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The isotopic composition of CO in vehicle exhaust

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ABSTRACT

We investigated the isotopic composition of CO in the exhaust of individual vehicles. Additionally, the CO_2 isotopes, and the $CO:CO_2$, $CH_4:CO_2$ and $H_2:CO$ gas ratios were measured. This was done under idling and revving conditions, and for three vehicles in a full driving cycle on a testbench. The spread in the results, even for a single vehicle, was large: for $\delta^{13}C$ in CO ~ −60 to 0‰, for $\delta^{18}O$ in CO ~ +10 to +35‰, and for all gas ratios several orders of magnitude. The results show an increase in the spread of isotopic values for CO compared to previous studies, suggesting that increasing complexity of emission control in vehicles might be reflected in the isotopic composition. When including all samples, we find a weighted mean for the $\delta^{13}C$ and $\delta^{18}O$ in CO of −28.7 ± 0.5‰ and +24.8 ± 0.3‰ respectively. This result is dominated by cold petrol vehicles. Diesel vehicles behaved as a distinct group, with CO enriched in ^{13}C and depleted in ^{18}O, compared to petrol vehicles.

For the $H_2:CO$ ratio of all vehicles, we found a value of 0.71 ± 0.31 ppb:ppb. The $CO:CO_2$ ratio, with a mean of 19.4 ± 6.8 ppb:ppm, and the $CH_4:CO_2$ ratio, with a mean of 0.26 ± 0.05 ppb:ppm, are both higher than recent literature indicates. This is likely because our sampling distribution was biased towards cold vehicles, and therefore towards higher emission situations. The $CH_4:CO_2$ ratio was found to behave similarly to the $CO:CO_2$ ratio, suggesting that the processes affecting CO and CH_4 are similar.

The $\delta^{13}C$ values in CO_2 were close to the expected $\delta^{13}C$ in fuel, with no significant difference between petrol and diesel vehicles. The $\delta^{18}O$ values in CO_2 for petrol vehicles covered a range of 20–35‰, similar to the $\delta^{18}O$ of CO. The $\delta^{18}O$ values in CO_2 for diesel vehicles were close to the $\delta^{18}O$ in atmospheric oxygen.

A set of polluted atmospheric samples, taken near a highway and inside parking garages, showed an isotopic signature of CO and a $H_2:CO$ ratio that were similar the high emitters in the individual vehicle measurements, with no significant differences between parking garage and highway samples. This suggests that in both environments, which are dominated by different driving conditions, the CO emissions from high emitters (either a few high emission vehicles, or many vehicles with brief bursts of high emissions) dominate the total traffic emissions.

1. Introduction

Carbon monoxide (CO) plays an important role in the atmosphere, in spite of its low atmospheric abundance (50–200 ppb (Holloway et al., 2000)). Most importantly, CO occupies a large fraction (~60% (Crutzen and Zimmermann, 1991)) of the cleaning capacity of the hydroxyl-radical (OH). OH oxidises reduced and partly oxidized compounds such as nitrogen oxides, methane and other hydrocarbons. If the CO burden increases, less OH will be available for reaction with other species (e.g. CH_4), which can lead to increased global warming and air quality issues. CO can also act as an ozone precursor, thus enhancing the dangers of ozone smog. CO has a lifetime of months, which means that it is long-lived enough to be influenced by transport, but short-lived enough to not be well-mixed. Therefore, CO concentrations can be significantly elevated around areas of high emissions.

An overview of the main CO sources and their strengths is given in Table 1. The different sources are of a comparable magnitude, which means the attribution of atmospheric variations in CO to a particular source is not straightforward. A useful tool for source attribution is the isotopic composition of CO. Table 1 also shows the isotopic composition of the different sources (for explanation of the δ definition, see section 2.2). Each source emits CO with a distinct isotopic signature, and these signatures can be used to improve constraints in atmospheric budgets (Manning et al., 1997) (Bergamaschi et al., 2000) (Wang et al., 2012), to study atmospheric pollution events (Röckmann et al., 2002), or to distinguish between different CO sources (Tarasova et al., 2007) (Saurer et al., 2009). However, current estimates of the isotopic signatures are uncertain, which limits the resolving power between

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Table 1
The strength (from (Bergamaschi et al., 2000)) and isotopic composition (from (Röckmann et al., 2002)) of the most important atmospheric CO sources, along with the isotopic composition of CO in the atmosphere.

Source	Strength (Tg yr^{-1})	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)
Fossil fuel combustion	600–700	−27.5	23.5
Biomass burning	600–800	−22.9	17.2
CH_4 oxidation	750–830	−51.1	0
NMHC oxidation	200–300	−32.2	0
Atmospheric comp.	–	−28 to −23	0 to 10

sources.

In this study, we focus on CO emissions from traffic, which constitute an important part of fossil fuel emissions, especially in urban areas. Our objective is to update the current estimate of the isotopic signature of CO from traffic. This value is also often adopted for fossil fuel combustion as a whole (Röckmann et al., 2002), and is thus of significant importance. The isotopic composition of CO from traffic has been investigated in previous studies, but these studies are few and sparsely spread through time (Stevens et al., 1972) (Brenninkmeijer and Röckmann, 1997) (Kato et al., 1999) (Tsunogai et al., 2003) (Popa et al., 2014) (Vimont et al., 2017), which can be a problem considering the quickly evolving vehicle industry. Moreover, the studies were limited in extent: in individual vehicle studies, only a small number of vehicles were measured ((Brenninkmeijer and Röckmann, 1997): 1; (Kato et al., 1999): 4; (Tsunogai et al., 2003): 6). In only one study ((Tsunogai et al., 2003)), measurements were done under full driving conditions. In atmospheric studies, samples are taken near polluted locations, such as tunnels or highways (Stevens et al., 1972) (Kato et al., 1999) (Tsunogai et al., 2003) (Popa et al., 2014) (Vimont et al., 2017). Such studies provide estimates integrated over a large number of vehicles, which makes them less sensitive to the strong variability in exhaust composition and thus results in more consistent estimates. A limitation is that results might be biased towards a restricted number of driving conditions (e.g. no cold start emissions in tunnels). Moreover, such an integrated signal provides no information on the most important contributors to CO emissions, both in terms of driving conditions and of differences between vehicles. Such information might be valuable in assessing the usefulness of different mitigation measures.

We investigated the emissions from individual vehicles through three different approaches. In the first approach, many different vehicles were sampled under idling conditions. Secondly, three vehicles were sampled on a testbench, each in a full simulated driving cycle. In this approach, the influence of driving conditions could be studied. Lastly, four vehicles were sampled while revving (the accelerator was pressed without coupling, so that the engine rotation was not transmitted to the wheels and the vehicle remained stationary). To put these individual vehicle measurements in context, two series of atmospheric samples were taken: one in and near parking garages and one near a highway. The measurements reported here constitute the most extensive study on the isotopic composition of CO from vehicles to date.

In addition to the isotopic composition of CO, we determined the CO:CO_2, the H_2:CO and the CH_4:CO_2 gas ratios of the exhaust samples. Gas ratios provide a method for estimating contributions from individual sources to changes in the atmosphere, complementary to isotope measurements. Most sources will emit different gases in different characteristic ratios. Since gas concentrations are easier to measure than isotope abundances, there are more results available for gas ratios in vehicle exhaust. We express CO and CH_4 emissions relative to CO_2, to have a robust measure for comparing emissions between vehicles. Also, since CO_2 emissions can be estimated from fuel consumption statistics, the ratios allow us to scale CO and CH_4 emissions to CO_2 emissions. The H_2:CO ratio is similarly used to scale H_2 emissions to CO emissions (Novelli et al., 1999) (Hauglustaine and Ehhalt, 2002) (Ehhalt and Rohrer, 2009) (Grant et al., 2010) (Bousquet et al., 2011), but may also provide a measure for the catalytic efficiency in petrol vehicles (Vollmer et al., 2010). Finally, for a subset of the samples, we measured the isotopic composition of CO_2.

2. Background

2.1. Processes affecting trace gas emissions from vehicles

It is generally considered that CO emissions from diesel vehicles are small compared to those from petrol vehicles (e.g. (Tsunogai et al., 2003)). Since diesel engines burn lean, there is an excess of oxygen available and carbon is almost completely oxidized to CO_2. Petrol engines, on the other hand, aim to run at the stoichiometric point, where just enough oxygen is available to burn all the fuel introduced into the engine. This results in less complete combustion and higher CO emissions. Partly for this reason, the three-way catalytic converter (TWC) was introduced in petrol vehicles in the early 1980s, to oxidise CO to CO_2. A modern TWC working at optimal efficiency can reduce CO concentrations in the exhaust by over 99% (Vollmer et al., 2010) (Shelef and McCabe, 2000).

However, a TWC only runs at optimal efficiency when it is sufficiently heated. Though progress has been made in pre-heating TWCs, in nearly all vehicles the TWC is still heated indirectly by exhaust air from the engine. Pollutants emitted before the TWC is hot, are called cold-start extra emissions (CSEE). A TWC also functions sub-optimally when the engine does not burn at the stoichiometric point, for example during rapid acceleration. Though there is an oxygen buffer included in modern TWCs to reduce this effect, there are limits to its efficiency. Both these deviations from optimal performance only occur for a relatively short period, but the corresponding emissions can be significant (Weilenmann et al., 2005) (Andrews et al., 2005) (Favez et al., 2009). Tsunogai et al. (2003) have reported that catalytic oxidation of CO may result in isotopic enrichment of both ^{13}C and ^{18}O, and thus these are important to consider in the interpretation of our results.

Modern vehicles are additionally equipped with more advanced engine control measures, which allow for much more complex emissions control, the explanation of which goes beyond the scope this paper.

2.2. Isotopes

As is conventional, we express isotope abundances in the relative δ-value. It is defined as:

$$\delta = \frac{R_{sample}}{R_{reference}} - 1, \tag{1}$$

where R is the ratio between the abundance of the isotope of interest and that of the most abundant isotope. The δ values are reported in permil (‰). The isotopes relevant to this paper are ^{13}C and ^{18}O. For ^{13}C, we report values relative to the standard Vienna Pee Dee Belemnite (VPDB) and for ^{18}O, we report relative to Vienna Standard Mean Ocean Water (VSMOW).

2.3. The isotopic composition of CO_2

In modern vehicles, effectively all carbon is emitted as CO_2. For this reason, the carbon isotopic composition of CO_2 from traffic is assumed to reflect that of fuel (~ -30 to -26‰ (Andres et al., 1994)). Since oxygen also leaves the vehicle as H_2O, and since CO_2 can undergo isotopic exchange with H_2O, the $\delta^{18}O$ value in CO_2 from traffic is less well constrained. It is generally considered that it reflects that of atmospheric oxygen (23.9‰ (Barkan and Luz, 2005)) (Cuntz et al., 2003), but deviations from this assumption have been observed (Horvath et al., 2012) (Schumacher et al., 2011).

2.4. Gas ratios

2.4.1. CO:CO_2

The CO:CO_2 ratio is measured to allow comparison between different vehicles and studies, since absolute CO concentrations can be influenced by the exact sampling approach and by dilution of the exhaust air. Since nearly all carbon is emitted by a vehicle as CO_2, expressing any emission relative to CO_2 emissions is analogous to expressing emissions relative to the quantity of fuel burnt. Additionally, when the source-specific CO:CO_2 ratio is known, the atmospheric CO:CO_2 ratio may provide a cheap and easy method for determining CO_2 emissions from fossil fuels, complementary to ^{14}C tracing (Gamnitzer et al., 2006). For petrol vehicles, CO:CO_2 values in the range of 5–50 mmol mol^{-1} have been reported (Frey et al., 2003) (Guo et al., 2006) (Pelkmans and Debal, 2006). For diesel, some studies report CO emissions around 25–50% of what is found for petrol vehicles (Grant et al., 2010) (Vollmer et al., 2007), while others estimate it in the range of only a few percent (Bond et al., 2010). For overall traffic, recently reported CO:CO_2 values cover a range of 4–9 mmol mol^{-1} (Popa et al., 2014) (Vollmer et al., 2007) (Bishop and Stedman, 2008).

2.4.2. H_2:CO

The main use of the H_2:CO ratio so far has been deducing H_2 traffic emissions from the CO budget (Novelli et al., 1999) (Popa et al., 2015), since traffic emissions of H_2 are poorly constrained (Hammer et al., 2009). Moreover, since it is understood that TWCs oxidise CO more efficiently than H_2, the ratio might provide a measure for catalytic efficiency (Vollmer et al., 2007). Widely varying H_2:CO values have been reported for individual petrol vehicles: the total range reported in studies spans 0.4–5.7 ppb:ppb (Vollmer et al., 2010) (Bond et al., 2010). Most studies report a relatively constrained fleet averaged ratio of 0.47–0.57 ppb:ppb (Grant et al., 2010) (Vollmer et al., 2007) (Aalto et al., 2009) (Yver et al., 2009) (Popa et al., 2011). For diesel vehicles, H_2 emissions are expected to be too small to lend the ratio any significance (Bond et al., 2010).

2.4.3. CH_4:CO_2

The CH_4:CO_2 ratio can be used to quantify CH_4 emissions from traffic. Reported values of the CH_4:CO_2 range from $4.6 \cdot 10^{-2}$ ppb:ppm (Popa et al., 2014) to 0.41 ppb:ppm (Nam et al., 2004). However, even the highest estimate shows that CH_4 emissions from vehicles are negligible in the overall budget (Nam et al., 2004).

3. Methods

3.1. Sampling

Samples were collected in 1-L glass flasks equipped with PCTFE seals (Normag, Ilmenau, Germany) (Rothe et al., 2005). The sampling setup consisted of a pre-evacuated flask, a 7 μm SS filter, a magnesium perchlorate ($Mg(ClO_4)_2$) drier and a 2 m long, 1/16” SS tube. For sampling, the tube was inserted a few cm into the vehicle tailpipe, after which the flask was opened. The flask then filled with exhaust air to atmospheric pressure in approximately 25–35 s. The sampling setup was flushed between measurements with outside air, using a syringe, to avoid memory effects between samples.

For each vehicle, the vehicle type, fuel type, mileage and the year of manufacture were registered. In the parking lot, only idling vehicles were measured. Arriving vehicles were labelled as hot, and departing vehicles as cold. There might be some convenience bias in the sampling, but the sample distribution in terms of age and vehicle type seemed to be roughly representative for the average Dutch traffic fleet (see detailed information in Supplement 3). In the revving measurements, the engine speed was increased to a certain number of rotations per minute (rpm). For each vehicle, samples were taken while idling (~650–850 rpm), at slightly increased speed (~1200–1300 rpm) and at strongly increased engine speed (~1800–1900 rpm). The revving samples provide a first approximation of how sensitive the exhaust emission composition is to variations in engine conditions.

Table 2
The characteristics of the vehicles used for the testbench measurements.

Vehicle number	Type	Manufacture year	Mileage (x 1000 km)
1	Smart Forfour	2007	103
2	Citroën Berlingo	2006	224
3	Ford Focus	2016	1

For the measurements on the testbench, three petrol vehicles were measured (see Table 2 for the characteristics). During the testbench sampling, an exhaust hood was placed near the vehicle tailpipe to prevent toxic gas levels. A large fan was placed in front of the vehicle, to simulate the cooling effect of wind while driving. The three vehicles were each sampled under similar driving cycles. Firstly, the vehicle was sampled while idling, for comparison with the previous idling results. Then the vehicle was driven at 50 km/h. To give an indication of how emissions evolved while the vehicle was heating up, 6 to 8 samples, over a period of 15–20 min, were taken at this speed. At this point the vehicle was assumed to be hot. The speed was then increased to 90 and 120 km/h and samples were taken at both these speeds. Next, the vehicle was accelerated from 0 to 50 km/h in ~30 s. Because of the switching of gears, constant acceleration was only maintained from ~15 to 50 km/h (in second gear), so that this was the period in which samples were taken. Finally, more idling samples of the now-hot vehicles were taken. Each driving cycle took 45–60 min.

The Ford Focus had several safety measures that enforced a speed limit of 25 km/h under conditions present on the testbench (e.g. only two rotating wheels). These measures were eventually deactivated, but at this point the vehicle was no longer cold. Therefore, for the Ford Focus, only the first idling samples were taken while the vehicle was cold.

The atmospheric samples were taken in and near three different parking garages on the campus of Utrecht University, and near a highway that borders the same campus. These samples provide an integrated signal of the vehicle exhaust composition at these locations. To derive the isotopic signature of the integrated vehicle emissions, a Keeling plot analysis was performed. A Keeling analysis works from the assumption that the CO in the samples consists of a constant background level, combined with one polluting source. This results in a measured $\delta^{13}C$ value given by:

$$\delta^{13}C_{ms} = (\delta^{13}C_{bg} - \delta^{13}C_{sc})\frac{[CO]_{bg}}{[CO]_{ms}} + \delta^{13}C_{sc}, \qquad (2)$$

where *ms*, *bg* and *sc* indicate measured, background and source values respectively. Since all other parameters are constants, the y-intercept of a plot of the $\delta^{13}C_{ms}$ value versus the reciprocal of CO_{ms} gives the source isotope signature. $\delta^{18}O_{sc}$ is derived similarly. We also performed a Keeling plot analysis for H_2:CO (for a derivation, see Supplement 2). A complete overview of the sampling distribution is given in Table 3.

3.2. Sample analysis

The H_2 and CO mole fractions were determined using a Peak Performer 1 Reduced Gas Analyser (RGA). Each sample was measured three times and a known reference gas was measured three times before and after the sample measurements. For the RGA measurements, a non-linearity correction was applied. The correction was determined by measuring a sample multiple times, and diluting the sample in between each measurement. The difference between the decrease in mole fraction predicted from the dilution, and the reduction in signal measured on the RGA provided the non-linearity correction. The instrumental error was estimated at 3 ppb for CO and 9 ppb for H_2. The non-linearity

Table 3
The sample distribution of the measurements presented in this paper. The parking lot samples contain exclusively idling samples. The testbench samples consist of three cars undergoing a full driving cycle. The revving sample series was taken from vehicles whose throttle was pressed without coupling, so as to change engine conditions without moving the car. Where possible the distinction between hot/cold and petrol/diesel vehicles is made. The number of idling samples are indicated in brackets.

Measurement series	Petrol vehicles	Petrol samples		Diesel vehicles	Diesel samples	
		Hot	Cold		Hot	Cold
Parking lot (*idling*)	20	11 (*11*)	12 (*12*)	8	4 (*4*)	4 (*4*)
Testbench (*idling*)	3	56 (*10*)		0	0 (*0*)	
Revving (*idling*)	2	23 (*9*)		2	16 (*7*)	
Parking garage	25					
Highway	16					
Total (*individual vehicles/ atmospheric*)	167 (*126/41*)					

correction introduced an additional error of 1% and the uncertainty in the mole fraction of the reference gas introduced an error of 3% in both species.

CO_2 and CH_4 mole fractions were determined using a Picarro G2301 analyser. A syringe was connected to the flask and, due to overpressure in the flask, filled with sample air. Then the syringe was connected to the Picarro analyser, which sucked in the sample air. The repeatability for CO_2 and CH_4 was 20 ppm and 20 ppb respectively. This error is relatively large for Picarro measurements. One explanation is that using the syringe introduced an additional error. Moreover, we often measured concentrations outside the conventional measurement regime (for CO_2, over 1000 ppm; for CH_4, over 20 ppm). However, due to these high concentrations, the relative error was generally small, and we found no non-linear behaviour at high concentrations.

CO isotopologues were measured using the measurement set-up described in (Pathirana et al., 2015), based on a Continuous Flow Isotope Ratio Mass Spectrometer. CO_2 isotopologues were measured on the same instrument, which has in the meantime been expanded with CO_2 isotope capability. The typical precision was 0.2‰ for $\delta^{13}C$ and 0.3‰ for $\delta^{18}O$, for both CO and CO_2.

Since initial gas concentrations were generally far above the typical measurement range of each instrument, dilution by several orders of magnitude was required before a sample could be measured. Dilution was done with CO-free synthetic air, which contained CO concentrations below the detection level of the RGA (< 10 ppb). The dilution setup was also used to create overpressure in the flasks. The dilutions introduced additional errors, but the instrumental errors dominated.

4. Results & discussion

4.1. CO isotopologues and gas ratios of individual vehicles

An overview of the isotopic composition of CO from all samples analyzed in this study is given in Fig. 1. In Figs. 2 and 3 the isotopic composition of CO is plotted versus the $CO:CO_2$ ratio and the $H_2:CO$ ratio, respectively, and Fig. 4 shows the correlation between $CO:CO_2$ and $CH_4:CO_2$ gas ratios. The results are grouped into idling, revving and testbench measurements (explained in Section 3.1). As a reminder, some of the testbench and revving measurements were idling measurements and are here indicated as idling. We distinguish between hot and cold vehicles (only possible for idling), and between diesel and petrol vehicles, since these are the characteristics between which we found the largest differences.

Overall, the isotopic composition of CO covers a surprisingly wide range, both for $\delta^{18}O$ (+10 to +35‰) and for $\delta^{13}C$ (−60 to 0‰). For $\delta^{18}O$, a few samples dominate the extremes of the spread: most of the petrol results range from 20 to 35‰. For $\delta^{13}C$, the spread is more uniform. Previous research (Tsunogai et al., 2003) also demonstrated that the spread in isotopic composition of CO can be significant, but the degree of enrichment and especially the depletion in $\delta^{13}C$ that we find are unprecedented. Moreover, unlike previous research (Tsunogai et al., 2003), we find no correlation between $\delta^{13}C$ and $\delta^{18}O$.

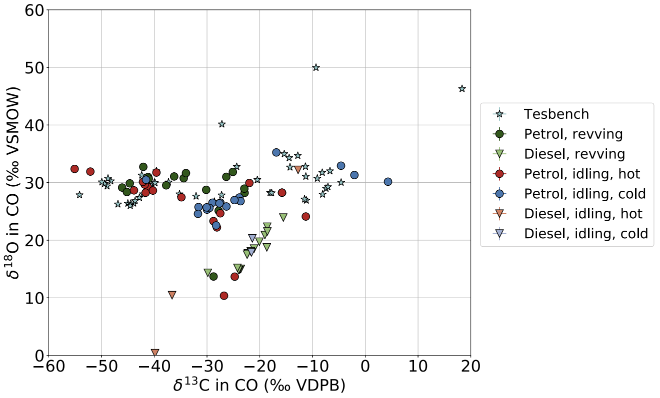


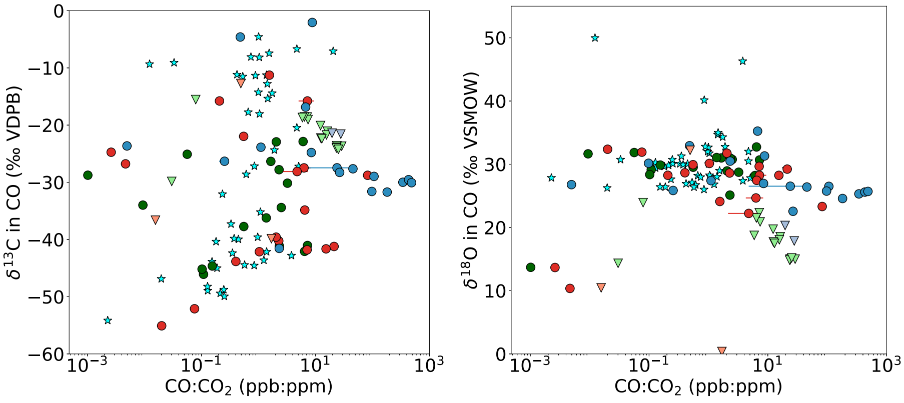
Fig. 1. The results for $\delta^{18}O$ in CO plotted against $\delta^{13}C$ in CO for the full dataset. Hot idling, cold idling and revving vehicles are shown in red, blue and green respectively. Dark-coloured circles indicate petrol vehicles and light-coloured triangles diesel vehicles. The non-idling samples taken on the testbench (all petrol) are indicated by cyan stars. Error bars are indicated for all points, but these are too small to distinguish. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The most well-defined group is that of cold diesel vehicles, which also includes some of the diesel revving samples. These vehicles emitted CO with an isotopic composition around $\delta^{13}C = -20‰$ and $\delta^{18}O = +20‰$. Within this subgroup there is a positive correlation between $\delta^{13}C$ and $\delta^{18}O$. A similar correlation for diesel vehicles was found in (Tsunogai et al., 2003), with a similar $\delta^{18}O/\delta^{13}C$ slope of approximately 1. The $CO:CO_2$ ratios (~10 ppb/ppm) and $CH_4:CO_2$ ratios (order of 10 ppb/ppm) are on the high end of the overall distribution, but they are still an order of magnitude lower than for most cold petrol samples. The exhaust from hot and cold diesel vehicles generally has very low ($< 10^{-1}$ ppb/ppb) $H_2:CO$ ratios.

Cold (idling) petrol vehicles, emit CO with an isotopic composition around $\delta^{13}C = -30‰$ and $\delta^{18}O = +25‰$. The $\delta^{13}C$ of CO is close to the $\delta^{13}C$ values of CO_2 (see Section 4.3), which we assume to reflect the $\delta^{13}C$ of fuel. The $\delta^{18}O$ value of this group is close to, but somewhat higher than that of atmospheric oxygen (23.9‰ (Barkan and Luz, 2005)). The $H_2:CO$ ratio is relatively closely centered around 0.5 ppp:ppb, which is similar to the ratio found in previous studies (Grant et al., 2010) (Vollmer et al., 2007) (Aalto et al., 2009) (Yver et al., 2009) (Popa et al., 2011). Cold petrol samples give the highest $CO:CO_2$ and $CH_4:CO_2$ ratios. Because of the large spread in $CO:CO_2$ ratios, this means that they are likely to contribute significantly to the overall traffic signature, even if vehicles are only cold for a short part of the driving cycle.

The remaining samples were mostly taken from hot vehicles and from non-idling measurements. This group shows little coherent behaviour and dominates the spread in the isotopic composition of CO and in the $H_2:CO$ ratio. The spread is largest for the testbench and revving measurements. The $CO:CO_2$ and $CH_4:CO_2$ ratios also cover a wide range, but are below the highest ratios found for the cold petrol group.

To test whether the exhaust composition from hot and cold vehicles deviate from one another significantly a Welch's *t*-test was performed. Because of the low number of diesel samples, the test was only performed for petrol vehicles. The parameters were tested at a significance level of 5%. A p-value below 5% means that the null hypothesis (that the two groups are similar) is rejected with 95% confidence. We find that the hot and cold petrol vehicle samples have significantly different means for $\delta^{13}C$, $H_2:CO$, $CO:CO_2$ and $CH_4:CO_2$ (Table 4). For $\delta^{18}O$, the



(a) (b)

Fig. 2. The isotopic composition of CO (**(a)**δ^{13}C; **(b)**δ^{18}O) of the sampled vehicle exhaust plotted against the CO:CO$_2$ ratio. The CO:CO$_2$ axis is logarithmic.

difference is not significant.

It is interesting to observe that despite the spread in the H$_2$:CO ratio and in the δ^{13}C of CO, only two samples are both depleted in ^{13}C and have a low H$_2$:CO ratio. In a sample size of 121, these two can be considered an anomaly. In (Vollmer et al., 2010), it was shown that when the air-to-fuel ratio in petrol vehicles approaches stoichiometry, i.e. when the TWC is most efficient, the H$_2$:CO ratio increases downstream of the catalyst. The distribution found here suggests that the same conditions that result in a high H$_2$:CO ratio, are the only conditions under which CO can become depleted in ^{13}C relative to fuel. No such relation is discernible between δ^{18}O and H$_2$:CO.

Previous studies found that the highest CO emissions correspond to δ^{13}C values close to fuel, and that, when CO emissions decreased, the δ^{13}C values in CO increased (Tsunogai et al., 2003) (Popa et al., 2014). A similar correlation has been found in the isotopic composition of CH$_4$ (Nakagawa et al., 2005). In both cases, the enrichment was attributed to isotopic fractionation by the catalyst. We find no clear correlation between CO:CO$_2$ and δ^{13}C or δ^{18}O (Fig. 2a and b). However, we do find that the highest emitters ($\geq$ 50 ppb/ppm), which are mostly cold petrol vehicles, emit CO with a relatively constant isotopic composition of δ^{13}C ~ -28‰, similar to the δ^{13}C for fuel (see section 4.3), and of δ^{18}O ~ +25‰, similar to atmospheric oxygen (23.9‰ (Barkan and Luz, 2005)).

Finally, we find a positive correlation between CH$_4$:CO$_2$ and CO:CO$_2$, especially for high emitters (Fig. 4). The correlation between CO and CH$_4$ might give information on the chemistry going on inside a vehicle. The correlation for high emissions indicates that the processes responsible for producing and destroying CO and CH$_4$ are similar in this range, but start to deviate when emissions decrease, be it through more efficient combustion or more efficient catalytic destruction. It has already been indicated that the behaviour of the isotopic composition of CO (Tsunogai et al., 2003) and that of CH$_4$ (Nakagawa et al., 2005) are similar.

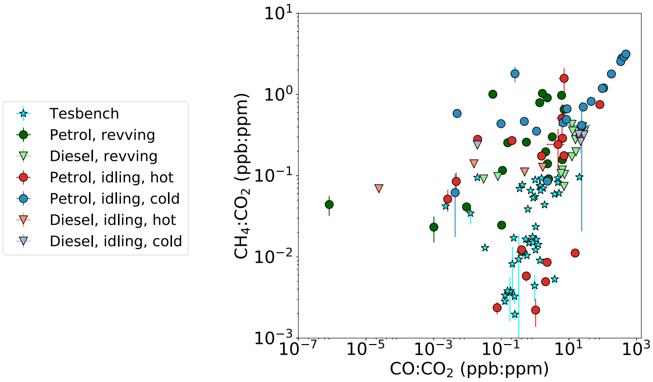
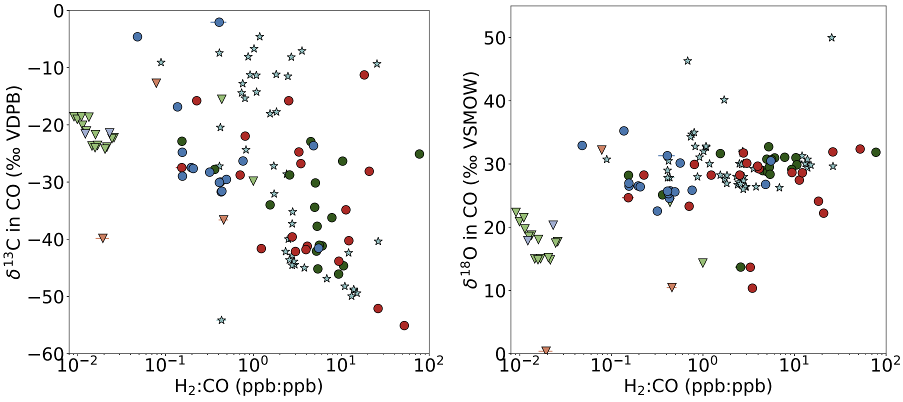


Fig. 4. Results for the CH$_4$:CO$_2$ ratio plotted against the CO:CO$_2$ ratio. Both axes are logarithmic.

4.2. Testbench results

Fig. 5 shows the results from the testbench measurements in more detail. There is a surprisingly large spread in the results, both for the gas ratios and for the isotopic composition. In some cases jumps off several tens of per mill between two subsequent samples are found. In general, CO emissions of these vehicles are quite low (CO:CO$_2$ < 10 ppb/ppm). The exceptions are the first idling sample for vehicle 1 and 2, which had CO:CO$_2$ ratios of 393 ppb/ppm and 44 ppb/ppm respectively (blue arrows in Fig. 5). The isotopic values that correspond to these high



(a) (b)

Fig. 3. The isotopic composition of CO (**(a)**δ^{13}C; **(b)**δ^{18}O) of the sampled vehicle exhaust plotted against the H$_2$:CO ratio. The H$_2$:CO axis is logarithmic.

Table 4
The mean and standard error of the mean (SEM) of the parameters for petrol vehicles, split between hot and cold vehicles. The last column gives the results of the Welch's *t*-test. For $p < 5\%$ the hypothesis that the two groups have equal means is rejected at the 95% (2-σ) confidence limit.

Parameter	No. cold	Mean cold	No. hot	Mean hot	p-value (%)
δ^{13}C (‰)	17	-24.5 ± 2.1	17	-34.2 ± 3.1	1.5
δ^{18}O (‰)	17	27.3 ± 0.7	17	28.2 ± 0.7	44.6
H_2:CO (ppb ppb^{-1})	19	1.2 ± 0.6	16	10.6 ± 3.4	1.6
CO:CO_2 (ppb ppm^{-1})	19	111.8 ± 37.9	16	9.9 ± 5.1	1.5
CH_4:CO_2 (ppb ppm^{-1})	19	1.3 ± 0.2	16	0.3 ± 0.1	0.05

CO:CO_2 ratios are close to −30‰ and +25‰ for δ^{13}C and δ^{18}O, respectively, and the H_2:CO ratio is between 0.1 and 0.6 ppb/ppb. Except for the same two samples, CH_4:CO_2 ratios were also low.

Given the wide range of results and the inconsistent behaviour among vehicles, it is not possible to deduce systematic drivers of the exhaust signatures from these measurements. When considering any one vehicle, changes in the driving conditions lead to differences in the emission signature. However, these changes are not consistent between the three vehicles. Higher driving speeds tend to correspond to elevated CO and CH_4 emissions, though not for every sample. For vehicle 3, changes in isotopic composition and gas ratios are very sudden, suggesting a strong influence of the driving speed. However, for vehicles 1 and 2, changes are more gradual, suggesting a memory effect. Acceleration is expected to push a vehicle's engine away from equilibrium, leading to sub-optimal performance and higher emissions. This is not directly seen in the results. It could be that the acceleration used in this test was too weak, or that modern vehicles have sufficient buffering capacity to remain largely unaffected by sudden changes in driving conditions. Overall, the testbench results show that emission composition varies strongly for each individual car, and that the response to changing driving conditions is different for each car, both qualitatively and quantitatively.

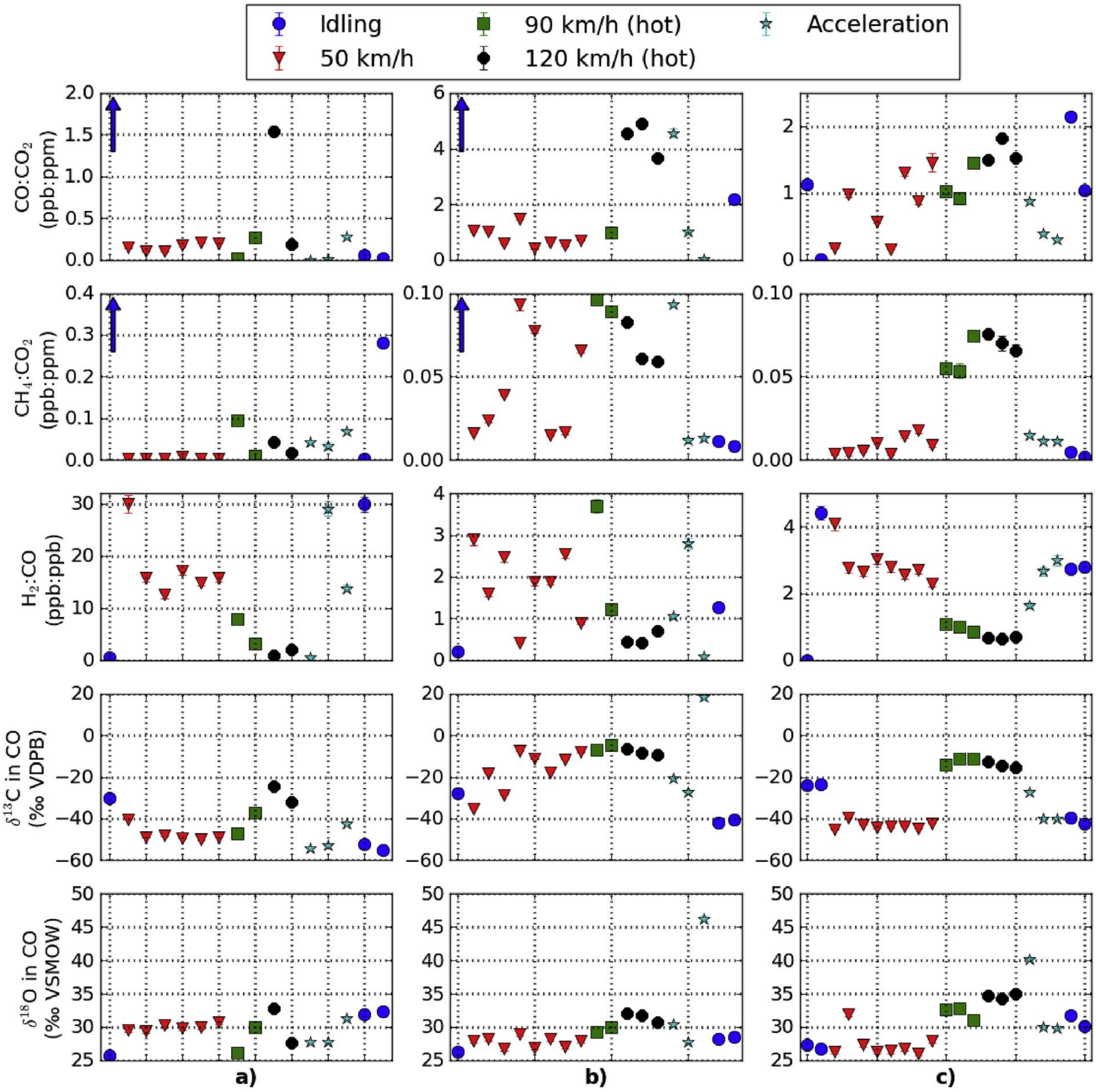


Fig. 5. The results from the testbench measurements. Results are plotted in the chronological order in which the samples were taken. Arrows indicate where measured values fall outside the plot range. Each column gives the result of one car: **a)** Vehicle 1: Smart Forfour (2007). **b)** Vehicle 2: Citroën Berlingo (2006). **c)** Vehicle 3: Ford Focus (2016).

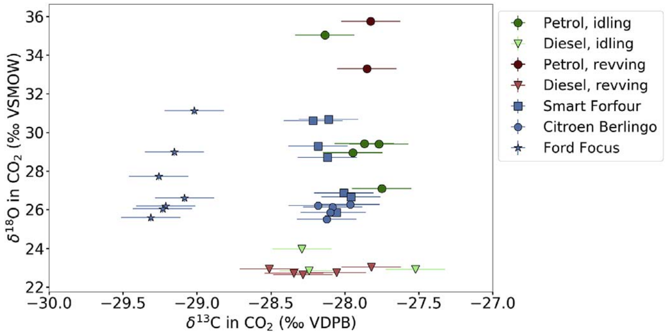


Fig. 6. The results of the CO_2 isotopologue analysis for a subset of samples. Idling samples are indicated in green, and revving samples in red. Diesel samples are indicated by light triangles and petrol samples by dark circles. Testbench samples are shown in blue and the different vehicles (all petrol) are distinguished by different symbols. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

4.3. CO_2 isotopes

Fig. 6 shows the results for the isotopic signature of CO_2, available for a subset of samples. The spread in $\delta^{13}C$ is much smaller than what we found for CO. Moreover, most of the spread comes from variations between vehicles. We assume the $\delta^{13}C$ value of CO_2 reflects that of the fuel burnt, since nearly all carbon leaves the engine as CO_2. As oil from different regions has different $\delta^{13}C$ values, small variations between vehicles are expected. The $\delta^{13}C$ values found here, fall within the range covered by $\delta^{13}C$ values of oil (− 30 to − 26‰ (Andres et al., 1994)). The $\delta^{18}O$ values cover a wider range, from + 22 to + 36‰. Interestingly, $\delta^{18}O$ values of CO_2 from diesel vehicles are a lot more constant. A possible explanation is that in petrol vehicles, a significant amount of carbon is first emitted as non-CO_2 compounds and only later converted to CO_2 by the TWC, as opposed to the more complete combustion in a diesel vehicle. This could also explain why the $\delta^{18}O$ values of CO_2 from diesel vehicles are closer to the $\delta^{18}O$ of atmospheric oxygen (23.9‰ (Barkan and Luz, 2005)).

4.4. Atmospheric samples

The Keeling plots for $\delta^{13}C$, $\delta^{18}O$ and H_2:CO are given in Fig. 7a, b and 7c. In Table 5 the source values, as derived from the Keeling plots, are given. We do not find a significant difference between the source values of the highway samples and those of the parking garage samples. This is striking, because the two environments are characterized by strongly different driving conditions. In a parking garage, roughly half of the vehicles contributing to the source signature are cold, and all are driven at low speeds. On a highway, most vehicles are hot, and all are driven at high speeds. Apparently this difference in driving conditions does not result in a significant difference in the integrated exhaust composition.

In both sample series, the source values are close to those that were found for the highest emitters in the individual vehicle samples. For $\delta^{13}C$, this is also the value for $\delta^{13}C$ in CO_2 (Section 4.3), which we assume to represent the $\delta^{13}C$ value of fuel. The $\delta^{18}O$ values are similar to what is reported in the literature (22.3 ± 0.3‰ (Kato et al., 1999); 25.3 ± 1.0‰ (Tsunogai et al., 2003); 24.1 ± 0.2‰ (Popa et al., 2014)). The H_2:CO source values are similar to the range reported in the literature (0.47–0.57 ppb:ppb (Grant et al., 2010) (Vollmer et al., 2007) (Aalto et al., 2009) (Yver et al., 2009) (Popa et al., 2011)).

Since the samples were taken on different days, background levels were not constant, so that some contamination by other sources might be present. However, in both sample series we found samples with CO concentrations exceeding 200 ppb, which is generally only reached through contamination by local sources. Near the highway sampling site, no other strong local CO sources were present, and in the parking garage CO concentrations were high enough, so that no such contamination would affect the results. The background isotopic composition of CO differs between the sample series. This is because the parking garage samples were taken in late April and early May, whereas the highway samples were taking in early August. The difference in the background isotopic composition is in agreement with the seasonal cycle of the isotopic composition of CO (e.g. (Röckmann et al., 2002)), and it does not affect the derived source values.

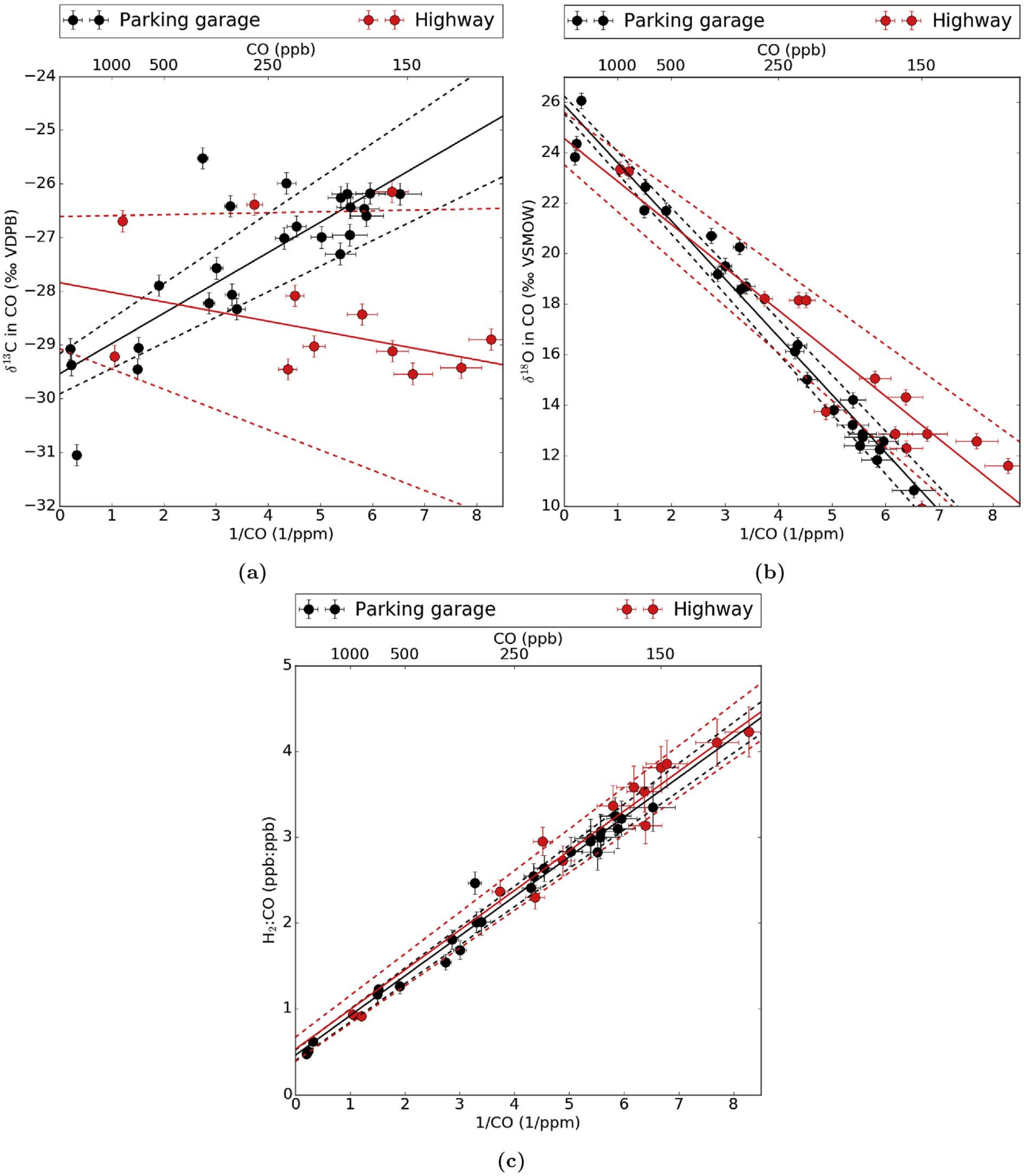
4.5. Relation between ambient samples and individual vehicles

To better relate the individual vehicle measurements to the parking garage measurements, we computed what the traffic signature would be for all the individual vehicle measurements combined. For the δ-values, this representative value is computed as a weighted mean of individual samples, with the CO:CO_2 ratios used as weights: $\delta_{final} = \frac{\sum_{i=1}^{N}(CO:CO_2)_i\delta_i}{\sum_{i=1}^{N}(CO:CO_2)_i}$. For the gas ratio X:Y, the result is given by $\frac{\sum_{i=1}^{N}[X]_i}{\sum_{i=1}^{N}[Y]_i}$. Separate weighted means were computed for each group that showed distinct behaviour.

The results, given in Table 5, show that the weighted means provide a remarkably well-defined isotopic composition for CO: the standard error of the mean is very small, considering the spread in the individual samples. This is because the samples with the highest CO:CO_2 ratios exert a strong influence on the weighted mean of the isotopic signature of CO (Fig. 8). Even if only the five highest emitters are discarded, both δ values are strongly affected and they both deviate from the isotopic signature derived from the atmospheric samples (Section 4.4). This is because the 10 highest emitters make up 80% of the sum of CO:CO_2 ratios of all samples (right y-axis in Fig. 8), so that these dominate the weighted mean calculations.

The dependence on a small number of high CO:CO_2 samples makes these types of studies sensitive to sampling biases. If the study were to be repeated with different vehicles, these outliers might not be found, resulting in a very different weighted isotopic signature for CO. However, we suggest that it is a reflection of the situation in the real world. Total traffic emissions of CO are likely dominated by a small number of vehicles or emission moments. The agreement between the weighted isotopic composition of CO in the individual vehicle samples and the atmospheric samples provides a strong argument in favour of this interpretation. The parking garage and highway samples correspond to very different driving regimes. Since the isotopic composition of CO in both driving regimes reflect the isotopic composition of CO from high CO emitters, it is reasonable to assume that overall traffic emissions are also dominated by high CO emitters. In our individual vehicle samples, we find that every high CO emitter is a cold petrol vehicle, but our highway results suggest that even in a different driving regime, with very few cold cars, high CO emitters dominate traffic emissions. Whether the high emissions originate from a few high emission vehicles, or from high emission episodes that more vehicles experience, or from a combination of both, is not clear at this point.

When the highest emitters are excluded, the resulting signature is enriched in ^{13}C, relative to the overall weighted mean. For ^{18}O, the effect is less clear, since leaving out the first ten samples leads to lower $\delta^{18}O$ values, whereas leaving out more than ten samples results in higher $\delta^{18}O$ values, compared to the overall mean. Under conditions where cold emissions are less important than for our specific sample distribution, it is likely that $\delta^{13}C$ in CO will shift towards higher values, whereas for $\delta^{18}O$ the direction of the shift is more uncertain. Note that this holds only for the idling samples, where we changed only one parameter (hot/cold). We have insufficient data to make a similar statement about for example the highway driving regime. In (Tsunogai et al., 2003) (individual vehicle measurements) a $\delta^{13}C$ of − 23.8 ± 0.8‰ was found for petrol and a $\delta^{13}C$ of − 19.5 ± 0.7‰ for diesel vehicles. In (Popa et al., 2014) (a tunnel study) a $\delta^{13}C$ of − 25.6 ± 0.2‰ was reported. These values are enriched compared to our overall



(a)

(b)

(c)

Fig. 7. Keeling plots of the atmospheric samples. Solid lines indicate least-squares linear fits, and the dashed lines outline the 68% confidence interval of the fit. Each figure shows two separate fits: one for the parking garage samples (black) and one for the highway samples (red). **a)** A Keeling plot of δ^{13}C versus 1/CO. The derived source signatures are -29.5 ± 0.4 and -27.8 ± 1.2 for the parking garage and highway respectively. **b)** A Keeling plot of δ^{18}O versus 1/CO. The derived source signatures are 25.9 ± 0.4 and 24.6 ± 1.0 for the parking garage and highway respectively. **c)** A Keeling plot of H_2:CO versus 1/CO. The derived source signatures are 0.46 ± 0.06 and 0.53 ± 0.14 ppb:ppb for the parking garage and highway respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

results. In our study, enriched signatures are found for the group of samples with not the highest, and not the lowest CO:CO_2 ratios (see Fig. 8). Thus, this middle group of samples might have provided a stronger contribution to the integrated CO signature measured in these studies. In a recent atmospheric study in Indianapolis (Vimont et al., 2017), where emission regulations for CO are absent, a δ^{13}C value of -27.7 ± 0.5‰ was reported: a value more in line with our most polluted samples. Similar to (Tsunogai et al., 2003), we find that δ^{13}C values of CO from diesel vehicles are higher than those for petrol vehicles. Different from (Tsunogai et al., 2003), we also find a significant number of samples that are depleted in ^{13}C relative to fuel. This is contrary to conventional understanding of catalytic oxidation of CO, which has been shown to result in isotopic enrichment (Ogrinc et al., 1997). Our findings suggest that the emission control systems in vehicles may have increased in complexity in such a way, that CO from vehicles can now be depleted in ^{13}C under certain conditions. To gain further insight in these variations, it would be interesting to study the exhaust composition upstream of the catalyst, or to check whether

Table 5
The main results found in this study for the vehicle exhaust composition. For the δ-values of the individual vehicle samples, we report the mean weighted by the CO:CO_2 ratios. For the individual vehicle samples, each gas ratio is computed as the ratio between the sum of the respective gas concentrations. For the atmospheric samples (parking garage and highway), the results from the Keeling plots (Section 4.4) are given. For the individual car samples, reported errors are the standard error of the mean. For the atmospheric samples, the errors indicate the 68% confidence interval of the fit.

Parameter	Overall (Individual vehicles)	Idling	Cold Petrol	Cold Diesel	Parking garage	Highway
$\delta^{13}C$ (‰)	−28.7 ± 0.5	−29.6 ± 0.6	−29.8 ± 0.6	−22.3 ± 1.9	−29.5 ± 0.4	−27.8 ± 1.2
$\delta^{18}O$ (‰)	24.8 ± 0.3	25.3 ± 0.3	25.6 ± 0.2	17.1 ± 2.0	25.9 ± 0.4	24.6 ± 1.0
H_2:CO (ppb:ppb)	0.71 ± 0.31	0.62 ± 0.29	0.45 ± 0.23	0.017 ± 0.018	0.46 ± 0.06	0.53 ± 0.14
CO:CO_2 (ppb:ppm)	19.4 ± 6.8	51.2 ± 19.3	121.2 ± 43.4	14.1 ± 12.2	n.a.	n.a.
CH_4:CO_2 (ppb:ppm)	0.26 ± 0.05	0.59 ± 0.15	1.23 ± 0.29	0.22 ± 0.12	n.a.	n.a

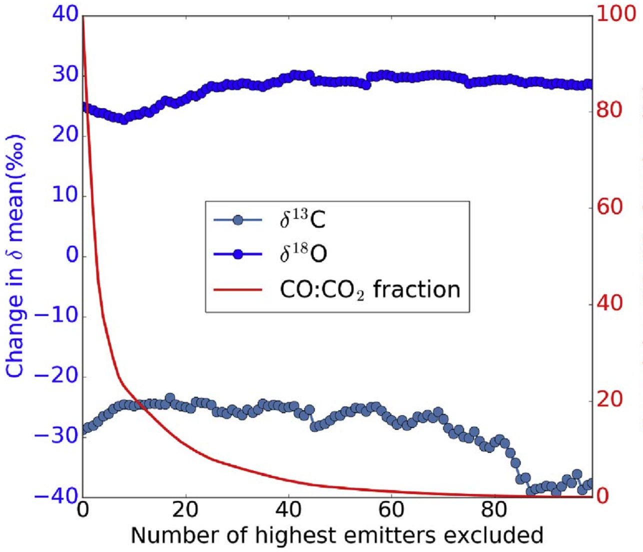


Fig. 8. The evolution of the weighted isotopic signatures of CO when gradually discarding the samples with the highest CO:CO_2 ratios. The x-axis gives the number of highest emitters that we do not include in the analysis. Only individual car samples are included in the analysis. The left y-axis shows the weighted means of $\delta^{13}C$ (dark blue) and $\delta^{18}O$ (light blue) of the new subset of samples. The right y-axis gives the fraction of the weight that the new sample subset made up in our analysis of the full dataset (red), which is quantified by the sum of CO:CO_2 ratios in the sample subset, relative to the full dataset. The total sample size was 121. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

similar isotopic variations are found for CH_4, which has been found to show isotopic variations similar to CO (Nakagawa et al., 2005). However, the CO emissions depleted in ^{13}C are not likely to contribute significantly to the atmospheric traffic signature, since they correspond to the lowest CO:CO_2 ratios.

In previous studies, it was found that samples with $\delta^{13}C$ values in CO similar to fuel, showed $\delta^{18}O$ values close to atmospheric oxygen (23.9‰ (Barkan and Luz, 2005)) (Kato et al., 1999) (Tsunogai et al., 2003). Here, we find higher $\delta^{18}O$ values (cold cars in Table 5). Since catalytic efficiency is presumably low for these samples, this enrichment in ^{18}O is likely a result of combustion in the engine.

The H_2:CO ratio reported in most atmospheric studies range from 0.47 to 0.57 ppb:ppb (Grant et al., 2010) (Yver et al., 2009) (Hammer et al., 2009) (Vollmer et al., 2007) (Aalto et al., 2009) (Popa et al., 2011). Studies that measured individual vehicle emissions found high variability in the H_2:CO ratio, dependent on the engine conditions (Vollmer et al., 2010) (Bond et al., 2010). In both studies, the best estimate differed from the atmospheric studies: 0.25 and 1.02 ppb:ppb respectively. Our best estimate of 0.71 ± 0.31 ppb:ppb falls well within the range of these values.

The weighted means confirm that the cold diesel vehicles indeed form a distinct group, with an isotopic signature distinct from petrol cars, which is in line with previous studies (Kato et al., 1999) (Tsunogai et al., 2003). Consistent with most existing literature, the H_2:CO ratio of these vehicles is very low. The CO emissions of cold diesel vehicles are actually quite significant compared to the overall results, though the few hot diesel vehicles sampled showed that these emissions sharply drop off when the vehicle heats up.

The CO:CO_2 and CH_4:CO_2 means are both elevated compared to recent literature (e.g. (Popa et al., 2014) (Frey et al., 2003)), suggesting that indeed our samples contained a relatively high number of high emission samples. Interestingly, in (Popa et al., 2014) both the CO:CO_2 and the CH_4:CO_2 ratios reported were a factor five lower than those found here. Additionally, the relative differences in Table 5 between the groups for CO:CO_2 are very similar to those for CH_4:CO_2. This again indicates that the two ratios behave similarly. A conservative estimate of global CH_4 emissions based on our average CH_4:CO_2 ratio and global carbon emissions from fossil fuels in the order of 10 GtC yr^{-1} (e.g. (Le Quéré et al., 2014)), would result in emissions of only a few Tg CH_4 yr^{-1}. The global budget of CH_4 is in the order of several hundreds of Tg (e.g. (Lelieveld et al., 1998)), so that even this upper bound on CH_4 emissions from traffic is insignificant.

4.6. *Implications*

Our results have interesting implications for research into vehicle exhaust in general. They show that determining a fleet average of traffic emissions from individual vehicle measurements is a complex task. The spread we find in the exhaust gas composition demonstrates that a large number of vehicles needs to be tested under a wide range of conditions to determine a fleet average. This is likely to become more challenging as emission control systems in vehicles become more complex, which may lead to complex emission patterns, as seen in the test bench results. In the interest of the mitigation of vehicle emissions, the strong variability of emission signatures emphasizes that this type of study may possibly provide further information to improve emission control systems. More specifically, the influence of strong acceleration on emissions is still uncertain. Our results also indicate that, since TWCs already work very efficiently under hot conditions, further improving the optimal performance of TWCs might not reduce traffic emissions by much, especially in urban areas. For these reasons it is important that research into individual vehicles, which are actually being driven in the real world, continues. Our results show that isotopic research can help to identify which driving conditions and which types of vehicles are contributing the most in different areas.

5. Conclusions

We find a large spread in the isotopic composition of CO in vehicle emissions ($\delta^{13}C$: 0 to −60‰; $\delta^{18}O$: +10 to +35‰), compared to previous studies. Hot and cold petrol vehicles behave significantly differently for $\delta^{13}C$, H_2:CO, CO:CO_2 and CH_4:CO_2, but not for $\delta^{18}O$. Diesel vehicles emitted CO with an isotopic composition distinct from petrol, and the gas ratios in the emissions were generally lower.

The weighted means of the isotopic composition were well-defined and close to what was found in the atmospheric samples. The $\delta^{13}C$ value was close to that of fuel and the $\delta^{18}O$ value slightly enriched relative to atmospheric oxygen. The weighted means were dominated by a small set of high-emitters, mostly cold petrol vehicles. This reflects the importance of a few moments of high emissions to total traffic emissions. The agreement between the weighted means of the isotopic composition of CO from the individual vehicle samples, and the signatures found for both the parking garage and the highway atmospheric sample series, suggests that the importance of a few moments of high emissions is not just a characteristic of our specific sample series, but also of traffic in general.

The H_2:CO ratio in the individual vehicle measurements showed large spread, but the weighted average agreed with values reported in the literature. It was also dominated by the high CO emitters, but to a lesser degree, since samples with low CO concentrations sometimes still showed significant H_2 emissions. We found a link between H_2:CO and $\delta^{13}C$, such that samples with low H_2:CO ratios rarely had low $\delta^{13}C$ in CO. The exact interpretation of this observation is uncertain, but it suggests that the H_2:CO ratio can perhaps give information on the state of the engine and/or of the TWC.

Results for the CO:CO_2 and CH_4:CO_2 ratios were less coherent than those for the H_2:CO ratio. For CO:CO_2, the range in the results covered eight orders of magnitude. Since all of the high emitters were cold petrol vehicles, this indicates the importance of CSEEs in modern vehicles. CH_4 emissions were dominated by the same high emitters. For these high emitters a linear correlation between CO and CH_2 concentrations was found. Our results support the finding from previous studies that CH_4 emissions from vehicles are negligible.

$\delta^{13}C$, $\delta^{18}O$ and H_2:CO values from samples collected in parking garages and near a highway were both similar to the weighted means of the individual vehicle measurements, as well as to each other. This indicates that high emitters dominate CO and H_2 emissions in a parking garage, as well as on a highway. High emitters could refer to a few high emission vehicles, or to high emission episodes that more vehicles undergo: the data do not conclusively point to either possibility.

The $\delta^{13}C$ values of CO_2 cover a range of 2‰, where most of the spread came from differences between vehicles (thus likely from the fuel). The $\delta^{13}C$ values of CO_2 were similar for diesel and petrol vehicles. The $\delta^{18}O$ values in CO_2 of petrol vehicles varied between 22 and 36‰, similar to the $\delta^{18}O$ values of CO. For diesel vehicles the $\delta^{18}O$ in CO_2 varied in a range of 1‰ around +23‰: close to the $\delta^{18}O$ of atmospheric oxygen.

Overall, the spread in the results showed that CO emissions from vehicles might be dominated by a small number of vehicles and driving conditions. Studies where results from only a handful of vehicles are extrapolated to an entire fleet, should therefore be considered with caution. A comprehensive study of a wide array of vehicles, measured under a wide range of conditions, could provide valuable information on the best methods for reducing emissions of CO and other pollutants.

Data availability

The full dataset is available in Supplement 3, including all recorded vehicle characteristics and more specifics on the ambient sample series.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2018.01.015.

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