions.[11] A constant volume sampler per critical venturi (Horiba CVS-CFV, model 20A), together with a total dilution tunnel, was used. This dilution tunnel comprised a stainless steel duct with a diameter that would create a turbulent flow to homogenize discharges with environmental air mixing.

An ambient air-mixing chamber was also used, receiving dilution air previously filtered by two particle filters, and one filter for organic compounds (hydrocarbons). This chamber was positioned as close as possible to the vehicles in order to prevent water condensation in the sampling system.

As shown in Figure 1, the sampling point was positioned downstream of the cyclonic separator, in the center, facing upstream. A diluted portion of the discharge gas was bubbled into gas washing flasks containing an absorbent solution, at a flow rate of two liters per minute, in accordance with directions of the ABNT/NBR 12026 method.[1]

In order to obtain the actual vehicle emissions, each phase of the test had an assemblage of two gas washing flasks in series and ambient air collecting had an assemblage of two flasks in series to subtract the ambient concentration from the total measured. These procedures comprised a total of eight flasks, placed in a sink containing chilled water (temperature ranging from 2ºC to 6ºC). The ambient air sampling point was located close to the aldehyde sampler.

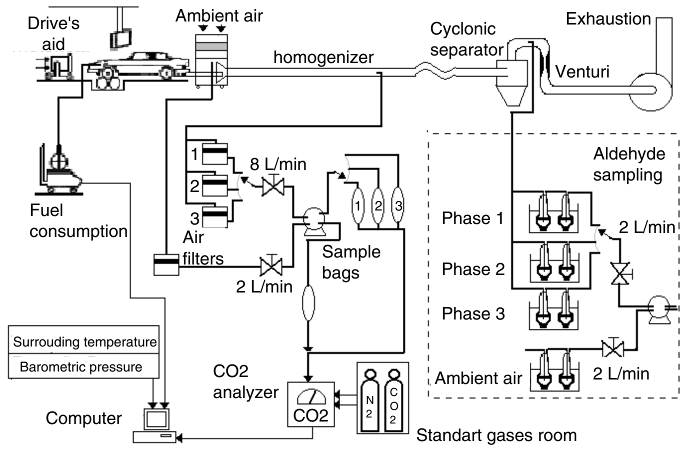

Figure 1 - Vehicle test diagram, displaying collection points for aldehyde and carbonic gas samples.

Each gas-washing flask contained 25 mL of an aldehyde absorption solution, so that any aldehyde in the discharge gas would generate carbonylic derivatives.

The absorption solution was prepared in the following proportion: 150 mg of 2.4 dinitrophenylhydrazine (purity equal to 99%, CAS 119-26-6) per liter of acetonitrile (high-performance liquid chromatograph – HPLC –, purity higher over 99.9%, CAS 75-05-8), and added five drops of a perchloric acid solution (170 ml of perchloric acid – 70% PA, formula $HClO_4$, CAS 7601-90-3 – per each distilled and deionized water liter). The samples were injected on the same day of their sampling.

Gases, after filtering, were collected in inert plastic bags (tedlar) for quantification of carbon dioxide (CO_2).

The method used to determine carbonylic derivative concentrations was based on the proportionality of the areas under standard and sample chromatographic peaks. Carbonylic derivatives were separated, identified, and quantified in a HPLC with a visible ultraviolet (UV/VIS) detector.

A Waters pump model 6000A and a Jasco UV/VIS detector model UV-970, 365 nm wavelength, equipped the HPLC. A reverse-phase octadecylsilane (ODS) column (C-18, 25 cm x 4.6 ID x 5 mm) was used with isocratic mobile phase containing 65% acetonitrile and 35% distilled water, at a flow rate of 1 mL/min.

In order to determine aldehyde linearity range, a stock solution was prepared by dissolving the standard of formaldehyde (99% purity, CAS 1081-15-8), and acetaldehyde (99% purity, CAS 1019-57-4) in acetonitrile with further homogenization. From this solution, five different dilutions were prepared and five injections of each solution were performed. Using linear regression, each aldehyde linearity stripe was determined, adopting the criterion of correlation coefficient (r^2) greater or equal to 0.9999.

Acetaldehyde linearity stripe ranged from 20.20 to 1,010 µg/L and its greatest standard deviation in the calibration curve was 0.01436 µg/L. Formaldehyde linearity stripe, however, ranged from 19.86 to 993 µg/L and its greatest standard deviation in the calibration curve was 0.02057 µg/L.

Aldehyde detection limit was determined by adopting threefold the standard deviation obtained relatively to the minimum measurement; acetaldehyde level was 0.30 µg/L and formaldehyde level was 0.67 µg/L.

Aldehyde quantification limit was determined by adopting tenfold the standard deviation obtained relatively to the minimum measurement; acetaldehyde level was 1.00 µg/L and formaldehyde level was 2.23 µg/L.

As a calibration daily standard one of the stock solution dilutions was used and its concentration was as close as possible to the samples' concentrations.

RESULTS

Table 2 displays the results of all tests performed. All tested vehicle acetaldehyde emission ranged from 5.9 up to 45.4 mg/km and formaldehyde emissions ranged from 16.5 up to 115.2 mg/km. Both aldehydes

Table 2 - Fuel autonomy and aldehyde emission in the vehicles tested (by km and fuel consumption) according to vehicle and test.

Vehicles	Tests	Fuel autonomy [km/L]	Acetaldehyde emission* [mg/km]	Formaldehyde emission* [mg/km]	Sum of aldehydes* [mg/km]	Aldehyde emission vs. fuel consumption [mg/L]
A	1st test	9.618	45.421	115.200	160.621	1406.402
	2nd test	9.011	31.689	89.156	120.845	993.477
	Average	9.315	38.555	102.178	140.733	1199.940
B	1st test	6.650	9.524	26.214	35.739	250.605
1st time	2nd test	6.538	8.663	25.330	33.992	221.991
	Average	6.594	9.094	25.772	34.866	236.298
B	3rd test	6.688	16.663	50.558	67.221	428.326
2nd time	4th test	6.745	17.986	53.293	71.279	452.038
	Average	6.717	17.324	51.926	69.250	440.182
C	1st test	7.732	7.004	20.081	27.085	204.843
	2nd test	7.795	6.565	17.611	24.176	176.485
	Average	7.764	6.784	18.846	25.630	190.664
D	1st test	7.096	5.907	16.544	22.450	151.006
	2nd test	7.127	5.897	17.521	23.418	161.217
	Average	7.112	5.902	17.032	22.934	156.111
All vehicles	Average	7.500	15.532	43.151	58.683	444.639
	SD	1.059	13.265	34.350	47.573	422.915

SD: standard deviation
*In accordance with CFR 40 (1977)

sum varied from 22.4 to 160.6 mg/km, while aldehyde sum emission relatively to fuel consumption varied from 151.0 to 1,406.4 mg/L.

DISCUSSION

Comparing vehicle B's urban* autonomy averages before and after engine reconditioning, they were 6.6 km/L for the two first tests before reconditioning and 6.7 km/L for the two tests after it. A practically inexpressive improvement of almost 2% was found. Nevertheless, the average aldehyde emission sum changed from 34.9% to 69.2 mg/km, a practically 100% increase. This unexpected value indicates the need for further evaluation, since a low pollutant emission is normally anticipated in well-regulated engines. Though according to Turns,[10] formaldehyde generation can be explained by methane or propane (obtained from combustion breakdown) stoichiometric oxidation with air under high temperatures, generating O, H, and OH radicals that attack methane and propane.

Sjogren[9] has studied emission of two diesel engines with several proportions of air/fuel and has found values that ranged from 6.2 to 128 mg/km for acetaldehyde and from 4.8 to 258 mg/km for formaldehyde. These results show a wider range and maximum values that are more than double of those obtained in the present study. However, these differences can be explained by differences found in the bus cycle, altering the pollutant emission profile, and of several air/fuel proportions; this provide fuel or oxygen in excess for an adequate combustion.

Since 1992, Brazilian legislation, through the Vehicle Air Pollution Control Program (Proconve), has set an aldehyde sum emission limit of 150 mg/km for new Otto-cycle light passenger vehicles. In 1997, this limit was reduced to 30 mg/km, i.e., a reduction of 80%. In 1998, this program has set the same limit of 30 mg/km for new Otto-cycle light commercial vehicles (with a test weight up to 1,700 kg) and an emission limit of 60 mg/km (for vehicles with a test weight greater than 1,700 kg).[7]

As of 2009 aldehyde emission limit has been anticipated to be 20 mg/km for the same categories of the vehicles with a test weight below or equal to 1,700 kg and 40 mg/km for vehicles with test weight greater than 1,700 kg. However, no inclusion has been anticipated for diesel cycle vehicle aldehyde emission.[6]

When compared with actual emissions of light spark

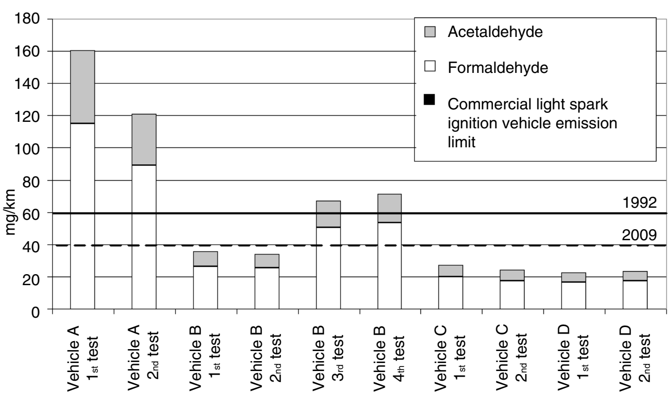

Figure 2 - Formaldehyde and acetaldehyde emission of the 10 tests performed, by run km, vehicle, and test. Comparison between PROCONVE limits in 1992 and 2009.

*Urban autonomy is inversely proportional to urban consumption, according to NBR 7024 (ABNT,[2] 1990).

ignition vehicles manufactured in 1995, diesel vehicle produce more aldehydes than gasoline ones and have the same magnitude as those of alcohol vehicles, given the emission average factor of 25 mg/km for gasoline vehicles and 42 mg/km for alcohol vehicles.[5]

In early Proconve implementation years, diesel vehicle aldehyde emission was considered insignificant, for their emission was much lower when compared with same category Otto-cycle vehicles. However, as seen in Figure 2, two of the four tested vehicles have violated the spark ignition limit, that is, 60 mg/km; one after its engine had been rectified and the other with 31,000 original km. The other two vehicles emitted on average approximately 46% of the limit already established for same category spark ignition vehicles.

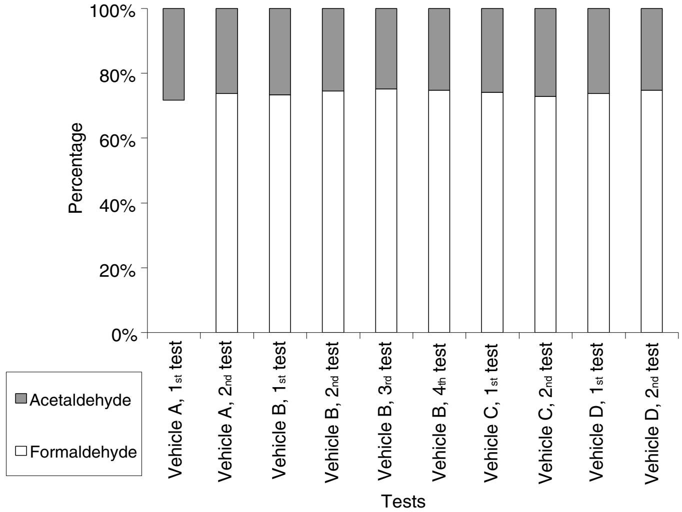

Figure 3 - Acetaldehyde and formaldehyde emission share (%), by vehicle tested and test.

In Brazil, no studies have been carried out aiming at determining deterioration factors related to diesel vehicle aldehyde emission, seen as highly important, for it is necessary to have a better knowledge of the profile of these compound emissions to the atmosphere.

The results suggest that, in some cases, diesel vehicles of the tested category emit much more aldehydes than spark ignition vehicles. The latter have already been equipped with catalytic converters, which significantly reduce these pollutant emissions.

Though aldehyde sum emission differences were significant from one vehicle to another – by analysis of variance (ANOVA), one can confirm that aldehyde emission average was different among vehicles (F*=28>Fc**=6.6). The proportion between acetaldehyde and formaldehyde remained practically the same in the ten tests performed, for it was around 74% of formaldehyde and 26% of acetaldehyde, as shown in Figure 3.

Performing studies with larger samples would be relevant, including the carrying out tests in motor dynamometers and in other vehicle categories in order to describe the in-use diesel vehicle fleet aldehyde emission profile, evaluate the deterioration factor of these vehicles as well as create an inventory of these pollutants emissions.

As a conclusion, the present study shows diesel vehicle aldehyde emission is significant and important and defining an emission limit for these substances, as for spark ignition vehicles, is also necessary for these vehicles. Brazilian legislation restriction for spark ignition vehicles with regards to aldehyde emissions showed to be effective and resulted in environmental improvements, especially with the use of catalytic converters. Its relevance is stressed considering diesel vehicle fleet growth, added to the fact that aldehydes pose risks to human health, contribute to an increase in biota morbidity and mortality rates, besides being significantly involved in ozone formation photochemical reactions in low troposphere.

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*F: Factor calculated in ANOVA test.
**Fc: Critical factor in ANOVA test.

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