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Original Research

Variability of Molecular Hydrogen in the Urban Atmosphere Based on Continuous Measurements in Kraków

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Abstract

With respect to the atmospheric budget of molecular hydrogen (H_2), Kraków represents a typical central European urban agglomeration with intense traffic and a relatively high proportion of low-level emissions associated with burning of fossil fuel (mainly coal and gas) for heating. The vehicle fleet in the city still contains a relatively high fraction of cars without properly operating catalysts, which constitutes a considerable source of atmospheric hydrogen. The mixing ratios of hydrogen in near-ground atmosphere were measured quasi-continuously over two years (from 01.2007 till 12.2008) at two different locations within the urban area of Kraków: close to the city center and at the outskirts of the city. Although both measurement locations were under the influence of local traffic, they differ with respect to the structure of local terrain (proportions of buildings, roads, and area covered by vegetation), as well as by local micrometeorological conditions.

A very wide range of H_2 mixing ratios was observed at both sites, with peak mixing ratios reaching 2,800 ppb. Distinct seasonality of H_2 mixing ratios was observed, with higher values recorded during winter months. Also, distinct daily variations of H_2 levels often were observed, with morning and evening H_2 maxima associated with traffic rush hours. Diurnal variation of hydrogen concentrations at both locations differs seasonally due to different micrometeorological conditions and source patterns, including car traffic intensity.

Keywords: atmospheric hydrogen, urban atmosphere, anthropogenic emission

Introduction

Regular observations of atmospheric concentrations of hydrogen were initiated in the 1970s [1-3]. The abundance of hydrogen in the troposphere was increasing until the 1990s, with a growth rate of approximately 3 ppb·year^{-1} [1]. The current mixing ratios of atmospheric H_2 vary between 450 and 550 ppb, depending on the location and season [4-7]. Although hydrogen is rarely mentioned as a greenhouse gas, it is expected that massive releases of this gas into the atmosphere, associated with a future hydrogen economy, may lead to a longer residence time of atmospheric methane and associated enhancement of the greenhouse effect [8-11]. The global budget of atmospheric hydrogen is not well constrained [12-16]. In particular, there are many estimations of the temporal and spatial variability of H_2

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uptake by soils, which constitutes the most important sink for atmospheric hydrogen [12, 17-20]. An important source of hydrogen, particularly in urban areas, is vehicle exhaust [5, 21-23].

Urban areas are under special interest, as the main anthropogenic source of hydrogen can be observed closely in cities [3, 7, 21, 24]. Interpretation of the results of hydrogen concentration analyses performed in an urban environment is difficult according to the little and usually unknown footprint of the sampling site [25, 26]. Direct application of dataset from urban area into the mesoscale model may cause disturbances that reduce chances of realistic interpretation of model results [27]. But the data are definitely valuable, especially the combination of different trace gases concentration measurements with micrometeorology parameters, which may lead to accurate estimation of the hydrogen source strength over the urban area [26, 28, 29]. But this it is not the aim of this work. To understand the influence of sampling site location on diurnal and seasonal hydrogen variability we decided to run parallel hydrogen analyses at two different locations in Kraków during the years 2007 and 2008.

Description of the Sampling Site

Kraków is located in southern Poland in the area of the Vistula and Rudawa river valleys connection. With about one million inhabitants, rapidly growing car traffic, and significant industrial activities, Kraków represents a typical urban environment. Two large highlands, Krakowsko-Czestochowska and Pogórze, surround the city. Morphology of the city territory induces frequent atmospheric inversion layer occupation even under fast air mass transport over the region [30]. In recent years large financial and infrastructural investment has reduced substantially the amount of so-called “low emission” sources from house heating systems. Road traffic, however, is now definitely more intense due to a greatly increasing number of cars [31]. Industrial emissions of trace gases (including hydrogen) belongs mainly to the HTS steel factory and the city power plant.

Measurements of hydrogen concentrations were carried out at stations located in two different parts of the city:

(i) AGH – close to the center of the city and next to the main roads leading from the northern to southern parts of the agglomeration. Large recreation grounds and parks are also in close vicinity to the sampling point.

(ii) IFJ – located in a suburban area at the northwest border of the city near the most frequently used roads leading from Silesia to Kraków and eastern Poland. Large grasslands covering neighboring areas close to the sampling point are expected to be a hydrogen sink in the area surrounding the station.

Analytical Methods

Two different approaches to quantify the atmospheric mixing ratio of hydrogen were studied:

(i) A dedicated commercial RGA (reduction gas analyzer) instrument (PP1 – Peak Performer 1 from Peak Laboratories) performed quasi-continuous measurements of atmospheric H_2 at Kraków – AGH station. The Peak Performer is equipped with the new generation of mercury detector with improved linearity and a backflush system using packed columns (Molsieve 5A 1.5 m as an analytical column and Unibeds 1S 1.5 m as a precolumn). The Peak Performer device scheme is plotted on Fig. 1. After installation and testing the instrument started regular measurements of H_2 in May 2007. Measurements were terminated in 2009 and the gas chromatograph was transferred to Kasprowy Wierch station.

The analog signal from PP1 was converted by ADC HP3553, and chromatograms were integrated by ChemStation software (produced by Agilent Technology Inc.). Typical uncertainty of individual H_2 analysis using reduction gas detection was on the order of ±3 ppb and the detection limit was close to 1 ppb. The inlet of the RGA instrument was connected in series with the inlet of another gas chromatograph (HP6890) measuring concentrations of other trace gases. Single hydrogen analysis was started

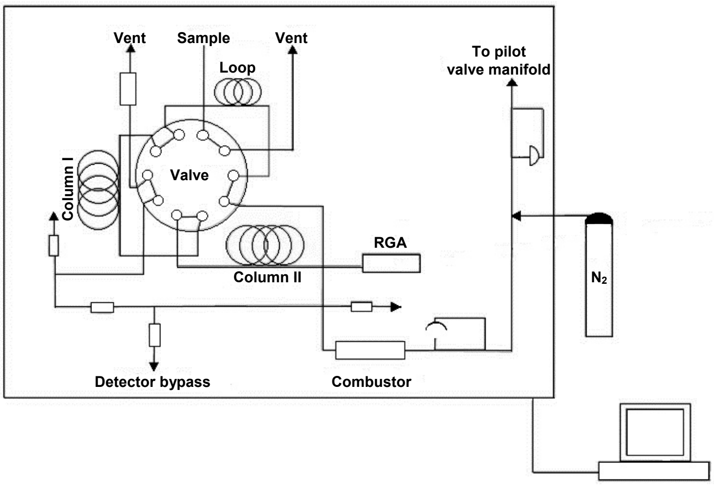

Fig. 1. Schematic diagram of the Peak Performer PP1 gas chromatograph used at the AGH site.

by external connection port of HP6890. During the measurement period the PP1 chromatograph suffered from different malfunctions causing short-term gaps in the data record. A UV lamp and its power supply was exchange twice in this period.

The local atmosphere was sampled on top of a 6-meter mast located on the roof of the laboratory building (ca. 25 m above the local ground). The air is sucked by pump through a 1/4 inch stainless steel tube at an average flow rate of 1 L/min. The inlet is split into 3 lines, each cryogenically dried. Moisture traps are kept in overpressure of 1bar to avoid contamination by the laboratory air. Dried air is injected to the RGA instrument and to HP6890 GC. Samples are injected every 37 minutes. A single analysis of hydrogen lasts 6 minutes, but HP6890 required 17 minutes for analysis of other species, and working standard was injected subsequently after each sample of ambient air. Combination of different analytical systems provides consistent information about concentration of six different gases (H_2, CO, CH_4, CO_2, N_2O, and SF_6) in the same air sample.

(ii) The Physicochemistry of Ecosystems Department at the Henryk Niewodniczański Institute of Nuclear Physics Polish Academy of Sciences has applied a different chromatographic method of hydrogen concentration measurement in the air since April 2007 [32]. The measurement program was finished in 2009.

The scheme of the measurement setup is shown on Fig. 2 [33]. This system consists of the pulsed discharge helium ionization detector (PDHID, Vici Inc. type PD-D2-I), 10-way Valco valve (V10) assembled with the sample loop and two chromatographic packed columns working in a backflush mode. The columns of 1/8 inch in diameter are packed with molecular sieves 5A, 2 m and 3 m long, respectively. Additionally, depending on the position of a 3-way valve, a sample loop can be filled with an air sample, delivered from the roof of a laboratory building or with reference gas. The T-connection between membrane pump and 3-way valve is added to prevent excessive pressure. 5.0 grade helium from Linde Gas AG, additionally purified by helium purifier HP2 (Valco Instruments), was used as the carrier gas with a flowrate of 18 ccm/min. Total helium consumption by the system was 50 ccm/min [32].

The air in the sample loop (Fig. 2), after switching the 10-position valve, is injected into column I, where it is partly separated. When neon and hydrogen are eluted the 10-position valve is switched again and the remaining gases in the first column (oxygen and nitrogen) are removed through the vent. Hydrogen and neon are separated by column II and subsequently introduced into the detector. During analyses the detector and column temperatures invariably hold at 80ºC and 50ºC, respectively. The backflush time (100 seconds) allows for sampling repetition every 10 minutes.

The whole system required occasional maintenance, including column conditioning and detector heating. Sensitivity of the instrument remains at the same level throughout the presented two-year period.

Quality Assurance

The calibration scale for hydrogen was established with the aid of three 20-liter stainless steel cylinders (Luxfer Co.) filled with synthetic air mixed with hydrogen, carbon dioxide, nitrous oxide, methane, carbon monoxide, and sulphur hexafluoride. The standard mixtures were calibrated at the Max Planck Institute for Biogeochemistry in Jena. Mixing ratios of hydrogen in the calibration cylinders are as follows: 447.0 ppb, 549.8 ppb, 1,174.2 ppb. The hydrogen mixing ratios presented in this paper are expressed in the scale "WMO-X2009" [34].

In 2008 a test leading to achieve reasonable precision was applied. The calibration of H_2 and CO was checked every 12 hours against three standards with contrasting mole fractions of H_2 and CO and corrected according to the cubic fit of detector response. However, this test resulted in

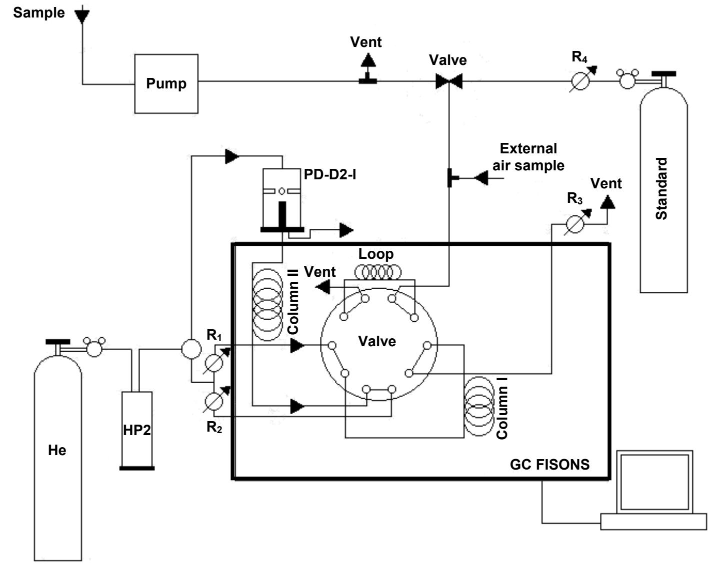

Fig. 2. Scheme of analytical setup for hydrogen measurements using PDHID detector applied at IFJ PAN site, R_1, R_2, R_3, R_4 – flow controllers, HP2 –Helium purifier, PD-D2-I – pulse discharge helium detector [33].

relatively small corrections applied in comparison to the assumption of the RGA's linear response function (0.01-1% in range 500-800 ppb). The mixing ratio of the hydrogen in Kraków air exceeds frequently 1,500 ppb. In the AGH laboratory high-value H_2 and CO mixtures also are available, which are occasionally used for dilution tests of detector linearity. Results of linearity tests performed regularly are optimistic, and the linearity of RGA detector in PP1 also for high concentrations may be expected. No correction for non-linearity was applied.

Tests of the linearity of the PDHiD detector allows us to state that linearity of the detector covers five orders of magnitude. For ambient air sample volume of 2 cm^3, the hydrogen detection limit is equal to 5 ppb (1 pg/cm^3) of hydrogen and typical uncertainty of individual H_2 analysis is in the order of ±5 ppb.

Comparison of the Instruments

To ensure full comparability of hydrogen data analyzed by both analytical techniques, the instruments were placed at the AGH station and connected to the same inlet system for 7 days a month before field deployment. The different lengths of the measurement sequences does not allow for direct comparison of the results, but we observed no significant differences in the level or amplitude of hydrogen mixing ratio variation (Fig. 3). Measurements presented here are representative for the whole period. However, some short term inconsistences were caused by sample inlet and finally after the reparation of sample delivery system only two days of parallel measurements remained for comparison.

The difference between mean values of 48 hourly averages of H_2 mixing ratio measured by both instruments during 8 and 9 of May 2007 is statistically insignificant (1.1±1.8 ppb). Variance of relative difference between mixing ratio records below 2% is acceptable for comparison of records with amplitude of 300 ppb, whereas variance of each hourly average frequently exceeds 90 ppb. Test results prooved the validity of further comparable analysis of both records.

Results and Discussion

Diurnal Variability

Short-term variation of hydrogen mixing ratio in Kraków seems to be irregular at first look. However, sources of this gas in city area are mostly connected to road traffic activity. It usually begins from 6 a.m. with maximum around 8 a.m. and decreases slightly at 10 a.m.. The afternoon rush-hour period begins at 3 p.m. and lasts until 7 p.m. Emission of hydrogen from car exhausts in Kraków is especially high due to the large number of old cars without catalysts or with catalyst not working properly. Additionally, most of the car engines function in the low oxygen regime according to the slow traffic movement [22, 35]. Hydrogen concentration in the air also depends on tropospheric mixing efficiency. Dynamics of the atmosphere depend on the solar radiation flux and the synoptic situation (high and low pressure systems and frontal situations). Kraków city air is frequently suffering from the long-lasting inversion layer with increased abundance of several trace gases [36].

Averaging the hourly mixing ratio throughout the month helps to distinguish differences between diurnal variation of hydrogen mixing ratio between both stations in relation to different seasons (Fig. 4).

Hydrogen released to the atmosphere by car exhausts during the evening rush hour [5] is consumed in the night by efficient soil sink [24]. The average amplitude of this process is the largest for winter months – 150 ppb in the city centre and rural area, when inversion of temperature begins early afternoon and remains sometimes for several days. This amplitude is exceptionally large in comparison to other European urban sites. The diurnal winter cycle in

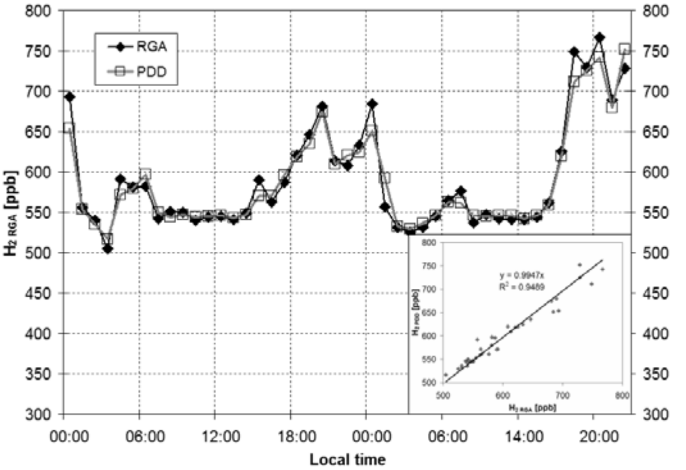

Fig. 3. Comparison of the hydrogen mixing ratio sampled from the same inlet system by two different instruments: PP1 with RGA detector (black diamonds and dark line) and GC Fissons with PDHID detector (empty squares with grey line). Each point represents hourly average of hydrogen mixing ratio results obtained by each system. The lower right panel represents correlation between both records.

Duebendorf near Zurich [5] and Bristol [7] are two times smaller, while in Helsinki diurnal variation remains at a level 10 times smaller [21]. In August diurnal variation amplitude decreases to 100 ppb at IFJ, however, remains at 150 ppb at AGH. However, in summer season clover, occasionally rising on most of the green recreation grounds, is balancing hydrogen soil uptake with substantial production [37] due to the enhanced mixing of the city air with the higher latitude troposphere concentration of hydrogen remains at a level close to the background values. Similarly, a seasonal effect may be noticed for the level of the diurnal mole fraction minima in relation to observations at the Jungfraujoch high-altitude station [38]. Due to Jungfraujoch's altitude of 3,580 m a.s.l. in the Swiss Alps, the H_2 data can be considered as primarily representative of free tropospheric background conditions over Central Europe [38]. Winter is characterized by large enrichment of the city atmosphere with hydrogen during early afternoon hours, even by 100 ppb in February observed at both stations. It also is precedent value in comparison to available reported data from other cities [5, 7, 21]. During summer the offset between both Kraków locations and background air decreases to negligible values. The difference between hydrogen observations at the stations is most obviously visible in October, when higher located suburbs of Kraków city, where the IFJ station is settled, are well ventilated, while the central district (AGH station) is frequently still within the inversion layer [30]. Then hydrogen mixing ratios at AGH are on average 100 ppb higher than at IFJ. Such a description may be applied for spring and autumn months (difference close to 50 ppb), but not for winter (when both records follow almost identically). The intensity of car traffic in the city decreases in summer parallel with the increase in soil sink efficiency [6] and in air turbulence [39]. In summer hydrogen concentrations reveal the smallest diurnal amplitude, but records from both stations still differ. During wintertime, according to the much slighter vertical temperature gradient in the troposphere, the concentrations recorded at these sites are equal. The diurnal cycle in this season is mainly driven by meteorological conditions in the Kraków atmosphere, but extremely extended concentrations are strictly connected with strong emissions occurring over the city.

Seasonal Variability

The seasonal pattern of hydrogen concentrations in Kraków is driven mainly by meteorological conditions over the city, in particular the frequency of temperature inversion in the lower troposphere. During the winter it occurs for a

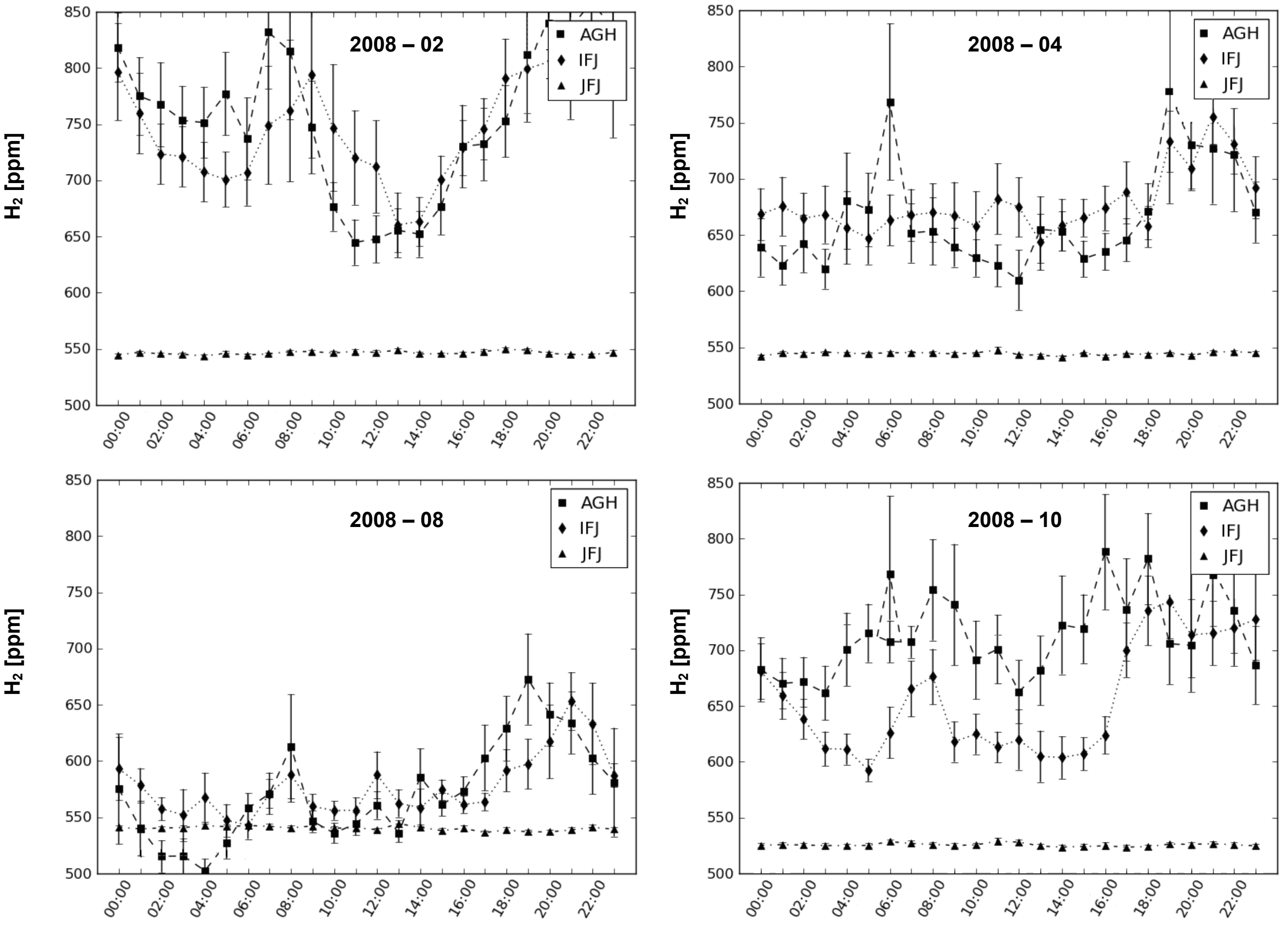

Fig. 4. Average diurnal variation of hydrogen mixing ratio in different seasons at 3 stations: AGH – University of Science and Technology, IFJ – Institute of Nuclear Physics, Polish Academy of Sciences, JFJ – Jungfraujoch mountain station in the Swiss Alps.

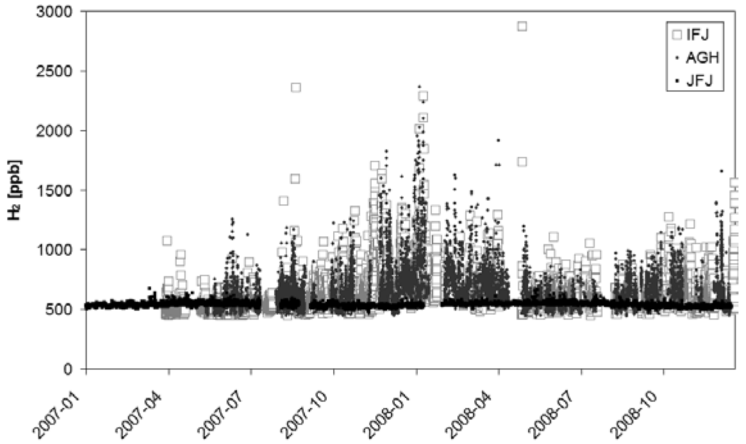

Fig. 5. Two years record of H2 mixing ratio at two different sites in Kraków (open squares – IFJ, gray dots – AGH), and at the mountain station Jungfraujoch (JFJ) in the Swiss Alps (black dots). The latter represents European background values of hydrogen mixing ratio.

several-day-period, elevating the hydrogen mixing ratio to the values even up to 1,500 ppb while values recorded in the free troposphere (station Jungfraujoch – 3,500 m a.s.l.) stays below the level of 540 ppb [38]. Efficient thermal mixing of the air within the whole troposphere over Kraków starts in May and disappears during late September. It is reflected in concentration levels of all measured trace gases at AGH station [34]. Monthly averages of hydrogen concentration are affected by its diurnal variations, which reflect both source efficiency and micrometeorological conditions in the city. Intensity of car traffic in Kraków decreases substantially during the holiday season (July and August). However, most of the green areas in the vicinity of the AGH station are becoming strong sources of hydrogen in summer months as they are lush with clover. The soil flux of hydrogen may vary strongly even on a local scale. Direct observations revealed the variability of hydrogen production from 0.5 up to 23 micromoles per hour per square meter in summer, while in winter the flux usually is slightly negative or negligible [37]. Nevertheless, hydrogen mixing ratios are definitely the lowest during the warm period (June – September) at AGH and at IFJ as well (Fig. 5).

Conclusions

A comparison of atmospheric hydrogen concentrations measured at two different locations of Kraków city underlines the role of the city in hydrogen balance with exceptionally high input from vehicle traffic emissions. Wintertime conditions favor frequent inversion of temperature, and strong emissions from car traffic over the city causes spatially homogenous enrichment of hydrogen over the whole city, which is not balanced by soil decomposition. The mixing ratio of hydrogen is frequently doubled during winter over the whole area of the city. During the summer season many different components (soil sink, biological production, car traffic sources, and air mixing) influence hydrogen concentrations in the lower troposphere, increasing its spatial variability.

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References

1. KHALIL M.A.K., RASMUSSEN R.A. Global increase of atmospheric molecular hydrogen. Nature **347**, 743, **1990**.
2. SCHMIDT U. The latitudinal and vertical distribution of molecular hydrogen in the troposphere. J. Geophys. Res. **83**, 941, **1978**.
3. SCRANTON M.I., BARGER W.R., HERR F.L. Molecular hydrogen in the urban troposphere: measurements of seasonal variability. J. Geophys. Res. **85**, 5575, **1980**.
4. SIMMONDS P.G., DERWENT R.G., O'DOHERTY S., RYALL D.B., STEELE L.P., LANGENFELDS R.L., SALAMEH P., WANG H.J., DIMMER C.H., HUDSON L.E. Continuous high-frequency observations of hydrogen at the Mace Head baseline atmospheric monitoring station over the 1994-1998 period, J. Geophys. Res., **105**, 12105, **2000**.
5. STEINBACHER M., FISCHER A., VOLLMER M.K., BUCHMANN B., REIMANN S., HUEGLIN C. Perennial observations of molecular hydrogen (H_2) at a suburban site in Switzerland. Atmos. Environ. **41**, 2111, **2007**.
6. HAMMER S., LEVIN I. Seasonal variation of the molecular hydrogen uptake by soils inferred from continuous atmospheric observations in Heidelberg, southwest Germany. Tellus B, **61**, (3), 556, **2009**.

7. GRANT A., STANLEY K.F., HENSHAW S.J., SHALLCROSS D.E., O'DOHERTY S. High-frequency urban measurements of molecular hydrogen and carbon monoxide in the United Kingdom, Atmos. Chem. Phys., **10**, 4715, **2010**.
8. PRATHER M.J., An environmental experiment with H_2?. Science **302**, 581, **2003**.
9. SCHULTZ M.G., DIEHL T., BRASSEUR G.P., ZITTEL W. Air pollution and climate-forcing impacts of a global hydrogen economy. Science **302**, 624, **2003**.
10. TROMP T.K., SHIA R.-L., ALLEN M., EILER J.M., YUNG Y.L. Potential environmental impact of a hydrogen economy on the stratosphere. Science **300**, 1740, **2003**.
11. WARWICK N.J., BEKKI S., NISBET E.G., PYLE J.A. Impact of a hydrogen economy on the stratosphere and troposphere studied in a 2-D model. Geophys. Res. Lett. **31**, L05107 doi:10.1029/2003GL019224. **2004**.
12. CONSTANT P., POISSANT L., VILLEMUR R. Tropospheric H_2 budget and the response of its soil uptake under the changing environment. Sci. Total Environ., **407**, 1809, **2009**.
13. EHHALT D.H., ROHRER F. The tropospheric cycle of H_2: a critical review. Tellus B, **61**, 500, **2009**.
14. RAHN T., EILER J.M., BOERING K.A., WENNBERG P.O., McCARTHY M.C., TYLER S., SCHAUFFLER S., DONNELLY S., ATLAS E. Extreme deuterium enrichment in stratospheric hydrogen and the global atmospheric budget of H_2. Nature, **424**, 918, **2003**.
15. NOVELLI P.C., LANG P.M., MASARIE K.A., HURST D.F., MYERS R., ELKINS J.W. Molecular hydrogen in the troposphere: Global distribution and budget, J. Geophys. Res., **104**, 30427, **1999**.
16. PRICE H., JAEGL´E L., RICE A., QUAY P., NOVELLI P.C., GAMMON R. Global budget of molecular hydrogen and its deuterium content: constraints from ground station, cruise, and aircraft observations. J. Geophys. Res., **112**, D22108, doi:10.1029/2006JD008152, **2007**.
17. CONRAD R., SEILER W. Influence of temperature, moisture and organic carbon on the flux of H_2 and CO between soil and atmosphere: Field studies in subtropical regions. J. Geophys. Res., **90**, 5699, **1985**.
18. RHEE T.S., BRENNINKMEIJER C.A.M., ROCKMANN T. The overwhelming role of soils in the global atmospheric hydrogen cycle. Atmos. Chem. Phys., **6**, 1611, **2006**.
19. SCHMITT S., HANSELMANN A., WOLLSSCHLAGER U., HAMMER S., LEVIN I. Investigation of parameters controlling the soil sink of atmospheric molecular hydrogen. Tellus B, **61**, 416, **2009**.
20. XIAO X., PRINN R.G., SIMMONDS P., NOVELLI P.C., HUANG L., LANGENFELDS R.L., O'DOHERTY S., KRUMMEL P.B., FRASER P.J., PORTER L.W., WEISS R.F., SALAMEH P., WANG H.J. Optimal estimation of the soil uptake rate of molecular hydrogen from the Advanced Global Atmospheric Gases Experiment and other measurements. J. Geophys. Res., **112**, D07303, doi:10.1029/2006JD007241, **2007**.
21. AALTO T., LALLO M., HATAKKA J., LAURILA T. Atmospheric hydrogen variations and traffic emissions at an urban site in Finland. Atmos. Chem. Phys., **9**, 7387, **2009**.
22. VOLLMER M.K., JUERGENS N., STEINBACHER M., REIMANN S., WEILENMANN M., BUCHMANN B. Road vehicle emissions of molecular hydrogen (H_2) from a tunnel study. Atmos. Environ., **41**, 8255, **2007**.
23. YVER C., SCHMIDT M., BOUSQUET P., ZAHOROWSKI W., RAMONET M. Estimation of the molecular hydrogen soil uptake and traffic emissions at a suburban site near Paris through hydrogen, carbon monoxide, and radon-222 semicontinuous measurements. J. Geophys. Res, **114**, D18304, doi:10.1029/2009JD012122, **2009**.
24. LALLO M., AALTO T., HATAKKA J., LAURILA T. Hydrogen soil deposition at an urban site in Finland. Atmos. Chem. Phys., **9**, 8559, **2009**.
25. BELLUCCI F., BOGNER J.E., STURCHIO N.C. Urban Geochemistry: Greenhouse Gas Emissions at the Urban Scale. Elements, **8**, 445, **2012**.
26. HAMMER S., VOGEL F., KAUL M., LEVIN I. The H_2/CO ratio of emissions from combustion sources: comparison of top-down with bottom-up measurements in southwest Germany, Tellus B, **61**, (3), 547, **2009**.
27. YVER C.E., PISON I.C., FORTEMS-CHEINEY A., SCHMIDT M., CHEVALLIER F., RAMONET M., JORDAN A., SØVDE O.A., ENGEL A., FISHER R.E., LOWRY D., NISBET E.G., LEVIN I., HAMMER S., NECKI J., BARTYZEL J., REIMANN S., VOLLMER M. K., STEINBACHER M., AALTO T., MAIONE M., ARDUINI J., O'DOHERTY S., GRANT A., STURGES W.T., FORSTER G.L., LUNDER C.R., PRIVALOV V., PARAMONOVA N., WERNER A., BOUSQUET P. A new estimation of the recent tropospheric molecular hydrogen budget using atmospheric observations and variational inversion. Atmos. Chem. Phys., **11**, 3375, **2011**.
28. BARNES D.H., WOFSY S.C., FEHLAU B.P., GOTTLIEB E.W., ELKINS J.W., DUTTON G.S., NOVELLI P.C. Hydrogen in the atmosphere: observations above a forest canopy in a polluted environment, J. Geophys. Res., **108**, 4197, doi:10.1029/2001JD001199, **2003**.
29. SANDERSON M.G., COLLINS W.J., DERWENT R.G., JOHNSON C.E. Simulation of global hydrogen levels using a Lagrangian three-dimensional model. J. Atmos. Chem., **43**, 15, **2003**.
30. WIOŚ Kraków – National report about state of environment – Malopolska province, **2008**.
31. A comprehensive assessment of the safety of traffic on the national road network subordinated to DODP Krakow for the years 1995-1997. Office of Design and Research Roads and Bridges “Transprojekt – Warszawa”,” Warszawa, maj, **1998**.
32. GROMBIK I. Elaboration a gas chromatographic method for the continuous hydrogen concentration measurement in the air, PhD Thesis, Institute of Nuclear Physics Polish Academy of Sciences, Krakow **2009** [In Polish], http://www.ifj.edu.pl/msd/rozprawy_dr/rozpr_Grombik.pdf
33. GROMBIK I., LASA J., ŚLIWKA I., MOCHALSKI P., PUSZ J., JACKOWICZ-KORCZYŃSKI M. The new methodology of hydrogen measurement in the air; Environment Protection Engineering, **32**, No.3/2006, PL ISSN 3024-8828, Index 357200, 75, **2006**.
34. JORDAN A., STEINBERG B. Calibrating Measurements of Atmospheric Hydrogen, Atmos. Meas. Tech., **4**, 509, **2011**.
35. VOLLMER M.K., WALTER S., BOND S.W., SOLTIC P., RÖCKMANN T. Molecular hydrogen (H_2) emissions and their isotopic signatures (H/D) from a motor vehicle: implications on atmospheric H_2. Atmos. Chem. Phys., **10**, 5707, **2010**.
36. ZIMNOCH M., JELEN D., GALKOWSKI M., KUC T., NECKI J., CHMURA L., GORCZYCA Z., JASEK A.,

RÓŻAŃSKI K. Partitioning of atmospheric carbon dioxide over Central Europe: insights from combined measurements of CO_2 mixing ratios and their carbon isotope composition. Isot. Environ. Healt. S., **48**, (3), 421, **2012**.

37. BARTYZEL J., NECKI J.M., ZIEBA D., ROZANSKI K., GASIOREK M. Uptake of atmospheric hydrogen by soils: a case study from southern Poland. Eur. J. Soil Sci., **64**, 597, **2013**.
38. BOND S.W., VOLLMER M.K., STEINBACHER M., HENNE S., REIMANN S. Atmospheric molecular hydrogen (H_2): observations at the high-altitude site Jungfraujoch, Switzerland, Tellus B, **63**, (1), 64, **2011**.
39. PAWLAK W., FORTUNIAK K., SIEDLECKI M. Carbon dioxide flux in the centre of Łódź, Poland – analysis of a 2-year eddy covariance measurement data set. Int. J. Climatol., **31**, 232, **2011**.