

SPECIATED HYDROCARBON EMISSIONS FROM ROAD TRAFFIC

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In Proceedings of the 16th International Clean Air & Environment Conference, Clean Air Society of Australia & New Zealand, 19-22 August 2002, Christchurch, New Zealand, pp. 746-757.

Summary

Internationally, speciated hydrocarbon emissions from road traffic are of growing environmental importance due to their significant contribution to several key air pollution problems. The group of hydrocarbons covers a broad range of individual species. The extent to which emission measurement data for each compound is available varies widely, depending on the compound. However, even in the case that an abundant source of information is available, direct use of this data in (urban) emission inventories should be carefully considered. The reason for this is that speciated hydrocarbon emissions are sensitive to many factors that underly the emission data, including vehicle technology, emission type, measurement methodology, fuel composition and driving conditions among others. Qualitative and possibly quantitative impact assessment of these issues could lead to improved (use of) emission inventories for speciated hydrocarbon emissions from road traffic.

Keywords: Traffic Emissions, VOC Profile, Speciated VOC emissions, Speciated HC emissions, Air Toxics, VOCs, NMHC, THC, Hydrocarbon Composition, Light-Duty Vehicles, Heavy-Duty Vehicles, Passenger Cars, Petrol, LPG, Diesel.

1. Introduction

This paper discusses several (emerging) issues with respect to speciated hydrocarbon emissions from road traffic. Australian data and their use in emission inventories is taken as a starting point and international literature is used for the discussion. This paper does not aim to cover the whole body of information on speciated hydrocarbons emissions from road traffic, which is widely available. Rather, it focuses on several key issues such as measurement methodology, fuel composition and driving conditions among others.

Historically, emissions standards and emission measurements have addressed only the mass of total hydrocarbons (THC) or non-methane hydrocarbons (NMHC), in addition to CO and NO_x. However, individual hydrocarbons (HCs) have vastly different health impacts due to different toxic, carcinogenic or mutagenic characteristics, different photochemical smog and secondary aerosol formation potentials and different greenhouse impacts (methane) and stratospheric ozone depletion potential (CFCs and HCFCs). This has led to an increasing interest in speciated HC emissions.

The hydrocarbon classes discussed in this paper include species with different physical and chemical behaviour and contain not only pure hydrocarbons containing only carbon and hydrogen, but also

hydrocarbons containing oxygen, e.g. aldehydes and ketones.

Individual HCs can be in the gas phase or particulate phase and include gas-phase VOCs¹, gas-phase SVHCs² (also commonly called SVOCs) and particulate-phase HCs, where condensation of SVHCs on aerosols occurs.

The acronyms VOC, THC, NMHC and HCs are frequently used but not clearly defined (EPAV, 1999). The exact definition of the HCs differs in literature and depends on the study objective, the selected measurement equipment and so forth. We roughly define VOCs as being C₁-C₁₂ hydrocarbons, SVHCs as C₁₀-C₂₆ (mainly alkanes and aromatics) and particulate phase hydrocarbons as C₁₄₊.

The major part of anthropogenic VOC emissions in urban areas come from light-duty petrol spark-ignition vehicles (LDPVs) (Watson *et al.*, 2001). Heavy-duty diesel vehicles (HDDVs) are particularly important with respect to SVHC emissions as they account for approximately 50% of the total NMHC emission rates from HDDVs, whereas this is approximately 10% for LDPVs (Zielinska *et al.*, 1996). The amount of NMHC

¹ Volatile organic compounds

² Semi-volatile hydrocarbons

in the particulate-phase can also be significant, especially with respect to diesel trucks (Pierson *et al.*, 1996).

There is much more information available in international literature on speciated HC emissions from spark-ignition vehicles (i.e. petrol fuelled, and to a much lesser extent LPG fuelled) than from compression-ignition vehicles (i.e. diesel fuelled), although there has recently been an increased interest in the measurement of speciated HCs above C₁₂ (e.g. Staehelin *et al.*, 1998; Siegl *et al.*, 1999). As a consequence, this paper mainly focuses on speciated HC emissions from SI-vehicles, i.e. speciated VOC emissions, although information on CI-vehicles is included where available.

There are different methods to estimate speciated HC emissions including laboratory studies³, tunnel studies, CMB modelling⁴ and roadway investigations. There have been a number of overseas tunnel studies and one recent Australian study specifically designed to develop speciated HC emission factors.

While both tunnel and roadside data have provided estimates of emissions from the entire vehicle fleet under specific operating conditions, most of the dynamometer studies have been performed using prototype, new or well-functioning vehicles.

Measured speciated HC emissions can be 'translated' into either emission factors (mg/km or µg/km) or HC profiles expressed as THC mass fractions (%w/w)⁵. The advantage of these normalised HC profiles is that they have been reported to be remarkably stable for most HCs under different conditions, particularly with respect to separate HC classes and the more abundant species.

Furthermore, HC profiles have the ease that they can be directly applied to the total hydrocarbon emissions or THC emission factors, provided that the sum of identified HCs and the corresponding THC measurements agrees reasonably well, say within 10-20%. However, in this respect it is important that all HC compounds have been taken into account. This issue is discussed further in section 3.3.

2. Australian Speciated HC Data

Most comprehensive studies investigating speciated HC emissions from motor vehicles have been performed in America (Auto/Oil Air Quality Research Program) and Europe (Auto-Oil Programme).

Until recently, there were little data available for the Australian car population. Although this applies to any local situation, this is important from the Australian perspective, as local data should be used for emission estimation as much as possible, in order to account for the unique vehicle fleet characteristics (vehicle emission

standards, engine calibration practice, fuel composition and so forth).

There have been different Australian studies into HC emission composition for the fleet and more specifically for different technology classes and fuel types and also for both exhaust and evaporative emissions. These include tunnel studies (Mitchell *et al.*, 1981; Duffy & Nelson, 1996), on-road studies (EPAV, 1999) and dynamometer studies (Nelson & Quigley, 1984; Nelson & Duffy, 1998; Duffy *et al.*, 1999). Some dynamometer studies specifically developed emission factors for certain VOC compounds, such as 1,3-butadiene (Ye *et al.*, 1997 and 1998) and BTX⁶ (Duffy *et al.*, 1998).

The recent laboratory investigation into the VOC profile of exhaust and evaporative emissions from 82 Australian vehicles by Duffy *et al.* (1999) is significant for the development of speciated VOC emissions in Australia. The strength of these data lies in the fact that in-service vehicles were tested 'as-received' using commercial fuel, therefore providing data that are potentially more representative of real-world emissions.

However, some aspects that influence speciated HC emissions should be carefully considered in order to prevent potential errors when this information is directly applied to develop (urban) emission inventories. These will be discussed in the next section.

3. Factors That Influence Speciated HC Emissions

Speciated HC emission factors are commonly determined by the combination of THC emission rates and HC profiles. Thus, consideration of both determinants is important. There are several factors that influence the THC emission rate and the HC profile:

- vehicle technology type;
- type of emission;
- measurement method;
- fuel composition;
- driving conditions;
- ambient temperature;
- cold-start operation; and
- tuning and maintenance practice.

Although these factors are not mutually exclusive, they are considered separately in the following subsections with respect to their impact on both THC emission rates and the HC profile.

³ Chassis dynamometer exhaust and SHED evaporative emissions testing.

⁴ e.g. McLaren *et al.* (1996).

⁵ This is the hydrocarbon composition, i.e. the weight fractions of individual compounds relative to total mass of HC emitted.

⁶ Shorthand for Benzene, Toluene and Xylenes.

3.1. Vehicle Technology Type

THC emission levels vary significantly with technology type⁷. In addition, exhaust and evaporative HC profiles vary significantly with vehicle technology.

Usually, the impact of vehicle technology is sufficiently covered by the development of speciated HC emission factors for the different technology classes. However, there is a constant need for new measurements and updated emission factors, due to a continually changing fleet composition. Some important differences between technology types are discussed in the following subsections.

Engine Type, Size & Fuel Type

Generally, gas-phase THC emissions from light-duty diesel vehicles (LDDVs) are relatively low when compared to light-duty petrol vehicles, but heavy-duty diesel vehicles emit higher amounts of gas-phase THC emissions and up to about twice those from light-duty vehicles have been reported (Zielinska *et al.*, 1996; Sagebiel *et al.*, 1996; Staehelin *et al.*, 1998).

CI diesel and SI petrol vehicles also have entirely different HC profiles. This is illustrated by the fact that fleet average HC profiles change significantly with small changes in fleet composition, for example, an increase in the proportion of catalyst petrol cars or diesel vehicles (Staehelin *et al.*, 1997).

Broadly speaking, (light) aromatic HCs and the lighter n-alkanes (<C₉) are more characteristic of spark-ignition vehicle emissions, whereas the heavier n-alkanes (>C₁₁) are more characteristic of diesel emissions. BTEX⁸ emissions are typical for petrol vehicles, whereas diesel vehicles contribute more significantly to higher aromatics such as iso-propylbenzene, 1,2,3-trimethylbenzene and p-ethyltoluene. Similarly, polycyclic aromatic hydrocarbons (PAHs) emission profiles are different for light-duty petrol and heavy-duty diesel vehicles.

The heavier gas-phase HC emissions (starting from n-undecane including PAHs such as fluoranthene, chrysene, benzo[a]pyrene etc.) from diesel heavy-duty vehicles are much higher than those for light-duty vehicles (Zielinska *et al.*, 1996; John *et al.*, 1999). Low molecular weight and particle-bound PAHs are generally regarded as the major toxic pollutants of diesel exhaust (Gorse *et al.*, 1991; Miguel *et al.*, 1998), although spark-ignition vehicles can exhibit similar emission levels of low molecular weight, (mainly) gaseous, PAHs and high molecular weight particle PAHs (Hampton *et al.*, 1983; Benner *et al.*, 1989).

Specific gaseous air toxics such as 1,3-butadiene, formaldehyde and acetaldehyde from light-duty diesel

vehicles have been reported to be both lower and higher than three-way catalyst petrol vehicles (Jemma *et al.*, 1992; Siegl *et al.*, 1999). In contrast, heavy-duty diesel vehicles have been reported to emit up to an order of magnitude more aldehydes than light-duty spark ignition vehicles (Pierson *et al.*, 1996; Schmid *et al.*, 2001).

Emission Control Technology

In addition to other engine type characteristics (carbureted versus fuel-injected), the presence of emission control technology (e.g. catalyst) has an important impact on THC emissions and the HC profile.

Since the late 1960s several studies have shown the significant impact of emission control technology on exhaust HC composition. For instance, Jackson (1978) reported that the use of oxidation catalysts and three-way catalysts greatly changed the exhaust HC composition by increasing alkanes and decreasing olefins and acetylene, when compared to those of non-catalyst cars.

The now commonly used three-way catalyst has not only reduced THC emissions by as much as 70% to over 95% compared to uncontrolled emissions, but has also drastically altered the exhaust HC composition. In other words, catalysts not only reduce total HC emissions but also cause a shift in the HC profile when compared to non-catalyst vehicles.

The reason for this is that catalyst conversion efficiency varies substantially from one HC to another, typically showing increased efficiency with increasing carbon-chain length within each class. For instance, alkanes can remain relatively uncontrolled, whereas reactive alkenes and alkynes are effectively oxidised, even at low catalyst temperatures (Rogak *et al.*, 1998). According to Ye *et al.* (1997) the order of the conversion efficiency observed for the various HCs is generally:

- methane, least effective: 9-37%;
- saturated hydrocarbons: 11-86%;
- aromatics: 78-90%; and
- unsaturated hydrocarbons, most effective: 80-95%.

This has important implications, for example with respect to ozone formation potential. According to several overseas and Australian studies, the highest ozone forming potential for light-duty vehicles is observed for non-catalyst cars due to the highest THC emission rates in combination with a high proportion of reactive substances like alkenes and aromatics, as catalysts preferentially oxidise these photochemically reactive species (e.g. Jackson, 1978; Duffy *et al.*, 1999; Schmitz *et al.*, 2000).

Finally, the presence of evaporative emission control technology (carbon canisters) impacts on THC emissions and on the evaporative THC profile.

It should be noted that despite the fact that shifts occur in the HC profile, the actual absolute emission levels of individual HCs are generally lower for newer

⁷ This includes differences in engine type (e.g. spark-ignition – SI versus compression-ignition – CI or carbureted versus fuel-injection), fuel type (e.g. petrol, diesel, LPG), engine size, vehicle mass and emission control configuration (e.g. non-catalyst, open-loop catalyst, closed-loop catalyst).

⁸ Benzene, Toluene, Ethylbenzene & (m-,o-,p-) Xylenes

technology vehicles when compared to older technology vehicles.

3.2. Type Of Emission

There are two 'types' of HC emissions: evaporative and exhaust or tailpipe emissions. Exhaust HC emissions are generated by the combustion process in the engine and by the survival of fuel HCs from this combustion process, i.e. unburnt HCs. Evaporative emissions consist of fuel (mainly petrol) HC losses through the vehicle's fuel system and include diurnal emissions and hot-soak emissions.

Evaporative and exhaust emissions have significantly different HC profiles. Moreover, there is also a spatial aspect to the type of emissions: evaporative speciation will be important to urban areas dominated by parking lots and exhaust speciation (including running-loss emissions) to those areas dominated by moving vehicles on streets and highways.

When exhaust emission HC profiles are compared to fuel composition, exhaust compositions are depleted in alkanes and aromatics, but enriched in alkenes and carbonyls. Alkanes in exhaust emissions are largely derived from unburnt fuel components. Aromatics come from unburnt fuel components and from partial oxidation or thermal degradation of larger aromatic fuel components.

Exhaust emissions of alkenes (olefins) are both from unburnt fuel components and partial oxidation products from alkanes. Typical combustion-derived HCs are the alkynes, light olefins and carbonyls. PAHs are constituents of diesel fuel, but they are also produced during combustion.

It is widely believed that the evaporative emissions from spark-ignition vehicles may constitute much or even most of the total HC emissions from road traffic (Pierson *et al.*, 1999). High emission factors for isopentane and n-butane, typical for evaporative emissions, were observed in a recent tunnel study, which supports these findings (Touaty & Bonsang, 2000).

Evaporative emissions are directly related to fuel composition. Emissions of low molecular weight alkanes (roughly C₅ to C₈) can be attributed to the presence of these compounds in petrol, whereas exhaust emissions of semi-volatile branched and cyclic paraffins (roughly C₁₈ to C₂₂) can be attributed to the presence of these compounds in diesel (Fraser *et al.*, 1998).

Evaporative emissions increase the relative proportions of alkanes (and to a much lesser extent aromatics) in THC emissions. As a result, evaporative emissions have much lower specific reactivities than exhaust emissions, owing to the much lower proportion of alkenes in the evaporative emissions.

When evaporative emission HC profiles are compared to fuel composition, evaporative emissions tend to be enriched in fuel components that have lower molecular weights, where diurnal emissions more closely represent the petrol headspace and hot-soak emissions are more

representative of the whole liquid fuel (Duffy *et al.*, 1999; Pierson *et al.*, 1999).

3.3. Measurement Method

Most speciated HC studies we have reviewed have investigated exhaust emissions, although some studies also include evaporative HC speciation. There is a wide range in the number of individual HCs that are reported in the literature, ranging from a (few) specific air toxic(s) to several hundreds of individual HCs. Even in the most comprehensive studies there will always be a complex mixture of unresolved individual HCs often included in the category 'unidentified'.

Most studies have been directed at studying speciated VOC emissions. Typically, Tedlar bags or more recently steel canisters are used for sampling alkanes, alkenes, alkynes, aromatics and cycloalkanes, followed by gas chromatography (GC) for separation and flame ionisation detection (FID) for quantification.

With the exception of a few studies, semi-volatile HCs in the molecular weight range above C₁₀ or C₁₂ are seldom measured at all, whereas individual HCs typically cover the range of C₁ to C₃₃. This practice clearly influences the accuracy of predicted impacts. For instance, Fraser *et al.* (1998) calculated that traditional VOC measurements only account for 93% of the photochemical reactivity that was predicted by more comprehensive measurements that included carbonyls and semi-volatile HCs.

Recently however, an increased interest in gas-phase semi-volatile HCs has led to more studies including or specifically investigating SVHCs. Typically Tenax adsorbent is used for sampling of mainly alkanes and aromatics, followed by thermal desorption, GC separation and FID quantification. GC/MS (mass spectrometry) techniques are sometimes used for verification of individual HC identification.

Emissions of carbonyls (aldehydes and ketones) have historically not been included in VOC profiles, as FID measurements did not capture a significant part of the carbonyls (Nelson & Quigley, 1984) and because bag, canister and adsorbent sampling are generally not suitable for oxygenated compounds due to poor recovery and artifact formation (Hewitt, 1999).

Compared with the HC compounds, carbonyl compounds are more reactive and thus more difficult to determine. However, carbonyl emissions cannot simply be neglected, as they make up a significant fraction⁹ of the VOC exhaust emissions.

Therefore, carbonyls from road traffic are now more commonly sampled, typically using adsorbent or acetonitrile solution containing 2,4-dinitrophenylhydrazine (DNPH), followed by high performance liquid chromatography (HPLC) for separation of hydrozones combined with UV detection. This separate measurement of carbonyl emissions has often resulted in the fact that

⁹ For example, 2-12% THC (w/w) for catalyst vehicles.

carbonyl emission factors are used separately from THC emission factors or VOC profiles (e.g. PAE, 2002).

Particle phase PAHs are commonly sampled using a filter or low-pressure cascade impactors, followed by solvent extraction, pre-concentration and separation/detection by GC/FID, GC/MS or HPLC. When individual HCs (e.g. PAHs) can exist both in the gas-phase and particle-phase, it is important to check whether reported emission factors apply to only one or include both of these phases. So-called 'filtration effects', i.e. where filters start to capture a significant amount of the total emissions of the individual compounds, have been suggested to begin at C₁₃ or C₁₄ n-alkanes (Hampton *et al.*, 1983).

There are several aspects of the measurement methodology that impact on the determination of speciated HC emission factors. Some of these issues are discussed in the following two subsections 'sampling' and 'analysis'.

Sampling

Sampling is the first and very critical step in the whole process of obtaining final results. In laboratory conditions exhaust emissions are usually diluted using constant volume sampling (CVS) devices, whereas ambient air samples are usually collected and analysed directly, either undiluted or with a pre-concentration step. Sampling set-up can introduce errors in predicted speciated HC emission rates.

For instance, Staehelin *et al.* (1997) measured quite low THC emission factors for heavy-duty diesel vehicles and they suggested that this may be due in part to possible trapping of higher alkanes on the particle filter that was mounted before the THC analyser.

It has been found that sampling with Tedlar bags and steel canisters can only reliably quantify truly gas-phase HCs (say < C₁₀). This is probably due to adsorption of the heavier compounds onto bag and canister walls, leading to underestimated concentrations.

Tenax samples have been reported to be more accurate starting from C₈ (Sigsby *et al.*, 1987; Zielinska *et al.*, 1996). However, Tenax also has several disadvantages including low capacity for very volatile organic compounds and polar VOCs, and artifact formation due to chemical reactions that occur during sampling (e.g. with ozone) or thermal desorption (Hewitt, 1999).

Staehelin *et al.* (1998) also found an artifact with canister sampling, where less volatile C₆-C₈ aromatic compounds such as ethylbenzene and toluene tended to irreversibly adsorb on the walls of canisters. According to Schmitz *et al.* (2000) Tedlar bags also showed substantial blank values for some HCs.

So, the choice of sampling method will influence the outcome in terms of speciated HC emissions. This is an important issue to check when measurement data are used for the development of speciated HC emission factors because certain individual HC emissions could be underestimated.

Another issue to consider when using measurement data is the stability of the sample for individual HC compounds. Sometimes, samples are stored for several months before being analysed. For some HCs rapid analysis after sampling is essential in order to prevent large emission underestimations.

For instance, Lipari (1990) found that THC and most of the alkanes and olefins are stable in the sample after 48 hours of sampling. However, some components such as xylene and ethylbenzene exhibited higher variations and especially the concentration of 1,3-butadiene decreased by over 25% within 24 hours and by over 70% within 48 hours of sample collection. This decay of 1,3-butadiene in exhaust samples has been confirmed in an Australian study (Ye *et al.*, 1997).

Zielinska *et al.* (1996) noted that longer-term sample stability (days-months) is even worse when compared to short-term stability. Again, the concentration drop is not the same for all HCs, although it was generally within 20% for most of the C₅-C₉ hydrocarbons. Greater drops were seen for some components, e.g. about 60% for styrene to complete disappearance for isoprene.

Furthermore, the variable quality of the canisters, their previous history, age, sample storage temperatures, cleaning methods, etc. may affect a compound's stability upon storage (Zielinska *et al.*, 1996).

Analysis

Although measurement methods for the different HC classes are quite uniformly used around the world, the details of the experimental procedures vary from one laboratory to another (e.g. pre-concentration step or not, calibration method used). Differences in the same sample analysis between different laboratories can be significant for individual HCs. For instance results have been reported to be usually $\pm 15\%$, but there can be up to a factor of 2 difference for specific HCs (e.g. Zielinska *et al.*, 1996).

An intercomparison experiment analysing ambient NMHC concentrations showed that 12 of 36 laboratories reported concentrations that differed by more than 20% from a standard two-component n-butane/benzene mixture. For a more complex 16-component mixture 12 of 28 laboratories were able to correctly identify all 16 components (Hewitt, 1999).

Sometimes, limitations in measurement equipment have prevented accurate analysis of individual HCs. For instance, the GC methods used a decade ago were not able to adequately measure certain VOCs such as 1,3-butadiene due to detection limits and resolution problems (e.g. Lipari, 1990). Therefore, 1,3-butadiene could only be reliably measured in emission samples from non-catalyst vehicles with GCs (Hoekman, 1992). Improvements in analytical equipment have now led to better HC speciation.

Also, the assumption that all non-methane HCs give the same FID response on a per-carbon basis might hold true for almost all compounds, but some HC compounds

(such as toluene and xylenes) could show lower response factors and emissions could therefore be underestimated.

In summary, the analysis method used will influence the outcome in terms of speciated HC emissions. Generally, the use of more recent measurement data will have an advantage over older data in terms of measurement accuracy.

3.4. Fuel Composition

HC emissions are strongly dependent on the fuel composition and individual HCs are affected differently by changes in fuel composition, which has been known for some time.

For example, Black *et al.* (1980) mentioned that exhaust and evaporative HC emission characteristics are very sensitive to petrol chemical composition, vapour pressure (not for exhaust) and the ASTM distillation curve. Reid vapour pressure (RVP) and distillation characteristics vary significantly and this is a primary source of variability between reported emission factors for individual HCs and those experienced in actual urban areas.

Similarly, HC emissions from diesel vehicles are significantly affected by fuel density, final boiling point, total aromatics and PAHs (Sjögren *et al.*, 1996).

There is a clear correlation for many individual HCs between the concentration in the fuel and the relative emissions rates. Changes in fuel composition, such as the addition of MTBE or methanol, do not only affect the VOC profile but also THC emissions (Lipari, 1990; Kirchstetter *et al.*, 1996).

Although there is a very close relationship between fuel and exhaust HC compositions, it is not simply produced by emissions of unburnt fuel. Enrichment also occurs for certain compounds. For example butanes and benzene are enriched due to formation in the combustion process.

The extent of specific HC survival from the combustion process varies with the chemical class of HCs, but is approximately constant within each class (Nelson & Quigley, 1984). Several studies have reported on (sometimes linear) relationships between petrol and exhaust HC composition (e.g. CONCAWE, 1999).

Several workers have investigated the impact of fuel composition on several speciated VOC emissions and found, for instance, that increasing olefins content of the fuel and high levels of substituted alkanes in the fuel leads to increased 1,3-butadiene exhaust emissions (e.g. Gorse *et al.*, 1991; Perry & Gee, 1994). The presence of fuel additives such as MTBE have been reported to increase 1,3-butadiene and formaldehyde exhaust emissions (Hoekman, 1992).

Similarly, the dependency of benzene emissions on the aromatics and benzene content of the fuel have been reported repeatedly. However, reducing fuel aromatic content in order to reduce for instance benzene emission rates could raise 1,3-butadiene and aldehyde emissions (Gorse *et al.*, 1991; Jemma *et al.*, 1992). With respect to diesel fuel, significant correlations between fuel PAHs

and PAH exhaust emissions have been observed (e.g. Sjögren *et al.*, 1996).

Generally, the impacts of any changes in fuel composition¹⁰ on speciated HC emissions should be carefully considered, because it could potentially lead to unwanted side effects such as increased ozone levels.

The fuel composition of the test fuel used is another issue that should be considered when emission factors or VOC profiles are developed from measurement data. Tests using 'certification fuel' instead of commercial fuel can lead to significant underestimation, up to a factor two, of specific air toxics emissions (Gorse *et al.*, 1991).

Even in cases where measurements are based on a commercial fuel, the results should be carefully considered. For example, the Australian study results from Duffy *et al.* (1998 & 1999) were based on a commercial fuel of 'standard' composition, but the average fuel characteristics of the test fuel and commercial fuel sold in Queensland are significantly different. In this case, the olefinic content particularly stands out, which is approximately a factor two higher in Queensland, whereas the aromatic content is about 15-25% lower compared to the test fuel. As discussed before, this has significant impacts on the HC profile. PAE (2002) estimated for instance that benzene dropped from 8.4 to 6.0 %THC (w/w).

3.5. Driving Conditions

The Australian ADR27 and ADR37 standards¹¹ regulate exhaust and evaporative emissions from petrol passenger cars and light-goods vehicles. These standards are based on the so-called 'CVS-C' and 'CVS-CH' driving cycles (Constant Volume Sampler – Cold cycle/Hot cycle), which are equivalent to the US FTP 1972 and FTP 1975 driving cycles. The only substantial difference between the ADR27 and ADR37 test cycles is the inclusion of a 10-minute engine-off period and a hot-start in the ADR37 cycle, making ADR27 a slightly more stringent test.

An important issue with respect to emission testing is the extent to which the driving patterns used in the tests are representative of real-world driving and this should be carefully considered (e.g. Smit *et al.*, 2002). Driving cycles or speed-time profiles are supposed to cover all driving patterns occurring in the real world, including a representative implicit weighting of the different driving patterns (or micro-trips) of which the driving cycle consists.

However, the ADR or FTP driving cycle, which is in fact based on outdated driving survey data taken in downtown Los Angeles during the 1960s, has long been known not to be representative of modern urban driving, due to low acceleration rates and limited speeds present in the cycle. These limitations are important as emissions

¹⁰ For instance, reformulated petrol and diesel fuels or introduction of unleaded fuels.

¹¹ Australian Design Rule (ADR)

increase with engine load, which is high during hard accelerations or high speeds (NRC, 2000). Similar findings have been reported for legislative European driving cycles (Joumard *et al.*, 2000).

An alternative urban driving cycle, which is considered to be more representative of urban driving than the ADR cycles, has been developed in Australia. This Australian Urban Cycle (AUC) is based on real-world driving conditions and incorporates information on driving obtained in Melbourne, Sydney and Brisbane. Watson (1995) found that HC emission levels in ‘real-world’ driving conditions (i.e. AUC cycle) are considerably higher than might be expected from the FTP cycle test, i.e. a factor 2.2 for catalyst vehicles and a factor 1.5 for non-catalyst vehicles. DoTRS (2001) measured even higher AUC/FTP ratios for individual catalyst vehicles up to a factor 16.

Several other studies investigating the impact of ‘real-world’ driving conditions have confirmed their substantial impact on HC emissions (Sjödin & Lenner, 1995).

Although it seems clear that THC emission factors based on ADR tests are likely to underestimate area-wide HC emissions, there is not a lot of information on the impact of driving cycles on HC profiles. Detailed study of the dependency of the composition of HC exhaust emissions and driving modes is the subject of ongoing research. However, there are a few overseas studies that present results on the impact of speed on VOC profiles, and they are discussed here.

An Australian tunnel study (Mitchell *et al.*, 1981) showed that C₂-C₆ emissions from motor vehicles were speed-dependent (e.g. decreasing acetylene content). Other overseas tunnel studies have confirmed non-proportional changes in individual HC emissions with respect to overall changes in THC emissions with changing speed (e.g. Sjödin & Lenner, 1995).

Bailey *et al.* (1990) more specifically investigated speed impacts on speciated HC emissions from non-catalyst vehicles by driving them over 5 different ‘real-world’ routes (average speed 20-113 km/h), using an on-board sampling system. It was found that the emission composition changed significantly with increasing speed. Generally, petrol components showed a fairly uniform decrease (e.g. n-pentane, toluene) or slight increase (e.g. benzene, ethane) with speed as a proportion of THC, while ‘pure’ combustion products (e.g. ethylene) showed increases in proportions, which differ between species.

Figure 1 depicts some of the results graphically. The characteristic drop in THC emissions with speed is shown together with the THC proportions of 9 speciated VOCs, which together make up approximately 50-60% (w/w) of the total HC emissions.

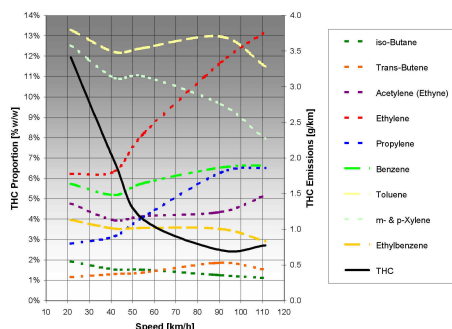


Figure 1. Change in HC profile with speed (Bailey *et al.*, 1990)

It is clear from Figure 1 that the individual VOC components do not maintain a constant proportionality over the speed range. Individual components can display quite different patterns amongst one another and in relation to the overall THC-speed relationship, which relate to their origins, i.e. whether petrol and/or combustion derived.

An earlier study in the US (Sigsby *et al.*, 1987) using three driving cycles under laboratory conditions, but this time with in-use catalyst vehicles, revealed apparently less dramatic results as is shown in Figure 2.

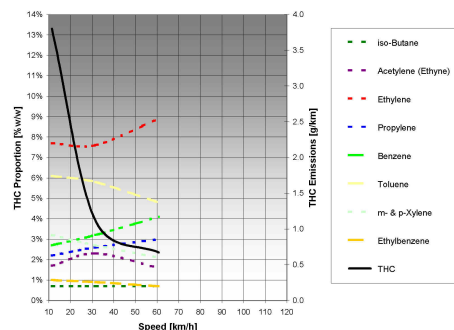


Figure 2. Change in HC profile with speed (Sigsby *et al.*, 1987)

However, the highest speeds tested by Sigsby *et al.* (1987) was much lower than tested by Bailey *et al.* (1990) and the low engine-load FTP driving cycle was used as one of the driving patterns.

Not shown in Figure 2 is the significant proportional change of methane from 9 to 17% with increasing average speed from 11 to 61 km/h. The HC composition was found to be most variable for the highest speed and least variable for the lowest speed, possibly due to lower concentration levels at higher speeds.

In a more recent study, Schmitz *et al.* (2000) investigated speciated VOC emissions (i.e. HC classes) using FTP75 and ‘Autobahn’ tests (maximum speed 162 km/h) and fuels representative of the German market. It was found that the change in VOC profile for non-catalyst cars is small and that it is only at higher speeds that a slight increase in the alkenes and hence a slight

decrease in the alkanes class is observed. It is noted that absolute emission levels do change significantly with speed. When this information is compared with the work of Bailey *et al.* (1990), the trends are very similar, i.e. a decrease in alkanes and aromatics and an increase in alkenes and alkynes with increased speed.

However, in contrast to non-catalyst vehicles, Schmitz *et al.* (2000) found strong variations in the VOC profile for three-way catalyst cars, e.g. at high speeds, aromatics and alkenes dominate the VOC profile (85%), whereas at low speeds alkanes and carbonyls are dominating the VOC profile (65%). Apparently, rich air-to-fuel ratios at high engine loads lead to an increase in THC emissions and to a change in the VOC profile.

In the US, a roadway sampling field study employing tracer gas techniques concluded that individual NMHC species from the 1983 on-road fleet did not vary significantly with different modes of traffic operation (cruise, acceleration, deceleration). For instance, the reported average percentages did not differ by more than 4% for individual HCs on a %NMHC basis, e.g. 3% for ethylene between the selected roadway sites. HC classes differed by less than 11% (w/w NMHC) between roadway sites (Zweidinger *et al.*, 1988).

Again, this study investigated the lower average speed range only (27 to 71 km/h), although no relationship between speed and emissions could be established due to inconsistent data. The presence of traffic signals and the morning rush hour resulted in variable and transient traffic. THC emission rates were substantially higher than those reported in Sigsby *et al.* (1987). When these data are compared to data from Bailey *et al.* (1990) and Schmitz *et al.* (2000), the observed shifts in VOC profiles seem quite similar.

A statistically significant and non-proportional change in the speciated HC profile with only a small change in average speed (i.e. 10 km/h) for an on-road fleet (including petrol cars, diesel trucks etc.) driving at high speeds (90-100 km/h) has been observed in Europe in a recent tunnel study (Staehelin *et al.*, 1995 & 1997).

Similar to petrol vehicles, absolute speciated HC emissions from diesel vehicles have been found to be strongly dependent on driving conditions. For instance, Bernaudat *et al.* (2000) reported increased emission rates of formaldehyde, acetaldehyde, BTX and PAHs in a change from freeway to congested driving conditions. The diesel VOC profile is nearly constant and is dominated by alkenes and carbonyls over the speed range (Schmitz *et al.*, 2000).

Other engine load impacts such as road grade have also been shown to impact on both absolute and relative speciated HC emissions, particularly in the case of heavy-duty vehicles (Sagebiel *et al.*, 1996; Pierson *et al.*, 1996).

It is clear from the discussion that 'real-world' exhaust emissions of individual HCs cannot be estimated by assuming a constant HC profile across the entire speed range or at driving conditions that require significant higher engine power output, particularly in

the case of petrol catalyst vehicles where the conversion efficiency of the catalyst complicates the situation.

There seem to be two distinct average speed ranges: urban speed and higher speeds, where the HC profiles are quite different. However, in the urban speed range with average speeds of typically 20-50 km/h, several studies show a much less significant impact on HC profiles. It seems that HC profiles are more stable at more congested driving conditions and are more sensitive to changes in speed at higher speeds. This could be due to the fact that transient driving results in enrichment conditions and less efficient catalyst conversion, which is reflected in elevated THC emissions that are less sensitive to change than low THC emissions.

Therefore, we could argue that HC profiles derived from ADR measurements are appropriate for low-dynamics 'urban driving' in Australia, which is simulated by the ADR (or FTP) driving cycle. It has to be kept in mind that for other driving conditions, for example high-speed freeway driving, driving under grade or possibly for the AUC driving cycle, the VOC profiles will deviate from the established HC profile.

3.6. Ambient Temperature

Ambient temperature impacts on THC emission levels. In general, THC exhaust emissions increase gradually with decreasing temperature from about 25°C and below about 10 °C the emissions increase dramatically in a non-linear fashion (e.g. Laurikko, 1995 & 1997; NRC, 2000). There is probably no significant increase in THC exhaust emissions (C₁-C₁₂) with temperatures above 25 °C (e.g. Stump *et al.*, 1992).

Evaporative THC emissions, and particularly diurnal emissions, increase with increasing ambient temperature and increasing fuel volatility. Ambient temperature also impacts on the HC profile, but little information could be found in the literature.

Ambient temperature influences the particle-phase to gas-phase ratio of the heavier HCs (Benner *et al.*, 1989) and will therefore impact on, for example, measured gas-phase SVHCs and emission factors. Therefore, HDV¹² THC emission factors could be higher or lower in comparable situations but with different ambient temperature (Pierson *et al.*, 1996).

Stump *et al.* (1992) investigated a limited number of catalyst petrol cars and found that there was no significant increase in VOC emissions (C₁-C₁₂) with increased FTP test temperature from 24 to 41°C. With respect to the VOC profile, some individual VOCs were rather insensitive to changes in temperature (e.g. acetaldehyde, 1,3-butadiene), whereas some slightly increased (e.g. n-butane, methane, ethylene) and some slightly decreased with increasing temperature (e.g. toluene, m,p-xylene), depending on the actual engine type (carbureted versus fuel-injected). With respect to

¹² Heavy-duty vehicles.

HC classes, paraffin and olefin emissions generally increased and aromatic emissions decreased as test temperature increased.

Importantly, data from Stump *et al.* (1992) shows that there is a significant shift in the diurnal and hot soak VOC profile, showing increased mass fractions of alkanes and decreased mass fractions of aromatics with increased temperature, whereas alkenes remained roughly constant. The opposite was found for carbureted vehicle hot-soak emissions, where increased mass fractions of aromatics and decreased mass fractions of alkanes with increased temperature were found. Again, alkenes remained roughly constant.

3.7. Cold-Start Operation

Both THC emissions and HC profiles are different for cold-start, hot-start and running emissions. This is due to differences in engine operation (fuel enrichment) and catalyst efficiency.

THC emissions are elevated under cold-start conditions, and to a much lesser extent under hot-start conditions. However, the relative increase of emissions caused by the cold-starts is most important for catalyst petrol vehicles and is less pronounced for cars with diesel engines and non-catalyst petrol engines.

The contribution of cold-start emissions to total trip THC emissions is dependent on the trip length and can be quite large. For instance, excess cold-start THC emissions (expressed as g/start) from an Australian ADR37/00 three-way catalyst car are estimated to make up 80-90% of the total THC emissions emitted during an entire trip of only a few kilometres. With longer trips, this contribution drops, for example to 40% for a 20 km trip (PAE, 2002).

Cold-start operation also substantially impacts on the HC profile. For instance, Schmitz *et al.* (2000) reported a dominant share in aromatics (52%) under cold-start conditions for three-way catalyst cars, but less dominant proportions under hot-stabilized driving conditions (21%), where alkanes are dominant. This, of course, is mainly due to reduced catalyst conversion efficiency and according to Singer *et al.* (1999) also due to a larger fraction of unburnt fuel in the cold-start profile. Also, Hoekman (1992) found, on average, that normalised reactivity (i.e. g ozone/g NMOC) for catalyst vehicles was highest under cold-start conditions.

This shift in the hydrocarbon profile is important as cold-start emissions account for a large part of THC emissions. Moreover, most cold-start excess emissions are emitted at the beginning of the trip and cold-start operation is not uniformly distributed in urban areas during the day. Therefore, speciated cold-start HC emissions should in principle be resolved spatially and temporally. A breakdown of HC profiles for each ADR phase could therefore be considered, possibly expressing start emissions as g THC per start with its own cold-start HC profile.

3.8. Tuning and Maintenance Practice

Both THC emissions and HC profiles are influenced by the efficiency of fuel combustion and the efficiency by which engine-out emissions are further reduced. At vehicle level, these factors are dependent on the actual state of tuning and the state of the emission control system.

Vehicles can be badly tuned or tampered with and can have malfunctioning or partly functioning emission control systems ('high-emitters'). As a result, speciated HC emissions from the entire vehicle fleet are influenced by factors such as the vehicle age distribution and the presence of inspection & maintenance programs.

High-emitters can make up a significant fraction of the vehicle fleet. For instance, remote-sensing data showed that about 10% of the vehicles in Melbourne are responsible for half or more of the total CO and HC exhaust emissions (Zhang *et al.* 1995). This highly skewed emission distribution, where the majority of the vehicles have low emissions but some vehicles exhibit very high emissions, is confirmed by Australian chassis dynamometer tests, as is shown in Figure 3.

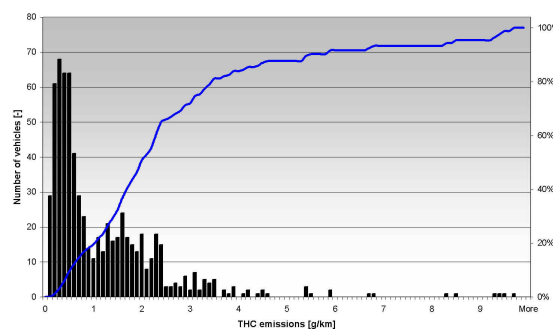


Figure 3. Histogram for HC emissions from petrol SI-vehicles (ADR37 test)

Figure 3 shows the distribution of THC emissions for a fleet of approximately 700 Australian petrol passenger cars including non-catalyst, oxidation catalyst and three-way catalyst vehicles. The line in Figure 3 shows the cumulative percentage of the total emissions. It can be derived that approximately 50% of the total HC emissions come from only 20% of the vehicles.

These high-emitting vehicles might exhibit high THC emissions, including alkenes and alkynes and have different HC profiles compared to their normal well-tuned and well-functioning counterparts.

This shift in HC profile is illustrated by dynamometer measurements carried out by Ye *et al.* (1997) in Australia, where THC emission rates from 24 catalyst cars varied from 0.5 to 4.2 g/km and 1,3 butadiene emissions varied from 1 to 25 mg/km, indicating that catalytic converters on 20% of the catalyst vehicles were not working properly. This percentage of malfunctioning or poorly operating catalysts was confirmed by another Australian study (Duffy *et al.*, 1998). As a result, the

1,3-butadiene proportion of THC varied between 0.04 and 1.4%.

The specific impact of catalyst ageing on the HC profile is illustrated by the fact that ageing of the catalyst dramatically decreases the conversion efficiencies for alkanes, e.g. a drop from 75% to 11% for ethane. It also significantly decreases the conversion efficiencies for aromatics.

For instance, catalyst efficiencies for BTEX typically dropped from 80-90% to 70-80% when considering a fresh and aged catalyst respectively (e.g. Andersson *et al.*, 1991). However, ageing has a smaller effect on the conversion efficiencies for alkenes and alkynes, where the most effectively controlled hydrocarbons with even an aged catalyst produced good results, e.g. complete oxidation for ethyne and 93% for propyne and 1,3-butadiene (Andersson *et al.*, 1991; Ye *et al.*, 1997).

Kirchstetter *et al.* (1996) conducted a tunnel study and found that although vehicles were operating under hot-stabilized conditions at average speeds between 65 and 80 km/h, the HC profile corresponded to a dynamometer-derived cold-start HC profile, but not to a stabilized HC profile. It was suggested that vehicles that have high emissions under stabilised operating conditions due to reduced or non-existent catalyst activity and lack of closed-loop air-to-fuel ratio control (i.e. high-emitters) would have caused this effect.

Maintenance impacts are not only restricted to catalyst vehicles. For instance, engine modifications such as spark retard, adopted by manufacturers in the past to satisfy emissions standards for non-catalyst vehicles, led to lower THC emissions, but also to some significant changes in the HC profile with respect to certain compounds such as ethylene and propylene (Nelson & Quigley, 1984).

Unfortunately, despite their relevance to total emission levels, absolute THC emissions from high-emitting vehicles are generally difficult to characterise statistically. This is because their fleet numbers are relatively small and variation in emission levels is relatively large. This complicates accurate emission modelling (Smit *et al.*, 2002).

On the other hand, the HC exhaust composition of non-catalyst cars, and therefore potentially cars with (partially) malfunctioning catalysts, has been found to be rather insensitive to variations in mass emission rates for most HCs. Measurement of a fleet sample, using in-service vehicles with a representative range in odometer readings, is probably the only means of further improving speciated HC emissions with respect to local maintenance practice and high-emitting vehicles.

3. Conclusions

Several factors that influence speciated HC emissions have been identified and discussed in this paper. Direct use of measurement data in (urban) emission inventories should be carefully considered, as speciated HCs emissions are sensitive to these factors. At least

qualitative and possibly quantitative assessment of these issues could lead to improved (use of) emission inventories for speciated HCs emissions from road traffic.

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