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# Water vapor release from biofuel combustion

R. S. Parmar<sup>1,\*</sup>, M. Welling<sup>1</sup>, M. O. Andreae<sup>1</sup>, and G. Helas<sup>1</sup>

<sup>1</sup>Max Planck Institute for Chemistry, Biogeochemistry Department, P. O. Box 3060, 55020 Mainz, Germany

\*now at: IIMT Engineering College, Department of Applied Science, Meerut – 250001 (UP), India

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Correspondence to: G. Helas (gth@mpch-mainz.mpg.de)

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## Abstract

We report on the emission of water vapor from biofuel combustion. Concurrent measurements of carbon monoxide and carbon dioxide are used to scale the concentrations of water vapor found, and are compared to carbon in the biofuel. Fuel types included hardwood (oak and African musasa), softwood (pine and spruce, partly with green needles), and African savanna grass. The session-averaged ratio of H<sub>2</sub>O to the sum of CO and CO<sub>2</sub> in the emissions from 16 combustion experiments ranged from 1.2 to 3.7 on average, indicating the presence of water that is not chemically bound. This biofuel moisture content ranged from 33% in the dry African hardwood, musasa, to 220% in fresh pine branches with needles. The moisture content from fresh biofuel contributes distinctly to the water vapor in biomass burning emissions, and its influence on meteorology needs to be evaluated.

## 1 Introduction

Water vapor production from biomass burning is generally considered to have little effect on atmospheric water vapor concentration. On a local scale, however, large open fires can trigger cloud formation and may even lead to thunderstorms (Stocks et al., 1997; Fromm et al., 2006). This is usually attributed to induced convection or pyro-convection. However, it is not clear what role water vapor released from biofuel combustion plays in the atmospheric conditions above the fire (Potter, 2005; Trentmann et al., 2006; Luderer et al., 2006; and Luderer, 2007; Clements et al., 2006).

Water vapor released from biofuel combustion may have two different sources, the release of fuel moisture that is not chemically bound to the organic molecules of the fuel, and the production of H<sub>2</sub>O by chemical reactions during combustion. The chemically not bound water in biofuels is designated as moisture content and is defined as the weight of water contained in the fuel expressed as a percentage of its oven dry weight. Dry weight, as an operational definition, is achieved, when the mass remains constant

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at an oven temperature of usually 105°C. This water in the biofuel would evaporate on heating, i.e., in the course of the combustion process.

In discussing fuel moisture content, it is useful to distinguish between live and dead fuels (Chuvienco et al., 2004). The latter refer to dead grasses, foliage, twigs, branch wood, and slash. Moisture exchange in dead fuel is controlled by physical processes, i.e., dew formation, adsorption, precipitation, desorption, and evaporation. Thus the fuel moisture of dead biofuel is strongly dependent on atmospheric variability. In contrast, the fuel moisture content of living plants is mainly related to soil moisture and plant physiology, i.e., length of the root system, stomatal resistance, transpiration rate and others, as well as medium-term (a few days or weeks) weather conditions (Chuvienco et al., 2004). While the fuel moisture content of dead biofuels usually is a few to some ten percent, the fuel moisture content of live foliage and needles is easily up to 200% or even more (Agee et al., 2002). Stem moisture content of more lignified material may range to above 100%, as reported by Chalk and Bigg (1956) for Sitka spruce. Moisture in sugar cane stems has been reported up to 600% (Asana, 1950) and sunflower stem moisture content was measured up to 800% by Wilson et al. (1953). Although such high moisture content will inhibit direct combustion by acting as a heat sink through the evaporation of water, ignition is still possible in the end if heat transfer from the surroundings of a biomass fire is large enough (Van Wagner, 1977).

Water vapor is also formed by chemical reaction. The combustible matter of plant biomass, the solid framework, consists of celluloses and hemicelluloses (typically 50–70% dry matter), lignin (15–35%), proteins, amino acids, and other metabolites, including volatile substances (alcohols, aldehydes, terpenes, etc.) (Andreae and Merlet, 2001). In complete combustion, carbon dioxide and water, together with other less prominent oxides such as NO<sub>x</sub>, are formed. Surrogates for biofuels, as for instance simple sugars in the form of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, produce one molecule of water per molecule of carbon dioxide. Celluloses and condensed hexosanes (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>) yield 0.83 and condensed pentosanes (C<sub>5</sub>H<sub>8</sub>O<sub>4</sub>) 0.8 H<sub>2</sub>O per CO<sub>2</sub>, while lignin, whose composition is

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variable but may be assumed to be close to  $C_6H_{6.4}O_2$ , releases 0.53 molecules of  $H_2O$  per molecule  $CO_2$ . Ward (2001) uses  $C_6H_9O_4$  as the average for biofuel (Byram, 1959) and calculates a  $H_2O/CO_2$  ratio of 0.75. Any additional water above that produced in the combustion must already have been present in the fuel.

5 There have been discussions recently on whether the water vapor produced from biofuel fires is essential for the formation of pyro-cumulus clouds. Potter (2005) suspected evidence of a contribution and proposed, in his study, the need to determine how much moisture a fire adds to the air and whether this amount is or is not important. Trentmann et al. (2006), Luderer et al. (2006), and Luderer (2007) for their  
10 modeling studies rejected this influence on pyro-convection on theoretical grounds. In contrast, Clements et al. (2006) showed in an experimental study that the atmospheric water vapor increase due to biofuel fires should not be neglected.

Therefore it would be of interest to know whether combustion experiments provide constraints on the actual production of water vapor from biofuel burning. Here we  
15 report on a re-analyzed data set, which originally had aimed at investigating aerosol formation from biofuel combustion (Wurzler et al., 2001; Chand et al., 2004; Dusek et al., 2004; Parmar et al., 2004; Zeromskiene et al., 2004; Chand et al., 2005; Dusek et al., 2005; Hungershoefer et al., 2005; Schmid et al., 2005; Hungershoefer et al., 2007; Iinuma et al., 2007).

## 20 **2 Experimental**

The experiments were conducted 2003 in course of the EFEU campaign at the combustion facility of the Max Planck Institute for Chemistry, in Mainz, Germany. It consists of a chamber for burning biofuel (Lobert, 1989, Lobert et al., 1991) and a container for smoke dilution, mixing and aging. The laboratory fires were sustained on a fuel bed  
25 housed in a container open to ambient air. In the burning chamber, an inverted stainless steel funnel with a 1.2 m diameter opening was positioned 0.5 m above the fuel bed. The smoke was lifted up via this funnel into the steel sampling container ( $32 m^3$ )

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at a typical flow rate of about  $63 \text{ dm}^3 \text{ s}^{-1}$  (min–max:  $53.3\text{--}68.3 \text{ dm}^3 \text{ s}^{-1}$ ) provided by a fan at the end of the sampling line. This gentle updraft of approximately  $5 \text{ cm s}^{-1}$  at the lower end of the sampling funnel ensured that any boosting of the combustion by the induced flow was minimized. The sampling container (a standard 20-foot container) is positioned on top of another one to avoid guiding the effluents of the fire downwards. A switch in the exhaust stack above the funnel was used to vent the emissions from the starting of the fires vertically out through the chimney. After stabilization of the combustion conditions, the switch redirected the effluents through a steel pipe of  $\sim 20 \text{ cm}$  diameter and  $500 \text{ cm}$  length into the sampling container. Assuming turbulent flow and complete mixing, the residence time in the transfer pipe would have been  $2.5 \text{ s}$  and in the container  $500 \text{ s}$ . Ceiling fans were used to circulate and mix the sample air in the container, which served to provide sufficiently homogenized air for the measurement and sampling devices. The duration of most continuous flow experiments was about one hour.

The fuel bed was continuously weighed with a Sauter E1210 balance. The effluents in the mixing container were monitored for temperature and relative humidity by a Vaisala Humicap 133Y, while carbon monoxide and carbon dioxide were measured by Heraeus Binos NDIR systems. The temperature and humidity of air entering the combustion facility was measured with the same type of Vaisala sensor. Data acquisition was in 10-s intervals.

The air-dried European biofuels used were oak (*Quercus spec.*), pine (*Pinus spec.*), and spruce (*Picea abies*) from Germany in the form of small sticks or twigs of ten to  $20 \text{ cm}$  in length. Pine and spruce were also combined with dry litter from underneath the respective trees, or fresh twigs with needles of pine or spruce were combusted after starting the fires with the corresponding air dried wood species. African biofuels comprised of musasa (*Brachystegia speciformis*) from Zimbabwe and savanna grass (mainly *Setaria flabellata*, and *Laudetia simplex*) were mixed with small amounts of acacia (*Acacia spec.*) from Namibia to ensure continuous combustion. Reloading of fuel during the combustion sessions ensured that both the flaming and smoldering

phases mimicked natural fires.

### 3 Results and discussion

The relative humidity and temperature data from 16 combustion sessions were converted to absolute humidity and are expressed on a mole per mole basis for the sake of comparison to the carbon species concurrently emitted. Figures 1 to 3 display the measured concentrations of water vapor, the sum of carbon monoxide and carbon dioxide, and the ratios  $\Delta\text{CO}/\Delta\text{CO}_2$  and  $\Delta\text{H}_2\text{O}/(\Delta\text{CO}+\Delta\text{CO}_2)$  for fires in which oak, spruce with greens, and savanna grass, respectively, were burned. After the evaporation of fuel moisture, the water vapor release in the experiments was largely proportional to the carbon oxides produced.

The diagrams for the oak fire in Fig. 1 can be interpreted as follows: At the beginning of the fire, the combustion efficiency, expressed by the emission ratio of emitted CO over CO<sub>2</sub>, changes from 4% to 12%, i.e., from a flaming toward a smoldering fire. During this time, the emitted water vapor relative to the carbon oxides is highest, indicating that this water vapor release stems from the fuel moisture and that the distillation process represents a heat sink. Once the chemically not bound water has evaporated, the emission of the carbon oxides increases, and the combustion efficiency rises, i.e.,  $\Delta\text{CO}/\Delta\text{CO}_2$  falls, indicating that the heat production is growing. In this phase, emitted water should mainly stem from the combustion process. However, the  $\Delta\text{H}_2\text{O}/(\Delta\text{CO}+\Delta\text{CO}_2)$  ratio of  $\sim 2$  indicates that a release of chemically not bound water is still taking place. In part, this is likely related to the fact that combustion of vegetation fuels is not a homogeneous process, but that different parts of the fuel bed are at different stages of combustion, so that fuel drying and pyrolysis continues in some parts of the fuel, while others are already in flaming combustion. The spruce with greens fire (Fig. 2) shows a similar behavior. For comparison, plots for savanna grass combustion are shown in Fig. 3. Note that the  $\Delta\text{H}_2\text{O}/(\Delta\text{CO}+\Delta\text{CO}_2)$  ratio in this fire is smaller due to the drier fuel.

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The  $\Delta H_2O/(\Delta CO + \Delta CO_2)$  ratios integrated over the combustion sessions are combined in Table 1 in the first column. Taking into account that the water emission stems from two different processes, the corresponding median values of the individual  $\Delta H_2O/(\Delta CO + \Delta CO_2)$  ratios are displayed in the second column. Interestingly, they do not differ much from the previous column. In the next two columns maxima and minima of the individual measurements are added. Minimum values point to inhomogeneities in the emissions, whereas the maximum values, which appear mostly at the beginning of the experiments, indicate the distillation of the excess water, i.e., the fuel moisture. The integrated values are always larger than unity, pointing to a distinct contribution of fuel moisture.

We estimate the fuel moisture content by assuming a fuel composition of  $C_6H_9O_4$  as given by Ward (2001) which accommodates a typical mixture of cellulose and lignin. The ratio of possible water formation per carbon is then 0.75 (9 hydrogen to form 4.5 molecules of water per 6 carbon; additional oxygen comes from the atmosphere). The difference between the observed  $\Delta H_2O/(\Delta CO + \Delta CO_2)$  and 0.75 must be chemically not bound water, i.e., the fuel moisture, which is related to the total biomass combusted assuming a carbon fraction of 0.5. The carbon oxides, CO and  $CO_2$ , are assumed to form the bulk of the carbon species during the combustion process. Their median emission ratios for the experiments are added to Table 1 for convenience.

Fuel moisture contents range between 33 and 220% (Table 1). The African fuels savanna grass and musasa, which had been stored for a long time, show fuel moisture contents of below 40%. Especially the fuels with fresh green needles have very high fuel moisture contents. Two additional columns in Table 1 give the fuel moisture content estimates assuming the fuel to be composed of pure cellulose and lignin. So for instance, a fuel moisture content of 32% using the water/carbon ratio of cellulose (0.83) as the reference for savanna grass may be more appropriate than 38%. Likewise for musasa, being much more lignified (0.53), the values of 56 and 50% may match better. The data found are within the range described above for typical biofuels. At fuel moistures larger than 56% their contribution to water vapor release will exceed that of water



vapor produced from combustion given the average chemical composition as stated above. The break-even points are 62% and 40% for cellulose and lignin, respectively.

The high moisture content of living fuels, e.g., leaves and needles, obviously contributes significantly to the water vapor in the emission plumes. It helps explain why pyro-cumulus clouds, over fires of living fuels, e.g., sugar cane, are optically quite dense in spite of low ambient atmospheric water content (Andreae et al., 1996). In their modeling study on pyro-cumulus clouds Trentmann et al. (2006) use an average fuel moisture content of 40%. This is a value more typical for dead biofuels, and may be unrealistically low for wildfires. Indeed, in most of our experiments, this threshold was surpassed.

The source of water above that which is chemically produced remains unclear. The individual 10-s data yields  $\Delta H_2O/(\Delta CO + \Delta CO_2)$  ratios above 0.75 most of the time, indicating a continuous water release from available reservoirs. This water seems to be released when the solid structure of the biofuel is disrupted by the combustion. Only during this phase of combustion is there a correlation between the release of carbon oxides and water vapor. It would suggest that the water is coming from inside the cells, i.e., the vacuoles. If this were the case, the standard procedure for determining fuel moisture content by heating until weight constancy is achieved may result in underestimation as the physical structure of the biofuel remains intact. Fuel moisture content of the fresh biofuels were not determined, as the experiments did not aim at such assessments. Determining the fuel moisture content of such inhomogeneous fuels, i.e., twigs, branches, leaves etc. would only have given a guess, as the fuel could not have been prepared as exact duplicates.

As a constraint for our data, we have to keep in mind that carbon monoxide and carbon dioxide are not the only carbon compounds emitted from the combustion. If the fuel carbon escaping in other forms is approximately 10%, the ratio  $\Delta H_2O/(\Delta CO + \Delta CO_2 + \Delta C_{\text{unknown}})$  would still remain above unity and the estimated fuel moisture contents would be reduced by 11 to 25%.

To the best of our knowledge, only Clements et al. (2006) report on concurrent wa-

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ter vapor and CO<sub>2</sub> flux measurements from a grass fire. They report on tethersonde measurements showing potential temperature and water vapor mixing ratio changes between 15 and 25 m height above the fire and deduce fluxes of the same parameters from tower measurements at 3, 22, and 32 m height. Their measurements show a temporal and local increase of water vapor of roughly 30% above ambient in the plume close to the ground. They cautiously discuss the problem of attributing the water vapor sources as being from the fire, advection, or soil moisture. Unfortunately, their data set is only given in condensed form as general values of  $\Delta\text{H}_2\text{O}$  of 3510 ppm (2.18 g kg<sup>-1</sup>) and  $\Delta\text{CO}_2$  of 2182 ppm, giving a ratio of 1.61. This is larger than the  $\Delta\text{H}_2\text{O}/\Delta\text{CO}_2$  value of 1.33 for our old savanna grass. The value of 1.61 would be lower, if  $\Delta\text{CO}$  could have been taken into account. For an assumed  $\Delta\text{CO}/\Delta\text{CO}_2$  emission ratio of 8%, the amount of released water to released carbon oxides would be 1.49, resulting in a fuel moisture content of approximately 60% with cellulose as reference.

Our results suggest that fuel moisture can make a significant contribution to the water vapor content of fire plumes and that the low contribution from “fire moisture” to pyro-cloud water proposed by Trentmann et al. (2006) and Luderer (2007) may be an underestimate as a result of their assumed low fuel moisture content of 40%. While this does not necessarily contradict their result that most of the humidity and condensed water within the cloud stems from entrained environmental air, their estimate that “fire moisture” accounts for less than 5–10% of their modeled pyro-cloud’s water budget may require some upward revision. Accurate measurements on water vapor release from biomass burning under field conditions are desirable to constrain future modeling efforts.

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**Table 1.** Measured  $\Delta\text{H}_2\text{O}/(\Delta\text{CO}+\Delta\text{CO}_2)$  and calculated fuel moisture contents of 16 combustion sessions with different biofuels.

Fuel	measured water to C ratio				calculated fuel moisture content in %			ER $\Delta\text{CO}/\Delta\text{CO}_2$ in %
	$\Delta\text{H}_2\text{O}/(\Delta\text{CO}+\Delta\text{CO}_2)$ ratio calculated from time integrated data	median $\Delta\text{H}_2\text{O}/(\Delta\text{CO}+\Delta\text{CO}_2)$ ratio calculated from individual data	maximum $\Delta\text{H}_2\text{O}/(\Delta\text{CO}+\Delta\text{CO}_2)$ ratio calculated from individual data	minimum $\Delta\text{H}_2\text{O}/(\Delta\text{CO}+\Delta\text{CO}_2)$ ratio calculated from individual data	using average water to C=0.75 according to Ward (2001)	using water to C=0.83 for cellulose	using water to C=0.53 for lignin	
oak	2.05	1.80	15.76	1.33	98	92	114	7.9
oak	1.51	1.40	2.13	1.02	57	51	74	6.6
musasa	1.27	1.29	1.61	0.53	39	33	56	8.1
musasa	1.19	1.17	1.77	0.63	33	27	50	9.2
pine	1.42	1.42	3.12	0.55	50	44	67	8.5
pine with green	3.71	3.52	4.47	0.25	222	216	239	4.8
pine with green	1.29	1.31	1.74	0.71	41	35	57	6.8
pine with dry underbrush	1.39	1.38	2.14	0.52	48	42	65	3.2
pine branch only	1.96	1.92	4.59	0.65	91	85	107	4.4
pine branch only	1.47	1.42	2.16	0.63	54	48	71	7.5
spruce	2.36	2.35	2.91	1.97	121	115	137	3.5
spruce	2.20	2.23	3.66	1.28	109	103	125	11
spruce with green	2.21	2.20	4.84	1.66	110	104	126	4.9
spruce with green	2.87	2.69	8.56	1.69	159	153	176	8.8
spruce with green	1.49	1.49	2.8	0.65	56	50	72	7.7
savanna grass	1.25	1.24	1.73	0.61	38	32	54	6.3

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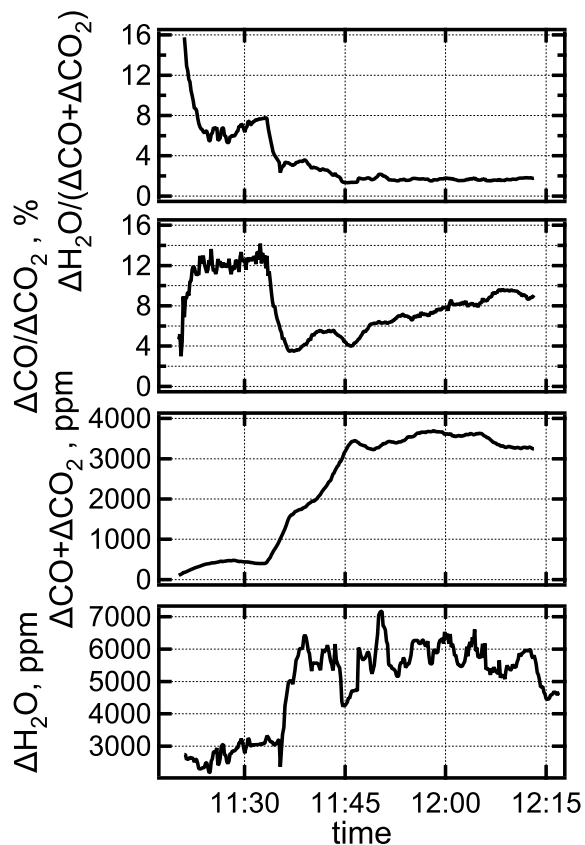
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Interactive Discussion



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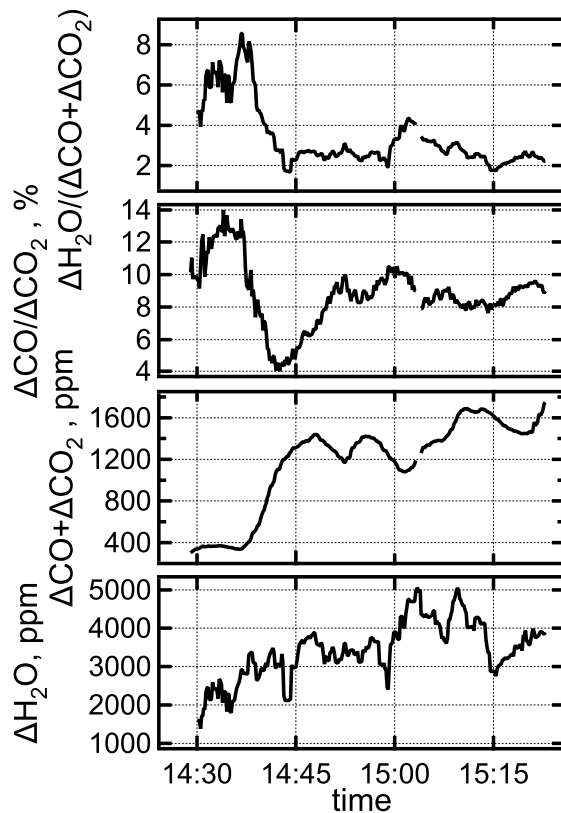


**Fig. 1.** Water vapor and carbon oxides released from an oak biofuel fire versus time. The panels show from below: water vapor emitted in the course of the combustion session; CO and CO<sub>2</sub> produced; the combustion efficiency expressed as  $\Delta\text{CO}/\Delta\text{CO}_2$  (mol per mol); the emitted water vapor per emitted carbon oxides expressed as  $\Delta\text{H}_2\text{O}/(\Delta\text{CO}+\Delta\text{CO}_2)$  (mol per mol).

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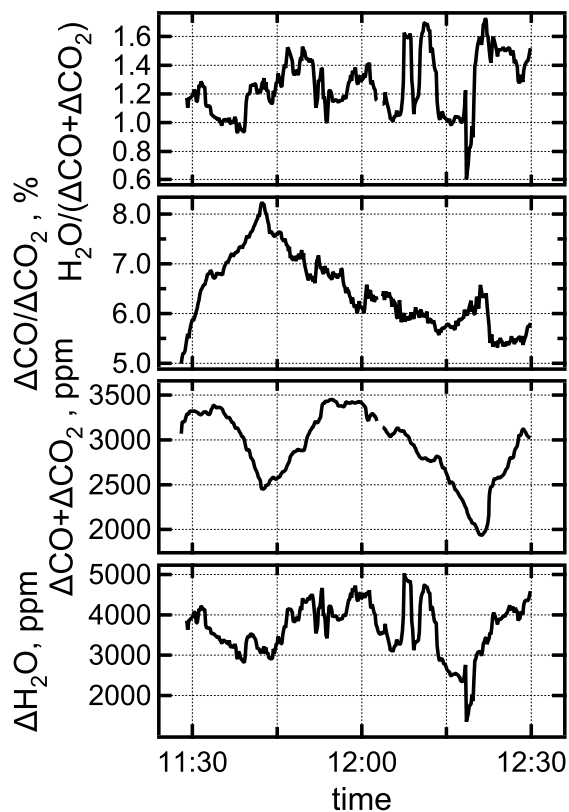
**Fig. 2.** Water vapor and carbon oxides released from a spruce with greens biofuel fire versus time. The panels are the same as in Fig. 1.

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**Fig. 3.** Water vapor and carbon oxides released from a grass biofuel fire versus time. The panels are the same as in Fig. 1.

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