Name of research institute or organization:

Physikalische Chemie / FBC, Bergische Universität Wuppertal

Title of project:

Measurements of nitrous acid (HONO) in the free troposphere

Project leader and team:

PD Dr. Jörg Kleffmann

Project description (summary):

In the present DFG pilot study, an optimized LOPAP instrument (DL 0.2 pptV, time response 6-7 min) for the detection of nitrous acid (HONO) in the atmosphere was tested on the high alpine research station "Jungfraujoch" at 3580 m altitude. The excellent performance of the instrument was confirmed in this study also under extreme weather conditions. HONO concentrations in the range <0.5-50 pptV with a mean value of 7.5 pptV were observed on the "Jungfraujoch". The diurnal profiles obtained showed clear maxima at noon and minima with very low concentration during the night supporting a proposed photochemical production of HONO on ground surfaces. It was also demonstrated, that interferences of wet-chemical HONO monitors can significantly influence the measurements. However, for the LOPAP instrument these interferences are corrected for, which was recently validated in different intercomparison campaigns with an optical instrument (DOAS). From the present pilot study, it can be concluded that the LOPAP instrument is capable for the ultra sensitive detection of HONO in polar regions.

1 Introduction

Nitrous acid (HONO) is of particular importance in atmospheric chemistry, since the photolysis of HONO at relatively long wavelength significantly enhances the rate of photooxidation processes, e.g. the formation of tropospheric ozone [1, 2, 3], not only early in the morning, but possibly also during daytime [4, 5, 6, 7, 8, 9, 10, 11, 12, 13] due to the rapid production of OH radicals:

(1) $HONO + h\nu\ (300\text{-}390nm) \rightarrow OH + NO$.

Despite its importance in atmospheric chemistry, the mechanisms leading to HONO formation are still not well understood at present. All gas phase reactions are to slow to explain the observed night-time HONO formation [2]. In addition, direct emissions can only explain atmospheric HONO levels partly [14]. It is commonly proposed that HONO is formed by heterogeneous processes, i.e. by the conversion of NO_2 on humid surfaces [15].

Recently, it was observed that HONO is significantly formed during sunlight on snow surfaces in the Arctic [4, 10, 16, 17, 18, 19]. It was estimated that the photolysis of HONO can be the dominant source of OH radicals for these regions [4, 10, 11] and thus possibly controls the oxidation capacity of the lower polar atmosphere. Accordingly, the mechanistic understanding of this process and a quantification of the HONO source strength are of paramount importance for a better understanding of atmospheric chemical processes in polar regions.

However, the mechanism of HONO formation in these regions is not well understood at present. It was proposed [10, 16, 17, 18, 19] that HONO formation is caused by the

photolysis of nitrate in the snow [20, 21, 22, 23, 24, 25], which is also suggested as the photolytic source of NO_x emitted from snow surfaces (e.g. [26, 27, 28, 29]). An alternative mechanism to explain HONO formation during daytime was recently proposed by the photoenhanced reduction of NO_2 on organic surfaces, like e.g. fulvic and humic acids [30, 31]. Since these organic compounds are ubiquitous, this mechanism could probably also explain the observed HONO formation on snow surfaces. The proposed mechanism could also help to explain the high $HONO/NO_x$ ratio often observed in polar regions, which is in contrast to the expected ratio based on laboratory studies about the nitrate photolysis (see also [10]).

Measurements of gaseous HONO have been made since many years in the atmosphere with various techniques (e.g. [32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42]). For measurements in the Arctic, dry carbonate denuders [4, 16], mist chambers with ion chromatographic detection [17, 18] and the HPLC technique [10, 19, 43] have been used. The common principle of these instruments is the sampling of HONO on humid or aqueous surfaces in the form of nitrite. Very recently, it was found that these chemical detectors could suffer from interferences by the reaction of different hydrocarbons with NO_2 [44], by which nitrite is efficiently formed on similar surfaces. In addition, in all polar HONO studies the air was sampled through Teflon/PFA tubes of up to 30 m length (e.g. [10]). Since it is well known that HONO is heterogeneously formed on surfaces (e.g. [45, 46]), the surfaces of the sampling lines could cause additional HONO formation and lead to incorrect results. Accordingly, there is an urgent need for the exact quantification of HONO concentrations in polar regions by an instrument for which interferences and sampling artefacts can be excluded finally leading to a better understanding of the impact of HONO on the oxidation capacity of the polar atmosphere.

2 Aim of the study

The proposed DFG pilot study was aimed to demonstrate that the recently developed LOPAP instrument for the detection of nitrous acid in the atmosphere is capable to work under polar conditions. In addition, it was planned to significantly improve the sensitivity of the instrument in order to quantify the expected extreme low concentrations in Antarctic regions. Thus, HONO measurements were performed with a modified HONO instrument in a field campaign on the high alpine research station “Jungfraujoch” in the period 02.-07.11.2005.

3 Experimental

Nitrous acid (HONO) was measured with a newly developed, ultra sensitive instrument (LOPAP), which is described in detail elsewhere [40, 41]. Briefly, HONO is sampled in a stripping coil by a fast chemical reaction and converted into an azo dye, which is photometrically detected by long path absorption in light conducting Teflon tubes. The two-channel set-up of the instrument suppresses interferences including those caused by mixtures of NO_2 and semi-volatile diesel exhaust components [44]. Artificial HONO formation in sampling lines by heterogeneous or photolytic processes [45, 46] is minimized by the use of an external temperature controlled sampling unit, in which the stripping coils are mounted and which can be directly installed in the atmosphere of interest. In recent intercomparison campaigns with the DOAS technique in the field and in a smog chamber, excellent agreement was obtained also for daytime conditions [47], which is in contrast to all other published intercomparison studies between chemical HONO instruments and the DOAS technique [48, 49, 50, 51, 52]. The detection limit of the instrument was 1-2

pptV for a time response of 5 min [41]. Further modifications of the instrument to improve the sensitivity were performed as part of a recent DFG pilot study [53] and is summarized in chapter 0.

4 Results and Discussion

4.1 Modifications of the LOPAP instrument

Prior to the field study on the "Jungfraujoch" the sensitivity of the LOPAP instrument was improved [53], which led to a detection limit of <0.2 pptV in the laboratory for a time response of 6-7 min, which is shown in Fig. 1 as an example. In this experiment, some laboratory air was added to zero air, leading to HONO concentrations of only 20 and 200 pptV at ca. 9:50 h and 12:40 h, respectively. Since both concentrations were still orders of magnitude higher than the detection limit of the instrument, the signal from the interference channel 2 is also show in the figure to demonstrate the sensitivity of the instrument. During the first addition of laboratory air over a period of ~20 min, a signal of 0.3 pptV was observed in channel 2, which can be easily resolved and which is still much higher than the noise (2 σ) of the instrument of ~0.1 pptV (see Fig. 1). However, since the detection limit was calculated from the noise of both channels, a detection limit of ~0.15 pptV was determined from the zero measurements during this experiment. During the second addition, laboratory air was injected only for 2 min, leading to a sharp peak from which a time response of 6.5 min can be determined, highlighting the high time response of the instrument even in this ultra sensitive set-up.

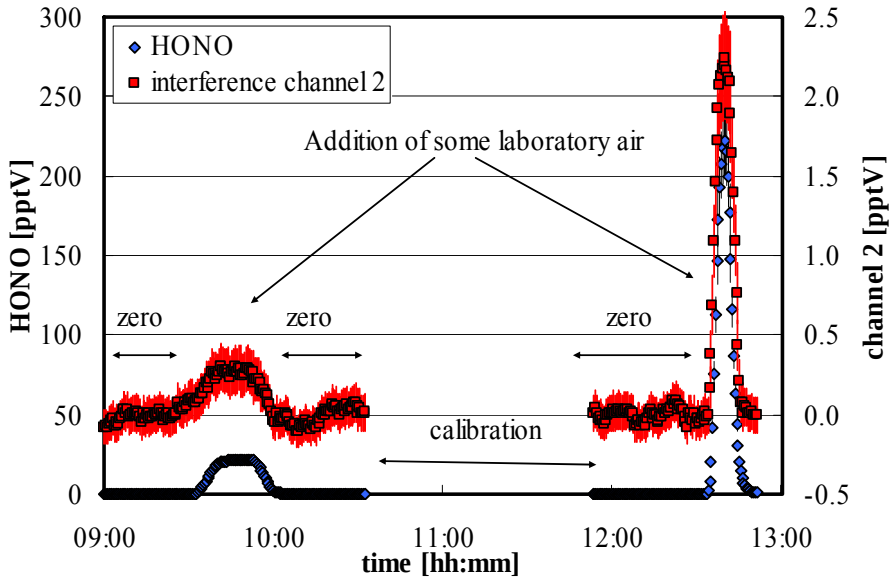

Fig. 1 Sensitivity and time response tests of the optimized LOPAP instrument. The instrument was running under zero air. HONO was added by decreasing the flow rate of the zero air slightly below the flow rate of the instrument, thus measuring very diluted laboratory air. To demonstrate the sensitivity of the instrument the signal from the interference channel 2 is also shown.

In conclusion, the modified LOPAP instrument is now the most sensitive known HONO instrument worldwide. The most sensitive HONO instrument in the literature is currently a HPLC system for which a detection limit of 0.5 pptV was recently achieved for a time response of 10 min [43].

4.2 Field campaign on the "Jungfraujoch"

4.2.1 Location and weather conditions

During the time period 02.-07. November 2005 a pilot field campaign was performed on the high altitude research station "Jungfraujoch". The station is located in 3580 m altitude between the mountains "Jungfrau" and "Mönch" in Switzerland. Measurements were performed at the "Sphinx" building (see Fig. 2), which is build on a rock, above the basement of the "Jungfraujoch". The station is surrounded by large snow and ice fields. Although the station is located in middle Europe, recent NO_y measurements showed that the air reaching the station could be often compared with measurements at remote stations [54]. Caused by the large snow and ice fields around the station, the temperature range during the campaign (see below) and the low pollution levels, the "Jungfraujoch" is considered as an ideal test station for polar measurements. Especially, when southeasterly winds were prevailing during three days of the campaign, the air flow was from the large glacier "Aletschgletscher" directly to the sampling location of the LOPAP instrument and thus, were in contact with large ice surfaces and not influenced by possible local emissions from the station.

Fig. 2 "Sphinx"-station on the Jungfraujoch (northeast side). The external sampling unit of the LOPAP instrument is shown by the yellow arrow.

The LOPAP instrument was installed in the GAW laboratory room below the roof of the "Sphinx" building (see Fig. 3). The external sampling unit was fixed on a plate in front of a window on the northeast side of the building (see Fig. 4). The instrument was calibrated two times, at the beginning and at the end of the campaign and zero measurements of 20 min duration were automatically performed every 4 h.

Fig. 3 LOPAP instrument in the GAW laboratory in the "Sphinx station" on the "Jungfraujoch".

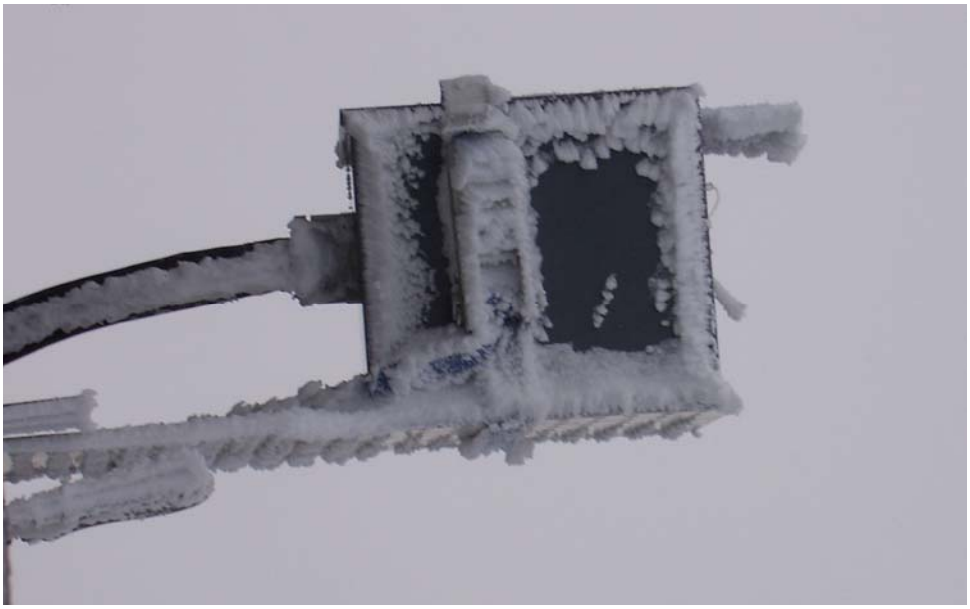

Fig. 4 External sampling unit of the LOPAP instrument during strong frost formation caused by a super saturated cloud event on the 04.-05. November 2005.

During the campaign the weather conditions varied significantly. On Nov. 02, 2005 clouds covered the sky and the station was frequently inside clouds. On Nov. 03, 2005 the weather was quite nice with maximum daytime temperatures around 0°C and low wind speed. However, at the afternoon strong winds from the southeast started while the weather was still nice up to the morning of Nov. 04, 2005. Then, the

station was inside clouds and snowfall started, while the wind was still strong. The temperature significantly decreased and super saturated cloud droplets lead to the strong formation of frost needles on the building in the night Nov. 04.-05, 2005 (see also Fig. 4). On Nov. 05, 2005 the wind speed decreased, while it was still snowing. During the end of this day until Nov. 06, 2005 high clouds covered the sky and the slow wind was reaching the station still from the southeast. During the afternoon of Nov. 06, 2005 the high clouds became thinner, leading again to higher irradiation. In addition, during this day the wind direction again changed from southeast to northwest. During the night Nov. 06-07, 2005 the weather became very nice again until noon of Nov. 07, 2005, when first high clouds covered the sky. Later the station was again inside clouds with wind from the north.

During the campaign, the temperature varied between -9.2 and +0.9 °C, the wind speed between 0-15 m/s and the pressure between 657-664 mbar.

4.2.2 HONO measurements

The HONO concentration varied between <0.5-55 pptV (see Fig. 5) with a mean value of 7.5 pptV, which is in the same range compared to polar measurements [4, 10, 16, 17, 18, 19] but also to remote measurements on mountain sites [43, 41, 42]. The HONO concentration showed a strong diurnal variation with highest concentrations during the day (see Fig. 5 and Fig. 6). This observation is in agreement with other measurements on mountains [41, 42], but also in arctic regions and is explained by photolytic processes.

While the relative diurnal variation was very similar during the campaign, the absolute values varied significantly for the different days. For example, the HONO concentrations were significantly lower on the morning of Nov. 04 compared to Nov. 03, although the weather was nice at this time of both days (see Fig. 5). This is most probably caused by stronger dilution of HONO generated on the surface, caused by the much stronger winds on the second day. On the third day the HONO concentration around noon was significantly higher compared to the second day, although for both days the weather was cloudy with some snowfall (see Fig. 5). This difference can be attributed to different air masses arriving at the measurement site. Thus, also the NO_2 concentration was much higher on the third day compared to the second day. This is an indication that probably NO_2 reactions are of importance for the daytime formation of HONO at the measurement site, in contrast to what was postulated in arctic studies.

The fourth day of the campaign was also quite interesting, since the HONO concentration increased from ~15 pptV to >40 pptV in between one hour around noon (see Fig. 5). At this time the wind direction changed from southeast (glacier "Aletschgletscher") to northwest (Interlaken Valley). Probably the observed fast increase in the HONO concentration can be attributed to the different air masses arriving at the measurement site.

For all data a mean diurnal HONO profile was calculated from the 10 min mean values of the instrument (see Fig. 6). Except some outliers, the mean HONO concentration varied between ~2 pptV in the night and ~17 pptV around noon. The variability of the data is much lower during the night compared to the day. This might be explained by a decreasing boundary layer height during the night and a much lower influence of variable pollution from the valleys around the measurement site

during the night. Accordingly, the mean night time concentration of 3.5 pptV (6:00-18:00) might be considered as a typical value for the free troposphere in mid Europe. The high daytime concentrations are most probably caused by photolytic formation of HONO, since the diurnal HONO profile nicely matches with the variation of the light intensity. However, since photolytic HONO formation is most probably caused by heterogeneous processes on the surfaces around the station, these high values are not representative for the free troposphere during the day. The mechanism of the photolytic daytime formation, i.e. nitrate photolysis versus photoenhanced NO_2 reduction, is still an open question, however, its clarification was not an objective of this pilot study.

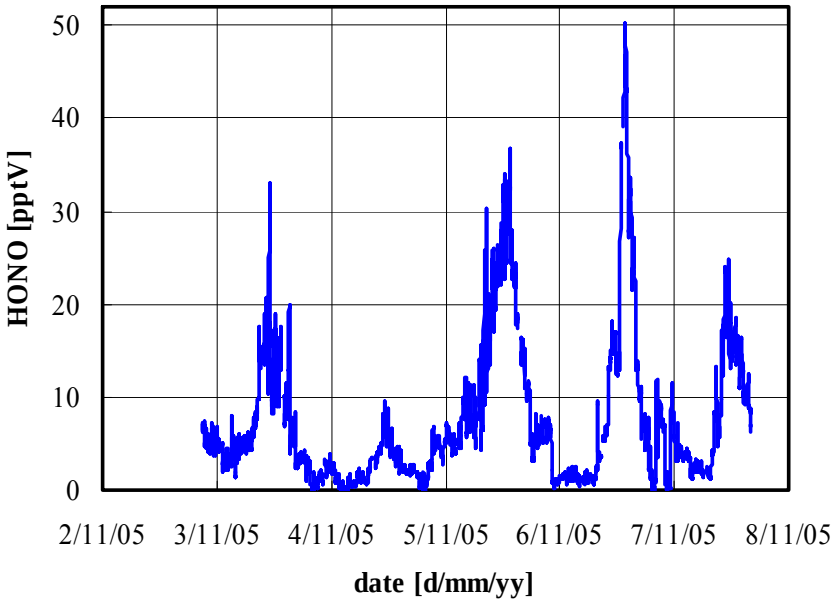

Fig. 5 HONO concentration during the field campaign on the "Jungfraujoch" in the time period Nov. 02-07, 2005.

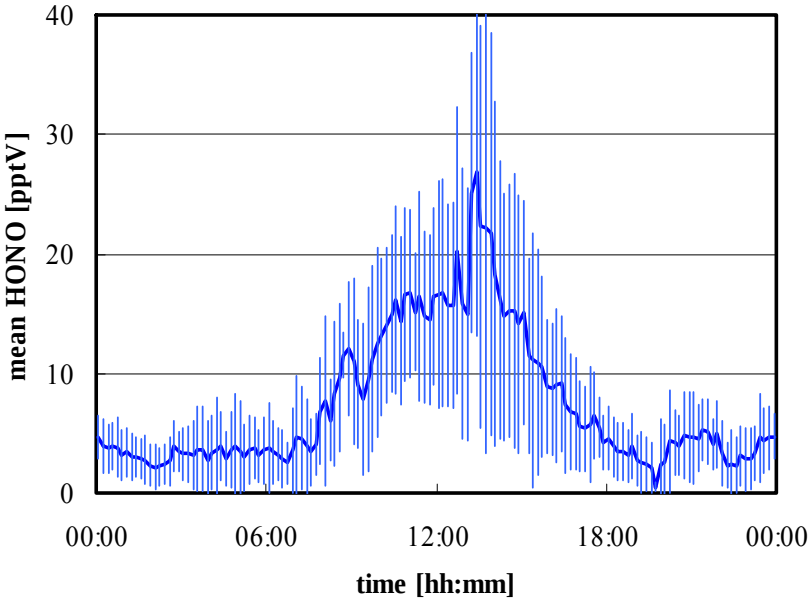

Fig. 6 Mean HONO concentration (10 min averages) during the field campaign on the "Jungfraujoch".

4.2.3 Performance of the instrument under "real world" conditions

During the campaign on the "Jungfraujoch", the weather conditions varied significantly. It was observed that the performance of the instrument, i.e. time response and detection limit, was not significantly effected by the different weather conditions. Especially during one night, super saturated clouds and high wind speed lead to the formation of ice needles on the sampling unit of the LOPAP instrument (see Fig. 4). However, the inlet of the temperature controlled stripping coil (20°C) was not affected by ice needles. Super saturated water droplets can easily form in clouds under remote conditions and thus are a typical problem for this mountain site [55], however, will be of less importance on ground stations. Thus, the field campaign on the "Jungfraujoch" demonstrated that the LOPAP instrument worked well even under extreme weather conditions.

The time response of the instrument was tested during the regular zero measurements and is defined as the time of the change of the signal from 90-10 % or 10-90 % of maximum during start and end of the zero measurements, respectively. For the field campaign, a mean time response of 7 min was achieved (see Fig. 7), in good agreement with the laboratory experiments.

The detection limit of the instrument was also determined during the campaign and is defined as two times the standard deviation of the signal from both channels during the zero measurements. For most of the zero measurements a detection limit of ~0.2-0.3 pptV was achieved (see Fig. 7), which is only slightly above the value determined in the laboratory. Thus, for most of the campaign the high performance of the instrument was confirmed also under extreme weather conditions.

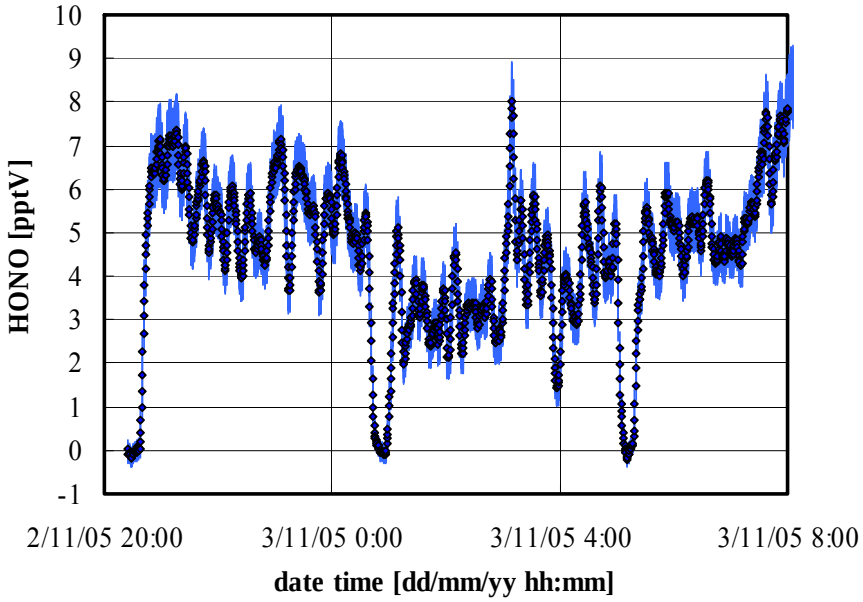

Fig. 7 Demonstration of the time response and sensitivity of the instrument during the field campaign. Each data point reflects a mean value of 30 s.

While typically the correction of interferences was in the range 10-50 %, very high interferences of >100% were observed during one night of the campaign (see Fig. 8). In this case, the signal of the interference channel 2 was nearly as high as the one of channel 1. The reason for these high interferences is still unclear. The small known

ozone and NO_2 interferences [41], can only explain a signal of ~1 pptV in channel 2 under the conditions shown in Fig. 8. Thus, other unknown interferences like e.g. the one caused by NO_2 and oxidisable hydrocarbons [44] might explain the observed high signal in channel 2. This again highlights the importance of using a two channel system for the detection of nitrous acid in the atmosphere by a wet-chemical instrument. Since it can be expected that also other chemical instruments will suffer from these interferences [44], HONO measurements might be afflicted with large errors especially at low HONO concentrations. For example, during the night shown in Fig. 8, the HONO concentration would have been overestimated by a factor of up to three, if only a one-channel LOPAP instrument were used. Caused by the high interferences and the large correction of the HONO signal during this night, a detection limit of only 0.7-0.8 pptV was determined for this special situation. In contrast, for the rest of the campaign, the correction by interferences was much lower and thus, the determination of the detection limit only by the zero measurements was not significantly effected. For example, for the measurements shown in Fig. 7, interferences of only 15-20 % were measured in channel 2 of the LOPAP instrument. This small correction has no significant influence on the accuracy of the data. Since it can be expected that interferences are of lower importance in polar regions with typically lower concentrations of interfering compounds such as NO_2 and oxidisable hydrocarbons [44], a detection limit of ~0.2 pptV can be expected also for polar measurements with the LOPAP instrument.

In conclusion, the high performance of the LOPAP instrument was also confirmed under the extreme weather conditions prevailing on the "Jungfraujoch" and thus, the aims of the pilot study were fully reached.

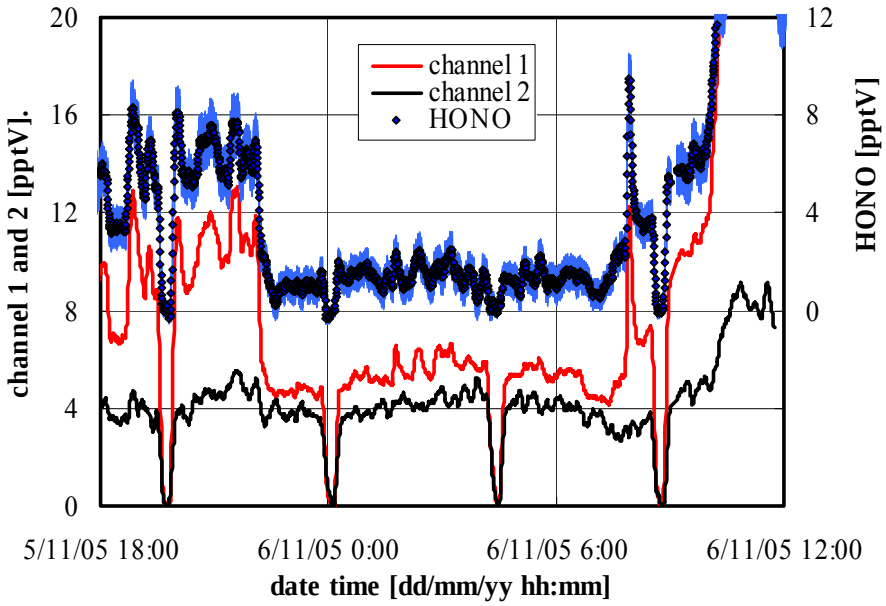

Fig. 8 Example of high interferences observed in the night Nov. 05-06, 2005, leading to a somewhat higher detection limit of ~0.7-0.8 pptV for these conditions.

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