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Hydrogen in the atmosphere: Observations above a forest canopy in a polluted environment

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[1] Long-term in situ observations of atmospheric concentrations of molecular hydrogen were monitored every 24 minutes for three years (1996–1998) above Harvard Forest, Massachusetts, in concert with measurements of carbon monoxide and twelve other trace gases. A seasonal cycle with a spring maximum and autumn minimum was observed. The diurnal cycle was characterized by a morning minimum and an afternoon maximum, reflecting the combined effects of uptake by soils and boundary height fluctuations. Enhancements of H_2 concentrations in pollution events, concurrent with winds from the southwest, were typically 100–200 ppb above the background seasonal cycle. The mean molar ratio of H_2 and CO ($\Delta H_2/\Delta CO$) in pollution plumes was 0.396 ± 0.050 ppb/ppb. The results agree with expectations from the water-gas equilibrium ($CO + H_2O \leftrightarrow CO_2 + H_2$) for conditions in automobile engines and with car emission data. These observations suggest that automobiles are the major anthropogenic source of atmospheric hydrogen and that the ratio of $\Delta H_2/\Delta CO$ has changed little as emission controls have taken effect. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; *KEYWORDS:* hydrogen, pollution, emissions, car exhaust, troposphere

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1. Introduction

[2] Molecular hydrogen is a major by-product of combustion, but because it is not itself deleterious to the atmosphere, little attention has been paid to it in the atmospheric literature. Nonetheless, H_2 is a major trace gas affecting a range of processes that directly impact concentrations of OH and O_3 in the troposphere and the stratosphere. The current ambient hydrogen mixing ratio of 531 ppb [*Novelli et al.*, 1999] is more than twice the estimated pre-industrial concentration of around 200 ppb [*Khalil and Rasmussen*, 1990]. This substantial global increase is consistent with the view that anthropogenic emissions of fossil fuel and biomass burning constitute ~40% of global hydrogen sources [*Novelli et al.*, 1999].

[3] The global budget of H_2 in the troposphere is comprised of four main sources (oxidation of CH_4, oxidation of non-methane hydrocarbons, fossil fuel combustion, and biomass burning) and two main sinks (oxidation by OH and uptake by soils) [e.g., *Novelli et al.*, 1999]. Additional minor sources include biogenic N_2 fixation by legumes [*Conrad and Seiler*, 1980] and emissions from oceans and volcanoes [e.g., *Schmidt*, 1974]. The oxidation of methane and non-methane hydrocarbons by the main atmospheric scavenger, OH, leads to the formation of the major carbonyl, formaldehyde (CH_2O), a precursor of tropospheric O_3. Roughly, 95% of the hydrogen found in the stratosphere originates in the troposphere and enters through the tropopause [*Hurst et al.*, 1999]. Once there, it represents a source of water vapor and plays a minor, but significant, role in the chemistry of HO_x [*Penner et al.*, 1977; *Khalil and Rasmussen*, 1990; *Hurst et al.*, 1999]. Thus, it is fair to consider anthropogenic hydrogen as a pollutant in the atmosphere.

[4] Before the 1970s, hydrogen research was motivated by a desire to monitor the atmospheric increase of the hydrogen isotope, tritium, released by nuclear explosions and leakage from the nuclear industry [*Ehhalt*, 1966; *Mason*, 1977]. In the 1970s, modeling attention focused on the escape flux of H_2 and atomic H from the exosphere of the Earth [*Liu and Donohue*, 1974a, 1974b; *Hunten and*

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Strobel, 1974]. More recently, in the stratosphere, direct measurements of H_2 have aimed at closing the total stratospheric hydrogen budget in order to better quantify the amount and production of water vapor there [*Dessler et al.*, 1994; *Hurst et al.*, 1999].

[5] In 1923, P. M. Schuftan made the first reliable tropospheric hydrogen measurements, finding 0.50 ± 0.10 ppm in air samples from liquid air plants in Germany [*Paneth*, 1937]. Since then, most tropospheric H_2 observations have been taken at remote surface locations, in an effort to characterize the global distribution in the background atmosphere. Beyond individual air samples analyzed before 1975 [*Glueckauf and Kitt*, 1957; *Scholz et al.*, 1970; *Ehhalt and Heidt*, 1973], research of the 1970s and 1980s employed systematic grab samples and continuous measurements over short durations taken during ocean-crossings by air and sea, during flights over unpolluted areas, and during aircraft ascents to define tropospheric vertical profiles [*Schmidt*, 1974, 1978; *Ehhalt et al.*, 1977; *Fabian et al.*, 1979]. Additional tropospheric studies have sought to both identify and quantify the sources and sinks of hydrogen: ocean releases [*Herr and Barger*, 1978]; soil uptake [*Seiler*, 1978; *Conrad and Seiler*, 1980]; nitrogen fixation by legumes [*Conrad and Seiler*, 1980]; biomass burning emissions [*Helas et al.*, 1995]; and car engine exhaust [*Starkman and Newhall*, 1965; *Jones et al.*, 1971].

[6] Long-term tropospheric studies by *Khalil and Rasmussen* [1990] in 1985–1989 and *Novelli et al.* [1999] in 1989–1996 involved weekly flask measurements taken at ground-based network stations in remote locales to define the meridional distribution of H_2 at the surface. Observations of hydrogen in pollution plumes (beside those data that were flagged and removed during remote measurement campaigns) have been reported by *Schmidt and Seiler* [1970] and *Schmidt* [1974], who monitored air continuously downwind of Mainz, Germany, over several months, by *King* [1970] in Bayway, New Jersey, near traffic, and by *Scranton et al.* [1980], who measured hydrogen continuously over the months of January–February and June–July, 1979, in Washington, D. C., near Interstate Route 295. Long-term, high frequency tropospheric measurements were made at Mace Head, Ireland, from 1994 through 1998 [*Simmonds et al.*, 2000].

[7] The present study provides measurements of atmospheric hydrogen concentrations in air sampled every 24 minutes from a 30-meter tower at Harvard Forest, Massachusetts, for three years, 1996 through 1998. The location of the sampling station (42.48°N, 72.18°W, 340 m), with 'clean' background air arriving from the northwest (Canada), 'dirty' polluted air arriving from the southwest (the New York City–Washington, D. C., corridor, including western and central Connecticut), and forest soils below, is ideal for analyzing the background signal and observing the effects of urban/industrial emissions and soil uptake of hydrogen. No other long-term, high frequency tropospheric measurements of H_2 have been reported for the United States, either in the remote troposphere or downwind of pollution sources. The results of this study are used to corroborate the background seasonal signal found by the flask networks, to characterize the diurnal cycle in light of sources and sinks, to establish the current $\Delta H_2/\Delta CO$ emission ratio from regional urban/industrial sources, and to develop an inventory of annual fossil fuel emissions of H_2 for 1996 through 1998 for the New York City–Washington, D. C., corridor.

2. Methods and Measurements

[8] Atmospheric mixing ratios of hydrogen were monitored by a fully automated, in situ gas chromatographic instrument called FACTS (Forest and Atmosphere Chromatograph for Trace Species). Air was drawn down from the tower through 3/8″ O.D. Dekabon tubing (DuPont type 1300, DuPont Dekaron Division, Aurora, OH) by diaphram pumps (KNF Neuberger, Princeton, NH, model UN010) at a continuous flow rate of approximately 5.75 L/min, dried by a glass bead trap and a Nafion drier (General Valve Co., Fairfield, NH), and then passed into a 5 cc sample loop from which it was injected onto the columns. The columns consisted of a 0.3175 cm (1/8″) I.D. Unibeads 1s pre-column (2 m in length) followed by a 0.3175 cm (1/8″) I.D. Molecular Sieve 5A column (4 m), both maintained at 85°C (Alltech Associates, Inc., Deerfield, IL, and Fisher Scientific, Hampton, NH). The Unibeads 1s pre-column retains any CO_2 in the air sample to prevent it from collecting on the Molecular Sieve 5A main column, from which it would slowly bleed into the detector causing an elevated baseline. Nitrogen carrier gas is pre-conditioned by a 350°C zirconium (Zr) getter whose high surface area adsorbs low-level impurities, a Hopcalite (MnO_2 and CuO) trap which combusts any CO into CO_2, and a Molecular Sieve 13X trap which removes the newly created CO_2, before flushing the air sample at a flow rate of 50 sccm from the sample loop through the columns and into a Shimadzu (Shimadzu, Tokyo, Japan) electron capture detector with a ^{63}Ni β source maintained at 350°C. The carrier gas is doped with N_2O flowing at $2.5*10^{-3}$ sccm to provide sensitivity to the hydrogen molecules as they elute from the columns. Due to their small size, the hydrogen molecules fit the pore size of Molecular Sieve 5A better than molecules of O_2, with the unusual result that H_2 elutes before the air peak.

[9] Air samples were alternated with calibration tank samples every 12 minutes. Two working standards, one of clean ambient atmospheric air and one of atmospheric air diluted by 10% with halocarbon-free zero air, are used on FACTS. Standards were prepared in Aculife-treated aluminum tanks (Scott Specialty Gases, Plumsteadville, PA), filled by NOAA/CMDL (National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory) at Niwot Ridge, Colorado, using an oilless air compressor (Model RIX SA6, RIX Industries, CA) with anhydrous magnesium perchlorate as a drying agent. Our working standards were calibrated against the NOAA/CMDL CCG working standards, which are tied to a set of gravimetric standards [*Novelli et al.*, 1999].

[10] Two additional data sets are available for intercomparison. First, to establish the relative concentrations of H_2 among the seven calibration tanks used over the course of the experiment, intercomparison tests were devised during which three calibration tanks were run in conjunction with one tower air for a week or more. Four such intercompar-

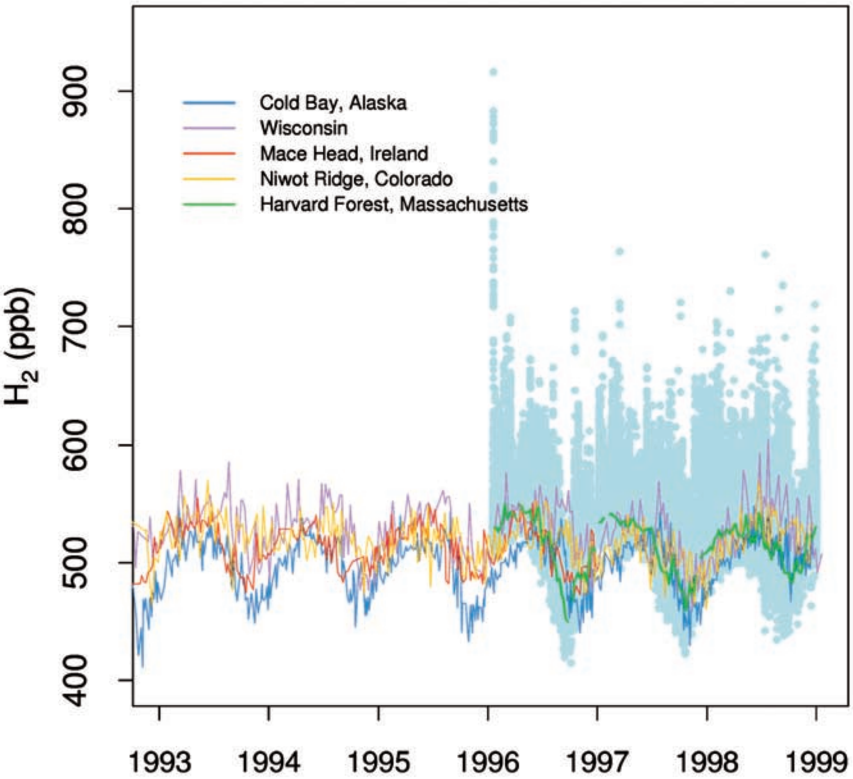

Figure 1. Comparison of background Harvard Forest hydrogen levels (green line) to those measured at Northern Hemisphere remote stations of NOAA/CMDL (as retrieved from the NOAA/CMDL web site: ftp://ftp.cmdl.noaa.gov/ccg/h2/flask). The full H_2 data set measured by FACTS at Harvard Forest is presented.

ison tests were performed in July 1996, May and June 1997, and December 1998, each with a different set of three tanks. Using the average H_2 peak height instrument response during each test, a fully consistent set of calibration values may be inferred (see *Barnes* [2000] for details). Second, the high degree of agreement between the FACTS background results and the measurements from NOAA/CMDL Northern Hemisphere remote station flask data reflects their common tie to the NOAA calibration scales (Figure 1).

[11] The FACTS instrument recorded atmospheric observations every 24 minutes over the three-year period of 1996 through 1998 (Figure 2), for H_2 plus thirteen other trace gases: CO, CH_4, PCE, CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 (CCl_2F-$CClF_2$), CH_3CCl_3, CCl_4, Halon-1211 ($CBrClF_2$), $CHCl_3$, TCE (C_2HCl_3), N_2O, and SF_6 [*Barnes*, 2000]. Field precisions were estimated on the average of 72 monthly precisions (36 months for the years 1996–1998 and two calibration tanks). Each monthly precision was based on one tank, run in sequence with the other tank and two airs, for a frequency of 1 in every 48 minutes. Measurements of standards were detrended by subtraction of a two-point running mean, and the precision was defined as the coefficient of variation (standard deviation/mean) of the residuals. The field precision of the hydrogen measurements was 1.10%, or 6.4 ppb, with the background ambient mixing ratio of around 530 ppb. The methods for defining the inter-annual trend, mean seasonal cycle, and monthly diurnal cycles for background H_2 and the seasonal character and inter-annual trend for urban/industrial H_2 emissions are summarized below and described in detail by *Barnes et al.* [2003a, 2003b].

3. Background Concentrations of Hydrogen

[12] The background signal for hydrogen (Figures 1 and 2) was estimated from the time series by computing a running quantile with an interval size of ten days and a quantile probability (i.e. rank order) of 0.2 over the three years of data [*Barnes et al.*, 2003a]. It has been shown that the running quantile probability of 0.2 captures the regional background level for several gases without the interference by low concentration stratospheric inputs [*Goldstein et al.*, 1995]. A sensitivity test on the window size, from 1/2 to 30 days, indicated that the 10-day window yields nearly the same result as the 30-day window.

3.1. Background Annual Trend

[13] The inter-annual trend for background H_2 over the years 1996–1998 at Harvard Forest is not statistically significant (−0.313 ± 1.688 ppb/year). This result falls outside the range found globally from 1991 to 1996 (−2.3 ± 0.1 ppb/year) but lies well within the range of shorter-term variability during the same years [*Novelli et al.*, 1999]. In contrast, European air (as measured at Mace Head, Ireland) exhibited a 1.2 ± 0.8 ppb/year increase in H_2 over 1994–1998 [*Simmonds et al.*, 2000]. This European increase agrees well with that determined from grab samples collected at Mace Head by NOAA/CMDL over the same

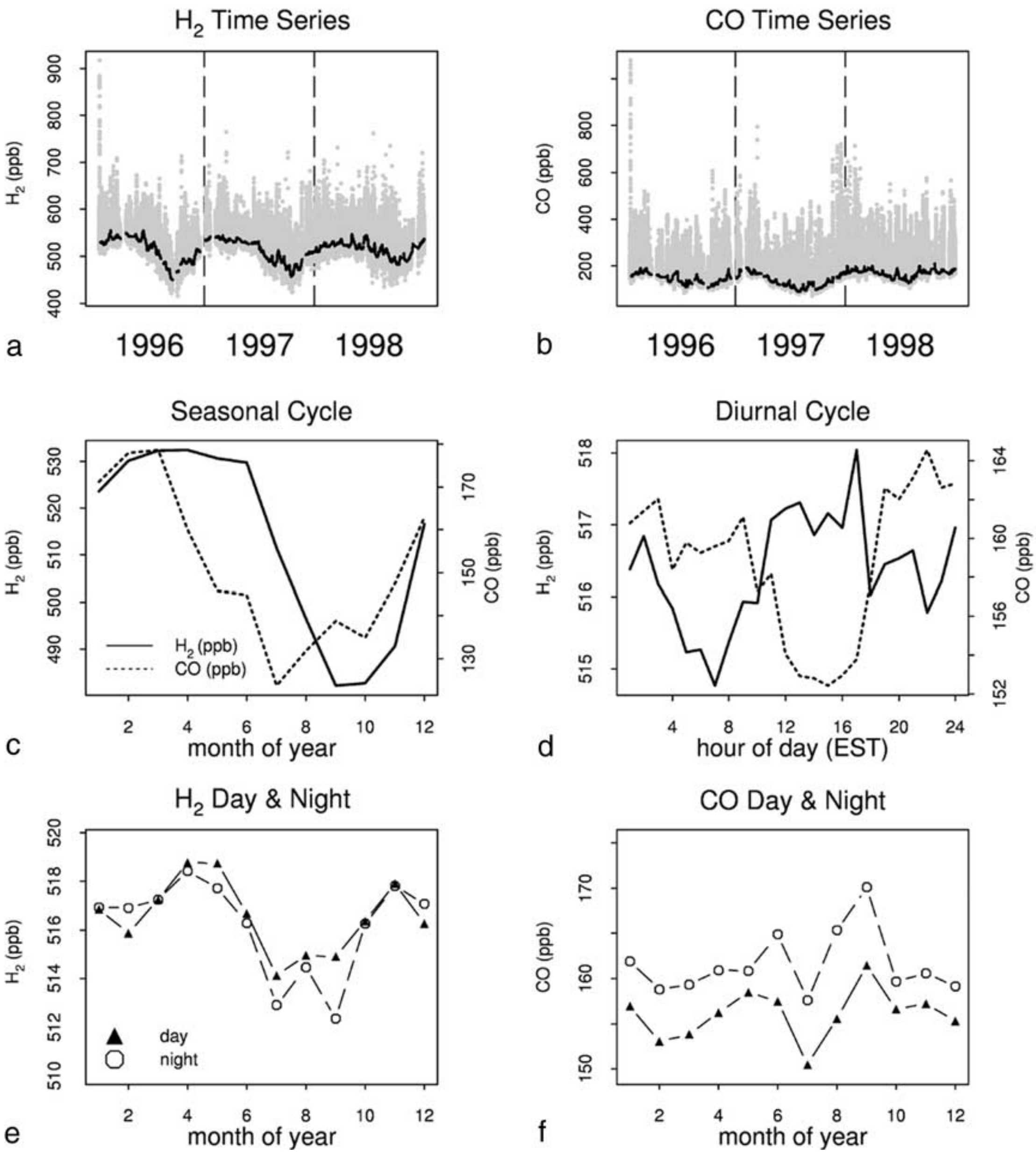

Figure 2. (a and b) Time series of H_2 and CO at Harvard Forest over the years 1996–1998. The background signals (black line) are based on a running quantile of 0.2 and an interval size of 10 days. Pollution plumes are clearly evident above the background. (c) The mean background seasonal cycles of H_2 and CO. (d) H_2 and CO diurnal cycles. Each hourly point represents the median concentration for all three years of data. (e and f) Median daytime (6 am to 6 pm) H_2 concentrations exceed their nighttime (6 pm to 6 am) counterparts throughout the year, except during the winter months when the soils are frozen. For CO, daytime oxidation by OH suppresses daytime values below nighttime ones throughout the year.

period (1.4 ± 0.41) [*Novelli et al.*, 1999; P. C. Novelli et al., unpublished data, 2001]. The absence of a significant H_2 trend at Harvard Forest contrasts with a measurable rise in CO (10.2 ± 2.9 ppb/year) over the period; that these trends are not of the same sign is noteworthy, considering that H_2 and CO share many of the same sources and sinks.

3.2. Background Seasonal Cycle

[14] The pronounced background seasonal cycles of H_2 and CO (Figure 2) both exhibit winter-spring maxima and summer-fall minima, a pattern that is consistent with maximum summertime loss rates by OH oxidation, the cumulative effect of soil uptake throughout the summer leading to a maximum in total drawdown by late summer and early fall, and strongest rates of soil uptake in late summer and early fall when soils are at their driest [*Conrad and Seiler*, 1985; *Schuler and Conrad*, 1991; *Yonemura et al.*, 2000]. The H_2 seasonal signal is slightly later in phase than that of CO by about 2–3 months. The lag arises in part from the longer atmospheric residence time for H_2 and in part from the greater role of soil uptake for H_2, which turns on later than the OH sink for both gases. For an atmospheric column

height of H = 7 km and soil deposition velocities of $\nu_d(H_2) \cong 7*10^{-2}$ cm/s [*Conrad and Seiler*, 1980, 1985; *Yonemura et al.*, 2000] and $\nu_d(CO) \cong 3*10^{-2}$ cm/s [*Moxley and Cape*, 1997; *Yonemura et al.*, 2000], the atmospheric residence times versus soil uptake are $t_{soils}(H_2) \cong 1*10^7$ s and $t_{soils}(CO) \cong 2.3*10^7$ s. For an average [OH] of 10^6 molecules/cm^3 [*Prinn et al.*, 1995] and OH reaction rate coefficients (T = 298 K) of $k(H_2) = 6.7*10^{-15}$ cm^3/(molecules*s) and $k(CO) = 1.5*10^{-13}$ cm^3/(molecules*s) [*DeMore et al.*, 1997], the OH lifetimes are $t_{OH}(H_2) \cong 1.5*10^8$ s and t_{OH} (CO) $\cong 6.7*10^6$ s. Thus soils represent the dominant sink for H_2 ($\lambda \cong 1*10^7$ s, where the atmospheric lifetime, $\lambda = t_{soils} + t_{OH}$), as compared to CO, which has a shorter lifetime ($\lambda \cong 5*10^6$ s) due mainly to removal by OH.

[15] The hydrogen seasonal pattern exhibits a broad maximum, spanning the winter-spring months of February through June, followed by a sharp decline to a short-lived minimum in September and October. The strength of the H_2 seasonal signal at Harvard Forest, with an average amplitude of 24.5 ppb, or almost 5% of mean ambient H_2 concentrations, reflects the seasonal character of its photochemically- or biologically-driven sources and sinks, fossil fuel combustion excepted. Similar seasonal patterns and amplitudes are reported by other Northern Hemisphere monitoring stations [*Khalil and Rasmussen*, 1990; *Novelli et al.*, 1999; *Simmonds et al.*, 2000]. Trace gases known to be released by anthropogenic activity are typically more concentrated in the Northern Hemisphere. For hydrogen, however, the opposite is true, with an average Southern Hemispheric autumn minimum hydrogen mixing ratio ~70 ppb higher than that found in the Northern Hemisphere [*Khalil and Rasmussen*, 1990; *Novelli et al.*, 1999]. This disproportion is attributed to the hemispherical asymmetry in the main hydrogen removal process, uptake by soils, with ~60–70% of the Earth's vegetated lands located above the equator [*Novelli et al.*, 1999].

3.3. Background Diurnal Cycle

[16] Both the diurnal and seasonal cycles of background CO have concentrations that drop during those time periods with highest solar irradiance, the mid-afternoon hours and the summer, respectively. These patterns are expected, given that OH is the main sink of CO. The diurnal pattern of H_2 background signal (Figure 2) shows a distinctly different pattern, with highest concentrations in the afternoon (2–8 pm, depending on season) and lowest in the early morning hours (6–7 pm), with an amplitude of ~5–10 ppb. Similar cycles were reported by *King* [1970], who observed a 2:00 p.m. maximum for his observations made near traffic, and *Simmonds et al.* [2000], who observed nocturnal depletion during conditions of a shallow, stable inversion layer at Mace Head, Ireland. With these two exceptions, however, the background diurnal cycle of hydrogen has received no attention at all.

[17] The diurnal cycles also reflect the sink strengths of OH and soils acting on CO and H_2. Rates for removal of H_2 by uptake by forest soils (75%) and oxidation by OH (25%) [*Novelli et al.*, 1999] are both most rapid in the afternoon. The dominant effect, however, is the influence of the soil sink which continues to deplete H_2 concentrations near the ground throughout the night, when the air is trapped in the stable canopy layer near the ground. Uptake of H_2 by soils at night has greater influence on this shallow layer (~100 m) than on the thicker daytime layer (~2000 m), and the associated drawdown of H_2 is correspondingly larger. By late-morning, convection breaks up the nocturnal stable layer, and the depleted gases are mixed with air of higher concentrations up to the height of the planetary boundary layer, leading to a rapid rise in H_2 concentrations at around 10 a.m. Thus CO daytime concentrations are lower than the nighttime ones throughout the year, due to the higher abundance of OH during the sunlit hours, whereas H_2 daytime concentrations are higher than at night except during winter months when the soils are frozen or snow - covered (Figure 2).

[18] Additional factors may contribute to the hydrogen diurnal signal. Sources of H_2, including fossil fuel combustion released predominantly from cars and the oxidation by OH of methane and of non-methane hydrocarbons (NMHCs), including isoprene and the terpenes released by plants, leading to the formation of formaldehyde (CH_2O), are both stronger in the daytime than at night. The formaldehyde produced may react with OH (producing no H_2) or undergo photolysis. Of the two photolytic pathways, one yields H_2 with an H_2:CO production ratio of 0.3. When removal of H_2CO by OH is included, the H_2:CO production rate from H_2CO is about 0.25. At Harvard Forest, concentrations of short-lived biogenic non-methane hydrocarbons from plants were found to rise with temperature and sunlight in the morning, peak in the afternoon, and then decline towards the evening [*Goldstein et al.*, 1995]. For example, the northern red oak that dominates the forest is a strong emitter of isoprene [*Goldstein et al.*, 1995]. Further, since both the OH reactions that produce CH_2O and the photolysis rate for formaldehyde peak during the sunlit hours, these reactions could play a role in producing the afternoon H_2 peak we observe.

4. Urban/Industrial Emissions of Hydrogen

[19] Pollution enhancements well above the background signal are clearly evident in the hydrogen time series (Figures 2 and 3). The plumes generally coincide with winds arriving at the tower from the southwest, the direction of the New York City–Washington, D. C., urban/industrial corridor, as opposed to the unpolluted background air carried by winds arriving from the northwest (Canada). The same spatial pattern is observed for almost all of the gases monitored by FACTS, reflecting sources that are predominantly anthropogenic in origin (Figure 3). The enhancements of hydrogen are typically 100–200 ppb, with some as high as 400 ppb, above the background; the overall range of hydrogen mixing ratios observed was 414–917 ppb with a mean of 533 ppb. The magnitude of these enhancements is comparable to those reported elsewhere. *Schmidt and Seiler* [1970] recorded values ranging from 400–1300 ppb outside of Mainz, Germany. *King* [1970] observed concentrations of 1000 ppb in Bayway, New Jersey. *Schmidt* [1978], measuring air masses in the English Channel, found maximum levels of 870 ppb due to contamination by the large cities and heavily industrialized regions of Western Europe. *Scranton et al.* [1980] detected

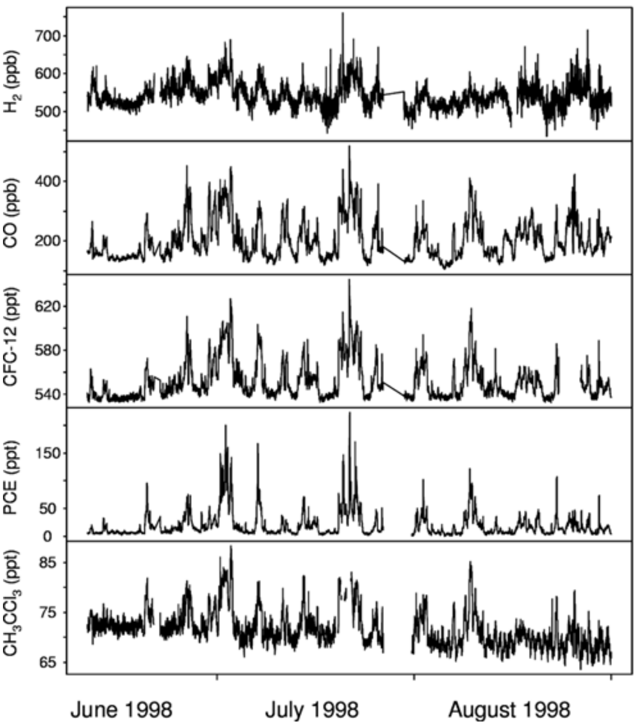

Figure 3. Pollution events from the southwest during Summer 1998 for the species H_2, CO, CFC-12, PCE, and CH_3CCl_3. The signals track each other closely.

an astonishing range of 600 to over 3000 ppb of hydrogen in Washington, D. C., near Interstate Route 295.

[20] To determine the annual per capita urban/industrial emissions of hydrogen for the New York City–Washington, D. C., corridor and to assess the predominant urban/industrial sources of hydrogen, we correlated H_2 plume events from the southwest with those of simultaneously measured CO and PCE (perchloroethylene, C_2Cl_4), a dry-cleaning and degreasing agent. Using the available emission inventories (inventory quantities are denoted with subscript I) for CO and PCE [*Environmental Protection Agency* (*EPA*), 1997; *McCulloch and Midgley*, 1996; P. M. Midgley, personal communication, 2001] (see also the U.S. Environmental Protection Agency web site: http://www.epa.gov/air/data/nettier.html and http://www.epa.gov/enviro/html/tris), full-year per capita emissions of CO (CO_I) and PCE (PCE_I) were previously calculated for 1996, 1997, and 1998 for the New York City–Washington, D. C., corridor [*Barnes et al.*, 2003a]. We have shown that for 1996 the ratio of the CO and PCE pollution enhancements measured by FACTS, $\Delta CO/\Delta PCE$ (where Δz is the magnitude of the enhancements above the background for species z), agrees with the ratio of their emissions inventories, CO_I/PCE_I, to within 11% [*Barnes et al.*, 2003a].

[21] We determined the H_2 emissions on a seasonal time scale by comparing pollution enhancements of H_2 to CO and of H_2 to PCE above their background levels. These ratios of $\Delta H_2/\Delta CO$ and $\Delta H_2/\Delta PCE$ were derived for the 12 seasons of the study (with winter = December, January, and February) and for seven separate cases: all data; northwest winds only (NW); southwest winds only (SW); day (6 am to 6 pm); night (6 pm to 6 am); high U* (>0.2 m/s); and low U* (<0.2 m/s) (where $U^* = \sqrt{(-1^*\text{momentum flux})}$, a measure of turbulent exchange with the overlying atmosphere) (Figure 4). In all cases and all seasons, the number of data points (between 168 and 4163) is sufficient for this study.

[22] Apart from the species ratios in the NW air parcels, where the signal-to-noise ratio was low, all the cases give coherent results, in particular day and night and high and low U*, suggesting that diurnal variations and stagnation episodes are inconsequential for this analysis. For SW winds, the ratio of $\Delta H_2/\Delta CO$ in emissions is relatively stable at an average value of 0.396 ± 0.050 (ppb/ppb); some seasonal variation in the SW $\Delta H_2/\Delta CO$ may result from excess CO produced from secondary reactions. The ratio of emissions of SW $\Delta H_2/\Delta PCE$ has an average value of 1.22 ± 0.19 (ppb/ppt) with little seasonal variability.

[23] To calculate annual per capita urban/industrial H_2 emissions, the SW $\Delta H_2/\Delta CO$ and $\Delta H_2/\Delta PCE$ seasonal results are multiplied, respectively, by the previously determined CO_I and PCE_I emissions (in kg/person/year) for the New York City–Washington, D. C., region [*Barnes et al.*, 2003a]. It is not always advisable when determining these yearly rates to simply take the average of all four seasons of the SW slopes of $\Delta H_2/\Delta CO$ and $\Delta H_2/\Delta PCE$, because secondary production of CO and H_2 from hydrocarbons may be significant in the summer, additional sources not covered by the inventories. Furthermore, in the summertime, weaker winds make for longer and more frequent stagnation events, during which local emissions from the forest and nearby towns may build up, offsetting the regional signal. In wintertime the system is more flushed out. To address these concerns, an overall average is taken of:

$$\frac{CO_I^*\langle(\Delta H_2/\Delta CO)_{SW}\rangle + PCE_I^*\langle(\Delta H_2/\Delta PCE)_{SW}\rangle}{2}$$

where $\langle(\Delta H_2/\Delta z)_{SW}\rangle$ is a weighted average of $\Delta H_2/\Delta z$ for all four seasons, for winter and spring combined, and for the winter season alone. The whole year case is retained in order to capture any summer or fall variations in the emissions of H_2 itself.

[24] By this method we determined that over the three years, 1996, 1997, and 1998, hydrogen urban/industrial emissions from the New York City–Washington, D. C., corridor were 5.13, 4.87, and 4.28 kg/person, respectively. Although the inter-annual rate of decline is uneven, the overall sign of the H_2 emissions trend (−0.42 ± 0.10 kg/person/year) agrees with that of CO emissions (−4.90 ± 1.22 kg/person/year) over the same period, not surprising given their many shared sources. Thus the urban emissions showed a statistically significant decline in contrast to the background, which showed no trend over the period.

5. $\Delta H_2/\Delta CO$ in Anthropogenic Sources

[25] Hydrogen is known to be a by-product of fossil fuel combustion and may be released by other manufacturing processes as well. Recent budgets have attributed these processes with as much as ~19% of total H_2 emissions [*Khalil and Rasmussen*, 1990; *Novelli et al.*, 1999], and

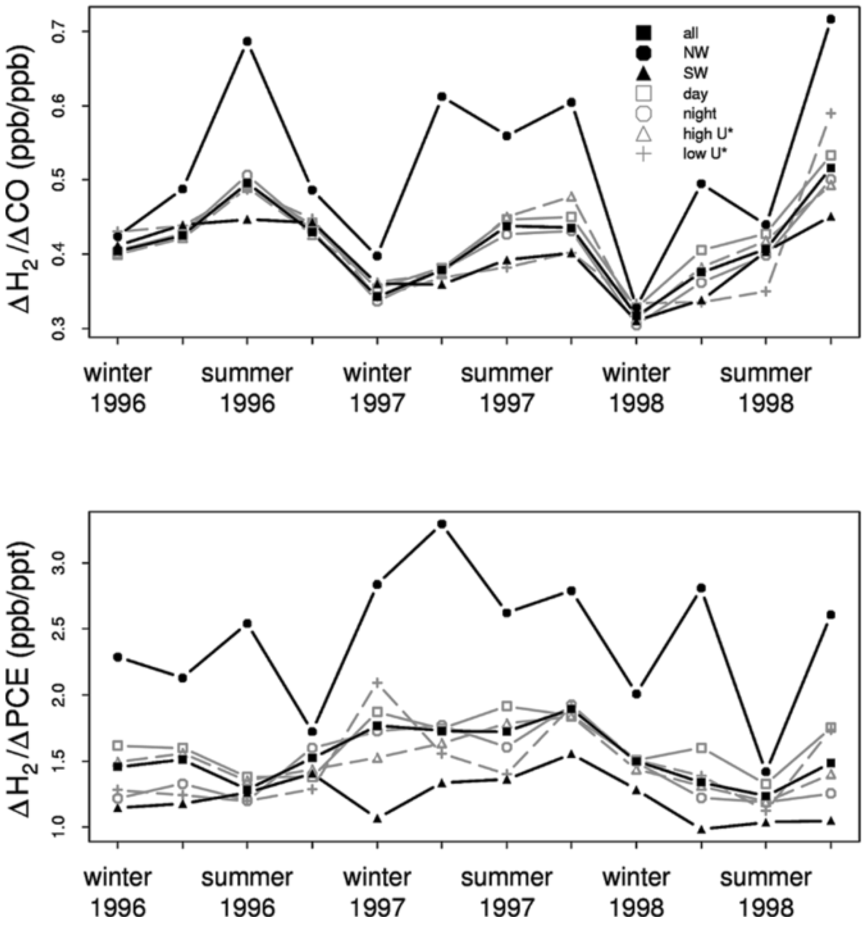

Figure 4. $\Delta H_2/\Delta CO$ (ppb/ppb) and $\Delta H_2/\Delta PCE$ (ppb/ppt) orthogonal distance regressions for each season and for seven cases of: all data; northwest winds only (NW); southwest winds only (SW); day (6 am to 6 pm); night (6 pm to 6 am); high U* (>0.2 m/s); and low U* (<0.2 m/s).

studies have sought to correlate and predict historic H_2 concentrations with the rise in global industrialization [*Penner et al.*, 1977; *Khalil and Rasmussen*, 1990]. These estimates are made, however, on the basis of very little field research; instead, the typical method for deducing total anthropogenic H_2 production has been to utilize known anthropogenic CO production rates along with simultaneous measurements of H_2 and CO [*Schmidt*, 1974; *Penner et al.*, 1977; *Novelli et al.*, 1999].

[26] With a number of field stations reporting a correlation between observed H_2 enhancements and local traffic flow [*Schmidt and Seiler*, 1970; *Scranton et al.*, 1980; *Novelli et al.*, 1999], the focus of anthropogenic H_2 source studies has centered almost entirely on automobiles, with little reference to other technological processes. The only direct evidence of the presence of H_2 in automobile exhaust dates back to a motor emission study by the Society of Automotive Engineers in 1965 [*Starkman and Newhall*, 1965], before the era of emission standards, fuel additives, catalytic converters, and other automotive changes. At that time, Starkman and Newhall attributed the hydrogen they observed to the well-known water-gas equilibrium reaction found in engines:

$$H_2 + CO_2 \leftrightarrow H_2O + CO.$$

Penner et al. [1977] judged that under the conditions typical of an internal combustion engine, with temperatures of around 1500–1700 K, the yield of H_2 from a water-gas reaction system would be about 40% that of CO. Any additional H_2 derived from photolysis of formaldehyde, which itself is released by incomplete combustion, was not included in the above calculation [*Calvert et al.*, 1972].

[27] Technological processes other than combustion by motor vehicles may also produce H_2, although direct emissions of H_2 from major combustion sources such as power plants are unlikely, given that they are very efficient, produce little CO, and would not be expected to produce significant H_2 on thermodynamic grounds. In industrialized areas, NMHCs and formaldehyde are emitted during manufacturing processes and by mobile and stationary sources [*Tanner et al.*, 1988; *Grosjean et al.*, 1990], leading to secondary production of H_2. Only *Scranton et al.* [1980], who measured H_2 in the Washington, D. C., area and found a diurnal cycle that was well correlated with local traffic patterns, considered the other potential hydrogen sources of home heating units (natural and oil gas burning), aircraft exhaust, a coal-burning power plant, and biological production from a large municipal sewage treatment plant. Based on the observed diurnal H_2 signal, they concluded

that these other processes were at best of only secondary importance as compared to the role of motor vehicle exhaust in the sources of urban/industrial H_2.

[28] Over the years, only a few other studies have reported observed or calculated $\Delta H_2/\Delta CO$ ratios in polluted environments (Table 1). *Starkman and Newhall*'s [1965] car engine experiment yielded an overall range of 0.27 to 0.78. *Jones et al.* [1971], using calculated hydrogen values based on CO measurements, derived $\Delta H_2/\Delta CO$ ratios of 0.33–0.39; the formula used to calculate H_2 emissions from CO was not provided. J. T. Kummer (cited by *Scranton et al.* [1980]) estimated a ratio of one third, based on conditions unknown. *Schmidt* [1974], W. Seiler and H. Zankl in 1975 (as referenced by *Conrad and Seiler* [1980]), *Novelli et al.* [1999] in 1989, and Y. Tohjima in 1995 (as referenced by *Novelli et al.* [1999]) all report $\Delta H_2/\Delta CO$ ratios based on atmospheric observations over short periods in urban plumes and/or near traffic flow. Of these, W. Seiler and H. Zankl's value of 1, recorded during a single aircraft pass through one urban plume, is higher than the 0.433, 0.6, and 0.5 results provided by the others. *Scranton et al.* [1980] present observations that suggest a ratio of ~0.65 (as judged from their Figure 6) but refrained from reporting $\Delta H_2/\Delta CO$ ratios due to their concern over the quality of CO data in the study. Finally, the *Simmonds et al.* [2000] measurements of European polluted air masses produced the lowest $\Delta H_2/\Delta CO$ ratio of only 0.15.

[29] We use here our three years of continuous H_2 and CO measurements, taken downwind of the major urban/industrial region of the New York City–Washington, D. C., corridor, to provide robust estimates for $\Delta H_2/\Delta CO$ ratios by season for polluted air in the late 1990s (Figure 4; Table 1). An average $\Delta H_2/\Delta CO$ value of 0.396 ppb/ppb (or 0.0285 kg/kg) was observed at Harvard Forest for winds issuing from the southwest. While this measurement reflects a mixture of common urban anthropological sources (direct emissions from transportation and other industrial processes plus secondary production from the oxidation of anthropogenic hydrocarbons), we note that this $\Delta H_2/\Delta CO$ value is entirely in harmony with that predicted by *Starkman and Newhall* [1965] from the water-gas reaction and is higher than that expected for production from formaldehyde photolysis. If automobile exhaust is indeed the primary source of H_2, the consistency of the $\Delta H_2/\Delta CO$ ratio since the mid-1960s is remarkable, considering the significant changes in the automotive industry, including the introduction of the catalytic converter, and the complexity of the chemistry in the internal combustion engine.

[30] Given the consistency of the $\Delta H_2/\Delta CO$ ratio in SW pollution plumes established above, we can use the 1996 $\Delta H_2/\Delta CO$ ratio of 0.0285 kg/kg and the 1996 CO emissions inventory of the EPA (http://www.epa.gov/air/data/nettier.html) to create a county-level map of H_2 fossil fuel releases for the northeastern U.S. in 1996 (Figure 5). As found for CO [*Barnes et al.*, 2003a], for which mobile combustion is the major source (~84%) of all CO sources [*EPA*, 2000], those counties that contain or neighbor large cities are responsible for the bulk of the H_2 anthropogenic output. Relative to Harvard Forest, most of these larger

Table 1. Literature Survey of $\Delta H_2/\Delta CO$ in Pollution Plumes

Year[a]	Source	Own Data?	$\Delta H_2/\Delta CO$, ppb/ppb	Time and Place	Notes
1965	*Starkman and Newhall* [1965]	Yes	0.28–0.57 0.27–0.78[b]	Car engine	Uncontrolled auto emissions
1971	*Jones et al.* [1971]	Calculated	0.33–0.39	Car engine	Decreases with air/fuel ratio
1977	*Penner et al.* [1977]	Calculated	0.4	Car engine	Based on temperatures of ~1600 K
1973	*Schmidt* [1974]	Yes	0.4333	May–June, Mainz, Germany	
1975	W. Seiler and H. Zankl[c]	Yes	1	Munich, Germany	Aircraft, one urban plume
?	J. T. Kummer[d]	?	1/3	?	?
1979	*Scranton et al.* [1980]	No	~0.65?[e]	Jan.–Feb., June–July Washington, D. C.	Near Interstate 295
1989	*Novelli et al.* [1999]	Yes	0.6 ± 0.1	Boulder, Colorado	30 m above traffic intersection
1995	Y. Tohjima[f]	Yes	0.5	Tsukuba, Japan	
1994–1998	*Simmonds et al.* [2000]	Yes	0.15	Mace Head, Ireland	Continuous measurements
1996	This Work	Yes	0.412, 0.439, 0.447, 0.443[g]	Harvard Forest, Massachusetts	Controlled auto emissions NYC–Washington, D. C., corridor
1997	This Work	Yes	0.360, 0.359, 0.392, 0.402[g]	Harvard Forest, Massachusetts	Controlled auto emissions NYC–Washington, D. C., corridor
1998	This Work	Yes	0.310, 0.338, 0.403, 0.451[g]	Harvard Forest, Massachusetts	Controlled auto emissions NYC–Washington, D. C., corridor

[a] Year of measurement or observation, to the best of our knowledge.

[b] Under the conditions of an 8:1 and a 15:1 compression ratio, respectively.

[c] As referenced by *Conrad and Seiler* [1980].

[d] Personal communication in 1978, cited by *Scranton et al.* [1980].

[e] Approximate ratio as judged from Figure 6 of *Scranton et al.* [1980]. Scranton et al. refrained from reporting $\Delta H_2/\Delta CO$ ratios due to concern about the quality of the CO values in their study.

[f] Personal communication, cited by *Novelli et al.* [1999].

[g] In winter, spring, summer, and fall, respectively.

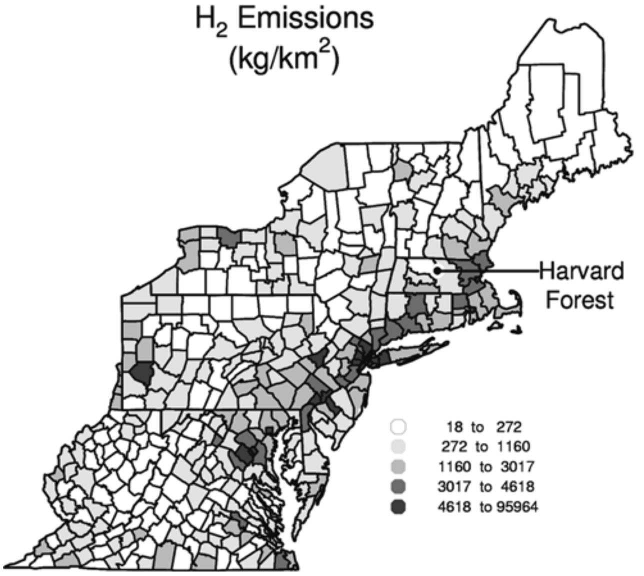

Figure 5. County-level map of the Northeast for hydrogen fossil fuel emissions in kg/area. These values are for the year 1996 and are based on the EPA inventory of CO emissions and 1998 county population and area statistics of the U.S. Census Bureau.

cities lie to the southwest, consistent with the polluted air masses observed from that direction.

6. Conclusions

[31] Measurements of atmospheric hydrogen were taken above a forest canopy and downwind of a major urban/industrial region at 24-minute intervals from 1996 through 1998, representing the first such data set of its kind.

[32] Diurnal, seasonal, and inter-annual variations in the background levels and seasonal and inter-annual variations in the pollution-related enhancements were recorded and characterized. The influence on H_2 of soil uptake over and above that of OH depletion is evident by comparing the seasonal and diurnal cycles of H_2 with CO. The H_2 seasonal cycle is slightly later in phase than that of CO, with a maximum spanning the winter-spring months of February through June, followed by a short-lived minimum in September and October. The H_2 diurnal cycle is opposite to that of CO, with a maximum occurring in the afternoon and lowest values in the early morning hours, except in the winter months when the ground is frozen over.

[33] Pollution plumes, associated with winds from the southwest, significantly enhance atmospheric concentrations above background levels. Hydrogen emissions from anthropogenic sources were determined to be on average 4.8 kg/person/year in the late 1990s. The ratio of pollution enhancements, $\Delta H_2/\Delta CO$, was found to be relatively uniform over all the seasons at 0.396 ± 0.050 ppb/ppb, in accord with $\Delta H_2/\Delta CO$ tailpipe and traffic plume studies dating back to 1965. The consistency of this result over the decades suggests that automobile exhaust may explain most of the enhancement of H_2 in polluted air. The water-gas reaction in the engines would remain in this case the major source mechanism for atmospheric pollution of H_2. If so, the influence of automobile emission controls over the decades on $\Delta H_2/\Delta CO$ has been minimal, with levels of H_2 in exhaust changing along with levels of CO.

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