Vehicle emissions of greenhouse gases and related tracers from a tunnel study: CO : CO 2 , N 2 O : CO 2 , CH 4 : CO 2 , O 2 : CO 2 ratios, and the stable isotopes 13 C and 18 O in CO 2 and CO

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Vehicle emissions of greenhouse gases and related tracers from a tunnel study: $CO:CO_2$, $N_2O:CO_2$, $CH_4:CO_2$, $O_2:CO_2$ ratios, and the stable isotopes ^{13}C and ^{18}O in CO_2 and CO

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Abstract. Measurements of CO_2, CO, N_2O and CH_4 mole fractions, O_2/N_2 ratios and the stable isotopes ^{13}C and ^{18}O in CO_2 and CO have been performed in air samples from the Islisberg highway tunnel (Switzerland). The molar $CO:CO_2$ ratios, with an average of (4.15 ± 0.34) ppb:ppm, are lower than reported in previous studies, pointing to a reduction in CO emissions from traffic. The ^{13}C in CO_2 reflects the isotopic composition of the fuel. ^{18}O in CO_2 is slightly depleted compared to the ^{18}O in atmospheric O_2, and shows significant variability. In contrast, the $\delta^{13}C$ values of CO show that significant fractionation takes place during CO destruction in the catalytic converter. ^{13}C in CO is enriched by 3 ‰ compared to the ^{13}C in the fuel burnt, while the ^{18}O content is similar to that of atmospheric O_2. We compute a fractionation constant of (-2.7 ± 0.7) ‰ for ^{13}C during CO destruction. The $N_2O:CO_2$ average ratio of $(1.8 \pm 0.2) \times 10^{-2}$ ppb:ppm is significantly lower than in past studies, showing a reduction in N_2O emissions likely related to improvements in the catalytic converter technology. We also observed small CH_4 emissions, with an average $CH_4:CO_2$ ratio of $(4.6 \pm 0.2) \times 10^{-2}$ ppb:ppm. The $O_2:CO_2$ ratios of (-1.47 ± 0.01) ppm:ppm are very close to the expected, theoretically calculated values of O_2 depletion per CO_2 enhancement.

1 Introduction

In densely populated areas, traffic emissions are a significant source of trace gases and pollutants. The main product of fuel burning is CO_2, but a wide series of other gases are emitted concurrently. Some of these are short lived and have mainly local health and environmental effects. Long lived gases, like CO_2, CH_4, N_2O, CO, and H_2, are (indirect) greenhouse gases and have global effects on atmospheric chemistry and climate.

CO_2 emissions from traffic can be computed fairly accurately from fuel consumption statistics. The emissions of other gases are more difficult to estimate and depend strongly on technology, vehicle type and driving conditions. The introduction of catalytic converters led to a strong decrease in the emissions of some gases, and emissions further decreased with each generation of emission standards. In Europe for example, the accepted CO emission for Euro 3 passenger gasoline vehicles was 2.3 g km^{-1}, and the Euro 4 and Euro 5 standards decreased the limit to 1 g km^{-1}. Other relevant gases, like for example H_2 and N_2O, are not controlled by the existing vehicle emission standards, while CH_4 is usually only included in the total hydrocarbon category. However, vehicle emissions of N_2O and CH_4 have to be estimated and included in annual reports by the United Nations Framework Convention on Climate Change (UNFCCC) partners. These estimations are based on traffic statistics and emission factors

(IPCC, 1997; UNFCCC, 2006), thus it is important that emission factors reflect the actual real-life emissions.

Because of the relatively fast evolution of vehicle technology and emission standards, emissions can change significantly on timescales of several years. Besides this, different composition and age of the car fleet lead to large regional differences in emissions.

Vehicle emission rates (or factors) are used together with traffic statistics to estimate traffic emissions at various scales. Emission rates are often obtained in laboratory setup by dynamometer studies, but it has been shown that the results do not always represent the real-life emissions (Ropkins et al., 2009 and references therein). Tunnel measurements proved to be very useful for estimating real-world fleet-wide emission rates (see Ropkins et al., 2009 for a review of emission estimation methods). The obvious advantage of a tunnel setup is that it allows observing real-life traffic emissions while keeping out other possible sources. Tunnel studies have, however, some limitations; for example, they are mostly representative for fluent traffic conditions and not for urban driving with frequent stops and accelerations. Thus tunnel measurements have to be complemented by other types of measurements in order to obtain a complete picture.

The Islisberg-2011 measurement campaign took place in June–July 2011 at the Islisberg highway tunnel located near Zürich, Switzerland, with the intention to update (where older estimates exist) or quantify emissions and isotopic signatures of several important long lived trace gases, characteristic to the western European vehicle fleet.

The purpose of the present paper is as follows:

- to quantify $CO:CO_2$, $N_2O:CO_2$ and $CH_4:CO_2$ emission ratios for the present vehicle fleet;
- to determine the present isotopic signatures of traffic-emitted CO_2 and CO;
- to verify the theoretically calculated $O_2:CO_2$ ratios of traffic emissions.

Results on the $H_2:CO$ emission ratios and H_2 isotopic signatures will be presented in a different publication.

The remainder of the paper is organized as follows. Section 1.1 contains background information on each species dealt with in the paper – we considered necessary to include this information, but it can be skipped by the expert reader. Section 2 presents the sampling and measurement methods. Section 3 starts with a general description of the data acquired and continues with a detailed discussion on the $CO:CO_2$ ratios and the isotopic composition of CO_2 and CO, followed by $N_2O:CO_2$, $CH_4:CO_2$ and $O_2:CO_2$ ratios. Section 4 contains a summary of our findings. The Supplement includes a more detailed description of the CO mole fraction measurements at the Institute for Marine and Atmospheric research Utrecht (IMAU) and the main numerical data used in the paper.

1.1 Background on the investigated species

$CO:CO_2$ ratios

CO is an atmospheric trace gas that results from incomplete oxidation of carbon. Anthropogenic emissions are responsible for a large part of the global CO; in Europe anthropogenic sources account for about 70 % of the total sources (Pfister et al., 2004). About a quarter of these emissions were in 2010 from road transport (EEA, 2013).

CO is important for the atmospheric chemistry, mainly due to its reaction with OH radicals. CO is also a toxic gas and, because some of its largest sources are associated with human agglomerations, it is a concern for human (and animal) health. Thus most urban air quality monitoring programs include CO. Besides these, CO is a good tracer for detecting and quantifying anthropogenic emissions from burning processes, since it is a product of incomplete burning. For example, the ratio between atmospheric variations of CO and CO_2 (the $CO:CO_2$ ratio) has been used to quantify the fossil fuel contribution to the CO_2 variability and the CO_2 fossil fuel fluxes (e.g. Gamnitzer et al., 2006; Levin and Karstens, 2007; Rivier et al., 2006; Turnbull et al., 2006, 2011; Zondervan and Meijer, 1996). The $CO:CO_2$ ratios are higher for poorer burning (e.g. forest fires), thus these ratios can be used to distinguish between different burning processes or to determine the burning efficiency (Andreae and Merlet, 2001; Röckmann et al., 2010; Suntharalingam et al., 2004; Wang et al., 2010).

Anthropogenic emissions of CO have been decreasing over the last two decades, according to various inventories (see e.g. Granier et al., 2011), and the decrease in emissions is reflected in decreasing atmospheric mole fractions in urban areas, background areas and in the atmospheric column (Angelbratt et al., 2011; von Schneidemesser et al., 2010; Worden et al., 2013; Zellweger et al., 2009); for Europe, the decreasing trends are larger than the global ones.

In populated regions like Europe one of the major sources of CO_2 and CO is road traffic. The CO_2 emission rate is relatively constant, as it depends directly on the quantity of fuel burnt. Emissions of CO, on the other hand, are strongly dependent on vehicle technology and thus on fleet composition. Emission standards gradually lowered the limits of allowed CO from Euro 1 to Euro 4. A gradual decrease in emissions from pre-Euro to Euro 4 cars has been confirmed by real-world measurements (e.g. Rhys-Tyler et al., 2011). The stricter vehicle emission standards and the mandatory introduction of catalytic converters in new cars at the beginning of the 1990s are partly responsible for the decrease in emissions.

It is expected that traffic CO emissions will continue to decrease while older vehicles are replaced by new ones. It is also likely that the overall anthropogenic emissions of CO in Europe (and in consequence the $CO:CO_2$ ratios) will continue to decrease with the evolution towards cleaner technologies, under the pressure of pollution reduction policies. Periodically updating the information on CO : CO_2 emission ratios for different sources will reduce uncertainties in CO emission inventories. This will on one hand improve the possibility to use these ratios for CO_2 source discrimination. On the other hand, for vehicle emissions, where CO_2 is relatively well known from fuel consumption, known CO : CO_2 ratios can help determining CO emissions, which is important for example for assessment and control of pollution in populated areas.

1.1.1 CO_2 stable isotopes ^{13}C and ^{18}O

Numerous studies have used the isotopic composition of atmospheric CO_2 in order to constrain various aspects of the carbon cycle (e.g. Battle et al., 2000; Gruber and Keeling, 2001; Yakir and Sternberg, 2000; Yakir and Wang, 1996). In general, the isotopic composition of atmospheric CO_2 is linked to the biosphere–atmosphere exchange and, in the case of ^{18}O, to the water cycle (Farquhar et al., 1993; Francey and Tans, 1987; Mills and Urey, 1940). However, especially in highly populated areas like Europe, a significant part of the CO_2 emitted originates from fossil fuel burning. Good knowledge on the isotopic composition of the fossil fuel-derived CO_2 can in principle help interpreting atmospheric measurements and partitioning sources and sinks at local and regional level (e.g. Meijer et al., 1996; Pataki et al., 2003, 2006, 2007; Zimnoch et al., 2004; Zondervan and Meijer, 1996).

In modelling studies so far, the ^{18}O isotopic ratio of combustion-derived CO_2 is considered to be equal to the ^{18}O isotopic ratio of atmospheric O_2 (e.g. Ciais et al., 1997; Cuntz et al., 2003). This assumes that atmospheric O_2 is consumed without fractionation; however, this has been questioned by some recent studies. For example, Affek and Eiler (2006), Horvath et al. (2012) and Schumacher et al. (2011) found the ^{18}O in vehicle exhaust CO_2 to be significantly different from the ^{18}O in atmospheric O_2; combustion of other materials has been shown to suffer fractionation processes affecting ^{18}O in CO_2 as well. More work appears thus necessary for better defining the source signatures of CO_2 resulting from different burning processes.

1.1.2 CO stable isotopes ^{13}C and ^{18}O

Stable isotopes have been used as a tool to distinguish between CO emission sources, for example to distinguish between traffic and wood combustion (Saurer et al., 2009), to identify large scale pollution from forest fires (Röckmann et al., 2002) and to identify various anthropogenic emissions (e.g. Tarasova et al., 2007). Also, modelling studies that included ^{13}C and ^{18}O provided more robust results than when considering CO mole fractions alone (Bergamaschi et al., 2000; Manning et al., 1997). For these uses, however, the source-specific isotopic signatures have to be known. It has been shown that the ^{13}C and ^{18}O isotopic signatures of CO from combustion sources are not necessarily the same as the ^{13}C of the material burnt and the ^{18}O in the atmospheric O_2 due to fractionation during the burning process (e.g. Kato et al., 1999a, b; Tsunogai et al., 2003). Relatively few estimates exist on the isotopic signatures of different CO sources, and in particular on traffic CO, although in some areas traffic emissions account for a large proportion of anthropogenic CO sources.

There are two main types of studies regarding the isotopic composition of CO emitted by traffic, which are complementary. One consists of fleet integrated measurements, with results representative for the real-world average traffic emissions. Only few such studies exist worldwide (Kato et al., 1999a; Stevens et al., 1972; Tsunogai et al., 2003); the most recent measurements in Europe were performed in 1997 by Kato et al. (1999a).

The other category of studies focuses on measuring emissions of individual vehicles or engines (e.g. Huff and Thiemens, 1998; Kato et al., 1999a; Tsunogai et al., 2003); upscaling their results to fleet level is not always straightforward, but these studies are particularly useful for understanding the factors controlling the emissions and the phenomena behind. As revealed by the studies above, the isotopic composition of exhaust CO is strongly dependent on vehicle technology. ^{13}C in CO in exhaust gas is approximately similar to that in the fuel for old vehicles without a catalyst, and it is enriched for gasoline vehicles with catalyst and for diesel vehicles. ^{18}O is enriched relative to atmospheric O_2 for gasoline vehicles with catalyst, and is depleted for old gasoline vehicles without catalyst and for diesel vehicles. The driving regime and the temperature of the catalyst have been observed to affect the isotopic composition of emitted CO as well.

The above implies that the isotopic composition of traffic CO should change in time with the change in technology, increasing proportion of vehicles equipped with catalytic converters, and changing shares for different fuel types. Such evolution is already clear when comparing the results of old and new estimates, and it is expected that the CO isotopic composition will continue to change and will have to be reevaluated periodically (Tsunogai et al., 2003).

1.1.3 N_2O : CO_2 ratios

N_2O is an important greenhouse gas, considered to be responsible for about 6 % of the anthropogenic radiative forcing (NOAA-AGGI, 2011); besides this, following the reduction of CFCs, N_2O is expected to become the most important ozone-depleting gas (Ravishankara et al., 2009). Atmospheric N_2O has increased from 270 ppb in preindustrial times to 324 ppb in 2011 (Flückiger et al., 2002; WMO (World Meteorological Organization), 2012), the main anthropogenic sources responsible for this increase being the use of nitrogen fertilizer, biomass burning, fossil fuel combustion, and industrial production of adipic and nitric acids. For NW Europe, road transport emissions are estimated to account for about 2.6 % of the total anthropogenic N_2O (UNFCCC, 2013).

It is known that vehicles equipped with a three-way catalyst have higher N_2O emission rates than old vehicles without a catalyst, as N_2O is formed inside the catalyst as an intermediary during NO reduction (Berges et al., 1993; Cant et al., 1998; Dasch, 1992). In the beginning of the 1990s, it was predicted that N_2O emissions from vehicles would continue to increase with the increasing proportion of catalyst-fitted vehicles. Berges et al. (1993) estimated that, if the entire car fleet would be equipped with the then-current type of catalysts, the global N_2O emissions from traffic could double and become responsible for 6–32 % of the atmospheric growth rate. However, later studies suggested that N_2O traffic emissions had been decreasing (e.g. Becker et al., 2000), possibly due to improvement in catalytic technology.

Emissions of N_2O, including the ones from traffic, have to be estimated, for example for reporting to the UNFCCC. The total N_2O emitted from traffic is difficult to estimate in a bottom-up way because, at vehicle level, the N_2O emission rate depends on a multitude of factors: presence, technology and age of catalyst; driving regime and catalyst temperature (largest emissions for cold catalyst); type of fuel; presence of sulfur in fuel; etc. (for a detailed discussion see Lipman and Delucchi, 2002). Studies of real-world traffic that integrate emissions from a large number of vehicles are particularly useful in such a case.

1.1.4 $CH_4 : CO_2$ ratios

CH_4 is the second most important anthropogenic greenhouse gas, being responsible for about 20 % of the anthropogenic radiative forcing (Forster et al., 2007), and it is also of major importance for atmospheric chemistry. CH_4 is a good candidate for greenhouse gases emission reduction measures, in the sense that its relatively short atmospheric lifetime of about 9 yr allows observing effects of such measures on timescales of several years.

Atmospheric CH_4 increased over the past centuries from a preindustrial level of about 700 ppb to the present level of 1800 ppb (Etheridge et al., 1998; WMO, 2012), mostly due to anthropogenic emissions from rice paddies, landfills, ruminants, biomass burning and energy production. Vehicle emissions are known as a minor or even insignificant source on global scale (Nam et al., 2004). It has been shown, however, that locally, in areas with high traffic density, they can account for a larger proportion, reaching even 30 % of the total emissions (Nakagawa et al., 2005). CH_4 vehicle emissions have to be estimated and included in annual reports by the UNFCCC partners.

1.1.5 $O_2 : CO_2$ ratios

During any burning process that produces CO_2, atmospheric O_2 is consumed, often in a fixed proportion. CO_2 and O_2 are also exchanged between the biosphere and atmosphere during photosynthesis and respiration, with a stoichiometric $O_2 : CO_2$ ratio assumed to be approximately -1.1 mol:mol. The $O_2 : CO_2$ ratios of fossil fuel burning (including road transport) and of land biosphere–atmosphere gas exchange have been used to estimate the partitioning of CO_2 uptake between land biosphere and ocean, to determine the geographical distribution of the CO_2 sink based on $N-S$ gradients, and to distinguish contributions of various sources to short-term atmospheric signals (e.g. Battle et al., 2000; Bender et al., 2005; Keeling and Shertz, 1992; Keeling et al., 1993, 1996; Manning and Keeling, 2006; Stephens et al., 2003).

The global $O_2 : CO_2$ ratio for fossil fuel burning was first computed by Keeling (1988) based on the chemical composition and the relative contribution of various fuel types, and updated by several other studies for different time periods; the resultant global $O_2 : CO_2$ ratio was around -1.4 mol:mol in all estimates. The fuel composition however may vary in space and time, and a global average cannot account for this. Manning and Keeling (2006) noted that improved estimates of the $O_2 : CO_2$ ratios of the source fuels are necessary for better constraining the land and oceanic carbon sinks. Recently, Steinbach et al. (2011) created a global database of $O_2 : CO_2$ ratios from fossil fuel burning (COFFEE; CO_2 release and O_2 uptake from Fossil Fuel Emission Estimate) calculated from fuel composition and updated production proportions; COFFEE is an hourly resolution data set with a grid of $1^\circ \times 1^\circ$ and covers the years 1999–2008.

We are only aware of one study that aimed to determine the fossil fuel $O_2 : CO_2$ ratio experimentally (Keeling, 1988), through atmospheric measurements in an urban environment influenced by vehicle emissions. Our estimation of $O_2 : CO_2$ ratios for the road traffic is the first one based on actual measurements of traffic signals isolated from other sources or sinks, and is useful for verifying the theoretically calculated ratios and to estimate the potential variability on short timescales of hours to days.

2 Methods

The Islisberg-2011 campaign had two components: (1) continuous, in situ measurements of CO and H_2 mole fractions, and (2) flask sampling for laboratory analysis of CO_2, CO, CH_4, N_2O, SF_6, H_2, O_2 / N_2, A / N_2, ^{13}C and ^{18}O in CO_2, ^{13}C and ^{18}O in CO, and D in H_2. The results reported here are based on the flask sample measurements.

2.1 Site description

The Islisberg highway tunnel is relatively new (2009); it is 4.6 km long and has separated bores for the two traffic directions, each with two lanes. In normal situations it has no active ventilation, which means that the air movement through the tunnel is created by the moving vehicles. The average traffic through the tunnel is about 25 000–30 000 vehicles per day in each direction (slightly lower during weekend); about 85 % are personal vehicles. This traffic load level is medium for the national roads in Switzerland, but relatively low compared to other roads around Zürich. Due to the relatively low vehicle load, the traffic in the Islisberg Tunnel is generally fluent. The proportion of heavy goods transport is in general about 5 %, which is a medium level for national roads in Switzerland. Like other roads used intensively for commuting, the traffic has morning and afternoon peaks during working days. The speed limit is 100 km h^{-1}. Our measurements took place in the tunnel bore that leads towards Zürich, which has an uphill slope of 1.3 %. Given the location of the tunnel it is likely that most vehicles were already warmed up, with the catalytic converters operating at optimal temperature.

Hourly traffic count data per vehicle category were obtained from the automatic traffic count network of FEDRO (Federal Roads Office) (data downloaded from www.portal-stat.admin.ch/sasvz/files/fr/03.xml).

2.2 Air sampling

Air was sampled in parallel at two locations in the same tunnel bore, close to each end of the tunnel. The "entrance" sampling site was located inside the tunnel, about 80 m from the tunnel entrance; the "exit" site was also inside the tunnel, about 50 m from the exit. The sampling equipment was installed in the maintenance spaces located below the traffic level. At each location, air was drawn from the traffic level via 14 mm OD, about 10 m long PTFE tubes, at a flow rate higher than 15 L min^{-1}. Air for flask samples was drawn from this main air stream via a glass distributor located before the main sampling pump (thus the sample air did not pass through this pump), with a flow of approximately 2 L min^{-1}. The other outlets of the distributor were used for our in situ measurements of H_2 and CO, and for other measurements made by the Zürich Office of Waste, Water, Energy and Air (WWEA).

At the end of the campaign, after the WWEA measurements had ended, we removed the glass distributor and filled several flasks with air drawn directly from the tunnel without dividing the stream; this was done for testing the influence of the distributor on the O_2 / N_2 values, as it is known that air stream divisions (e.g. a tee-junction) can lead to oxygen fractionation (Keeling et al., 2004). No significant difference was found between the flask sampled with and without the glass distributor.

2.3 Flask sampling

The two flask samplers that were employed used 1/4″ Synflex-1300 tubing and KNF Neuberger N86 diaphragm pumps. Air was dried using stainless steel traps (20 cm long, 1″ OD) filled with magnesium perchlorate, which was changed every one or two samplings. We used glass flasks equipped with PCTFE seals, made by Normag, Ilmenau, Germany: one set of 1 L flasks from IMAU (referred to in what follows as *imau*-flasks), one set of 1 L flasks from the Max-Planck Institute for Biogeochemistry (MPI-BGC, *mpi*-flasks) and one set of 2 L flasks from Empa (*empa*-flasks).

The standard sampling procedure was as follows. At the entrance site, two flasks were installed in series, one *mpi* and one *imau* flask (the *mpi* flask was always the first after the pump). At the exit site, three flasks were filled in series: *mpi*, *imau* and *empa*, in this order. The flushing time was 15 min, at a flow rate of 2 L min^{-1} and a pressure of 1.7 bar abs; the pressure was kept constant through the sampling time. The normal sampling action involved sampling at both entrance and exit site in parallel, with a delay of 15 min for the exit site. Unless otherwise specified, our analysis is based on the difference between these exit and the entrance flasks sampled in parallel. A total of 133 flasks were filled, most of them during a 30 h intensive sampling period on 21–22 June 2011.

2.4 Flask measurements

Different measurements were performed on the flask samples at MPI-BGC and IMAU. The *mpi* flasks were analysed at MPI-BGC for CO_2, CH_4, N_2O, SF_6, H_2, CO, O_2 / N_2, A / N_2, and the stable isotopes ^{13}C and ^{18}O in CO_2. The *imau* flasks were analysed at IMAU for CO, H_2, ^{13}C and ^{18}O in CO, and D in H_2. The *empa* flasks travelled to MPI-BGC and IMAU and were analysed for all species. The results for H_2 and its isotopic composition are not discussed in this paper.

2.4.1 Flask measurements at MPI-BGC

Two sets of flasks (the *mpi* and *empa* flasks) were analysed at MPI-BGC as mentioned above. MPI-BGC routinely performs flask sample analyses following well-established methods (Jordan and Brand, 2003; Jordan and Steinberg, 2011), thus we will only give a summary here.

CH_4, CO_2, N_2O and SF_6 were analysed using Agilent gas chromatographs with flame ionization (FID) and electron capture detectors (ECD). Typical 1-σ precisions are on the order of 0.075 % for CH_4, 0.017 % for CO_2, 0.05 % for N_2O and 0.4 % for SF_6. The mole fractions reported are traceable to WMO calibration scales (CO_2: NOAAX2007 scale, CH_4: NOAA2004 scale, N_2O: NOAA2006A scale, SF_6: NOAA2006 scale). Out of the 70 flask samples analysed, CO_2 mole fraction was above the range set by the WMO laboratory calibration standards in 38 samples and N_2O mole fraction in 9 samples. No significant extrapolation error is assumed for these extrapolated data as for CO_2 the FID is very linear, whereas N_2O mole fractions (detected with the more non-linear ECD) were not much above the calibrated range.

CO was analysed (together with H_2) using a RGA3 Reduction Gas Analyzer (Trace Analytical), with a typical CO precision of 0.2 %. CO results are traceable to the NOAA2004 scale. The calibration range covered by WMO tertiary standards at MPI-BGC extends up to 484 ppb. From the total of 70 flasks, 24 had CO mole fractions above the cut-off range of the instrument, thus could not be analysed. Additionally, 17 flask samples had mole fractions above the calibrated range; due to the significant non-linearity of the RGA instruments, the results of these flasks are possibly affected by large errors and will not be used here.

O_2 / N_2 and A / N_2 were analysed with a mass spectrometric method (Brand, 2005), with a typical precision of 2 per meg for O_2 / N_2 and 5 per meg for A / N_2 ("per meg" definition is given in Sect. 2.5). O_2 / N_2 results are traceable to the SIO (Scripps Institute of Oceanography) calibration scale. A / N_2 results were only used in our work as a quality check, in order to detect potential problems that could have led to O_2 fractionation (Battle et al., 2006; Keeling et al., 2004). Following this check, the results of two flasks that showed abnormal A / N_2 ratios were excluded from further analysis for O_2 / N_2.

^{13}C and ^{18}O in CO_2 were analysed with a mass spectrometric method (Brand et al., 2009; Ghosh et al., 2005; Werner et al., 2001), with a typical precision of 0.013 ‰ for ^{13}C and 0.025 ‰ for ^{18}O. The results are reported by MPI-BGC on the VPDB (Vienna Pee Dee Belemnite) scale in the case of $\delta^{13}C$ and on the VPDB-CO_2 scale in the case of $\delta^{18}O$, using JRAS air as the principle anchor to the VPDB scale (JRAS = Jena Reference Air Set, Wendeberg et al., 2013). In this paper, for direct comparison with previous works and with the CO results, we converted the ^{18}O in CO_2 data to the VSMOW (Vienna Standard Mean Ocean Water) scale considering that $\delta^{18}O$ (VPDB-CO_2, VSMOW) $= +41.5$ ‰.

2.4.2 Flask measurements at IMAU

Two sets of flasks (the *empa* and *imau* flasks) were analysed at IMAU for CO (and H_2) mole fractions and the stable isotopes ^{13}C and ^{18}O in CO.

CO mole fractions were measured (together with H_2) with a Peak Performer 1 RGA, using synthetic air as a carrier gas. The CO results are traceable to the NOAA2004 scale. A total 40 out of the 75 flasks measured had CO mole fractions above the cut-off range of the instrument and were diluted with CO-free synthetic air in order to make the analysis possible. A dilution series was produced in order to calibrate the RGA instrument over the whole measurement range (up to approx. 1000 ppb for CO) and to correct for the instrument non-linearity. Typical repeatability of the instrument, when measuring a constant gas with mole fraction in the normal atmospheric range, is better than 1 % for CO. The overall uncertainty that we assigned to the CO mole fractions, accounting for the dilution and calibration errors, is 5 %. Further details on the CO mole fraction measurements at IMAU are given in the Supplement.

^{13}C and ^{18}O in CO were measured with a continuous flow mass spectrometry system, which is described in detail in Pathirana et al. (2014). $\delta^{13}C$ and $\delta^{18}O$ values were calibrated against one calibration cylinder with a known isotopic composition (Brenninkmeijer, 1993) and are reported on the VPDB and VSMOW international scales respectively. These measurements were performed after the CO mole fraction measurements, thus after the flasks with very high CO mole fractions had been already diluted. The analytical precision (repeatability) during these measurements was estimated at 0.12 ‰ for $\delta^{13}C$ and 0.16 ‰ for $\delta^{18}O$. Additionally, based on the drift observed in the reference gas measurements, we assume a possible systematic error of the results of up to 0.2 ‰ in $\delta^{13}C$ and 0.1 ‰ in $\delta^{18}O$.

2.5 Units, conventions and calculations

Atmospheric mole fractions are given in the commonly used units of ppm (parts per million) and ppb (parts per billion); these are equivalent to the "official" $\mu mol\,mol^{-1}$ and $nmol\,mol^{-1}$ units.

We report variations in atmospheric O_2 in terms of $\delta O_2 / N_2$, as defined by Keeling and Shertz (1992):

$$\delta O_2/N_2 = \left(\frac{(O_2/N_2)_{sample}}{(O_2/N_2)_{reference}} - 1 \right).$$

$\delta O_2 / N_2$ values are given on the SIO scale in "per meg" units, with 1 per meg $= 10^{-6}$. For comparing to CO_2 on a mol:mol basis, we converted the variations of O_2 / N_2 ratios to ppm units, considering that a variation of 4.8 per meg is equivalent to 1 ppm.

We express all isotopic data using the common δ definition:

$$\delta X = \left(\frac{R_{sample}}{R_{reference}} - 1 \right),$$

where X is the heavy isotope of interest (^{13}C or ^{18}O), R_{sample} is the ratio between the heavy and the lightest isotopes of the species (e.g. $^{13}C / ^{12}C$) in the sample air, and $R_{reference}$ is the same ratio for the reference material specific to the scale considered. The δ values are multiplied by 1000 and expressed in ‰ (permil) units. $\delta^{18}O$ values in both CO_2 and CO are given on the international scale VSMOW. $\delta^{13}C$ values in CO_2 and CO are given on the VPDB scale.

The isotopic fractionation factor (α) for ^{13}C during CO destruction is defined as

$$\alpha = k_{^{13}C} / k_{^{12}C},$$

where $k_{^{12}\mathrm{C}}$ and $k_{^{13}\mathrm{C}}$ are the rate constants for the reaction of ^{12}CO and ^{13}CO, respectively, during the removal process. The fractionation constant (ε) is defined as

$$\varepsilon = \alpha - 1.$$

With this definition, negative ε means that ^{13}C reacts slower than ^{12}C. In this paper we express ε in ‰ units.

The $CO : CO_2$, $N_2O : CO_2$, $CH_4 : CO_2$ and $O_2 : CO_2$ ratios were computed for each group of entrance – exit flasks as follows. First, for each sampling action, "entrance" and "exit" mole fractions were computed for each species as averages of all available results from entrance and exit respectively (1 to 3 results). The ratio was then computed for each sampling action as a slope of the line defined by the two points corresponding to the entrance and exit. The error for each ratio result was computed by standard error propagation at 1-σ (68 % confidence) level. Keeling plot intercepts for ^{13}C and ^{18}O in CO_2 were computed in a similar way (δ values were averaged weighted by the corresponding mole fractions).

The ± intervals reported for the mean results are 68 % confidence intervals (CI), assuming the data normally distributed; CI are computed as one standard deviation divided by the square root of the number of data points minus one.

3 Results and discussion

3.1 Data overview

Most samples were collected during an intensive sampling period on 21–22 June and on 25 July 2011. For an impression on data variability, we show in Fig. 1 the measurement results of the flasks sampled during 21–22 June 2011 (plots a–i), together with the traffic characteristics during the same time interval (plot j). For the quantitative results in the later sections we also include the data from 25 July. The flask data from the entrance site are shown in blue, the ones from the exit site are shown in red and, for CO, the measurement results from MPI-BGC are shown by green dots. (CO in most samples exceeded the instrument range at MPI-BGC; the IMAU data set is more complete because the samples were diluted prior to measurement and thus they could all be analysed).

As expected for working days, traffic peaks were observed during the morning and evening, with a total vehicle count of around 2000 vehicles per hour (Fig. 1j). These traffic peaks are due to the personal vehicles, which account for most of the traffic (about 85 %) through the day. The heavy transport has a different evolution, with relatively constant intensity over the day and a decrease around 16:00 LT, just at the start of the evening peak.

The exit samples show for CO_2, CO and N_2O much higher values and higher variability than the entrance samples; thus we can consider for these species that all the variability at the exit site is due to the traffic inside the tunnel. (The traffic influences the mole fractions both through emissions and by controlling the air flow through the tunnel.) For CO_2 and N_2O, the exit site mole fractions and the difference between the exit and entrance data seem to follow a diurnal variation, with lower values during night. This feature is not that obvious in CO mole fractions, except for the largest peak at 10:00 LT on 22 June. $\delta O_2 / N_2$ values are as expected anticorrelated to CO_2. Unlike the mole fractions, the isotopic composition does show a significant variability at the entrance site, which in the case of ^{18}O in CO is even larger than the variability at the exit site. ^{13}C and ^{18}O in CO_2 are depleted at the exit site compared to the entrance site, while both isotopes are enriched in CO at the exit compared to the entrance. For CH_4, most of the exit data are slightly higher than the corresponding entrance data, but the difference is small compared to the overall variability in mole fractions. This is discussed in more detail in a following paragraph. No significant traffic influence was found in the SF_6 data; thus this species is not shown and not discussed further.

The mole fractions at the exit are somewhat correlated to the traffic intensity, in the sense that they are higher during day when the traffic is more intense. Apart from this, there is no finer correlation; the mole fractions do not seem to follow the hourly evolution of traffic. For example the mole fractions do not drop at midday between the morning and evening traffic peaks, but instead a large peak can be observed in CO_2, CO and N_2O mole fractions, with corresponding variations in O_2 / N_2 and in CO_2 isotopes. None of the tracers we describe in detail in the rest of this paper showed any significant correlation with the traffic count or with the proportion of heavy duty vehicles. The explanation could be in the fact that more intense traffic results not only in higher emissions but also in faster air flow through the tunnel, which in turn leads to a stronger dilution of emitted gases and thus partly counteracts the effect of higher emissions on the mole fractions.

One issue that must be mentioned is the following. The air in the tunnel is not perfectly and instantaneously mixed, which, corroborated with the large emissions, leads to large spatial gradients, and, when sampling at a fixed point, to large temporal variations even over seconds to minutes. One consequence of this is that the air in two or three flasks installed in series and sampled at the same time is not identical, because each flask contains a different weighted average of the incoming air during the sampling time, with increasing smoothing towards the last flask. A second consequence is that this variability will introduce additional "noise" when comparing flasks sampled in parallel at the entrance and the exit of the tunnel. This noise is expected to have however a normal distribution and it should not affect the average results.

During the night, the CH_4 mole fractions at the entrance were actually higher than the ones at the exit. A possible scenario to explain this observation is that under low traffic conditions, the flow of air through the tunnel slowed down and the entrance site was influenced by the accumulation of CH_4

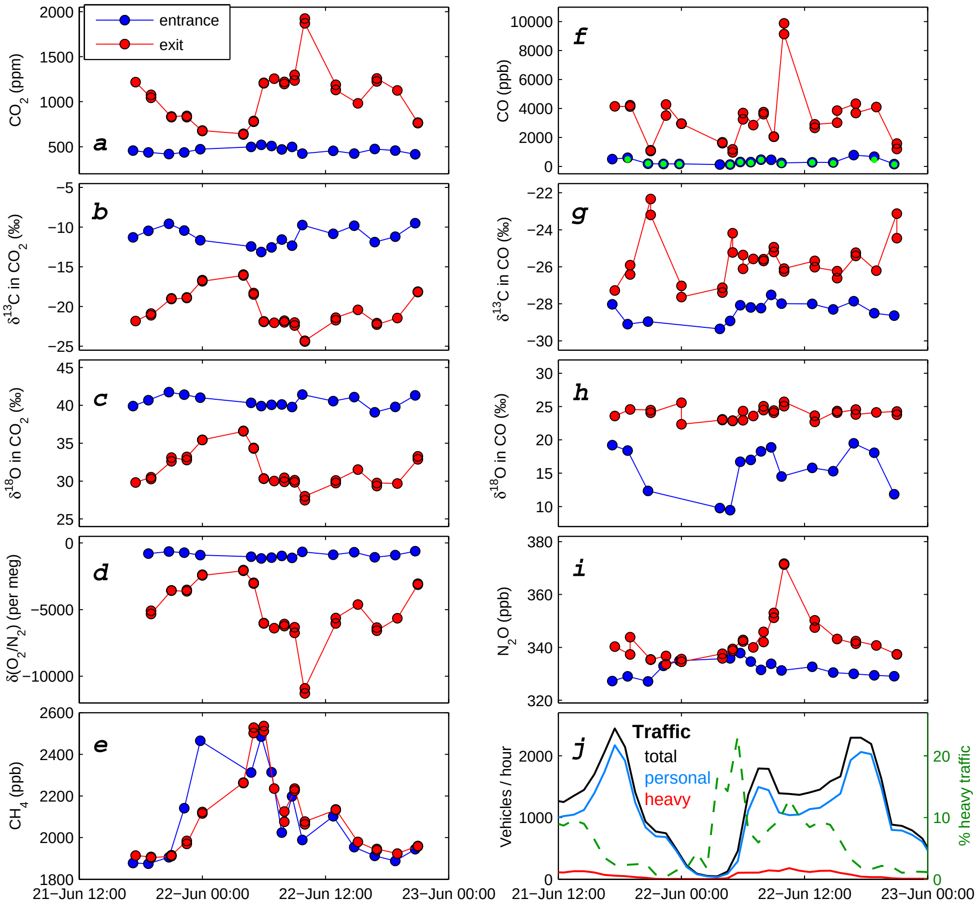

Fig. 1. (a–i) Results of the flasks sampled during 21–22 June 2011 (the intensive flask sampling campaign). O_2/N_2, CO_2, ^{13}C and ^{18}O in CO_2, N_2O and CH_4 were measured by MPI-BGC. ^{13}C and ^{18}O in CO were measured at IMAU. CO mole fractions were measured both at MPI-BGC and IMAU; the green dots show the results from MPI. **(j)** Traffic count hourly data during the same time interval, showing separately the personal vehicle category and the "heavy traffic" category (which includes all large vehicles: trailers, trucks and busses). The dotted green line shows the proportion of heavy traffic (right-hand axis).

in the shallow night-time boundary layer (outside tunnel) of gases from other sources. This influence apparently did not reach the exit site. In these conditions the entrance site could not be considered as "background" for the exit site; thus we excluded the data from this period from further analysis for all species.

3.2 CO : CO_2 emission ratios

The ΔCO : ΔCO_2 results for each parallel sampling action are plotted in Fig. 2 against time of day. CO : CO_2 emission ratios range approximately between 2 and 6 ppb:ppm, with an average of (4.15 ± 0.34) ppb:ppm. This is significantly lower than previously measured ratios for traffic, and than the overall CO : CO_2 emission ratio reported for fossil fuel combustion. Table 1 lists reported CO : CO_2 ratios for traffic emissions and for fossil fuel combustion from previous studies. Of particular interest is a comparison of our results with the ones of Vollmer et al. (2007), who performed measurements in 2004–2005 in another highway tunnel in the same region of Switzerland. Our CO : CO_2 ratios are roughly half the value of those from 2004. Although other factors may have a small contribution (differently sloping tunnels; different seasons), the observed difference in CO : CO_2 ratios shows a significant decrease in vehicle CO emissions, which likely reflects the technological improvement of vehicles in the actual fleet over 7 yr.

It has been shown that gasoline vehicles emit much larger quantities of CO during the cold start phase (when the catalyst is not yet working at optimal temperature), and that these cold start emissions and the CO : CO_2 ratios strongly increase for very low ambient temperatures (Weilenmann et al., 2009). Our estimate is representative for fluent highway traffic and does not include cold start conditions or other driving regimes where CO : CO_2 ratios could be different, likely higher. The same applies, however, to the results of Vollmer et al. (2007); thus we can safely compare the results

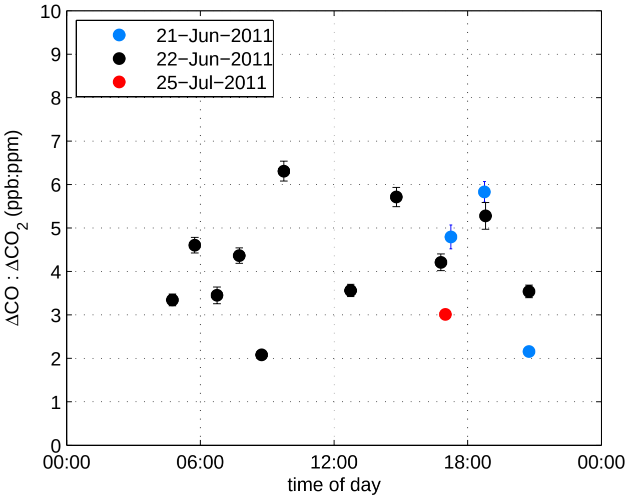

Fig. 2. $\Delta CO : \Delta CO_2$ ratios for groups of exit-entrance flasks sampled in parallel, shown against time of day. Different colours indicate different sampling dates.

and conclude that $CO : CO_2$ ratios have been decreasing between 2004 and 2011. For an overall estimate of traffic-related $CO : CO_2$ ratios, other traffic conditions must be taken into account.

3.3 CO_2 isotopes

CO_2 isotopic ratios are clearly anti-correlated to the CO_2 mole fractions, and both ^{13}C and ^{18}O are depleted at the tunnel exit compared to the entrance (Fig. 1). ^{13}C and ^{18}O of CO_2 at the exit are a mixture of the isotopic composition of the traffic-emitted CO_2 and the isotopic composition of the "background" CO_2 (typical values for $\delta^{18}O$ and $\delta^{13}C$ in background CO_2 are +41 ‰ VSMOW and −8 ‰ VPDB respectively). In order to estimate the isotopic signature of the fuel-derived CO_2 and its variability, we employed the Keeling plot approach for each entrance-exit pair of results; that is, we computed the slope of the isotopic variation versus variation in the inverse of CO_2 mole fraction ($1/CO_2$). The resulting isotope signatures are shown in Fig. 3 versus time of day; samples from different days are distinguished by colour.

The average isotopic signature is (-28.49 ± 0.04) ‰ for $\delta^{13}C$ and $(+23.57 \pm 0.13)$ ‰ for $\delta^{18}O$. By computing a Keeling plot intercept separately for each sampling action (and not for all data together) we minimize the influence of isotopic variability of the air entering the tunnel, which is otherwise not negligible (see Fig. 1).

The ^{13}C signature has to represent the average isotopic composition of the fuel burnt, since fuel is the major source of C in CO_2, and almost all C in fuel is combusted to CO_2.

The average $\delta^{18}O$ value is close to the $\delta^{18}O$ of atmospheric O_2 ((+23.88 ± 0.02) ‰ VSMOW, Barkan and Luz, 2005). The small difference of 0.3 ‰ is significant at the 3 % confidence level. The range of variability in our $\delta^{18}O$ signature values is relatively large, and larger than the computed uncertainty in the individual Keeling plot intercept values. Taking into account that each of our data points represents the integrated influence of many vehicles, we can assume that the variability of $\delta^{18}O$ in CO_2 from individual emitters is even larger.

Several recent studies suggested that CO_2 emitted from vehicles could have a different isotopic composition than atmospheric O_2. Affek and Eiler (2006) sampled tailpipe and exhaust air from two vehicles and found an average $\delta^{18}O$ signature of +29.9 ‰, which is by 6 ‰ enriched compared to the atmospheric O_2. They explained this value by isotopic equilibration between CO_2 and water vapour at a temperature of 200 °C. Schumacher et al. (2011) analysed the exhaust of several vehicles and obtained variable $\delta^{18}O$ values in the range +22.2 to +29.6 ‰, thus both depleted and enriched relative to the atmospheric O_2. Horvath et al. (2012) analysed the exhaust CO_2 of one gasoline vehicle and found a 9 ‰ enrichment in ^{18}O-CO_2 compared to the atmospheric O_2; they suggest the cause could be isotopic exchange between CO_2 and liquid or gaseous water.

Partial equilibration of CO_2 with water in the tailpipe at different temperatures is possibly one of the causes of variability in the $\delta^{18}O$ of CO_2 emitted. Two of the studies mentioned above suggested that CO_2 thermodynamically equilibrates with water in the vehicle catalyst or exhaust. However, the thermodynamic equilibration would always lead to ^{18}O enrichment in CO_2 compared to water (Friedman and O'Neil, 1977 and references therein). When the only oxygen source for both water and CO_2 is atmospheric O_2 and the supplied oxygen is consumed completely (most modern vehicle are set to run near the stoichiometric equilibrium), enrichment of CO_2 relative to water implies enrichment in CO_2 relative to the source oxygen. We do not observe a systematic enrichment in our CO_2 results relative to the atmospheric O_2, which suggests that the thermodynamic equilibration of CO_2 with water is not the dominant process that influences the final CO_2 isotopic composition. As the catalytic chemistry is quite complex, it is possible that other reactions involving oxygen influence the final $\delta^{18}O$ in CO_2, depending on catalyst type, temperature, other chemical species present, etc.

The studies mentioned above show a large variability in the $\delta^{18}O$ of CO_2 from individual vehicles, and our results (which represent the integrated signals of a large number of emitters) are consistent with this. It follows that the results from only one or several vehicles cannot be considered to represent the general behaviour of ^{18}O in traffic-emitted CO_2. Such studies are useful for understanding the processes, while our approach leads to results that are more representative for the integrated traffic emissions to the atmosphere. In summary, we find a large variability in the $\delta^{18}O$ of traffic CO_2 and only a small average deviation of 0.3 ‰ relative the $\delta^{18}O$ of atmospheric O_2.

Table 1. CO : CO_2 ratios for traffic and fossil fuel emissions. Results from Europe are shown in bold.

Reference	CO : CO_2 (ppb:ppm)	Location	Measurement year
CO : CO_2 traffic			
Bradley et al. (2000)	50 ± 4^a	Denver, CO, USA	1997
Bishop and Stedman (2008)	9.3 ... 18.4	US cities	2005–2007
Vollmer et al. (2007)	**9.19 ± 3.74**	**Gubrist Tunnel, Switzerland**	**2004**
This study	**4.15 ± 0.34**	**Islisberg Tunnel, Switzerland**	**2011**
CO : CO_2 fossil fuel			
Graven et al. (2009)	18.6 ± 2.7^b	flights US	2004
Turnbull et al. (2011)	14 ± 2	Sacramento, CA, USA (flight)	2009
Meijer et al. (1996)	**7.8 ± 1.5^c**	**Kollumerwaard, Netherlands**	**1994–1996**
Gamnizer et al. (2006)	**11.0 ± 1.1^d**	**Heidelberg, Germany**	**2002**

[a] OP-FTIR measurements, [b] average of the 5 data points given in Graven et al. (2009), [c] average of the 8 data points given in Meijer et al. (1996), [d] event sample measurements.

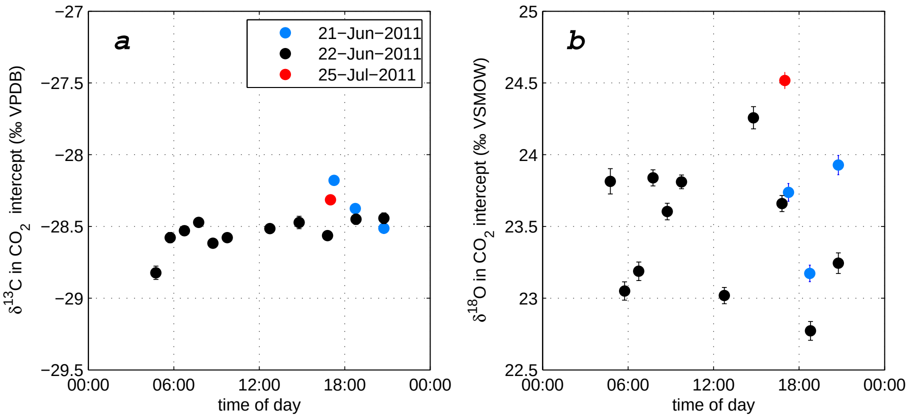

Fig. 3. Intercepts of Keeling plots for ^{13}C in CO_2 **(a)** and ^{18}O in CO_2 **(b)** for groups of entrance-exit flasks, plotted versus time of day. Different colours indicate different sampling dates. The error bars show the error of the intercept.

3.4 CO isotopes

In the case of CO, the mole fractions at the tunnel exit are a few tens of times larger than the ones at the entrance, thus we can consider that essentially all CO observed at the exit is produced by traffic. In this case we estimate the traffic signature directly from the exit site data, without using the Keeling plot approach. Figure 4 shows the $\delta^{13}C$ and $\delta^{18}O$ in CO, with the entrance and exit data shown in different colours. In the absence of fractionation, the ^{13}C isotopic composition should be the one of the fuel burnt, and the ^{18}O isotopic composition should derive from atmospheric O_2.

$\delta^{13}C$ in CO at the tunnel exit is consistently enriched compared to the $\delta^{13}C$ value of the fuel of (-28.49 ± 0.06) ‰ as estimated from the $\delta^{13}C$ in CO_2 (assuming that ^{13}C in CO_2 represents the composition of the fuel, see previous section). The average $\delta^{13}C$ in CO for the exit site is (-25.6 ± 0.2) ‰.

For $\delta^{13}C$ there is a subset of data that stands out of the general trend, with CO more enriched in ^{13}C. These are the data with the lowest CO mole fractions from the tunnel exit. This suggests that the enrichment in ^{13}C in CO could take place not during the CO formation, but during its subsequent destruction. Fig. 5 shows $\delta^{13}C$ in CO at the exit site, averaged for each sampling action, plotted against the CO : CO_2 ratio of the same groups of flasks. Although quite noisy, a tendency is evident of higher $\delta^{13}C$ values for flasks that have a lower CO : CO_2 ratio.

^{13}C enrichment during CO destruction has been observed before by Tsunogai et al. (2003), who tested individual engines in various running and idling conditions. A similar phenomenon is documented for other gas species emitted by vehicles with catalyst, like N_2O (Toyoda et al., 2008), CH_4 (Chanton et al., 2000; Nakagawa et al., 2005) and H_2 (Vollmer et al., 2010). Although CO destruction takes place both in the engine and in the catalyst, it is most likely that the ^{13}C enrichment mainly happens in the catalyst, since it has not been observed in the case of vehicles without a catalyst (Tsunogai et al., 2003).

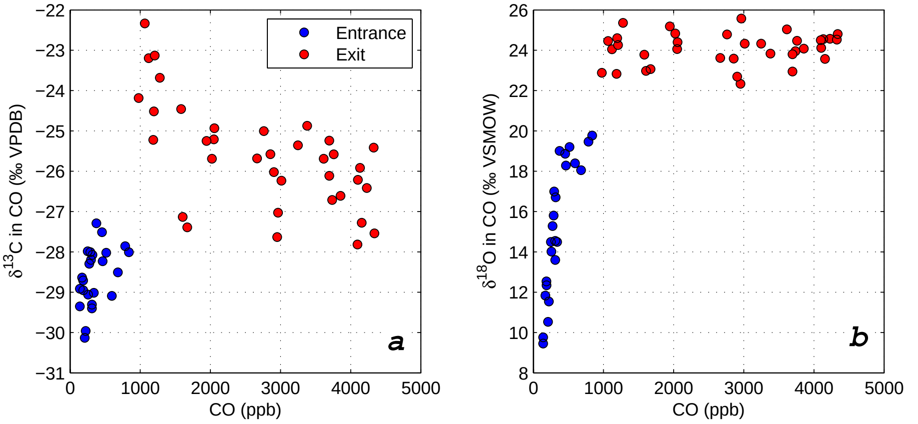

Fig. 4. δ^{13}C in CO **(a)** and δ^{18}O in CO **(b)**, with entrance and exit data shown in blue and red colours respectively. Two data points with CO around 10 000 ppb are not shown.

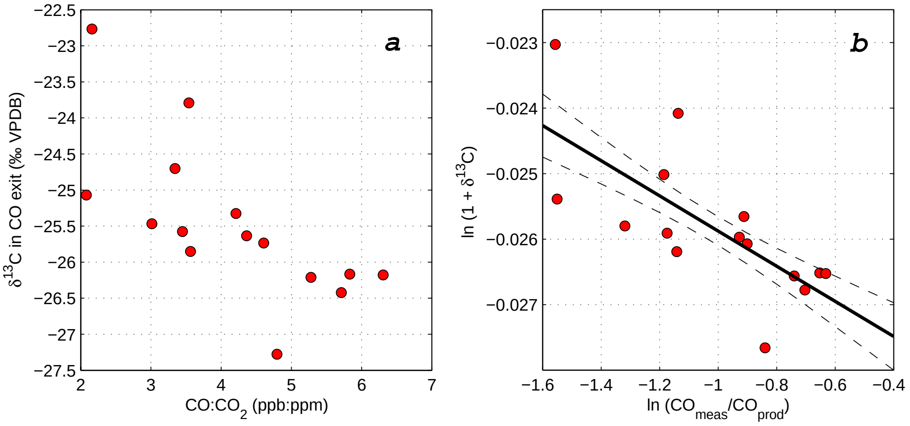

Fig. 5. (a) δ^{13}C in CO at the exit site, averaged for each sampling action, plotted against the CO : CO$_2$ ratios computed for the same sampling action. **(b)** Rayleigh plot used to determine the fractionation during CO destruction. The slope of the linear fit gives the fractionation constant ε. The dashed lines represent the 68 % confidence bounds for the linear function.

Our data allow estimating a Rayleigh fractionation constant for the supposed CO destruction. We assume for this that CO is produced in the engine with a constant CO : CO$_2$ ratio $R_{\text{CO-CO}_2}$; thus we can compute for each sampling action the CO produced (CO$_{\text{prod}}$) as

$$\text{CO}_{\text{prod}} = \Delta\text{CO}_2 \times R_{\text{CO-CO}_2}$$

where ΔCO$_2$ is the difference between the CO$_2$ at the entrance and at the exit of the tunnel. The ratio between the CO we measured and the calculated CO$_{\text{prod}}$ is then the CO fraction remaining after removal by the catalyst. For removal with isotopic fractionation constant ε of CO, the following equation is valid:

$$\ln\left(1+\delta^{13}\text{C}\right) = \varepsilon \times \ln\left(\frac{\text{CO}_{\text{meas}}}{\text{CO}_{\text{prod}}}\right) + \text{const.}$$

The fractionation constant ε can be computed as a slope of $\ln(1+\delta^{13}\text{C})$ versus $\ln(\text{CO}_{\text{meas}}\,/\,\text{CO}_{\text{prod}})$, as shown in Fig. 5b. We obtained a fractionation constant ε of (-2.7 ± 0.7) ‰, equivalent to a fractionation factor α of 0.9973. The result does not significantly depend on the $R_{\text{CO-CO}_2}$ ratios that we consider. Note that our assumption of constant CO : CO$_2$ ratios after combustion in the engine is quite strong; thus this fractionation result should be taken with caution. However, our result is surprisingly close to the one of Tsunogai et al. (2003), who calculated a fractionation constant of −2.6 ‰ for gasoline vehicles equipped with catalyst (their calculation implies the same assumption of constant CO : CO$_2$ produced).

δ^{18}O in CO values at the exit site, shown in Fig. 4b, are quite variable, similarly to ^{18}O in CO$_2$, and have an average of $(+24.1 \pm 0.2)$ ‰. This value is not statistically different from the δ^{18}O of atmospheric O$_2$ (+23.88 ‰), considering the 0.2 ‰ random error and the potential systematic error of 0.1 ‰ in our ^{18}O in CO measurements (as mentioned in Sect. 2.4). ^{18}O in CO seems however slightly enriched compared to the ^{18}O in CO_2 (+23.57 ‰). Unlike the δ^{13}C , the exit site δ^{18}O values do not depend on CO mole fractions; thus they are not significantly affected during the CO destruction in the catalytic converter.

Previous studies reported enrichment in ^{18}O in CO for gasoline vehicles with a functioning catalyst, and depletion in ^{18}O for vehicles without a catalyst, for vehicles with catalyst during a cold start (when the catalyst is not yet functioning efficiently), and for diesel vehicles (e.g. Huff and Thiemens, 1998; Kato et al., 1999a; Tsunogai et al., 2003). Our result integrates the emissions of many vehicles with potentially contrary effects, and the large variability in ^{18}O results show that individual emitters could have very different signatures.

In summary, our fleet averaged results show net enrichment in ^{13}C relative to fuel and no significant difference in ^{18}O relative to atmospheric O_2. For comparison, we show in Fig. 6 our results together with results of several previous studies that reported CO isotopic composition for the entire fleet, and separately for gasoline and diesel vehicles.

Part of the differences in ^{13}C among studies can probably be explained by the different isotopic composition of the fuel. The results of our study and of Tsunogai et al. (2003) (Japan fleet, 2000) are similar and show the highest δ^{13}C values for fleet averages; in addition, both studies find a ^{13}C enrichment phenomenon during catalytic CO destruction. This could be thus a characteristic of modern vehicles and could probably be related to the efficiency of catalytic destruction. Our ^{18}O results are very close to the ones of Tsunogai et al. (2003) and Stevens et al. (1972) (world average, 1971), but differ significantly from the estimate of Kato et al. (1999a) (German fleet, 1997).

As gasoline and diesel vehicles were reported to emit CO with very different isotopic signatures, the isotope values measured for the entire fleet could in principle be used to determine the relative emissions from gasoline and diesel vehicles. In the two studies shown in Fig. 6 that include separate estimates per fuel type, the fleet averages tend to be closer to the gasoline signatures, which show a larger share of gasoline emissions in the total CO. It would be useful to determine the share of gasoline and diesel CO emissions for the present fleet, if data on isotopic signatures of recent vehicles became available.

Modelling studies that include the isotopic composition of CO (Bergamaschi et al., 2000; Manning et al., 1997) have used until now, for the traffic-emitted CO, the δ^{13}C and δ^{18}O values of fuel and atmospheric O_2 respectively. Our study adds to the already existing evidence that significant fractionation can occur during the formation and subsequent destruction of CO, and that the traffic signatures can vary with time and place. Better characterizing these signatures through additional measurements and updating the information used in models would help constraining the CO budget.

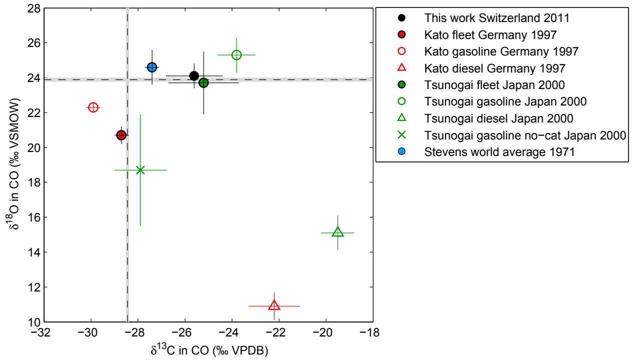

Fig. 6. δ^{18}O versus δ^{13}C in traffic CO from our work and previous studies: Kato et al., 1999a (Kato); Tsunogai et al., 2003 (Tsunogai); Stevens et al., 1972 (Stevens). The year shown in legend is the year when measurements were done. The dotted black lines indicate the δ^{18}O in atmospheric oxygen (Barkan and Luz, 2005) and the average δ^{13}C value of the fuel in our study, as estimated from the δ^{13}C value of CO_2; the shades indicate their standard errors, and their intersection shows the hypothetical CO isotopic composition in the absence of fractionation. The CO isotopic composition of gasoline vehicles from Kato et al. (1999a) is based on vehicles without a catalyst and one vehicle with catalyst functioning with cold engine.

3.5 $N_2O : CO_2$ emission ratios

Figure 7 shows the ΔN_2O: ΔCO_2 ratios for the mole fraction differences of groups of exit-entrance flasks sampled at the same time; the average ratio is $(1.8 \pm 0.2) \times 10^{-2}$ ppb:ppm (equivalent for $N_2O : CO_2$ to mg:g). The results exhibit a wide spread, with an upper limit of about 3×10^{-2} ppb:ppm. The $N_2O : CO_2$ ratios seem to vary with the time of day and it is interesting to note that samples taken on different dates at about the same hour tend to give comparable results. However no significant correlation was found with any of the traffic parameters available.

As the early morning data could have been influenced by N_2O emissions outside the tunnel entrance in conditions of slower air flow through the tunnel (see Sect. 3.1), we also compute the $N_2O : CO_2$ ratios when removing the data earlier than 08:30 LT. The $N_2O : CO_2$ average ratio is then $(2.1 \pm 0.1) \times 10^{-2}$ ppb:ppm.

Table 2 summarizes results of traffic $N_2O : CO_2$ emission ratios from several previous studies. Our results are obviously lower than all the previous ones, and it can be observed that the $N_2O : CO_2$ ratios in Europe decreased monotonically over the past 20 yr. Since in general the emission of CO_2 per kilometre decreased, the N_2O emission rate per kilometre travelled has decreased even more during this period than the $N_2O : CO_2$ ratio.

After the introduction of catalytic converters, it had been observed that vehicles fitted with a catalyst emitted more N_2O than older vehicles without a catalyst. N_2O is formed at relatively low catalyst temperatures as an intermediate in

Table 2. Traffic emission $N_2O:CO_2$ ratios from various studies. The bold text shows the studies concerning European traffic.

Reference	$N_2O:CO_2$ (g:g) × 10^5	Location	Measurement year
Berges et al. (1993)	**14 ± 9**	**Klara Tunnel, Sweden**	**1992**
Berges et al. (1993)	**6 ± 3**	**Elbtunnel, Germany**	**1992**
Jimenez et al. (2000)	8.8 ± 2.8	Los Angeles, CA, USA	1996
Jimenez et al. (2000)	12.8 ± 0.3	Manchester, NH, USA	1998
Becker et al. (2000)	**4.1 ± 1.2**	**Kiesberg Tunnel, Germany**	**1997**
Becker et al. (2000)	4.3 ± 1.2	Ford Research Laboratory (USA)	1996–1998
Bradley et al. (2000)	18.7 ± 1.3	Denver, CO, USA	1997
This study	**1.8 ± 0.2 (2.1 ± 0.1)***	**Islisberg Tunnel, Switzerland**	**2011**

* When excluding the early morning data.

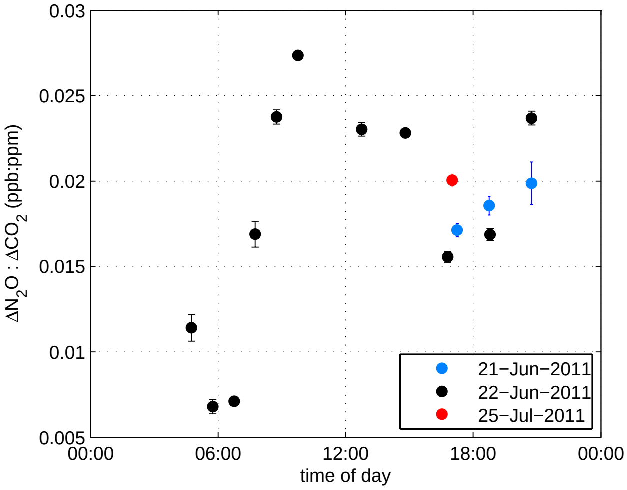

Fig. 7. $\Delta N_2O:\Delta CO_2$ ratios for groups of exit-entrance flasks sampled in parallel, shown against time of day. Different colours indicate different sampling dates.

nitrogen oxides reduction. The concern appeared that the quantity of N_2O emitted by traffic would increase with the increasing proportion of catalyst vehicles (e.g. Berges et al., 1993; Dasch, 1992). Our study clearly does not support this concern; on the contrary, we find for the present fleet significantly lower $N_2O:CO_2$ emission ratios than reported in the past. This is in line with the decreasing trend already observed from the study of Becker et al. (2000), when compared to the older ones. We assume that with improving catalytic technology, less N_2O is produced and a larger proportion of N_2O is completely reduced.

The following issue may affect our $N_2O:CO_2$ emission ratio estimate. N_2O can be formed inside containers from NO_x, in the presence of water and SO_2, with a time constant for N_2O formation on the order of hours; for dried samples the effect is smaller but is still present (Muzio et al., 1989). Since NO_x, SO_2 and water are present in vehicle emissions and consequently increased in the tunnel atmosphere, it is possible that part of the N_2O excess we observed is not directly emitted by vehicles but formed later either in the tunnel or inside the glass flasks during the few months' storage. In this case our estimate is a sum of direct and indirect traffic emissions in tunnel conditions. If N_2O resulted from NO_x makes a significant proportion, then in open air conditions the total traffic-resulted N_2O may be even lower than our estimate.

3.6 $CH_4:CO_2$ emission ratios

As already mentioned, the variability in the CH_4 mole fractions of the air entering the tunnel is large compared to the traffic signal (see Fig. 1). Thus, for the $\Delta CH_4:\Delta CO_2$ ratios, we only used the afternoon data, when the CH_4 variability at the entrance was smallest, because we considered that the other data would give unreliable $CH_4:CO_2$ emission ratio results. This leaves us with only seven data points for the $CH_4:CO_2$ emission ratios (not shown in figures); the average $\Delta CH_4:\Delta CO_2$ ratio is $(4.6 \pm 0.2) \times 10^{-2}$ ppb:ppm.

It is general knowledge that vehicles emit small quantities of methane, and (indirect) measurements of methane are included in certification vehicle testing, but we are not aware of comprehensive studies focusing on the recent European vehicle fleet. We can compare our results to the ones of Nam et al. (2004), who performed measurements on US vehicles of model years 1995 to 1999. For hot running vehicles, they obtained an average $\Delta CH_4:\Delta CO_2$ ratio of 3.8×10^{-2} ppb:ppm, which is close to our result. Their overall result that includes cold start emissions is much larger (14×10^{-2} ppb:ppm); this supports that, for estimating the overall traffic $CH_4:CO_2$ emission ratios, other traffic conditions must be taken into account.

Nakagawa et al. (2005) estimated the contribution of traffic emissions to the total CH_4 fluxes to be up to 30 % in a Japanese large urban area (based on isotope measurements). In our case it is obvious that the mole fraction increase due to traffic emissions (represented by the difference between the tunnel exit and entrance) is small compared to the overall variability; thus the traffic emissions account for a much smaller proportion of the total CH_4 fluxes.

3.7 $O_2 : CO_2$ ratios

As obvious in Fig. 1, variations in O_2 / N_2 ratios are anti-correlated to the CO_2 variations. Figure 8 shows the $\Delta O_2 : \Delta CO_2$ ratios computed from groups of exit-entrance flasks sampled in parallel. All $\Delta O_2 : \Delta CO_2$ ratios lie within the narrow interval −1.48 to −1.46, with an average of -1.47 ± 0.01 ppm:ppm.

Overall our $\Delta O_2 : \Delta CO_2$ results are similar to the ratios of approximately −1.5 calculated theoretically based on fuel composition by Steinbach et al. (2011) for this region. We note that the oxidative ratios from Steinbach et al. (2011) include other fossil fuel burning processes, not only road traffic.

Interestingly, our $\Delta O_2 : \Delta CO_2$ ratios are also very close to the average reduction level (or oxidative ratio) of the fuel burnt of 1.5 ± 0.06 obtained by Keeling (1988), based on O_2 and CO_2 simultaneous measurements in an urban atmosphere dominated by traffic. For determining the reduction level, Keeling (1988) corrected the measured $\Delta O_2 : \Delta CO_2$ ratios, assuming that a proportion of (8.5 ± 8.5) % of the carbon in fuel is emitted as CO. With the actual technology in Europe, a much smaller proportion of the fuel is burnt to CO (see Sect. 3.2); thus we can consider that the $\Delta O_2 : \Delta CO_2$ ratios we obtained directly represent the reduction level of the fuel burnt, without a correction being necessary.

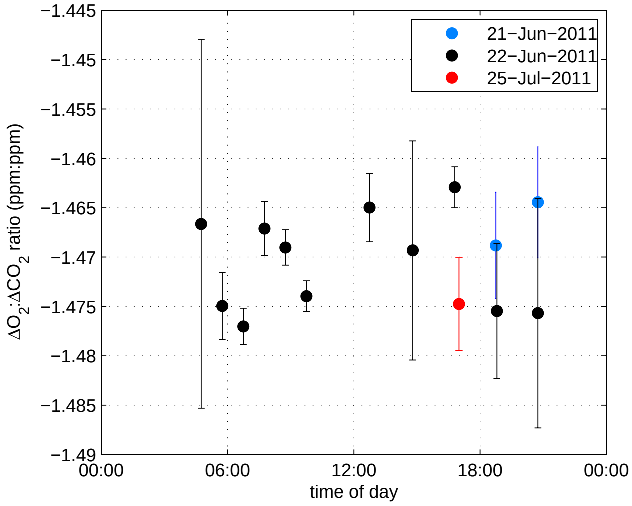

Fig. 8. $\Delta O_2 : \Delta CO_2$ ratios for groups of exit-entrance flasks sampled in parallel, shown against time of day. Different colours indicate different sampling dates. The negative ratios are due to the fact that O_2 is consumed while CO_2 is produced.

4 Summary and final remarks

The main results of our paper can be summarized as follows.

a. The $CO : CO_2$ emission ratios, with an average of (4.15 ± 0.34) ppb:ppm, are lower than the ratios presently available from databases and used in models, and than older experimental estimates. This is probably due to the evolution of the vehicle fleet associated with the evolution of vehicle emission standards. The $CO : CO_2$ emission ratio is likely to continue decreasing in the future, as older vehicles are replaced by new ones, thus it will have to be continuously updated if used for estimating the fossil fuel CO_2.

b. According to our measurements, the $\delta^{18}O$ in traffic-emitted CO_2 has an average value of +23.6 ‰, and thus is depleted by 0.3 ‰ relative to the atmospheric O_2. The variability of our $\delta^{18}O$-CO_2 data suggests the possibility that individual vehicles do emit CO_2 with different $\delta^{18}O$ signatures, which is in line with measurements of individual vehicles in other studies. However, our results do not show a large systematic deviation in $\delta^{18}O$-CO_2 at fleet level.

c. $\delta^{13}C$ in CO is enriched by 3 ‰ compared to the isotopic composition of the fuel, and its variability seems to be dominated by a destruction phenomenon in the catalyst, with highest $\delta^{13}C$ values associated to low $CO : CO_2$ emission ratios. For $\delta^{13}C$ we compute a fractionation constant ε of (-2.7 ± 0.7) ‰ for the catalytic CO oxidation. $\delta^{18}O$ in CO is similar within the uncertainty to the isotopic composition of atmospheric O_2, and, unlike $\delta^{13}C$, is not correlated to the $CO : CO_2$ emission ratios.

A potential application of integrated fleet measurements of CO isotopic composition is to estimate the relative contribution of emissions from gasoline and diesel vehicles; for this, more knowledge on the isotopic signature of CO emitted from recent vehicles is necessary.

d. The $N_2O : CO_2$ emission ratios of $(1.8 \pm 0.2) \times 0^{-2}$ ppb:ppm ($(2.1 \pm 0.1) \times 10^{-2}$ ppb:ppm when excluding the early morning data) are lower than older estimates, suggesting a decrease in N_2O emissions with improving technology. The concern that N_2O emissions will increase with the proportion of vehicles fitted with catalyst converters is not supported by our results. It is possible that the technological improvements will lead to an even further decrease in traffic N_2O emissions.

e. We find an average $CH_4 : CO_2$ emission ratio of $(4.6 \pm 0.2) \times 10^{-2}$ ppb:ppm. Our results confirm that the traffic CH_4 source is small compared to the other emissions.

f. The $\Delta O_2 : \Delta CO_2$ ratios from traffic emissions of (-1.47 ± 0.01) ppm:ppm are very close to previous theoretical and experimental estimates.

The main limitations of our study are as follows. (1) The fleet composition in the Islisberg Tunnel during our campaign may be different from the fleet composition in other locations in Europe and not fully representative for the overall European fleet. Thus our results may not be representative for different places and times, and an upscaling of our results to the entire western Europe must be done with caution. (2) The tunnel has a highway driving regime and the traffic was fluent during our measurement campaign. In different traffic conditions, like in urban areas or during traffic jams, emissions and the ratios between the emitted species are likely to be different. Emission rates reported for such cases are usually higher.

We recommend

- a periodical update of $CO : CO_2$ emission ratios if they are to be used for quantifying fossil fuel contributions;
- further studies on the possibility of using CO isotopes to distinguish between emission sources, and the possibilities of combining this with other tracers; for this purpose more information is needed on the isotopic signatures of CO sources and sinks;
- more studies characterizing the isotopic signature of traffic (and other fossil fuel) derived CO_2 to address the discrepancy between modelling studies that assume that burning processes occur without significant fractionation, and measurements that find fractionation induced alterations of CO_2 isotopic signatures;
- complementary studies for estimating traffic emissions in different conditions that are necessary to complete the picture: locations with different fleet composition, traffic type (e.g. city or traffic jams), and atmospheric conditions (e.g. different temperatures during winter);
- increasing the number of atmospheric oxygen measurements and testing new possibilities to use oxygen data for distinguishing between sources and sinks, making use of the well-defined $O_2 : CO_2$ ratios for certain combustion processes.

Supplementary material related to this article is available online at http://www.atmos-chem-phys.net/14/2105/2014/acp-14-2105-2014-supplement.zip.

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