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Estimation of hydrogen deposition velocities from 1995–2008 at Mace Head, Ireland using a simple box model and concurrent ozone depositions

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ABSTRACT

During stable nocturnal inversions with low wind speeds, we observed strong depletions of both hydrogen and ozone caused by deposition to the peat bogs in the vicinity of the Mace Head Atmospheric Research Station, Connemara, County Galway, Ireland. From these temporally correlated fluxes and using a simple box model, we have estimated the strength of the molecular hydrogen soil sink over a 14-yr period (1995–2008). Over this entire period 269 nocturnal deposition events were identified that satisfied the strict selection criteria. The average hydrogen deposition velocity determined from these events was 0.53 mm s^{-1}, covering a range of 0.18–1.29 mm s^{-1}, which is in agreement with the range of deposition velocities reported in the literature for similar peaty biomes. By annually averaging all of the nocturnal inversion events over the most seasonally active period from April–September we reveal a positive correlation with ambient temperature in the relative deposition velocities of hydrogen and ozone, which is not readily apparent in all of the individual events. Furthermore, average hydrogen deposition velocities and accumulated rainfall from 48 h before and during each event were to a reasonable extent anti-correlated. However, due to the large uncertainties in determining monthly mean H_2 deposition velocities there is no statistically significant trend in the hydrogen deposition velocities over time.

1. Introduction

Molecular hydrogen (H_2) is a major component of the atmosphere with a tropospheric average mole fraction of about 530 ppb (Novelli et al., 1999; Xiao et al., 2007). H_2 is also an indirect greenhouse gas and through various atmospheric processes impacts both tropospheric and stratospheric chemistry (Ehhalt and Rohrer, 2009 and references therein). Recent interest in the budget of atmospheric H_2 has arisen from the potential implications of adopting a H_2 fuel economy (Prather, 2003; Schultz et al., 2003; Tromp et al., 2003; Warwick et al., 2004) although, at present, there appears to be no observable trend in the global background H_2 mixing ratio (Grant et al., 2010).

Four major H_2 sources have been identified, two photochemical oxidation of methane (CH_4) and the non-methane hydrocarbons, via formaldehyde photolysis and two combustion sources fossil fuel and biomass burning (Langenfelds et al., 2002; Barnes et al., 2003; Xiao et al., 2007; Ehhalt and Rohrer, 2009). Minor sources include biogenic N_2 fixation (Conrad and Seiler, 1980; Constant et al., 2009) and emissions from the oceans (Schmidt, 1974). There are two major H_2 sinks, oxidation by OH and uptake by soils, the latter having the greatest uncertainty (Prather, 2003) and which may account for about 70–80% of the total H_2 loss (Liebl and Seiler, 1976; Rahn et al., 2002; Sanderson et al., 2003; Rhee et al., 2006; Xiao et al., 2007; Lallo et al., 2009; Yver et al., 2009). There is also a minor sink, oxidation by OH in the stratosphere (Price et al., 2007).

H_2 mole fractions in the southern hemisphere are higher than those in the northern hemisphere (NH), due to the larger land mass area in the NH and consequently greater loss through the soil sink. Furthermore, there is a seasonal component to this soil loss with higher uptake in the summer months and more significantly on an annual average basis approximately 2/3 of the total H_2 soil loss occurs in the NH (Novelli et al., 1999; Ehhalt and Rohrer, 2009).

Most recent studies suggest that soil uptake of H_2 is diffusion controlled and therefore dependant on soil properties of texture and moisture as well as biological factors (Smith-Downey

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et al., 2006; Yonemura et al., 1999, 2000; Gerst and Quay., 2001; Hammer and Levin., 2009; Schmitt et al., 2009). H_2 consumption is dominated by abiotic enzymes in upland soils and by methanogens, sulphate, and ferric ion reducers, and knallgas bacteria in wetland soils (Conrad and Seiler, 1981; Conrad, 1996; Guo and Conrad, 2008; Constant et al., 2008). H_2 deposition velocities in subtropical regions were reported to be independent of soil temperature but affected by soil hydrology and soil properties (Conrad and Seiler, 1980, 1985). From studies in forest, andisol fields and arable fields (Yonemura et al., 1999) concluded that H_2 deposition velocities were inversely related to soil moisture.

The continuous, high-frequency, in situ observations of greenhouse gases at the Mace Head Atmospheric Research Station, as part of the AGAGE programme (Prinn et al., 2000), provide evidence of local sources and sinks that may be attributed to the peat bogs in the vicinity of the station. Using the long-term atmospheric baseline air observations, under a stable boundary layer with strong night-time inversions, low wind speeds and a simple box model, we estimate the deposition of H_2 from the temporally correlated nocturnal depositions of ozone (O_3). The diurnal cycle of O_3 observed at rural locations has been attributed to the destruction of O_3 below the nocturnal inversion, the morning increase being due to downwards mixing of air from aloft as the height of the well mixed layer (the boundary layer) increases (Garland and Derwent, 1979). O_3 deposition at night requires that turbulent mixing continues near the surface but depletion of surface layers needs suppression of turbulence at greater heights.

This box model method has been used to determine natural methane (CH_4) and chloroform ($CHCl_3$) emissions from the peat bog biomes, which surround the Mace Head site (Derwent et al., 2009; Simmonds et al., 2010). This study extends our earlier investigation of the simultaneous deposition of H_2 and O_3 (1994–1998) from which we derived a H_2 deposition velocity of 0.26 mm s^{-1} (Simmonds et al., 2000). From concurrent H_2 and O_3 observations we construct a 14-year record (1995–2008) of H_2 deposition velocities at Mace Head, Ireland, which to our knowledge is the longest record available and provides an opportunity to assess if there has been any long-term trend in H_2 depositions driven by changing climatic conditions.

2. Mace head atmospheric research station

The Mace Head Atmospheric Research Station is located in Connemara, Co. Galway on the Atlantic Ocean coastline of Ireland at 53°19′33″N, 9°53′58″ W and offers a clean sector from 180° through west to 300°. Meteorological records show that on average approximately 70% of the air masses arrive at the station in the clean air sector (Manning et al., 2003). Air is sampled at a height of 14 m above sea level from a tower situated 90 metres from the shore-line and 50 m from high water.

Blanket peat bogs cover the surface in the immediate vicinity of Mace Head with about 20% exposed rock. The soil is a mixture of peat, peaty gleys and peaty podzols, with a depth that varies from a few centimetres on hill slopes to a few metres on flatter ground, extending many kilometres to the east (http://maps.epa.ie/InternetMapViewer/mapviewer.aspx). There are few trees, with the vegetation consisting mainly of grasses, sedges, ferns, rushes, gorse and heathers (Dimmer et al., 2001; http://macehead.org).

Calibrated H_2 measurements are recorded every 40 min using an automated custom-built sampling module coupled with a Reduction Gas Analyzer RGA-3 (Trace Analytics, Inc). Standard calibration and ambient air analyses were alternated 36 times throughout each day, (Prinn et al., 2000). Non-linearities were determined at regular intervals using H_2 standards with higher and lower mixing ratios relative to ambient values and by dynamic dilution of a high concentration primary standard. Calibration standards were referenced against a calibration scale developed at CSIRO (Commonwealth Scientific and Industrial Research Organization; Simmonds et al., 2000) intercalibrations have also been carried out between the CSIRO and Max Plank Institute (MPI2009) scales with the MPI2009 values approximately 16 ppb higher than CSIRO (Grant et al., 2010).

O_3 measurements were acquired every 10s using a commercial UV spectrometer (Model 8810, Monitor Labs, San Diego, CA, USA). The measurements were recorded as 1 min averages which were filtered for invalid data prior to calculation of hourly averages. The instrument calibration is checked every 3–6 months (www.netcen.co.uk) against a primary UV photometer (Sweeney and Stacey, 1992). On 10 March 2003, the Monitor Labs instrument was replaced with a new analyser (Model 49C, Thermo Electron Inc, CO, USA). Both instruments have been regularly validated by a system and performance audit conducted by the World Calibration Centre for surface O_3, (WCC-EMPA, 2002) and the performance criteria have consistently been passed as good (Derwent et al., 2007).

3. The box model

To quantify the H_2 depositions to the peat bogs surrounding the Mace Head Atmospheric Research Station we have used the same box model as described in Derwent et al. (1995, 2009). The box model has been formulated to represent the time behaviour of a trace gas, x, undergoing deposition within a shallow nocturnal inversion under poor dispersion conditions. An imaginary box of unit base area is placed on the ground above the peat bog with its top surface at a height, h, which represents the effective mixing height of the trace gas in the shallow boundary layer.

For a depositing trace gas, x, the rate of depletion of the trace gas concentrations c_x (g m^{-3}) in the box is given by equation (1):

$$Dc_x/dt = -j_x/h, \quad (1)$$

where j_x is the flux or mass deposition rate of the trace gas per unit area per second (g m^{-2} sec^{-1}).

In equation (1), the box depth, h, is chosen to represent the vertical spread of the trace gas driven by the turbulent motions of the air as it moves across the peat bog. The deposition of the trace gas, the volume (and thus h) from which the gas is mixed needs to be severely limited by a strong inversion at a low altitude.

From the definition of the deposition velocity, v_x, of a trace gas (Chamberlain et al., 1979; Hammer et al., 2009), then:

$$-1/c_x \; dc_x/dt = v_x/h \tag{2}$$

and rearranging for the case of two independently depositing trace gases, i and x:

$$-1/c_1 \; dc_i/dt \; 1/v_i = -1/c_x \; dc_x dc_x/dt \; 1/v_x. \tag{3}$$

Thus, the simultaneous rates of deposition of two different trace gases (i and x) should provide an assessment of the relative deposition velocities for the trace gases. If the deposition velocity of one trace gas can be estimated, then that of the other can be deduced from equation 3. Further details of the 'nocturnal box method' for determining trace gas fluxes in terrestrial and aquatic ecosystems is given by Fowler (1999) and Denmead et al. (1999).

4. Data selection

For the box model approach, detailed in equation 3 above, to work reliably, a number of conditions have to be satisfied so that erroneous estimates are not generated. These conditions were considered satisfied if:

(1) measured wind speeds were less than 4 m s^{-1},

(2) the well mixed mid-afternoon trace gas concentrations were close to baseline levels, which define the concentration before the onset of the depletion event and hence the rate of subsequent depletion. The baseline concentrations levels were determined using the NAME (Numerical Atmospheric dispersion Modelling Environment) model (Manning et al., 2003),

(3) no transport from Europe. Determined using the NAME model (Manning et al., 2003),

(4) no local emissions due to biomass burning events. Determined by the absence of carbon monoxide (CO) pollution events.

The NAME model is a Lagrangian atmospheric dispersion model that uses 3-D meteorology from the UK Met Office's numerical weather prediction model to predict how material dilutes in the atmosphere (Manning et al., 2003). Here the model has been used to predict the recent (12 day) history of the air as it travels to the observation station and in particular the impact of recent surface depositions.

A total of 269 local events satisfied the conditions required for the application of the simple box model to estimate the rates of deposition of H_2. The duration of these events ranged from 2–10 h and the number of events in each month are summarised in Table 1. Events that did not satisfy these criteria or were less than 2 h duration were excluded from the analysis. Due to instrumental problems no data were available during April–May 2006.

5. Results and discussion

Under stable nocturnal atmospheric conditions with low wind speeds, we observe fluxes of trace gases to and from the peat bogs surrounding the Mace Head site during each month between April and September. Generally there are far too few events in the winter period (October–March) to be statistically meaningful, due to fewer strongly stable nocturnal inversions. Of special interest to this study is the near simultaneous decrease in night-time molar fractions of O_3 and H_2 due to deposition under a stable boundary layer. Figure 1(a–c) records the temporally correlated decreases in H_2 and O_3 concentrations during several night-time events. For example, during the afternoon of 17 July 1997 (Fig. 1a), H_2 and O_3 mole fractions were close to their baseline monthly mean concentrations of ~500 and 31 ppb, respectively. Both gases then decline beginning around 2200 h reaching minimum concentrations of 460 ppb (H_2 loss of 40 ppb) and 18 ppb (O_3 loss of 13 ppb) at about 0600 h, before recovering back to their baseline levels. Over this 8-h period there was a strong correlation between the nocturnal depletion of both gases ($r^2 = 0.72$, $n = 8$). Similar decreases in the magnitudes of the H_2 and O_3 mixing ratios were observed in Fig. 1b during the nights of 18th, 19th, and 20th July 2000 ($r^2 = 0.72$; 0.76; 0.71, $n = 8$) and the 11th and 12th of May 2007 (Fig. 1, $r^2 =$ 0.75; 0.94; $n = 8$). This close temporal correlation between O_3 and H_2 provides confidence that ozone can be used to estimate H_2 deposition. Therefore, using the nocturnal box method and the mass balances between H_2 deposition and O_3 depletion, we have determined average monthly H_2 deposition velocities from 1995–2008. Even with the relatively large spatial integration, depositions are still quite variable during individual nocturnal events. It is further assumed that the blanket peat bog extends uniformly away from the sampling position and the extent of the peat bog is greater than the horizontal dimensions of the nocturnal box model.

Figure 2 shows a plot of the hourly H_2 deposition rate versus the hourly O_3 deposition rate during the local deposition events shown in Fig. 1(a–c). The points show a reasonable degree of correlation with a slope of 0.18 ± 0.07, $R^2 = 0.22$. The hourly points are subject to considerable error because the inaccuracies in their respective measurements ($\pm 2\%$ for O_3 and $\pm 1.0\%$ for H_2) are amplified in estimating the mole fraction differences used to estimate destruction rates. To the authors' knowledge, the study of ozone depletion to the blanket peat of Auchencorth Moss, an extensive blanket bog in the Scottish Borders by Fowler et al. (2001) is the most appropriate study of deposition to peat

Table 1. H_2 deposition velocities (mm s^{-1}) during stable nocturnal events from 1995 to 2008

Year	Month	Number of events	Mean H_2 deposition velocities mm s^{-1} (range mm s^{-1})	Average temperature (°C) during events[a,b]	Accumulated rainfall (cm)[c]
1995	April	3	0.53 (0.49–0.61)	6.5	0.81
	May	3	0.43 (0.21–0.59)	8.8	1.2
	June	2	0.37 (0.33–0.41)	11.0	2.04
	July	3	0.47 (0.27–0.59)	15.4	2.67
	August	5	0.5 (0.34–0.79)	16.1	0.58
	September	2	0.6 (0.37–0.84)	10.7	1.13
1996	April	3	0.39 (0.21–0.5)	6.0	4.1
	May	3	0.72 (0.43–0.87)	5.6	0.06
	June	3	0.39 (0.17–0.74)	10.7	2.68
	July	3	0.4 (0.26–0.38)	12.3	1.52
	August	4	0.48 (0.37–0.56)	11.5	3.01
	September	2	0.42 (0.35–0.49)	16.3	0.36
1997	April	5	0.56 (0.35–0.9)	8.4	2.14
	May	3	0.51 (0.31–0.76)	13.1	2.93
	June	4	0.47 (0.29–0.8)	11.0	4.29
	July	5	0.6 (0.26–1.43)	13.8	7.16
	August	5	0.41 (0.17–0.6)	13.8	2.54
	September	1	0.26	10.2	0.45
1998	April	4	0.38 (0.2–0.63)	5.4	2.96
	May	2	0.22 (0.2–0.24)	8.7	2.27
	June	3	0.62 (0.17–0.93)	12.1	1.31
	July	4	0.33 (0.2–0.44)	12.7	4.22
	August	2	0.62 (0.43–0.81)	9.9	5.16
	September	2	0.3 (0.12–0.48)	12.0	6.42
1999	April	2	0.93 (0.24–1.62)	6.5	3.78
	May	2	0.21 (0.17–0.25)	11.7	2.32
	June	5	0.63 (0.36–1.17)	11.6	1.23
	July	3	0.54 (0.18–0.9)	15.2	2.44
	August	4	0.41 (0.28–0.59)	15.2	5.22
	September	2	0.7 (0.32–1.07)	15.5	5.26
2000	April	1	0.613	7.7	0.6
	May	2	0.49 (0.4–0.58)	9.1	1.77
	June	7	0.46 (0.19–0.63)	12.3	0.66
	July	6	0.47 (0.29–0.58)	14.6	1.91
	August	5	0.53 (0.22–0.94)	11.3	4.31
	September	1	0.18	11.7	0.96
2001	April	3	0.36 (0.24–0.625)	7.9	4.59
	May	8	0.58 (0.12–1.24)	10.0	3.56
	June	6	0.37 (0.23–0.61)	11.8	5.44
	July	3	0.47 (0.31–0.56)	11.9	2.25
	August	3	0.4 (0.17–0.54)	11.6	2.08
	September	3	0.54 (0.11–0.87)	9.0	0.62
2002	April	3	0.74 (0.43–0.94)	5.7	1.77
	May	2	0.36 (0.23–0.49)	7.8	2.34
	June	1	0.5	11.6	3.16
	July	3	0.42 (0.36–0.51)	13.1	1.77
	August	2	0.81 (0.51–1.1)	12.5	7.35
	September	2	0.66 (0.49–0.84)	12.8	5.11

Table 1. Continued

Year	Month	Number of events	Mean H_2 deposition velocities mm s^{-1} (range mm s^{-1})	Average temperature (°C) during events[a,b]	Accumulated rainfall (cm)[c]
2003	April	3	0.53 (0.41–0.68)	7.5	0.84
	May	3	0.83 (0.38–1.59)	8.1	6.12
	June	2	1.05 (0.83–1.26)	14.4	0.26
	July	2	0.49 (0.45–0.52)	15.3	4.38
	August	8	0.62 (0.3–0.98)	14.9	3.05
	September	7	0.68 (0.16–1.1)	12.2	5.03
2004	April	3	0.56 (0.2–0.87)	7.3 (7.6)	2.58
	May	3	0.77 (0.33–1.25)	8.6 (9.8)	0.63
	June	2	0.9 (0.75–1.04)	12.1 (12.2)	0.56
	July	5	0.48 (0.37–0.7)	12.5 (12.7)	4.39
	August	4	0.88 (0.31–1.45)	11.6 (12.9)	2.38
	September	2	0.27 (0.26–0.27)	15.7 (15.1)	2.22
2005	April	2	0.58 (0.56–0.61)	6.5 (7.9)	4.84
	May	2	0.82 (0.79–0.84)	7.9 (9.2)	0.26
	June	3	0.55 (0.2–0.85)	12.5 (12.7)	0.57
	July	4	0.5 (0.31–0.74)	13.9 (13.7)	2.95
	August	6	0.62 (0.34–0.96)	13.5 (13.9)	4.57
	September	5	0.63 (0.35–0.98)	12.6 (13.7)	3.41
2006	April	No Data[d]			
	May	No Data[d]			
	June	5	0.73 (0.12–1.42)	11.2 (11.3)	0.4
	July	2	0.64 (0.53–0.75)	17.0 (16.8)	2.72
	August	4	0.54 (0.20–1.04)	11.8 (12.1)	3.86
	September	2	1.29 (1.20–1.37)	14.7 (16.0)	1.4
2007	April	3	0.57 (0.42–0.67)	7.4 (8.6)	0.28
	May	6	0.61 (0.39–1.02)	8.6 (9.5)	5.44
	June	2	0.55 (0.52–0.58)	7.6 (9.5)	1.86
	July	3	0.5 (0.40–0.58)	12.7 (13.3)	3.28
	August	3	0.44 (0.36–0.49)	12.8 (13.0)	3.29
	September	1	0.48	15.2 (15.2)	0.0
2008	April	2	0.66 (0.57–0.75)	7.3 (7.4)	1.1
	May	3	0.43 (0.17–0.72)	11.4 (11.5)	3.25
	June	4	0.46 (0.13–0.95)	11.8 (12.5)	1.66
	July	4	0.51 (0.32–0.75)	13.0 (13.8)	1.47
	August	2	0.48 (0.25–0.7)	15.0 (15.1)	1.26
	September	1	0.28	14.2 (13.2)	1.66

[a]Average ambient temperatures were recorded during the time course of the deposition events using the mean of the temperatures recorded at the Irish meteorological stations of Bellmullet and Shannon (1995–2008), courtesy of Met Éireann.
[b]From 2004–2008 local ambient temperatures recorded at Mace Head were used. Values in parenthesis.
[c]Accumulated rainfall (cm) from 48 h before and during the course of each event were obtained from the meteorological records of the Connemara State Park adjacent to Mace Head, courtesy of Met Éireann.
[d]No H_2 measurements were available in April–May 2006 due to instrumental failure.

bogs in the British Isles covering similar climatic conditions. Furthermore, we have successfully employed ozone deposition and the nocturnal box method to infer methane and chloroform emissions during local pollution events (Derwent et al., 2009; Simmonds et al., 2010). On this basis, the deposition velocity for O_3, v_d, is of the order of 2.6 ± 0.2 mm s^{-1} and combining this estimate with the slope from Fig. 2, an estimate can be made of the H_2 deposition velocity of 0.46 ± 0.18 mm s^{-1}. This is a reasonable order of magnitude estimate of the H_2 deposition velocity to the blanket peat bog.

When we have applied the nocturnal box model method during the most active period of deposition (2200–0600 h) and

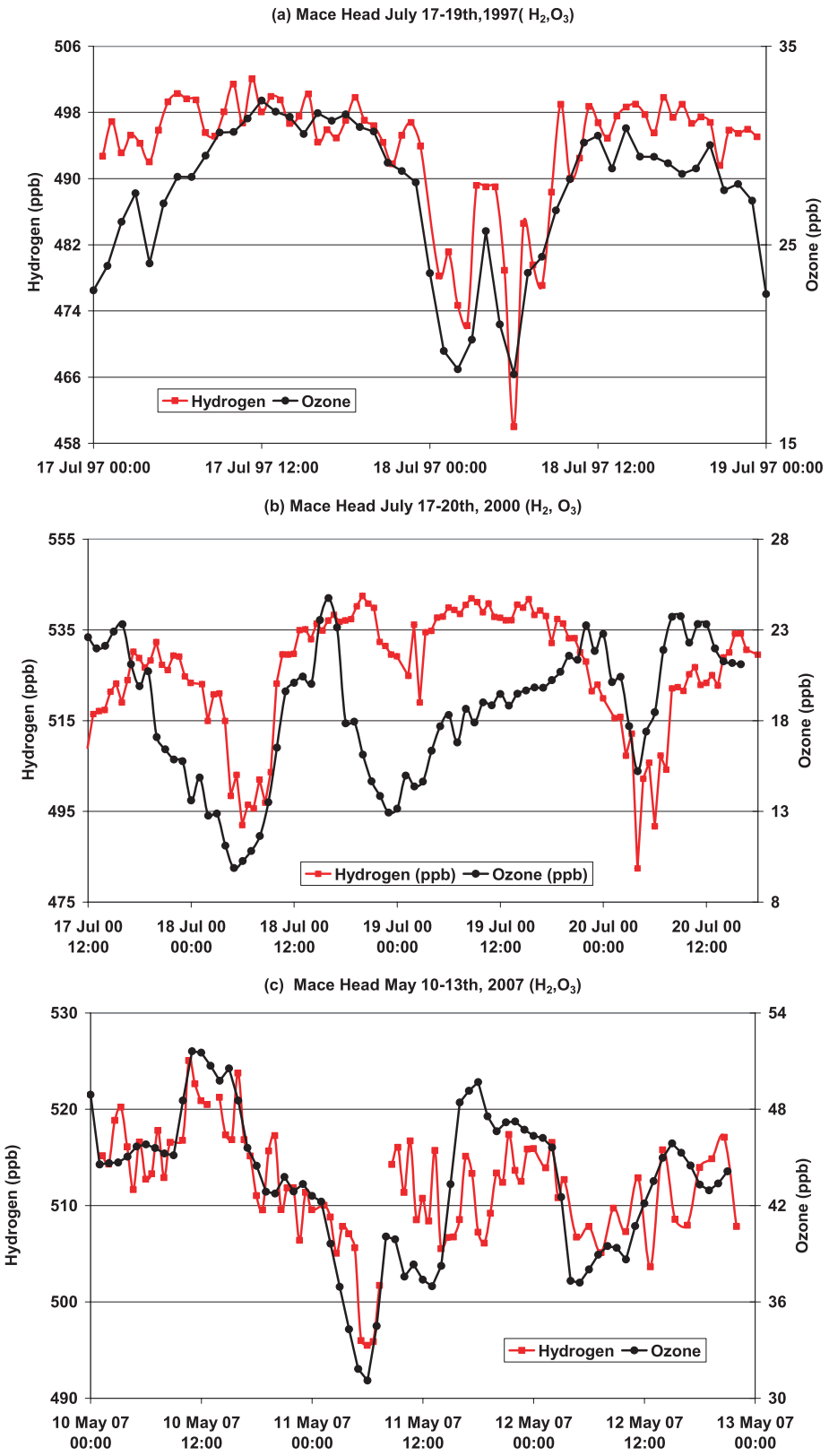

Fig. 1. Temporally correlated nocturnal depositions of hydrogen and ozone.

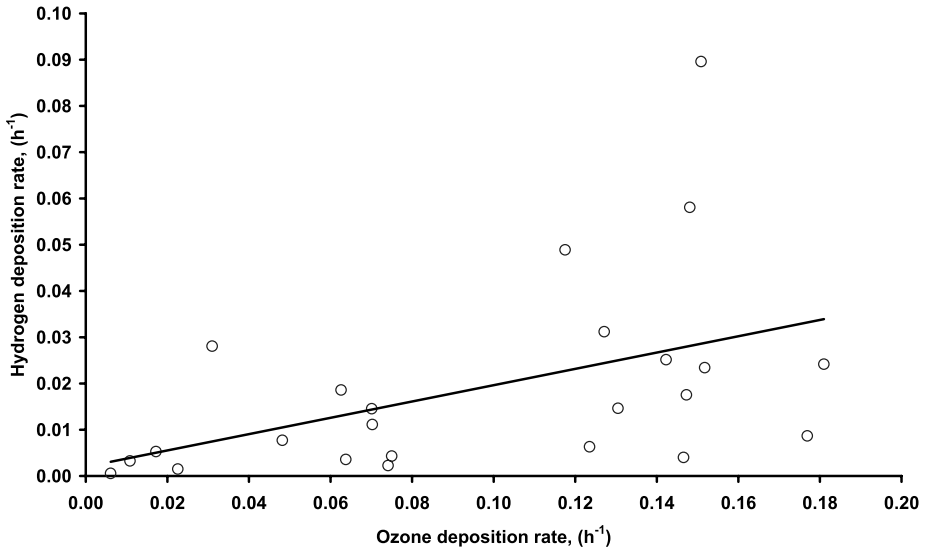

Fig. 2. Hourly H_2 deposition rate versus the hourly O_3 deposition rate.

deposition velocities are at a minimum, our assumption is that O_3 deposition to the blanket peat bog is controlled by non-stomatal resistances (Fowler et al., 2001). An important issue is then the choice of the single value (2.6 ± 0.2 mm s^{-1}) for the O_3 deposition velocity, since Fowler et al. (2001) show how it varies diurnally, seasonally and interannually. However, Coyle (2006) presents a more complete analysis of the observations, splitting them by wet, dry and freezing surface conditions. Under wet conditions, there is little apparent temperature sensitivity over the temperature range from 5 to 30 °C. Because of the marine location of the blanket peat bogs in the vicinity of the Mace Head station and the temperate climate, we consider that the assumption of a constant O_3 deposition velocity over our set of observations is justified. Nevertheless, it should be borne in mind that our observations provide only an estimate of the relative dry deposition of H_2 and O_3. A major limitation of our study is the lack of surface observations of temperature, humidity and soil moisture data at the Mace Head location.

The events in each month were averaged and the results of the 269 events, which satisfied the data selection criteria are presented in Table 1, with H_2 deposition velocities reported in mm s^{-1}. Also in Table 1 we report the measured average ambient temperature over the time course of the events and the accumulated rainfall of each month's events from 48 h before and during the time of each event. The rainfall records were obtained from the Connemara National Park adjacent to the Mace Head location, in lieu of soil moisture measurements, which were not recorded at the station. The long-term average H_2 deposition velocity from all 269 nocturnal events was 0.53 mm s^{-1} (s.d 0.16 mm s^{-1}) with a range of 0.18–1.29 mm s^{-1}, relative to an O_3 deposition velocity of 2.6 ± 0.2 mm s^{-1}.

To explore the possible causes of the monthly and interannual variability of the molecular H_2 soil sink, Fig. 3(a–f) plots the average H_2 monthly deposition velocity versus the monthly average temperature over the duration of the local events in each month (April–September) and also the accumulated rainfall for each months events (48 h before and during each event). Routine temperature measurements began at Mace Head in 2004, therefore prior to 2004 we have averaged the temperature records of the two closest Irish meteorological stations of Bellmullet and Shannon, at a distance of approximately 130 and 205 km, respectively. Where the temperature records of Mace Head and the two other stations overlap from 2004–2008 there is generally good agreement with Mace Head average temperatures generally about 0.5–1.5°C above the mean temperature of the other two meteorological stations (see Fig. 4). This provides some confidence that the temperature records for the two other stations are a reasonable proxy for Mace Head prior to establishing temperature measurements at the station. These are, of course, air temperature since soil temperature records were not available.

Unlike the comparable study with CH_4 (Derwent et al., 2009), where there was generally good correlation between increasing CH_4 emissions with higher ambient temperature; there appears to be no consistent relationship between average H_2 monthly fluxes and ambient temperature with deposition velocities both increasing and decreasing with higher ambient temperatures. Similarly, in some months it could be argued that H_2 fluxes are anti-correlated with accumulated rainfall but again with no consistent pattern. Previous reports have also noted a lack of correlation, or only a weak dependence, between soil deposition velocities of H_2 and temperature (Lallo et al., 2008; Schmitt et al., 2009). Therefore the large variability observed in the natural fluxes of H_2 is perhaps explained, not only by the inhomogeneity of soil microbial and enzymatic activity, but more importantly by the porosity of the soil and its degree of saturation,

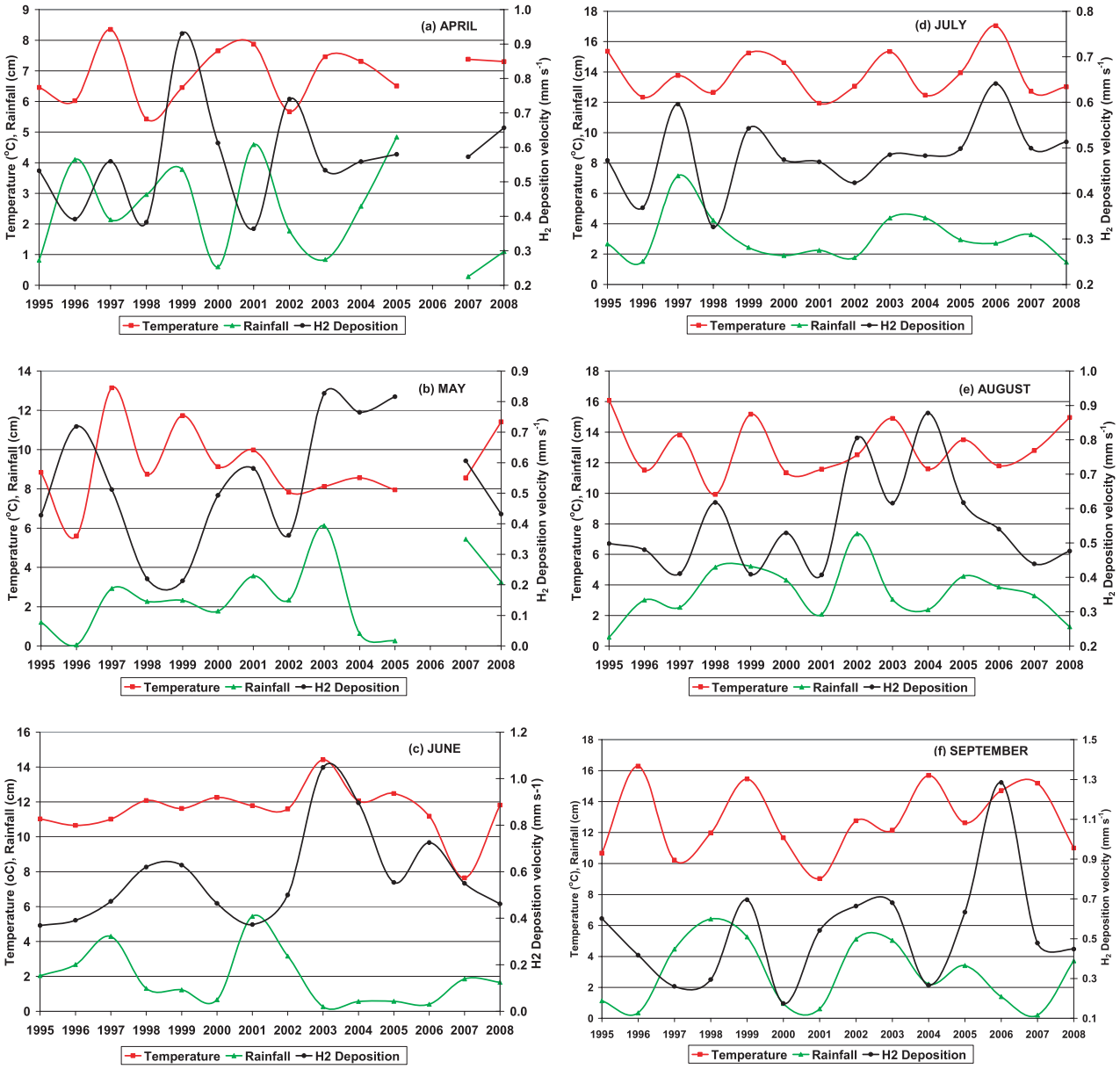

Fig 3. Average monthly H_2 deposition velocities versus average monthly temperatures during the time course of the events and the monthly accumated rainfall (48 h before and during event).

with higher soil moisture contributing to lower gas diffusivity (Yonemura et al., 1999; Ehhalt and Rohrer, 2009).

In Table 2, we compare the average H_2 deposition velocities determined in this study (0.53 ± 0.16 mm s^{-1}) with published literature estimates from various biomes. There is close agreement with the H_2 flux from a similar biome of peaty soil (0.57 mm s^{-1}) reported by Lallo et al., 2008, although our observations cover a much wider range of H_2 deposition velocities. A wide range of H_2 fluxes were also obtained for arable and andisol fields (Yonemura et al., 2000; Schmitt et al., 2009), with the lowest deposition velocities (0.24 mm s^{-1}) reported for an urban site using the radon tracer method (Yver et al., 2009). Also shown is our previous estimate (0.26 mm s^{-1}) for 1994–1998 for the peaty soils around Mace Head, Ireland using an identical approach. This value is at the low end of our range of estimated H_2 deposition velocities, with the mean value reported here for 1995–2008 higher then our earlier estimate. This is suggestive of perhaps an increasing trend through the extended period.

To assess if indeed there has been a long-term trend during the 14 yr of H_2 observations, we plot in Fig. 4 the annually averaged (April–September) H_2 deposition velocities against the annual average temperature and the average accumulated rainfall for

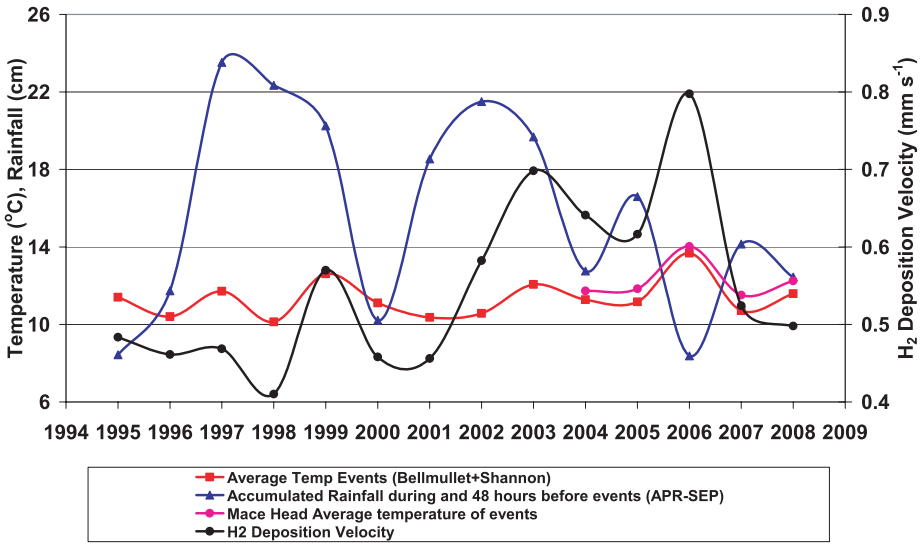

Fig. 4. Annually averaged H_2 deposition velocities versus average temperature and accumulated rainfall for each 6 months of events (April–September).

Table 2. Literature comparison of H_2 deposition velocities calculated using a range of different methods

Reference	Site	Method	V_d [mm s^{-1}] Mean	Range
This study	Peat soil	Ozone box	0.53 ± 0.16	0.18–1.29
Simmonds et al. (2000)	Peat soil	Ozone box	0.26	
Yonemura et al. (2000)	Arable field	Chamber	0.63	0–0.9
	Forest			0.6–0.8
Yonemura et al. (1999)	Andisol field	Open flow chamber	0.51	0–1.0
Gerst and Quay (2001)	Forest	Chamber	0.48 ± 0.13	
Schmitt et al. (2009)	Arable field	Chamber		0.1–0.8
Rahn et al. (2002)	Boreal forest	Concentration gradients	0.73 ± 0.15	0.09–0.56
Smith-Downey et al. (2008)	Forest	Chamber	0.63 ± 0.29	
	Desert		0.51 ± 0.36	
	Marsh		0.35 ± 0.13	
Hammer and Levin. (2009)	Urban	Radon tracer	0.3 ± 0.07	0.23–0.37
Yver et al. (2009)	Urban	Radon tracer	0.24 ± 0.13	0–0.51
Lallo et al. (2008)	Peat soil	Flux chamber	0.57[a]	0.46–0.66[a]
	Mineral soil		0.50[a]	0.44–0.55[a]
Lallo et al. (2009)	Urban park	Radon tracer May-Oct)		0.13–0.7
		Flux chamber (May-Oct)		0.14–0.93

[a]Soil temperature > 5°C

each six months of events (April–September). By averaging all of the emission events over the full 6 months we reveal a significant correlation ($r^2 = 0.53$, $n = 14$) between hydrogen fluxes and average ambient temperature during each year's events. Visually it might also appear that the magnitude of the H_2 deposition velocities have increased over time, principally due to the greater deposition velocities during 2003–2006. However, using a Mann-Kendall test (Salmi et al., 2002) we find that this apparent trend is not statistically significant, due to the large uncertainties in the estimates of H_2 deposition velocities listed in Table 1. It should be recognised that our approach provides only an estimate of the relative deposition velocities of H_2 and O_3.

Conversely, we note that the H_2 flux is, in some years, anti-correlated with the annual average accumulated rainfall, which if we assume is a proxy for the degree of soil moisture, would then imply that gross saturation of the peat bog has restricted efficient diffusion. However, this correlation is statistically insignificant ($r^2 = 0.04$, $n = 14$). As noted by others, the high variability in the observed H_2 deposition velocities of individual events

is largely determined by soil enzymatic activity, the amount of soil carbon and the competition between soil temperature and soil moisture; which we can only infer from our surrogate measurements of ambient temperature and rainfall. However, when the relatively large numbers of deposition events were averaged over many years we expose a more significant correlation, which was not previously evident. That H_2 deposition velocities should increase with soil temperature is expected given that the principal mechanism of H_2 loss is driven by enzymatic and microbial activity.

6. Conclusions

H_2 depositions velocities have been estimated over a 14-year period using a simple box model and the co-incident nocturnal fluxes of H_2 and O_3 under a stable boundary layer. Strict selection criteria indentified 269 deposition events with an average deposition velocity of 0.53 ± 0.16 mm s^{-1}, in close agreement with deposition velocities reported for similar peaty biomes. This approach could be used to estimate the soil sink for H_2 on a larger spatial scale, provided either information is available on the boundary layer height, or there are sufficient high frequency O_3 observations.

In the absence of surface soil moisture and temperature data we examined the relationship of the monthly averaged H_2 deposition velocities with averaged ambient temperature during the time period of the events and also with the accumulated rainfall 48 h before and during each event. While in some months deposition velocity and ambient temperature were positively correlated and similarly inversely correlated with rainfall there was no consistent pattern to these relationships. However, when the entire 14-yr period of H_2 deposition velocities were annually averaged from April–September and compared with the annual average temperature and the average accumulated rainfall for each 6 months of events (April–September), then a reasonable correlation with ambient temperature was observed, although was not statistically significant. Conversely there was a much weaker anti-correlation between accumulated rainfall and H_2 deposition velocities. In our previous paper on chloroform emissions from the Mace Head peat bogs (Simmonds et al., 2010) we noted a statistically significant (1σ) increase in the average temperature of about 0.6 °C over the same 14-yr period reported here. However, we cannot rule out the possibility that the change in H_2 deposition velocities we observed may also be is related to other environmental factors. This suggests that a longer period of observations is needed to see if the relationships noted above become more apparent.

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