

Supplement for: Molecular hydrogen (H₂) combustion emissions and their isotope (D/H) signatures from domestic heaters, diesel vehicle engines, waste incinerator plants, and biomass burning

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1 Methods Section for Supplements (Some text is overlapping with the content of the Methods Section in the main paper)

1.1 Residential fossil fuel and wood heaters

The samples were taken from a large variety of burner types, fuel systems, and burning capacities.

5 If not specified differently, two samples (A and B) were taken at the same location, typically ~5 min apart. The exhausts of two old (>20 yrs) oil-burner systems were sampled, both from single-family houses. In the first case (S-1), the samples were taken from a chimney access in the attic, about 4 m above the combustion chamber. The first sample (S-1A) was drawn shortly (~2 min) after starting the burner, such that the potential differences between this presumably non-optimal burning and the
10 more optimized burning (S-1B ~20 min after S-1A was collected) could be later investigated. The samples of the second oil-burner system (dating to 1992) were taken from the exhaust pipe at ~1 m from the burner where an exhaust temperature of 170 °C was measured (S-2).

A variety of natural gas burners were also sampled. The samples S-3 were taken from the roof-top chimney exhaust of a 4-party apartment house. The samples S-4 were also taken from the roof-top
15 chimney exhaust of a tall 25-party apartment block. The samples S-5 were taken at the roof-top chimney exhaust (S-5A was 55 °C and S-5B was 50 °C) from two different burner systems of a school complex, where S-5B was from a burner system with a H₂O condensation-recovery system.

The samples S-6 were both taken from a 3.7 MW gas burner system (1984) at Empa, which combusts $\sim 330 \text{ Nm}^3 \text{ hr}^{-1}$ of natural gas. These samples were taken $\sim 5 \text{ m}$ downstream of the burner where an exhaust temperature of $220 \text{ }^\circ\text{C}$ was measured. The samples S-7 were taken from the exhaust system of a single-family house, a few meters downstream of the burner (built in 1999) at a temperature of $52 \text{ }^\circ\text{C}$.

In addition to the fossil fuel-based heating systems, two wood-burning systems were also sampled. The samples S-8 were taken from a modern (2007) fully automated wood-pellet burning system of a 2-family house. Both samples were drawn from the exhaust pipe $\sim 2 \text{ m}$ downstream of the burner. The first sample (S-8A, temperature at $108 \text{ }^\circ\text{C}$) was collected only a few minutes after the start of the system. The second sample (S-8B, temperature at $114 \text{ }^\circ\text{C}$) was collected after $\sim 10 \text{ min}$ when the system was in full burning mode. The samples S-9 were taken from an indoor open fire place of a single family house, in which pieces of local beech were burnt. The samples were drawn through an opening in the chimney system $\sim 4 \text{ m}$ above the fire. The first sample (S-9A) was taken when the fireplace door was left open, which resulted in a reduced air draft and slower burning with a sample temperature of $155 \text{ }^\circ\text{C}$. The second sample (S-9B) was taken with the fireplace door almost entirely closed. This created a stronger air draft with a more rigorous flaming and an exhaust temperature of $170 \text{ }^\circ\text{C}$ at the sample location. Finally, ambient air samples were also collected during this campaign in order to determine approximate concentrations of the air drawn for combustion. They were collected in the vicinity of the sampled buildings, one air sample was collected at the end of the S-2 sampling, and two air samples were collected during the I-1 sampling.

Analysis on the RGA-3: Analysis was conducted on the Empa laboratory RGA (RGA-Frog). This instrument was characterized for nonlinear system response using a series of flasks containing various dilutions of a high-concentration mixture. For the dilutions, synthetic air was used from which traces of H_2 and CO were removed using a catalyst (Sofnocat 514, Molecular Products, Thaxted, UK). Based on the measurements of these flasks samples, the nonlinearities were characterized and correction functions derived. A function of the form $y = a + b \times x + c \times x^{0.5} + d \times x^{0.3333} + e \times x^{0.25}$ was applied (available within the GCWerks software used for all RGA measurements), where x is the normalized peak height (with respect to the bracketing standard), and y is the normalized sensitivity, see e.g. Vollmer and Weiss (2002). The ranges, for which these functions were applicable, were approximately 50 ppb to 3.5 ppm for H_2 and 20 ppb to 1.2 ppm for CO . The dilutions were made using pressure measurements using a Keller (Switzerland, www.keller-druck.com) pressure gauge (-1 to 3 bar) with a stated accuracy of 0.1% of the full scale.

Some of the heater samples were diluted using synthetic air, from which traces of H_2 and CO were removed using a catalyst (see above). The dilutions were made based with the above-mentioned pressure gauge. These samples, with their dilution factors in parentheses, were 7A (4.09), 8A (20.8), 9A (106), and 9B (26.7). These dilutions resulted in H_2 mole fractions, which were within the calibrated non-linearity range of the RGA. However, with regard to the CO mole fractions, some of

55 these diluted samples were still saturating the detector or they were exceeding the calibrated CO non-linearity range. Subsequent measurements on a GC-FID/ECD and/or a FTIR yielded quantifiable CO results.

Analysis on the GC-FID/ECD: The samples were also analyzed (May 2009) on a GC (Agilent Technologies 6890N and controlled through GCWerks) located at the Jungfraujoch observatory and
60 equipped with a flame-ionisation detector (FID) for CO and CH₄. The sample measurements were bracketed by those of a working standard at ambient concentrations of CO and CH₄. This instrument has linear detector response in the ambient concentration range as found through earlier experiments (Steinbacher and Vollmer, unpubl. data), but needed to be calibrated for high-concentration CO samples at concentrations >2 ppm. Additional analysis of two high-concentration standards
65 (2.01 ppm and 8.25 ppm, NIST-2612a calibration scale) revealed a slight CO nonlinearity at higher concentrations, which was characterized and for which the sample measurements were corrected. The measurement precisions were 0.2 % for CH₄ and 1.1 % for CO. CO results are reported on the WMO-2000 calibration scale (with NIST and WMO-2000 in very close agreement, Zellweger et al. (2009)) and CH₄ results are reported on the NOAA-2004 calibration scale (Dlugokencky et al.,
70 2005). The overall accuracies, including calibration scale and nonlinearity uncertainties, are estimated at ~5 % for each compounds. This GC was also equipped with an electron-capture detector allowing for the measurements of nitrous oxide and sulfur hexafluoride, which, however, are not further discussed here.

1.2 Waste incinerator exhaust

75 Exhaust gas was sampled at six waste incinerator facilities throughout Switzerland. These incinerators are typically designed for the combustion of household and industrial waste on a regional scale (equipped with one to four boilers and yearly waste throughput of 90'000 – 220'000 t) and are equipped with a sequence of catalysts and filters to remove most particles and toxic substances. The samples were collected on the occasion of extensive measurement and sampling campaigns serving
80 other purposes. The first incinerator (I-1) was sampled in 2008. CO was measured in-situ along with other parameters, and 6 stainless steel flask samples were taken for measurements of H₂ and CO on the RGA-3. The second incinerator was sampled in November 2008 using five 2-L glass flasks, which were measured on the RGA-3. In addition to the routine in-situ measurements, including CO, an on-line mass spectrometer (H-sense, V&F Analyse- und Messtechnik GmbH, Austria)
85 was used at this site for a full day of measurements (see Bond et al. (2010) for a description of the instrument). As this instrument is not suited for very accurate H₂ measurements in the ambient concentration range, these data are not further discussed here. However, these measurements support the independently performed flask sample measurement results and also revealed little H₂ variability in the incinerator exhaust over the course of the measurement day. During this second incinerator
90 sampling, ambient air samples were also drawn to characterize the composition of the intake air.

Flue gas samples were taken from a large set of incinerators from September to December 2010 (sample groups I-3 to I-9) by collection of integrated (1 week) dried (MD-070-24S-4, Perma Pure, USA) exhaust gas samples in Cali-5-BondTM sampling bags (GSB-P/44, Ritter Apparatebau, Germany), employing a peristaltic pump (ECOLINE VC-MS/CA8-6, Ismatec, Switzerland) at a flow rate of 3 ml min⁻¹. Some of these Tedlar bag samples were cryogenically transferred into pre-evacuated stainless steel flasks, which were immersed in liquid nitrogen. The transfer flow rates through the connecting 1/4" OD stainless steel tube were >0.6 L min⁻¹. We assume that back diffusion of H₂ becomes negligible under these conditions. These samples were measured on the RGA-3 a few days after transfer. Some samples with large CO concentrations were transferred directly from the Tedlar bags into a small (50 ml) pre-evacuated stainless steel container, immediately diluted with purified (H₂ and CO free) synthetic air, and subsequently measured on the RGA-3. CO, CO₂, CH₄, and other trace gases were also measured from the Tedlar bag samples using FTIR instrumentation. However, no H₂ isotope analysis was conducted on these samples.

Exhaust gas samples were stored in the Tedlar bags for less than two weeks before transfer and/or analysis. In order to assess potential diffusive exchange/loss of H₂ through the Tedlar bags during storage, a stability experiment was conducted. A reference gas sample of ~3 ppm H₂ (also including ~2 ppm CO and other compounds) was collected in a Tedlar bag stored in an ambient laboratory air H₂ and CO environment, similar (in temperature and light exposure) to that used for storage of the waste incinerators. The sample was repeatedly (4 times, nearly monthly) analyzed on the RGA-3 along with the original reference gas (stored in a cylinder). Over the course of 3.5 months, an increase of ~7% (~210 ppb) in H₂ and ~12% (~240 ppb) in CO was detected. At the same time, a similar experiment was conducted with synthetic air samples that contained small concentrations of H₂ (~20 ppb) and virtually no CO. Here, an increase of ~130 ppb H₂ and 65 ppb CO was detected over that same time span. The cause for these increases has not been further investigated but could possibly be related to potential H₂ and CO production from plastic under the influence of light. We originally suspected that diffusive exchange could potentially alter the H₂ concentration in the Tedlar bags. However, the fact that we observe an increase in H₂ over time in the bag with the ~3 ppm H₂ (and the ambient air having lower concentrations) indicates that this would not be the only process that might alter the H₂ composition/concentration. If we scale the results to the storage time of our incinerator samples, then the potential H₂ and CO concentration increases are relatively small and do not change our scientific interpretation. However, for longer storage, Tedlar bags may not be suitable for H₂ and CO experiments. Also, potential alterations of the D/H during storage in Tedlar bags may be expected.

1.3 Diesel powered vehicles

Exhaust gas analysis of diesel-powered vehicles was conducted at Empa in 2008 as part of an extensive dynamometer test stand emission study that included H₂ emissions, and that were part of a

larger fleet study also including gasoline vehicles (Bond et al., 2010). This included the measurements of 5 light-duty diesel delivery vehicles and 1 passenger car, most of which were tested under 6 different driving cycles. All diesel vehicles were classified by the Euro-4 emission standard. They
130 were equipped with oxidation catalysts and three had diesel particle filters. On-line direct exhaust measurements were conducted for a suite of compounds. H₂ was measured using the H-sense MS described in 1.2. For most of the diesel exhaust measurements with low H₂ concentrations (<1 ppm), this instrument was not suitable for accurate quantification because of its blank concentrations of similar size. The CO instruments used (Mexa 7100 AIA-721A and AIA-722, Horiba, Japan) exhibit
135 similar limitations. However, large H₂ and CO concentrations (up to several hundred ppm) occurred during all cold starts and during some of the acceleration phases making these two measurement techniques suitable for these periods. We have extracted these periods for further investigation of H₂/CO and have selected the duration based on the criteria of blank-corrected H₂>1 ppm. Mean H₂ and CO concentrations were calculated over the typically 1 min–2 min phases of the cold starts
140 and the 15–30 sec periods during some of the accelerations. The two driving cycles Ra and Rb (see Bond (2010) for details) had H₂ mole fractions exceeding 1 ppm in very rare cases only, thus these did not qualify for inclusion in our analysis. For our H₂/CO ratio calculations, we have also chosen to use the cumulative H₂ and CO mole fractions for each period (rather than the mean of the ratio of all 1-sec measurement pairs) to avoid potential mismatches of response time characteristics
145 of the H₂ and CO instruments. The results are shown in Table 1. This results in a mean H₂/CO ratio of 0.080 ± 0.082 (1σ) and a median of 0.031 (interquartile range is 0.12) suggesting that the distribution is not normal. For the final H₂/CO ratio, we have further weighed the individual ratio of each selected period by duration of the period. This reduces the above ratio to 0.058 ± 0.075 (1σ), with a median of 0.026, an interpercentile range of 0.12, and a median absolute deviation (MAD)
150 of 0.0550. Using these weights, and the fact that we base the initial calculation on the ratio of the cumulative H₂ and CO of each period, we better represent the ratio of the cumulative amounts of H₂ and CO emitted to the atmosphere (during the experiments). These results suggest that the molar H₂/CO for diesel is more than ten times smaller compared to gasoline combustion (Vollmer et al., 2007).

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Table 1. Diesel vehicle dynamometer exhaust results for H₂ and CO during events of elevated emissions for a variety of standardized driving cycles. Periods were selected where the H₂ mole fraction exceeded 1 ppm. Entries on the same lines do not indicate occurrence of the events at the same time within a cycle. Some vehicles have more events than others, hence dashes indicate no more events in a particular cycle. H₂-m is the mean H₂ mole fraction over the selected range, n is the number of measurement points (1 sec measurements), H₂/CO is the molar ratio of H₂ to CO for the selected periode, and the classification 'Phase' is either emission during cold start (CS) or during acceleration phases (Acc). The Audi A4 is a passenger vehicle, all others are light-duty delivery vehicles. For details on the experiments see Bond et al. (2010) and Bond (2010)

Make Model	Fiat Ducato	Renault Traffic T29	Citroen Jumper	Volkswagen T5	Ford Transit	Audi A4
Empty Mass [kg]	2000	1930	2650	2089	1735	1620
Displacement [cm ³]	2287	2464	2198	2461	2198	1968
Power [kW]	88	107	88	96	63	103
Gearbox	m5	m6	m6	m6	m5	m6
Diesel Particle Filter	No	Yes	No	Yes	No	Yes
Mileage [km]	24'867	38'158	13'482	32'203	23'485	25'806

Driving Cycle	H ₂ -m	n	H ₂ /CO	Phase	H ₂ -m	n	H ₂ /CO	Phase	H ₂ -m	n	H ₂ /CO	Phase	H ₂ -m	n	H ₂ /CO	Phase	H ₂ -m	n	H ₂ /CO	Phase				
IUFCl5	4.1	[22]	0.019	CS	29.2	[77]	0.095	CS	12.9	[15]	0.112	CS	28.8	[168]	0.117	CS	6.2	[165]	0.010	CS	44.5	[71]	0.193	Acc
IUFCl5	-	[-]	-	-	1.5	[12]	0.098	Acc	-	[-]	-	-	4.0	[7]	0.035	Acc	-	[-]	-	-	7.1	[14]	0.012	Acc
IUFCl5	-	[-]	-	-	54.0	[37]	0.219	Acc	-	[-]	-	-	2.9	[6]	0.027	Acc	-	[-]	-	-	14.0	[17]	0.021	CS
IUFCl5	-	[-]	-	-	128.5	[45]	0.238	Acc	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	41.5	[71]	0.159	CS
IUFCl5	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	40.0	[17]	0.240	Acc
L2	6.7	[89]	0.007	CS	17.5	[92]	0.015	CS	17.7	[81]	0.018	CS	4.8	[287]	0.015	CS	10.5	[158]	0.010	CS	-	[-]	-	-
L2	149.8	[35]	0.247	Acc	5.7	[15]	0.014	CS	-	[-]	-	-	-	[-]	-	-	11.6	[83]	0.009	Acc	-	[-]	-	-
L2	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	11.0	[42]	0.007	Acc	-	[-]	-	-
L2	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	6.6	[25]	0.024	Acc	-	[-]	-	-
LA	3.3	[63]	0.006	CS	20.8	[87]	0.036	CS	9.6	[34]	0.100	CS	1.2	[67]	0.011	CS	8.1	[121]	0.008	CS	61.7	[57]	0.114	CS
LA	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	2.0	[16]	0.012	Acc	-	[-]	-	-	14.4	[14]	0.219	CS
LA	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	7.2	[9]	0.161	Acc	-	[-]	-	-	-	[-]	-	-
CADC	-	[-]	-	-	198.8	[25]	0.143	Acc	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-
CADC	-	[-]	-	-	62.5	[19]	0.092	Acc	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-	-	[-]	-	-