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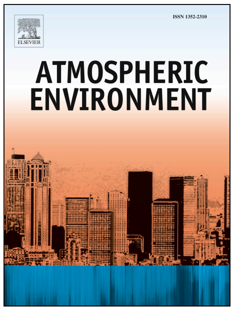

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S. Naus, T. Röckmann, M.E. Popa

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The isotopic composition of CO in vehicle exhaust

S. Naus[a,b], T. Röckmann[a], M.E. Popa[a]

[a] *Institute for Marine and Atmospheric research Utrecht, Utrecht University, Princetonplein 5, 3508TA Utrecht, The Netherlands*

[b] *Department of Meteorology and Air Quality, Wageningen University and Research Center, 6708 PB, Wageningen, The Netherlands*

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 $\sim$ -60 to 0 ‰, for $\delta^{18}O$ in CO $\sim$ +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 $\pm$ 0.5 ‰ and +24.8 $\pm$ 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 $\pm$ 0.31 ppb:ppb. The $CO:CO_2$ ratio, with a mean of 19.4 $\pm$ 6.8 ppb:ppm, and the $CH_4:CO_2$ ratio, with a mean of 0.26 $\pm$ 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 to 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.

Keywords: CO, CO_2, isotopes, vehicles, emissions, H_2

1. Introduction

Carbon monoxide (CO) plays an important role in the atmosphere, in spite of its low atmospheric abundance (50-200 ppb [1]). Most importantly, CO occupies a large fraction ($\sim$ 60 % [2]) 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