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Innovative Emissions Measurement and Perspective on Future Tailpipe Regulation

Real-world measurement and role of VOCs and N_2O emissions

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The Euro 7 exhaust emissions regulation will be important both from the perspective of how it further improves air quality, but also of certain greenhouse gas emissions and the economics of the internal combustion engine. This paper sets out the ongoing importance of ozone to urban air quality, and how tailpipe volatile organic compound (VOC) emissions contribute to that as well as having direct human health effects through inhalation. The paper then sets out a novel method for the measurement of speciated VOCs and nitrous oxide (N_2O) at the tailpipe in real-world conditions, and presents initial results across a range of modern light-duty vehicles. Based on the results, it may be the case that VOCs should be a higher priority for future regulation than N_2O, although more research is required to achieve a consensus on typical real-world N_2O emissions.

Introduction

“Concentrations of every air pollutant in Europe have declined since the year 2000, with the exception of ozone” – European Environment Agency

A potential Euro 7 regulation was being negotiated at the time of writing this article with the stated aim of pollutant reduction, building on the big advances thanks to the Real Driving Emissions (RDE) regulation. Taking a longer perspective, Europe has been regulating tailpipe emissions for over three decades, and the current ‘Euro stages’ system was first introduced in 1992. The system sets limit values for a range of pollutants, which are regularly reviewed. For a vehicle to be compliant, emissions must be under the limit on the certification test. This test was the New European Driving Cycle (NEDC) until 2017/2018, when it was replaced by a combination of the laboratory Worldwide Harmonised Light Vehicle Test Procedure (WLTP) and the on-road validation through the RDE test. As part of the consideration of next, Euro 7, stage, the Consortium for ultra Low Vehicle Emissions (CLOVE) performed a detailed analysis of the priority pollutants and measurement possibilities (1). This article looks at the remaining challenges, assesses evidence and makes some recommendations to inform the evolution of Euro 7.

Nitrogen oxides (NOx) emissions for the latest diesels average 43 mg km^{-1} (46% below the Euro 6 regulatory limit of 80 mg km^{-1}, excluding any conformity factor) and for the latest gasoline vehicles average 12 mg km^{-1} (80% below the Euro 6 limit of 60 mg km^{-1}) according to data from the Emissions Analytics’ RDE database. Carbon monoxide and total hydrocarbons remain well under control over the combined cycle as well. Further, particulate number emissions are 92% below the limit of 6×10^{11} particles per kilometre, while particulate mass in laboratory tests more than 99% below the Particle Measurement Programme (PMP)-based limit of 4.5 mg km^{-1}.

These emissions levels mean that policy must focus on removing the old, dirtier, vehicles from the road as quickly as possible. Taking the current vehicle car parc in Europe, Euro 5 vehicles are the most common. The average real-world NOx emissions of Euro 5 diesel vehicles, according to the Emissions Analytics' EQUA^{TM} test programme, is 806 mg km^{-1}, almost 19 times higher than the latest models.

Remaining Challenges

A number of challenges do, however, remain with current vehicles.

First, significant carbon dioxide emissions from the internal combustion engine remains a big challenge, but this is not relevant for air quality and the related regulations. Rather, reductions in CO_2 emissions are targeted and incentivised through fleet-average requirements for each manufacturer.

Second, there are difficulties with the administration of Euro 6. RDE, also known as Euro 6d-TEMP and subsequent 'sub-stages', in most ways has been a significant success. However, the large number of diesel vehicles sold at stage 6b have NOx emissions on average 10 times higher than RDE diesels. Furthermore, it is difficult for the end consumer to determine whether a vehicle is stage 6b or 6d. Introducing Euro 7 presents an opportunity to rationalise.

Third, there remain some areas of high emissions from the latest vehicles that need addressing. An increasingly high proportion of emissions are emitted under cold start, but these are easily under-represented if cold start forms too small a share of the official test cycle compared to real-world behaviours. With the switch away from diesel back to gasoline vehicles, and with the evolving gasoline and gas technologies, ultrafine particles below 23 nm may well get added to the particulate number regulation.

Fourth, the issue on non-exhaust emissions is now being considered for regulations. The most relevant to vehicle regulation are tyre and brake wear emissions. As vehicles become heavier with greater torque, tyre wear emissions are on an increasing trend. Brake wear is currently a significant source, but is likely to decline as regenerative braking becomes more widespread on all types of vehicles, not just battery electric cars. This topic is out of scope for this paper, but is being considered separately by Emissions Analytics.

From the tailpipe, the new pollutants to consider for regulation are methane (CH_4), nitrous oxide (N_2O) and VOCs including formaldehyde (CH_2O) and acetaldehyde (C_2H_4O). The first two are both air pollutants and greenhouse gases with warming potential far in excess of CO_2 (with global warming potential of around 30 times CO_2 and 273 times CO_2 over 100 years, respectively). While they are both referred to more often in the literature for their global warming potential, the suggestion is to regulate them as air pollutants on the basis of research cited by CLOVE, which would bring them within the scope of the 'Euro' structure and therefore make them relevant for Euro 7. Within VOCs, of which there are hundreds of potentially relevant compounds, only the two mentioned are being considered in any depth for the purposes of this paper, as they have been proposed for Euro 7. The same testing approach could be used to quantify any of the VOCs identified.

To form an independent view, Emissions Analytics set out to develop a practical method for measuring these compounds in real-world conditions, and to form a view on their importance for Euro 7.

Volatile Organic Compounds

When the various pandemic lockdowns across Europe failed to bring about the overall improvements in air quality that might have been expected, Emissions Analytics decided to focus in on VOCs and their potential role. While NOx emissions fell with traffic levels, often ground-level ozone rose, leading to similarly bad air quality from a human health point of view, just of a different complexion. In fact, this should not have been a surprise as the complex interaction of NOx, VOCs and ozone has long been studied in the USA. The South Bay in Los Angeles has grappled with this problem since motor vehicles proliferated, and many US air quality regulations have stemmed from the experiences there (2).

As well as their contribution to smog, inhalation of certain VOCs can have direct health effects. Therefore, it was important to develop a real-world test methodology that identified as many individual compounds as possible. The results from an initial test programme are set out below. This is aimed at taking understanding beyond the 'total hydrocarbons' regulated using a laboratory test in Europe, and non-methane hydrocarbons that are regulated in a number of territories including the USA.

Test Methodology

Measuring a wide range of organic compounds and other volatile species at the tailpipe is a challenge due to the large number of different compounds, many hundreds, if not thousands; as well as their volatility, which can make them hard to capture. While this can be done in the laboratory, it is an even greater challenge on the road. Traditional portable emissions measurement systems (PEMS) measure total hydrocarbons (THC) using a flame ionisation detector (FID). This can deliver robust measurements, but it creates some operational challenges, not least from the need for a supply of combustion gas. Furthermore, only a single figure for total hydrocarbons is produced; it does not include non-hydrocarbon VOCs, such as aldehydes, and does not separate the different species of hydrocarbons. This method can measure, for example, acetaldehyde, which has also been suggested for regulation under Euro 7. This is relevant due mainly to the combustion of alcohols in biogasoline.

One proposed approach for controlling VOC emissions is to lower the THC limit value under Euro 7. This would be a blunt and potentially ineffective approach because many of the most toxic compounds for humans, for example nitroaromatics, can be harmful at the low concentrations that tend to be found in exhaust. The two-dimensional gas chromatography method allows the separation and identification of hundreds of organic compounds in the exhaust, which typically shows relatively high-concentration hydrocarbons and low-concentration aromatics. The former can have health effects, but tend to be less carcinogenic than the latter. A lower THC would likely reduce the former, but have no impact on the latter.

To address these challenges and limitations, Emissions Analytics has developed a proprietary, patent-pending system (3), that harnesses sample collection from the exhaust onto tubes (**Figure 1**) while driving, which are then analysed later using laboratory gas chromatography. Using this, we can measure the concentrations of VOCs as well as semi-volatile organic compounds (SVOCs), together covering compounds from with two carbon atoms (C_2) up to at least 44 carbon atoms (C_{44}), CH_2O, N_2O, sulfur dioxide (SO_2) and many others. This is achieved by sampling simultaneously onto multiple tubes with different characteristics. In this case, the specific tubes were a molecular sieve (for N_2O), two Tenax® tubes (with different packing materials to cover the range of compound volatilities) and one 2,4-dinitrophenylhydrazine (DNPH) cartridge (which derivatises the CH_2O to ensure this volatile compound is fully captured). In this way, both the breadth of compounds measured, and the speciation challenges are solved. Furthermore, the measurements can be highly sensitive, picking up very low concentrations, which may be critical for highly toxic species. The chromatogram in **Figure 2** illustrates the large number of distinct compounds that are present in a typical exhaust, with the height of the peaks generally indicating relative amounts.

Fig. 1. Thermal desorption tube

To allow interpretation of this wealth of data, it is possible to group the compounds on the chromatogram into functional groups with similar properties, as shown in **Figure 3**. In the case of both images, the units of both axes are time, which represents the nature of chromatographic separation of the compounds.

When deployed together with a traditional PEMS unit, with its capability for measuring total exhaust flow, the concentrations of VOCs can be turned into mass values. Combined with the global positioning system (GPS) speed data, the distance-specific emission rates can be calculated, giving milligrams per kilometre values as is the basis for regulating most gaseous emissions.

The limitation of this approach is that the sample collection on tubes is cumulative over the test cycle and, therefore, there is no second-by-second signal. This creates two problems. First, when the average concentrations are multiplied by the total exhaust flow, the result is biased due to the highly variable nature of both the target gas concentration and exhaust flow at the instantaneous level. Second, the result is a combined value for the whole test cycle, without any breakdown between different driving modes.

The proposed approach addresses both limitations. The sample bias issue is overcome using a proprietary on-board constant volume sampling and proportional flow dilution system. As a result, the sample concentrations on the tubes can be adjusted for the fixed dilution factor and then multiplied by the total exhaust flow from the PEMS flow meter in order to derive distance-specific mass emission rates.

The lack of real-time signal is partially addressed by a geofencing system that automatically switches between different sample tubes at pre-set geographical points on the test cycle. In this case,

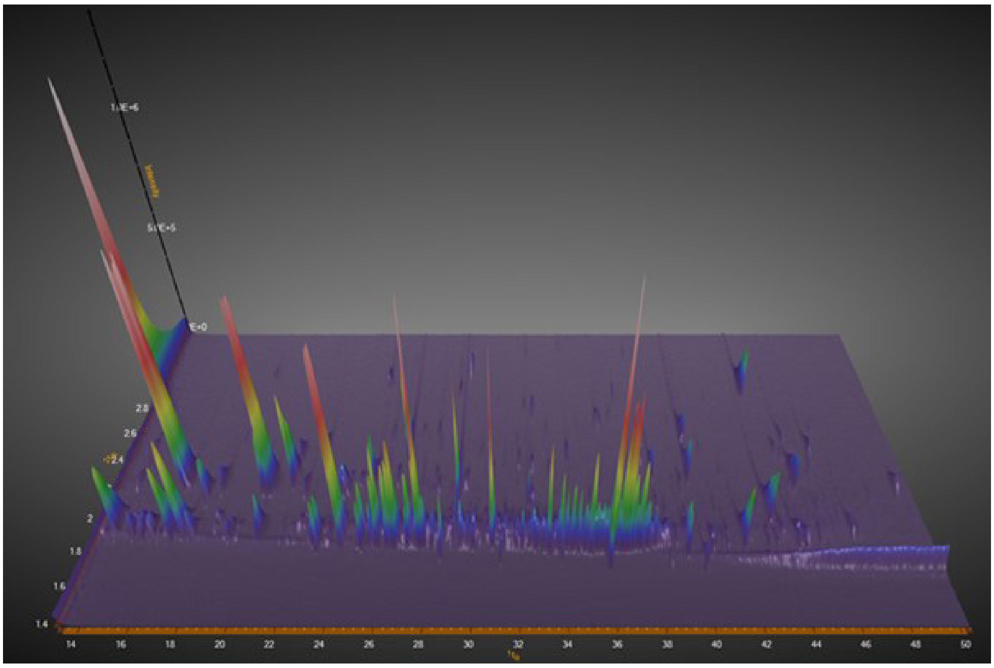
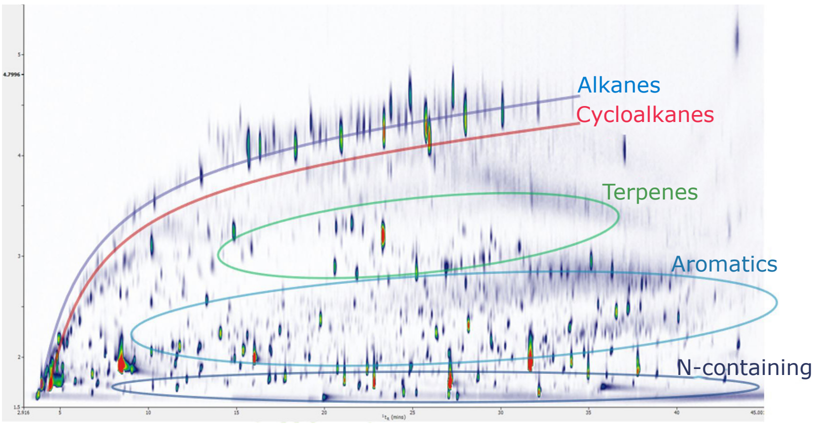


Fig. 2. Two-dimensional chromatogram showing compounds present in a typical exhaust. Height of peaks indicates relative quantity



- Wide-ranging analytes identified
- Alkanes: lungs, liver, kidney, brain
- Cycloalkanes: headaches, dizziness
- Terpenes: aromas
- Aromatics: carcinogens
- N-containing: carcinogens

Fig. 3. Chromatogram with functional groups marked

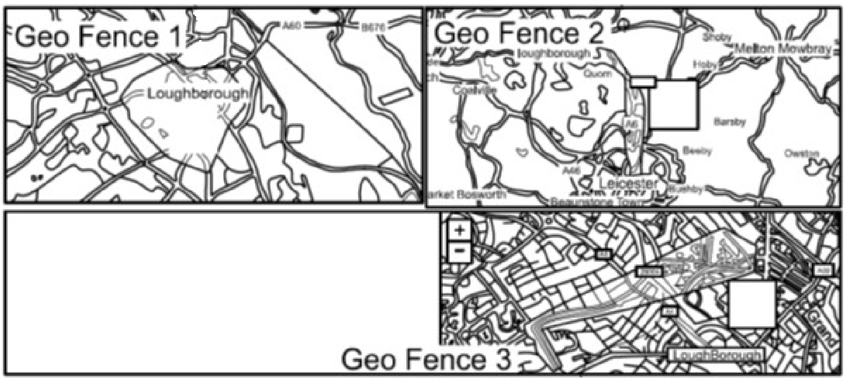


Fig. 4. Example geofencing of test routes

the geofences were set up to create urban, rural and motorway segments, as shown in **Figure 4**. The maximum number of segments is four. **Figure 5** shows the arrays of tubes, where each row corresponds to a geofenced segment and, within that segment, the different sample tubes described above sit. While the system switches automatically between segments, the overall system can be monitored and controlled from a laptop in the vehicle cabin.

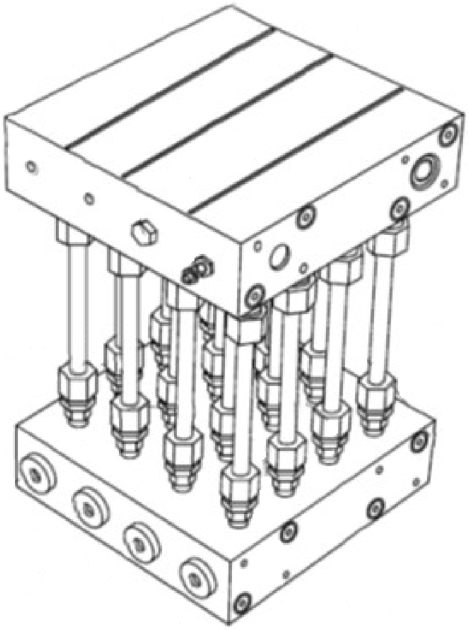


Fig. 5. Sampling tube array

A notable advantage of the sample tube approach, from a practical and analytical point of view, is that it separates sample collection from sample analysis. This reduces the complexity of the vehicle test itself, which improves the success rate. Having the sample captured on a tube means that it can be analysed later, in batches for efficiency, and each sample can be analysed multiple times, which is useful for validation and uncertainty analysis. For the purposes of our tests, we use a comprehensive two-dimensional gas chromatography (GCxGC) system coupled with a time-of-flight mass spectrometer (TOF-MS) from SepSolve Analytical (UK) and Markes International (UK). The GCxGC achieves a separation of the hundreds of compounds that would not be possible in a one-dimensional system. The TOF-MS is crucial for identification of the compounds, as well as quantification, which is aided by other detectors such as a FID and electron capture detector (ECD) for N_2O.

Experimental

Putting these techniques into practice, Emissions Analytics tested nine passenger cars in Europe across a range of ages and powertrains. **Figure 6** shows the experimental setup. There were three full hybrid electric vehicles (FHEVs), two from 2018 and one from 2021. Also from 2021 were two gasoline plug-in hybrid electric vehicles (PHEVs), a gasoline mild hybrid electric vehicle (MHEV) and a diesel internal combustion engine (ICE) vehicle. Making up the group was an old gasoline ICE vehicle, from 2005, and a 2013 diesel ICE vehicle. These were drawn from five different manufacturers, using a range of different aftertreatment systems. All were tested on our standard EQUA^{TM} Index test cycle, which is the basis of all data in the Emissions Analytics' subscription database, between September 2021 and October 2021. While similar to a certification RDE test, it has a wider range of dynamic driving and is about twice as long. It includes a cold start phase as well as urban, rural and motorway driving with a warm engine.

For the purposes of this testing, the cold-start VOC emissions were collected over 5 min from switching the engine on, the vehicle having been soaked overnight. The final column of the tables of VOC results expresses these cold-start emissions

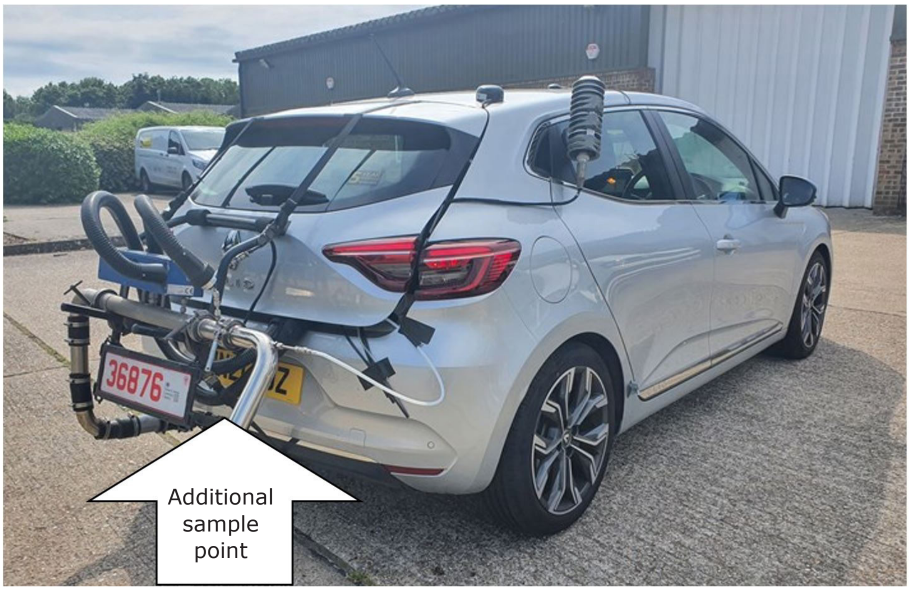


Fig. 6. Experimental measurement set-up

relative to the emissions over the first 5 km of the warm-start test. The cold-start emissions from a gasoline vehicle are collected until the engine temperature shows the vehicle is fully warmed up, which is after around 2 min for a gasoline vehicle and 15 min for a diesel. As 5 km is the approximate length of an average journey in Europe, this ratio is a measure of the importance of cold-start emissions both relatively between vehicles and in overall journeys.

Results and Discussion

The N_2O results are set out in **Table I**, split between urban, rural and motorway driving. In each case the highest and lowest emitting cars are indicated. Greatest emissions were seen in rural driving, with urban driving the lowest.

Emissions of N_2O are potentially important as the gas is a much more powerful greenhouse gas than CO_2. Over a 100-year horizon, it has warming potential around 273 times greater than CO_2. Therefore, small amounts of N_2O could undermine the extensive efforts to reduce primary CO_2 from engines. On average, across the nine vehicles and three driving modes, the N_2O emissions were 0.86 mg km^{-1}. Converted to an equivalent CO_2, this is 0.23 g km^{-1}. Real-world CO_2 emissions of these test vehicles averaged 124 g km^{-1}. Therefore, these N_2O emissions were equivalent to about 0.2% of total CO_2, within the measurement error of the CO_2 value.

Putting these results in the context of Emissions Analytics' database, which contains tests on 29 passenger cars in total, all on the same EQUA^{TM} route, the average warm-start, combined N_2O emissions are 1.5 mg km^{-1} for unhybridised gasoline vehicles and 1.0 mg km^{-1} for diesels. Therefore, the results quoted above are close to, albeit slightly lower than, this overall average. Across all 29 vehicles, the greatest value is 5.0 mg km^{-1}, in motorway driving on a 2016 Euro 6b (WLTP) diesel vehicle.

These values are lower than those quoted by CLOVE. On what has been publicly presented, the range of values is around 7 mg km^{-1} to 21 mg km^{-1}. It is unclear how many vehicles were tested on what test routes, although they were all RDE diesels and the ambient temperatures of the tests are quoted. There could be many reasons for the differences, starting with the different instruments and test set-ups. The data above are for warm-start, while the CLOVE data may be cold-start. Some of the CLOVE values may be higher when tested at lower ambient temperatures. While the EQUA^{TM} tests were on a standardised route, what is considered 'normal' under RDE has wider possible variation in driving style. There may be a selection bias, in that the diesel vehicles presented may not be representative.

Formaldehyde is a pollutant of concern as it is believed to be carcinogenic and causes a wide range of irritation in humans, including to skin, eyes and lungs. The results from the same nine vehicles are shown in **Table II**.

Again, lowest emissions were seen in urban driving. Although the exact human health effects depend on factors such as the dilution and dispersion of the emissions, it can be seen from the data that there is about a factor of three difference between the cleanest and dirtiest cars. The average combined emissions from these cars was 0.385 mg km^{-1}. In the context of the EQUA^{TM} test database, the average emissions were 0.271 mg km^{-1} across all

Table I Nitrous Oxides Results

Model year	Make	Model	Fuel and powertrain	N_2O warm start, mg km^{-1}			
				Urban	Rural	Motorway	Combined
2018	Toyota	C-HR	Gasoline FHEV	0.424	0.038 [a]	0.026 [a]	0.163 [a]
2018	Toyota	Prius+	Gasoline FHEV	0.016	0.092	3.786	1.298
2021	Toyota	Yaris	Gasoline FHEV	0.000 [a]	0.992	0.381	0.458
2021	Fiat	500	Gasoline MHEV	0.021	0.059	1.204	0.428
2021	Audi	A3	Gasoline PHEV	0.251	0.117	0.842	0.403
2021	Jeep	Renegade	Gasoline PHEV	0.010	1.446	1.423	0.960
2021	Volkswagen	Passat	Diesel ICE	0.434	0.504	0.154	0.364
2013	Audi	A6	Diesel ICE	0.581 [b]	2.160 [b]	3.768	2.170 [b]
2005	Fiat	Panda	Gasoline ICE	0.330	1.699	2.392 [b]	1.474

[a] Lowest emitting vehicle
[b] Highest emitting vehicle

Table II Formaldehyde Results

Model year	Make	Model	Fuel and powertrain	CH_2O warm start, mg km^{-1}			
				Urban	Rural	Motorway	Combined
2018	Toyota	C-HR	Gasoline FHEV	0.096 [a]	0.151 [a]	0.222 [a]	0.156 [a]
2018	Toyota	Prius+	Gasoline FHEV	0.269	0.359	0.530	0.386
2021	Toyota	Yaris	Gasoline FHEV	0.349	0.196	0.272	0.273
2021	Fiat	500	Gasoline MHEV	0.258	0.323	0.417	0.333
2021	Audi	A3	Gasoline PHEV	0.572 [b]	0.733 [b]	1.001	0.769 [b]
2021	Jeep	Renegade	Gasoline PHEV	0.385	0.268	0.455	0.369
2021	Volkswagen	Passat	Diesel ICE	0.212	0.189	0.474	0.292
2013	Audi	A6	Diesel ICE	0.374	0.482	1.147 [b]	0.668
2005	Fiat	Panda	Gasoline ICE	0.195	0.185	0.283	0.221

[a] Lowest emitting vehicle
[b] Highest emitting vehicle

Table III Common Volatile Organic Compounds from the Exhaust

Compound	Group	Toxicity	Toxicity potential factor
Tridecane	Alkane, alkene, alkyne and cyclo	Damaging to lungs	10
Tetradecane	Alkane, alkene, alkyne and cyclo	Damaging to lungs	10
Dodecane	Alkane, alkene, alkyne and cyclo	Damaging to lungs	8
Toluene	Aromatics, aldehydes and ketones	Damaging to lungs; skin irritant; dizziness	35
Pentadecane	Alkane, alkene, alkyne and cyclo	Damaging to lungs	12
Benzene, 1,3-dimethyl-	Aromatics, aldehydes and ketones	Damaging to eyes and skin	19
***p*-Xylene**	Aromatics, aldehydes and ketones	Damaging to lungs; skin and eye irritant	23
Undecane	Alkane, alkene, alkyne and cyclo	Damaging to lungs	11
Octane	Alkane, alkene, alkyne and cyclo	Damaging to lungs; skin irritant; dizziness	15

powertrains, with a highest value of 1.211 mg km^{-1} in high speed rural driving on a 2017 Euro 6b (NEDC) diesel.

Turning to other VOCs and SVOCs, the tubes captured over 500 different compounds from each vehicle. Some of these were common to most or all, but other compounds were characteristic of specific vehicles. Taken together, each vehicle has its own chemical signature. **Table III** shows the top compounds that were common to each vehicle, together with their toxic effects. It should be noted that the actual effects on humans depend on the concentrations experienced.

The final column in the table above gives a quantification of the potential toxicity, developed by Emissions Analytics, and on a scale starting at zero representing no toxicity. It uses the hazard codes submitted by product manufacturers to the European Chemicals Agency, and weighs the number of hazard codes with the potential seriousness of the human health effects of each. The values above should only be used as a relative assessment. As reference, a known carcinogen, naphthalene has a toxicity potential of 36 on this scale, similar to the toluene found in these samples.

Using the functional groups, we can then express these results as distance-specific emissions, as shown in **Table IV**. For quantitation, a toluene-equivalence method was used.

Conclusion and Recommendations

The test programme shown demonstrates the capability of the measurement system to quantify a wide range of currently unregulated pollutants with high sensitivity in real-world conditions using GCxGC and TOF-MS. The key is to decouple the sample collection on tubes from the off-line measurements. This is coupled with a proportional dilution system and a traditional PEMS unit to derive unbiased mass emissions. Finally, the use of geofencing allows results to be split into urban, rural and motorway segments to match how data is assessed under existing regulations.

Table IV Volatile Organic Compounds Emissions

Model year	Make	Model	Fuel and powertrain	VOCs warm start, mg km^{-1} Alkanes, alkenes, alkynes, cyclo	VOCs warm start, mg km^{-1} Aromatics	VOCs warm start, mg km^{-1} Polycyclic aromatic hydrocarbon, nitro-aromatics	Cold start, %
2018	Toyota	C-HR	Gasoline FHEV	0.179	0.096	0.006	27
2018	Toyota	Prius+	Gasoline FHEV	0.266	0.255 [b]	0.007	20
2021	Toyota	Yaris	Gasoline FHEV	0.441	0.176	0.017 [b]	7
2021	Fiat	500	Gasoline MHEV	0.129	0.065	0.003	30
2021	Audi	A3	Gasoline PHEV	0.576 [b]	0.202	0.010	16
2021	Jeep	Renegade	Gasoline PHEV	0.029	0.019 [a]	0.001 [a]	89
2021	Volkswagen	Passat	Diesel ICE	0.020 [a]	0.019 [a]	0.001 [a]	9
2013	Audi	A6	Diesel ICE	0.023	0.019 [a]	0.001 [a]	62
2005	Fiat	Panda	Gasoline ICE	0.088	0.058	0.007	44

[a] Lowest emitting vehicle
[b] Highest emitting vehicle

On this first pass, therefore, there is good reason to move beyond the simple measure of THCs and non-methane hydrocarbons in various regulations around the world. The next stages are to consider the absolute quantities of the compounds, model their dispersion in the environment, understand their toxic effects, and study their propensity to create secondary organic aerosols, i.e. solid airborne particles created as the SVOCs react in the atmosphere. While in absolute terms these amounts look relatively low, they can be concentrated during the short, cold-start period, and some compounds are potentially toxic even at low concentrations.

These initial results demonstrate the capability to identify and measure a wide range of VOCs and SVOCs in real-world driving: compounds that can have a wide range of deleterious effects on human health and the environment. The N_2O results suggest that further work is required to determine whether the emissions levels are problematic enough to warrant regulation as an air pollutant under Euro 7 or *via* other mechanisms as a greenhouse gas. It may prove more relevant to focus on the ongoing effects of VOCs, whether the direct effect on humans and the biosphere, as precursor to ozone and smog, or as they lead to formation of airborne particulate matter.

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The Author

Oxford graduate Nick Molden has more than fifteen years' experience in the information sector, specialising in advanced modelling techniques to help businesses extract profit from data. Through real-world testing Nick is profoundly committed to improving vehicle emissions. As well as leading Emissions Analytics and the EQUA Index, he is the cofounder of Allow Independent Road-testing (AIR).