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Supplementary Material to: Molecular hydrogen (H_2) 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 Supplementary Materials (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. For each location, two samples (A and B) were taken 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 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 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 H_2O 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 $\mathrm{Nm}^3\,\mathrm{hr}^{-1}$ of natural gas. These samples were taken $\sim$5 m downstream of the burner where an exhaust temperature of 220 °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 °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 m downstream of the burner. The first sample (S-8A, temperature at 108 °C) was collected only a few minutes after the start of the system. The second sample (S-8B, temperature at 114 °C) was collected after $\sim$10 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 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 °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 °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.

Analysis on the RGA-3: Some of the samples were diluted using synthetic air, from which traces of H_2 and CO were removed using a catalyst (Sofnocat 514, Molecular Products, Thaxted, UK). These samples, with their dilution factors in parentheses, were 7A (4.09), 8A (20.8), 9A (106), and 9B (26.7).

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 equipped with a flame-ionisation detector (FID) for CO and CH_4. The sample measurements were bracketed by those of a working standard at ambient concentrations of CO and CH_4. 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 (2.01 ppm and 8.25 ppm, NIST-2612a calibration scale) revealed a slight CO nonlinearity at higher concentrations, which was corrected. The measurement precisions were 0.2 % for CH_4 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 CH_4 results are reported on the NOAA-2004 calibration scale (Dlugokencky et al., 2005). The overall accuracies, including calibration scale and nonlinearity uncertainties, are estimated at $\sim$2 % for both 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

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 filter systems to remove most particles and toxic substances. The samples were collected on the occasion of extensive measurement and sampling campaigns serving 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 H_2 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 online mass spectrometer (H-sense, V&F Analyse- und Messtechnik GmbH, Austria) 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 H_2 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 H_2 variability in the incinerator exhaust over the course of the measurement day. During this second incinerator sampling, ambient air samples were also drawn to characterize the composition of the intake air.

A large set of incinerators was sampled from September 2010 to March 2011 by collection of integrated (1 week) dried (MD-070-24S-4, Perma Pure, USA) exhaust gas samples in Cali-5-Bond$^{\text{TM}}$ sampling bags (GSB-P/44, Ritter Apparatebau, Germany), employing a peristaltic pump (ECOLINE VC-MS/CA8-6, Ismatec, Switzerland) at a flow rate of $3\,\text{ml}\,\text{min}^{-1}$. Some of these Tedlar bag samples were cryogenically transferred ($>0.6\,\text{L}\,\text{min}^{-1}$) into evacuated stainless steel flasks and subsequently 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) stainless steel container, immediately diluted with purified (H_2 and CO free) synthetic air, and subsequently measured on the RGA-3. CO, CO_2, CH_4, and other trace gases were also measured from the Tedlar bag samples using FTIR instrumentation. However, no H_2 isotope analysis was conducted on these samples.

Exhaust gas samplesi 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 H_2 through the Tedlar bags during storage, a stability experiment was conducted. A reference gas sample of $\sim$3 ppm H_2 (also including $\sim$2 ppm CO and other compounds) was collected in a Tedlar bag stored in an ambient laboratory air H_2 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 $\sim$7 % ($\sim$210 ppb) in H_2 and $\sim$12 % ($\sim$240 ppb) in CO was detected. At the same time, a similar experiment was conducted with synthetic air samples that contained small concentrations of H_2 ($\sim$20 ppb) and virtually no CO. Here, an increase of $\sim$130 ppb H_2 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 H_2 and CO production from plastic under the influence of light. We originally suspected that diffusive exchange could potentially alter the H_2 concentration in the Tedlar bags. However, the fact that we observe an increase in H_2 over time in the bag with the $\sim$3 ppm H_2 (and the ambient air having lower concentrations) indicates that this would not be the only process that might alter the H_2 composition/concentration. If we scale the results to the storage time of our incinerator samples, then the potential H_2 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 H_2 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 H_2 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 standards. They were equipped with oxidation catalysts and three had diesel particle filters. On-line direct exhaust measurements were conducted for a suite of compounds. H_2 was measured using the H-sense MS described in 1.2. For most of the diesel exhaust measurements with low H_2 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 similar limitations. However, large H_2 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 H_2/CO and have selected the duration based on the criteria of blank-corrected $H_2>1$ ppm. Mean H_2 and CO concentrations were calculated over the typically 1 min–2 min phases of the cold starts and the 15–30 sec periods during some of the accelerations. We also limit the analysis of H_2/CO to these compounds' mean concentrations over these periods in order to avoid potential mismatches of response time characteristics of the two instruments.

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