Identification of spikes in continuous ground-based in-situ time series of CO_2, CH_4 and CO: an extended experiment within the European ICOS-Atmosphere Network

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Impact of the spike detections on diurnal cycles

In this section, we provide a complete description of the impact of the SD and REBS methods to the seasonal averaged diurnal cycles of CO_2, CH_4 and CO at the test sites.

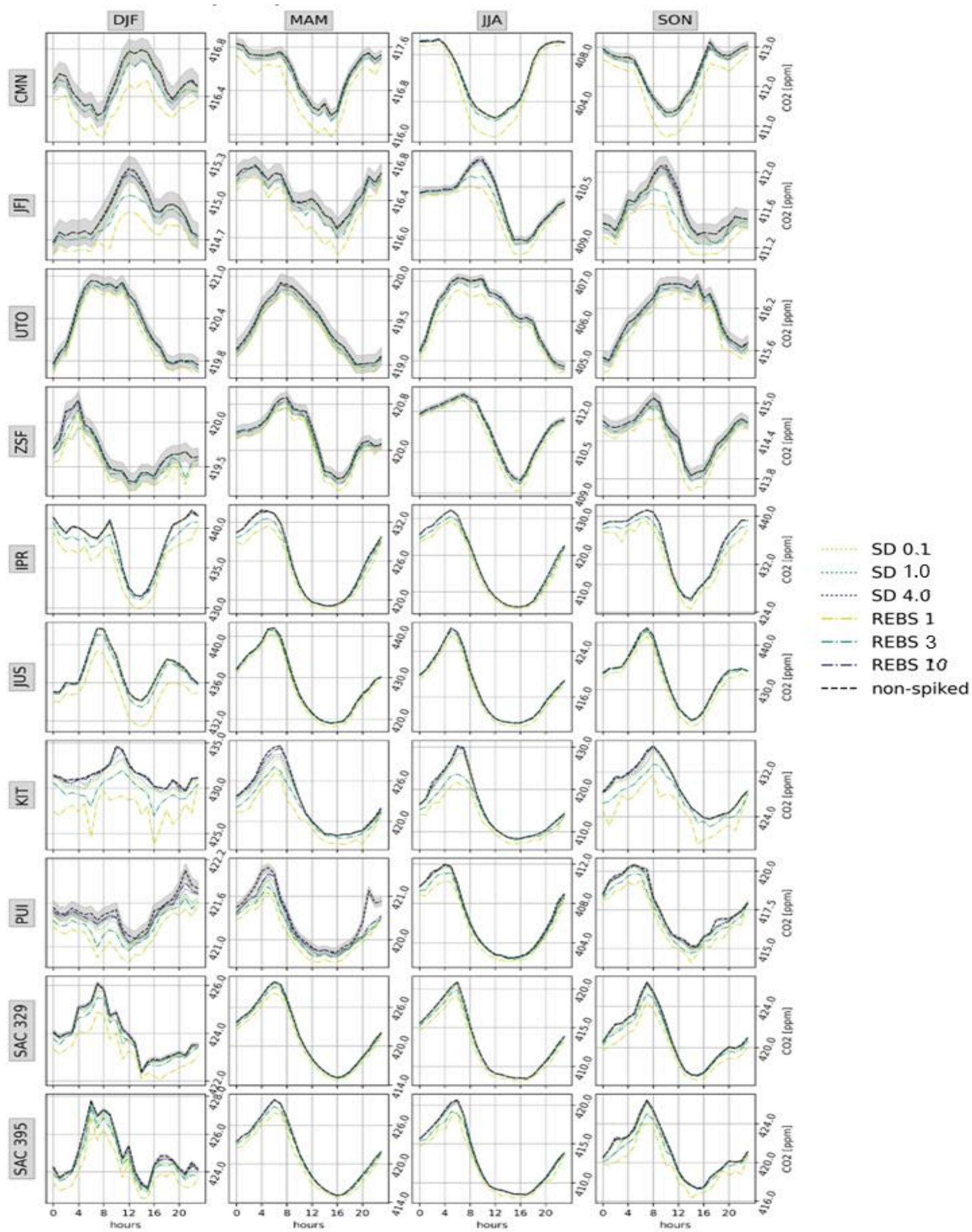

Figure S1: Mean seasonal diurnal cycles of CO_2 at selected sites and sampling heights for different data selection: results for the original data are shown ("non-spiked") together with those after de-spiking for SD with α = {0.1, 1, 4} and REBS with β = {1, 3, 10}. The grey areas indicate the WMO network compatibility goal referred to the original dataset. Time is expressed as UTC.

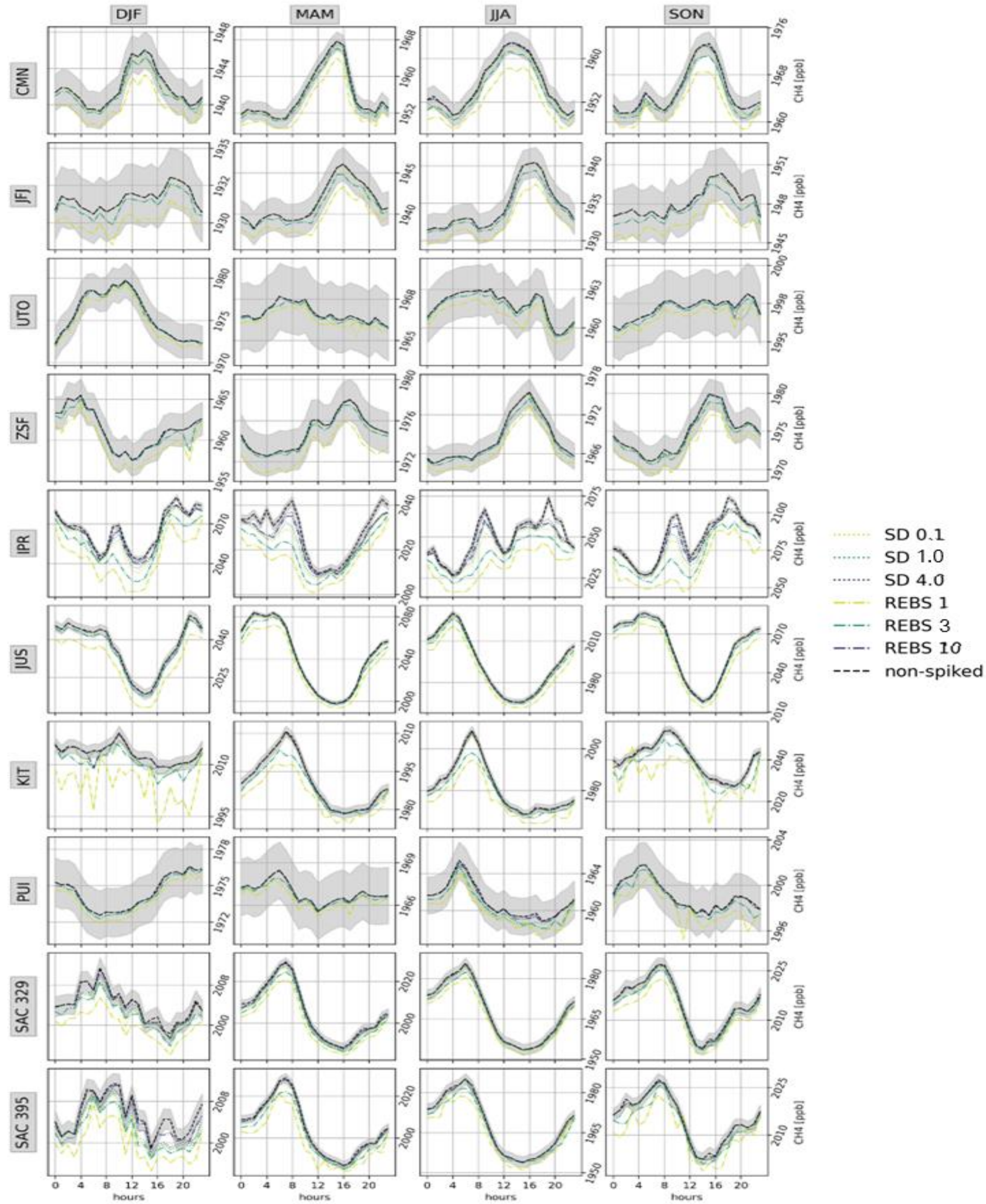

Figure S2: As for Figure SM1 but for CH_4.

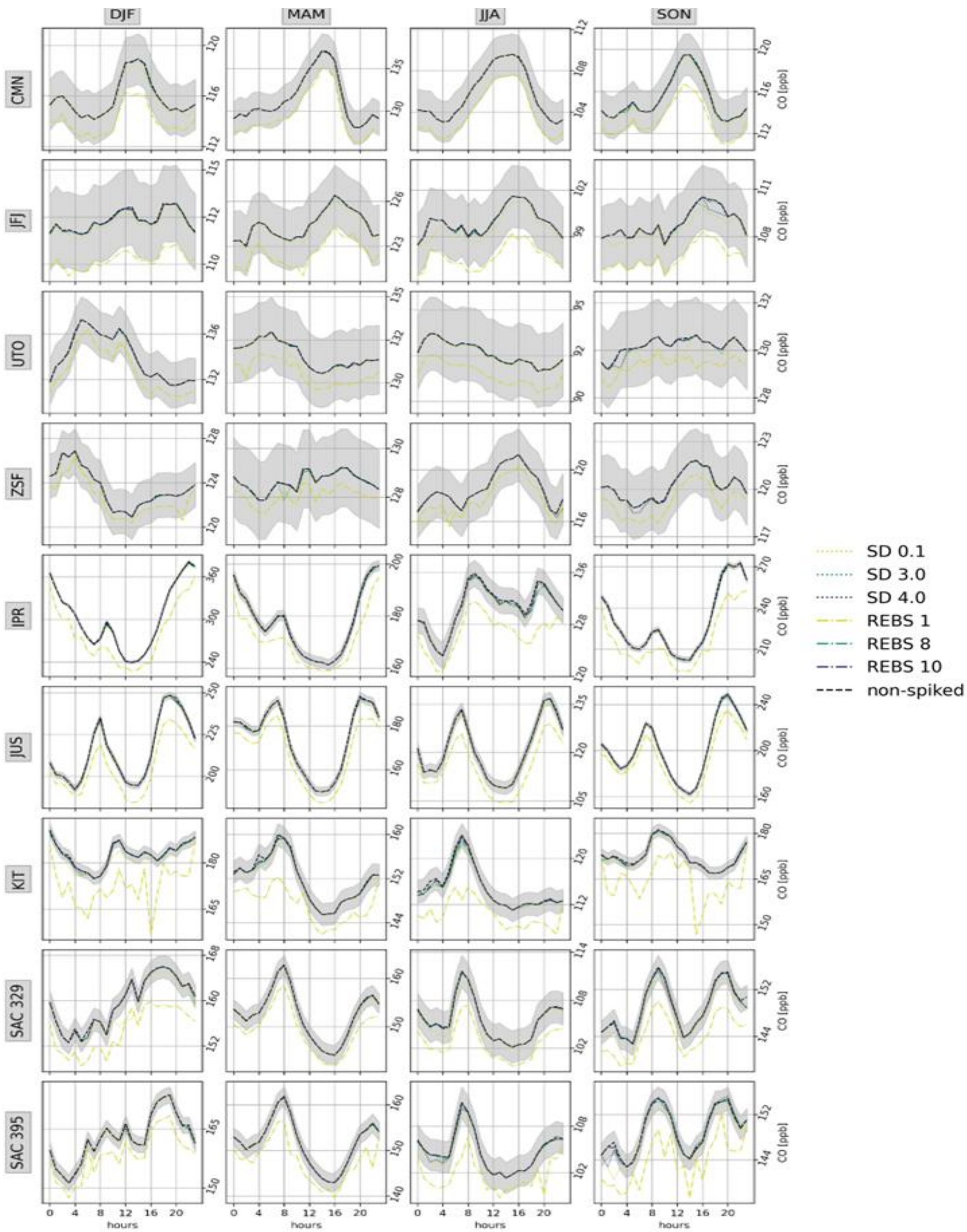

Figure S3: As for Figure SM1 but for CO with de-spiking for SD with α = {0.1, 3, 4} and REBS with β = {1, 8, 10}.

Comparison of SD and REBS spike detections during case studies

In this section, we provide further indications about the ability of the SD and REBS methods in detecting spike events during specific case studies selected by the site PIs at JFJ, UTO, PUI, IPR, SAC and JUS. For each of the considered sites, a list of specific periods (lasting from a few days to a few weeks) affected by the occurrence of spikes were provided by the site PIs for CO_2, CH_4 and CO. SD and REBS were run for the standard configurations as well as for the other α and β values. Then, the spike identifications were inspected and evaluated by the site PIs. For each considered site and case study, a short description of the spike identification results were reported in the supplementary material (Tables S1 - S6), together with the expert assessment about the performance of the two methods. When possible, we also provided an evaluation about which algorithm was in better agreement judged by the stations PIs' expertise for these specific case studies. To achieve the best agreement between the expert judgement of the statistical de-spiking, we varied the standard configurations (α and β values) and provided the optimal method configuration based on the visual inspection of the de-spiking method results for each case studies.

Based on the case study analyses, at JFJ (Table S1), both SD and REBS tended to overestimate spike occurrences with "standard" settings. For REBS, this overestimation was reduced when β = 8 was used. As an example, the case study for 19 - 21 November 2020 was reported in the main manuscript (Figure 10) for JFJ.

For UTO, we used the spike events related to ship emissions reported by Grönholm et al. (2021) to compare the ability of SD and REBS in detecting spikes (Table S2). At UTO, SD was not able to select any of these spikes. However, these short-lasting spikes were recognized for CO_2 and CH_4 by REBS. Nevertheless, an overestimation appeared to affect REBS detection by adopting the standard setting, while a more accurate spike detection occurred when β = 8 was used. Here we detailed the case study reporting the spikes occurred on 19 July 2020 (please note that we did not report SD results due to the absence of detected spikes). In this case, the occurrence of spikes was confirmed by REBS at UTO (Figure S4), even if a slight overestimation of spikes was documented. For comparison, Figure SM4 also reports the spike detection performed by running REBS with β = 8. In this latter case, a more consistent spike detection was evident with a reduction of spike overestimation.

Moving to "continental" sites, by inspecting case studies at IPR, SD appeared to detect less spikes than REBS with "standard" settings for CO_2 and CH_4; by looking to CO also REBS appeared to provide under detection of spikes (Table S3). As an example, the case study 2 - 4 July 2019 was reported in the main manuscript (Figure 11) for IPR.

A good test case was provided by observations at PUI, since this site can occasionally be under the influence of local emissions from a paper mill, the nearby district heating plant and a biogas power plant. The site PI was able to trace back the spikes to these local sources by inspecting the local wind direction regime. The comparison between SD and REBS for five case studies (Table S4) led to similar results to IPR: REBS showed higher skills in detecting the spikes. A case study characterized by the occurrence of several CH_4 spikes from 2 to 21 June 2020 was reported by Figure S5. In this case, a significant day-to-day variability affected CH_4 at PUI. The occurrence of CH_4 spikes related to local emission sources was over-imposed to this variability. While REBS was able to catch almost all the detected spikes (only one event missed, and one partially identified, see Figure S5), SD was only able to partially detect a few events.

The situation appeared to be different for the other continental site SAC. As deduced by the inspection of case studies, SD appeared to have more skills in detecting spikes than REBS when the standard configuration was used (Table S5); an improvement in the REBS performances was detected by adopting β = 8 for CO_2 and CH_4 for specific case studies. Due to this complexity, we reported two case studies for SAC. The first is related to 9 - 10 January 2019 and it was described in the main manuscript (Figure 12). For the case study of 22 - 31 March 2019 (Figure S6), a diurnal variability was evident for CO_2 and CH_4, with maxima in night-time/early morning and minima during afternoon. This variability was temporarily disrupted on 29 March. CO_2 and CH_4 spikes superimposed to the diurnal variability from 25 to 28 March, while a very high variability affected observations on 29 March. For CO_2, SD was not able to catch these spikes which were detected by REBS, instead. For CH_4, either method was able to identify the spikes on 25-28 March, but SD only partially detected the high variability on 30 March.

SD and REBS were also applied to CO_2, CH_4 and CO observations at JUS (Table S6). Overall, the analysis of the selected case studies lead to the conclusion that both the methods overestimated the spike occurrence at this site. Only for CO, REBS appeared to provide consistent detections. A sensitivity study (here not shown) suggested that REBS performed better (i.e. less false spikes) for CO_2 and CH_4 when β = 8 was used. As being located in the urban area of Paris, JUS is characterized by strong diurnal variability of the observed species: both SD and REBS had the tendency to detect as spikes the diurnal peaks related with this systematic variability (Figure S7).

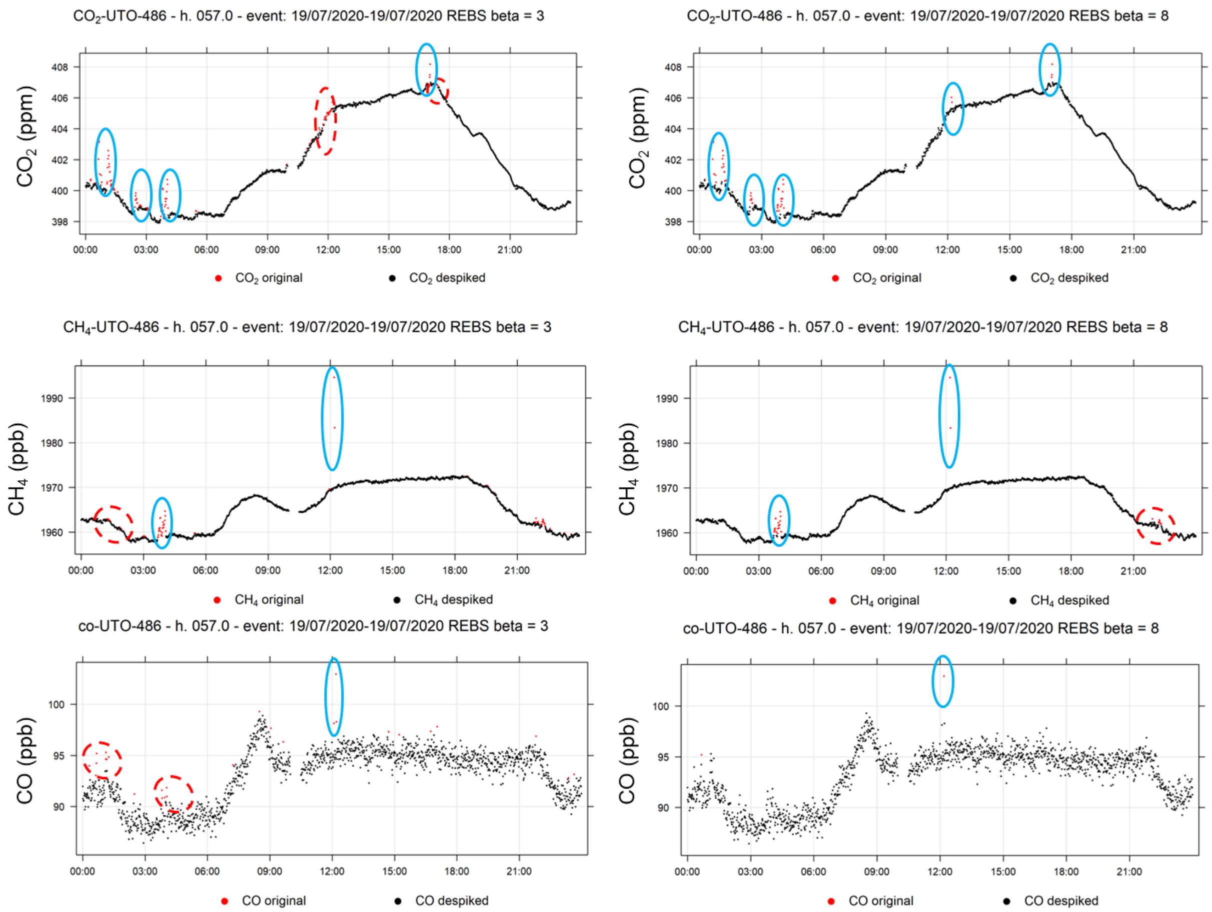

Figure S4: CO_2, CH_4 and CO observations at UTO (19 July 2020). No-spike data are reported by the black points (”despiked”); red points (“original”) denote the data flagged as spikes using SD (left) and REBS (right). Continuous (dotted) circles represent the spike attribution manually confirmed (not confirmed) by site PI.

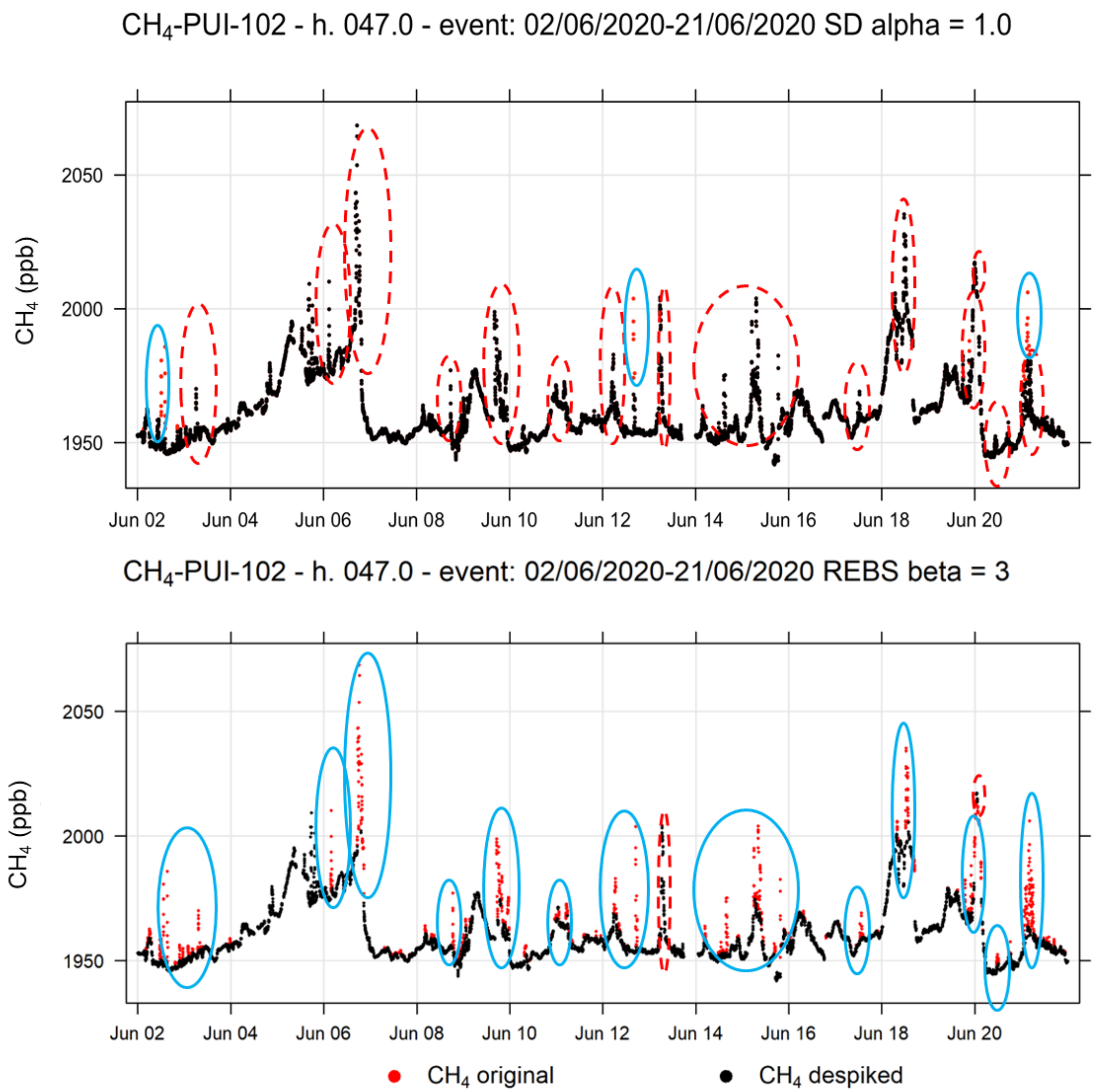

Figure S5: CH_4 observations at PUI (2-21 June 2020). No-spike data are reported by the black points (”despiked”); red points (“original”) denote the data flagged as spikes using SD (left) and REBS (right). Continuous (dotted) circles represent the spike attribution manually confirmed (not confirmed) by site PI.

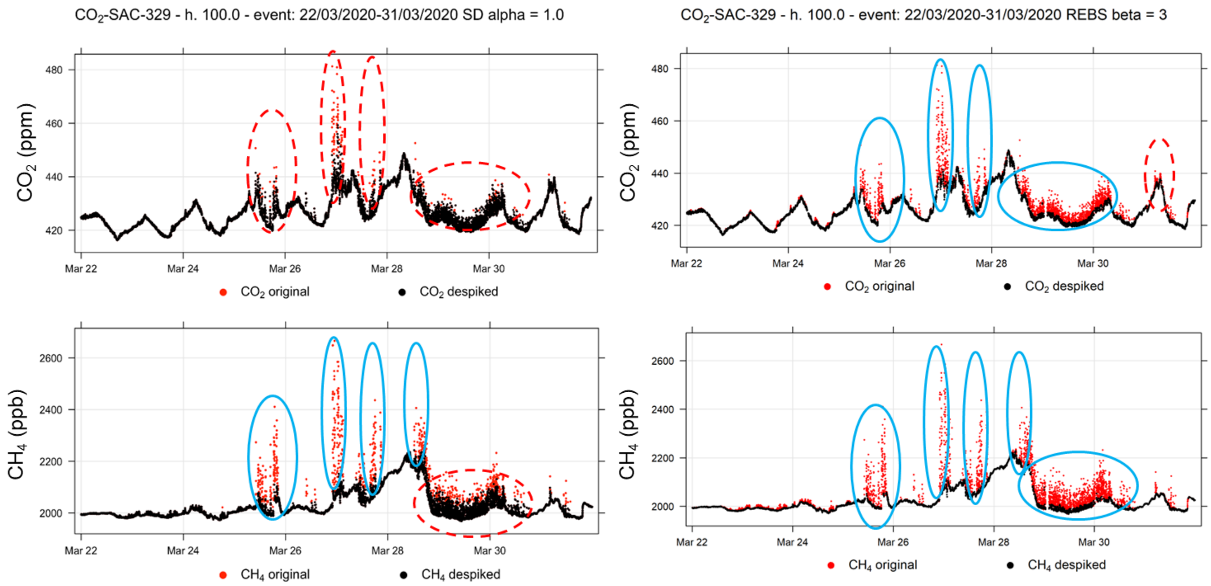

Figure S6: CO_2 and CH_4 observations at SAC (22-31 March 2019). No-spike data are reported by the black points ("despiked"); red points ("original") denote the data flagged as spikes using SD (left) and REBS (right). Continuous (dotted) circles represent the spike attribution manually confirmed (not confirmed) by site PI.

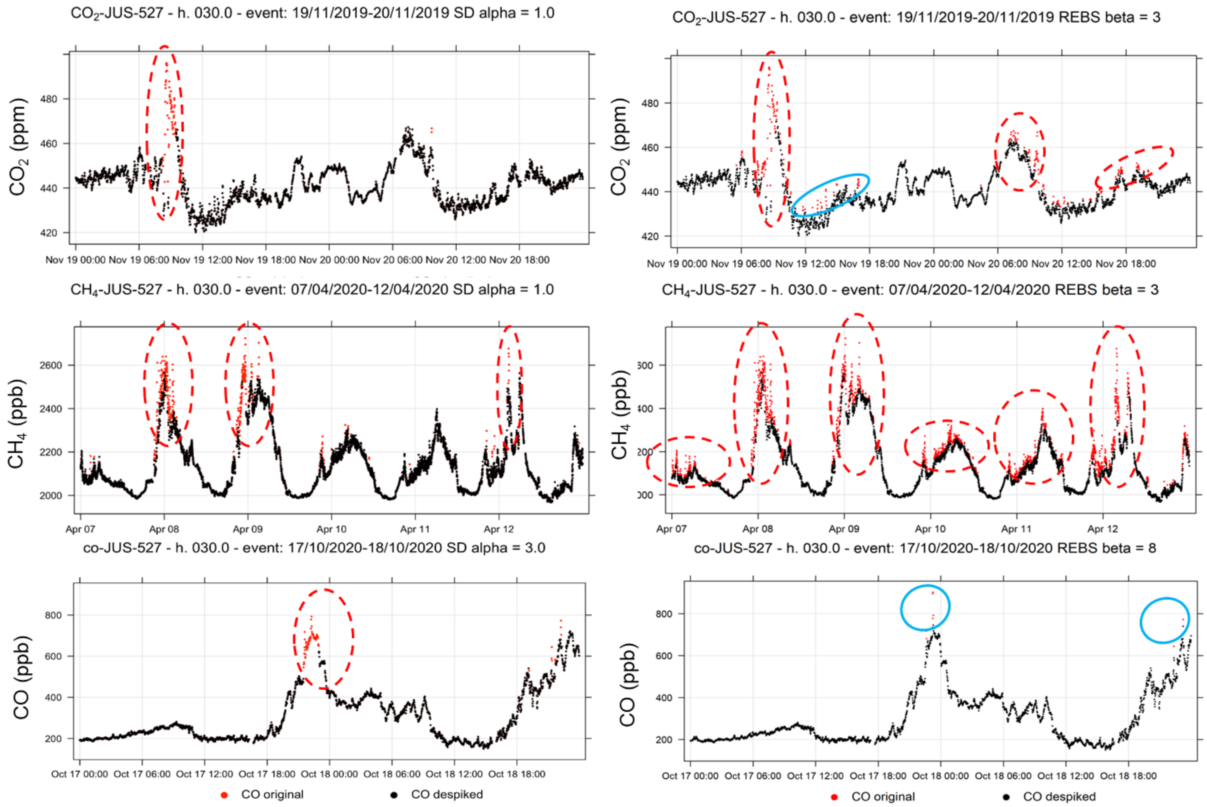

Figure S7: CO_2 (19-20 November 2019), CH_4 (7-12 April 2020) and CO (17-18 October 2020) observations at JUS. No-spike data are reported by the black points (”despiked”); red points (“original”) denote the data flagged as spikes using SD (left) and REBS (right). Continuous (dotted) circles represent the spike attribution manually confirmed (not confirmed) by site PI.

Table S1: Analysis of spike case studies at JFJ. For each case study, italic characters denote the better performing method after subjective analysis. The notation "significant" or "not-significant" impact refers to the WMO network compatibility goals.

Case studies	**JFJ (method: SD; α = 0.1 for CO_2 and CH_4; α = 3 for CO)**	**JFJ (method: REBS; β= 3 for CO_2 and CH_4; β= 8 for CO)**
2019/2/2-3 (Pollution event)	For CH_4 and CO_2, wrong spike detections with significant impact on hourly mean values. For CO, wrong spike detections but not significant impact on hourly mean values.	*For CO_2 and CO no spike detections: correct. For CH_4 wrong detection of spikes with significant impacts on hourly values.*
2020/3/24-26 (Pollution event)	For CH_4, wrong spike detections but several short small spikes were missed. For CO_2, detected spikes as well as high variability but also wrong spike detections.	For CH_4, mixture of wrong and correct spike detections. For CO_2, spike overdetection.
2020/10/25-26 (Pollution event)	For CO_2, wrong spike detections.	For CO_2 and CH_4, wrong spike detections (improvements with β = 8).
2020/11/19-21 (Diurnal cycles for all the species)	*No spikes detected for CH_4 correct. Mixture of correct and wrong spike detections for CO_2.*	For CO_2, one event correctly identified but several wrong detections. For CH_4, wrong spike detections.

Table S2: Analysis of spike case studies at UTO. For each case study, italic characters denote the better performing method. The notation "significant" or "not-significant" impact refers to the WMO network compatibility goals.

Case studies	**UTO (method: SD; α = 0.1 for CO_2 and CH_4; α = 3 for CO)**	**UTO (method: REBS; β= 3 for CO_2 and CH_4; β= 8 for CO)**
2020/3/1 (Ship emission with small spikes for CO_2 and CH_4)	No spike detected.	*Too much data detected as spikes for CO_2 and CH_4. Improvements by setting β = 8 (less wrong spikes selected).*
2020/6/6 (Ship emission with small spikes for CO_2 and CH_4)	No spike selected.	*Too much data detected as spikes for CO_2 and CH_4. Improvements by setting β = 8 (less wrong spikes selected). Correct spike selection for CO.*
2020/7/19 (Ship emission with spikes for CO_2 and CH_4)	No spike selected.	*Reasonable spike selection with standard setting but improvements with β = 8 for CO_2 and CH_4 (less wrong spikes selected). Correct spike selection for CO.*
2020/10/5 (Ship emission with spikes for CO_2 and CH_4)	No spike selected.	*Too much data detected as spikes for CO_2 and CH_4. Improvements by setting β = 8, but wrong detections still occurred. Correct spike selection for CO.*
2020/11/6 (Ship emission with spikes for CO_2 and CH_4)	No spike selected.	*Too much data detected as spikes for CO_2 and CH_4. Improvements by setting β = 8, but wrong detections still occurred. Correct spike selection for CO.*

Table S3: Analysis of spike case studies at IPR. For each case study, italic characters denote the better performing method. The notation "significant" or "not-significant" impact refers to the WMO network compatibility goals.

Case studies	**IPR (method: SD; α = 0.1 for CO_2 and CH_4; α = 3 for CO)**	**IPR (method: REBS; β= 3 for CO_2 and CH_4; β= 8 for CO)**
2019/4/8-25 (Diurnal cycles and spikes for all the species)	For all the species, several spikes detected but also a few missed.	*For all species, effective spike detection. A few missed spikes for CH_4 and CO.*
2019/4/14 (Diurnal cycles and spikes for CH_4)	For CH_4, very large spikes (> 2200 ppb) were detected but other spikes (<2100 ppb) were missed.	*For CH_4, effective spike detections but also large spikes (> 2100 ppb) were missed.*
2019/7/2-4 (Diurnal cycles and spikes for all the species)	For CH_4 and CO, spikes were missed or only partially identified. For CO_2, two spikes missed (about 10 ppm for a few minutes).	*Effective spike detections for CO_2 and CH_4. but also wrong detection for CO_2. For CO, missed spikes (improvements for β = 3).*
2020/2/25 (Spikes for all the species)	For all the species, spikes were detected.	*For CO_2 and CH_4, effective spike detections. For CO, missed spikes (improvements with β = 3).*

Table S4: Analysis of spike case studies at PUI. For each case study, italic characters denote the better performing method. The notation "significant" or "not-significant" impact refers to the WMO network compatibility goals.

Case studies	**PUI (method: SD; α = 0.1 for CO_2 and CH_4; α = 3 for CO)**	**PUI (method: REBS; β= 3 for CO_2 and CH_4; β= 8 for CO)**
2020/06/02-21 (Mixture of spikes and daily cycles for CH_4)	Several spikes not detected related to local emission sources.	*For all the species, effective spike detection: a few spikes missed.*
2019/1/1-17 (Mixture of spikes and daily cycles for CO_2)	Large single spikes (> 460 ppm) detected. Only a few points of lower spikes (< 430 ppm) were detected.	*For all the species, effective spike detection.*
2019/11/1-14 (Spikes for CO_2)	Spikes (small and large) only partially detected.	*For all the species, effective spike detection: a few spikes missed.*
2019/11/16-28 (Spikes for CO_2)	Only partial spike detection.	*For all the species, effective spike detection*
2020/3/1-17 (Spikes for CO2)	Many spikes (> 430 ppm) correctly detected.	*For all the species, effective spike detection.*

Table S5: Analysis of spike case studies at SAC. For each case study, italic characters denote the better performing method. The notation "significant" or "not-significant" impact refers to the WMO network compatibility goals.

Case studies	**SAC (method: SD; α = 0.1 for CO_2 and CH_4; α = 3 for CO)**	**SAC (method: REBS; β= 3 for CO_2 and CH_4; β= 8 for CO)**
2019/1/9-10 (Spikes for CO_2 and CH_4)	*For all the species, effective spike detections but the lower part of spikes were missed.*	For all the species, spike over-detections. Improvements with β = 8.
2019/3/17-29 (Spikes for CO_2 and CH_4)	*For all the species, effective spike detections, but a few data within a spike missed.*	For all the species, effective spike detections, but a few data within a spike missed.
2019/7/21 – 29 (Spikes for CO_2 ,CH_4 and CO)	*For CO_2, effective spike detections. For CH_4 , major spikes were detected. For CO, not all the major spikes were detected.*	For CO_2 and CH_4 , spike over-detection. For CO, several spikes missed.
2019/2/1-12 (Spikes for CO_2 and CH_4)	*For CO_2, not effective spike detection. For CH_4, effective spike detections.*	For CO_2, not effective spike detection. For CH_4 , spike over-detection.
2020/03/22-21 (Spikes for CO_2 and CH_4)	For CO_2 and CH_4, missed spikes. Improvements with α = 0.1.	*For all the species, effective spike detection.*
2020/8/5-13 (Mixture of daily cycles + spikes for all the species)	For all the species, spike over-detection.	For all the species, spike over-detection. Improvements with β = 8 .
2020/11/24-30 (Mixture of synoptic-scale and spikes for all the species)	*For CO_2, spike over-detection. For CH_4 , effective spikes detection but some events only partially detected. For CO, two large spikes detected but also wrong detections.*	For CO_2 and CH_4 spike over-detections (Improvements with β = 8). For CO, effective spike detection.

Table S6: Analysis of spike case studies at JUS. For each case study, italic characters denote the better performing method. The notation "significant" or "not-significant" impact refers to the WMO network compatibility goals.

Case studies	**JUS(method: SD; α = 0.1 for CO_2 and CH_4; α = 3 for CO)**	**JUS (method: REBS; β= 3 for CO_2 and CH_4; β= 8 for CO)**
2019/11/19-20 (Diurnal cycles and spikes for CO_2)	Wrong spike detections on 19 November.	Wrong spike detections. Improvements with β = 8.
2020/10/17-18 (Diurnal cycles for CO)	Wrong spike detection over the diurnal peak on 17 October.	*Effective spike detection over the diurnal peak on 17 October.*
2020/4/7-12 (Diurnal cycles and spikes for CH_4)	Wrong detections during large diurnal peaks.	Wrong detections during large diurnal peaks. Improvements with β = 8.