Determination of Nitrous Acid mixing ratio in the troposphere using LOng Absorption Photometry technique

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Table of Contents:

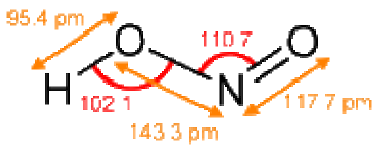
Abstract:

A research study was performed using a LOng Path Absorption Photometry (LOPAP) technique towards determination of Nitrous acid (HONO) concentration in the lower atmosphere, specifically troposphere in urban areas of Toronto, Ontario. The instrument was located on the rooftop of Petrie Science and Engineering building of York University Keele campus. The detection limit of the LOPAP instrument is 5 pptv. The sources of HONO represent a major research area since it plays a very important role in production of OH radicals and therefore tropospheric ozone (O_3) – a very strong oxidizing agent and human health hazard. The obtained experimental data suggest a specific trend of a night time build-up of HONO and continuous photolysis at sunset, which is compliant with theoretical assumptions. Experiments were performed at different times of day and show an average of 20-30 pptv mixing ratio of HONO in the atmosphere during the night and 5-10 pptv mixing ration during the day. The possible sources of HONO taken from these experimental measurements are the vehicle emission of NO_2 molecules and humic acid pollution from the forested regions located close to the instrumental setup and carried with wind gust. A suggested further research needs to be performed for better quantification of possible sources of nitrous acid evolved into the troposphere.

1.1 Introduction

Nitrous acid (HONO) is an important chemical species that is included in the atmosphere and has been a subject of research for quite some time by atmospheric chemists around the world. The reason for such high interest in this compound is an important role that it plays in chemical processes in atmosphere, the most important of which is the formation of OH radicals in the troposphere (9). A better understanding of the formation of HONO is needed for improvement of the existing air pollution models, which account for very oversimplified Nitrous acid production mechanisms. This research field might have a significant impact on these models as well as understanding a photochemical smog formation and possible future political decisions regarding emission control strategies (8).

Nitrous acid is weak monobasic acid with molecular weight of 47.013 g/mol and exists in the gas phase at room temperature. Judging from the IR spectra of Nitrous acid, it predominantly exists in trans conformation and is 2.3 kj/mol more stable than its cis conformation (3):



The physical properties of nitrous acid include its non-flammability with relative density of 1 g/mL, and appear as a pale blue coloured solution.

The chemical relevance of Nitrous acid includes the most important reaction in the atmosphere – the photolysis of HONO into OH and NO radicals in the troposphere with the first sunlight through the following reaction:

HONO + hν (λ <400 nm) → OH + NO (R1)

The importance of this reaction is the production of OH radicals which is a major contributor to the production of ozone in the troposphere as well as it reacts with NOx and SO_2 to produce constituents of the acid rains (17).

Since the air pollution problem is still at hand, it is crucial to find out the exact sources of Nitrous acid in the atmosphere. The following are the sources of HONO in the atmosphere known to this day:

Homogeneous Chemistry through the reverse of reaction R1 (15):

$NO + OH \rightarrow HONO$ (R2)

This reaction is irrelevant during the night, since the concentrations of OH are too low, however there are still studies undergo towards the relative significance of this reaction during the day (19).

Heterogeneous Formation of Nitrous acid by a first order mechanism on surfaces in the presence of water and NO_2 (7):

$H_2O + 2NO_2 \rightarrow HNO_3 + HONO$ (R3)

Even though this reaction seems to be valid, the laboratory measurements performed does not provide an exact mechanism for this reaction as well as the lack of understanding about the surfaces on which this reaction occurs (20). The reaction of water, NO and NO_2 in production of Nitrous acid is also possible (2), however the observations suggest that NO is not necessarily included in the formation of HONO (23, 26). In addition, the production rate of HONO in the laboratory environments present the rates two orders of magnitude lower than in the atmosphere, therefore it is still unknown whether these assumptions can be used in real life model (25).

Formation of Nitrous acid on soot particles in the presence of NO_2 and perhaps water is another possible source of HONO as laboratory studies have shown, however the relevance of this source is still under investigation (1).

Direct Emission from combustion processes in engines is yet another source of HONO in the atmosphere (16). Studies have shown that Nitrous acid is emitted by diesel engines (24). Other studies have shown that gas space heaters and stoves also produce HONO in high concentrations indoors (4). The following is the list of all of the equations that contribute to the production of OH in the troposphere (5):

$O_3 + h\nu\ (340\ \text{nm}) \rightarrow O(^1D) + O_2$ (R4)

$O(^1D) + H_2O \rightarrow OH + OH$ (R5)

$HONO + h\nu\ (\lambda < 400\ \text{nm}) \rightarrow OH + NO$ (R1)

$HCHO + h\nu\ (\lambda < 370\ \text{nm}) \rightarrow H + CHO \rightarrow H_2 + CO$ (R5)

$H + O_2 + M \rightarrow HO_2 + M$ (R6)

$HCO + O_2 \rightarrow HO_2 + CO$ (R7)

$HO_2 + NO \rightarrow OH + NO_2$ (R8)

The reaction R8 of HO_2 with NO is also important to keep in mind when studying the nitrous acid contribution to the overall OH radical formation in the troposphere since NO molecules are directly produced from R1.

2.1 Techniques of determination of HONO concentration in the atmosphere

There are different methods of determination of concentration of Nitrous acid in the atmosphere available to this day:

Chemiluminescent method - is a continuous–flow method for measuring HONO concentrations that uses a chemiluminescent NO_x monitor. A Na_2CO_3 solution strips HNO_2 from the atmosphere by means of pulling an air sample and the solution through a glass coil and mixing continuously with ascorbic acid solution which reduces nitrite to NO. The mixture is led into a gas-liquid separating coil consisting of micriporous PTFE tubing. The NO evolved from the separating coil is swept out by a stream of clean air and detected with a chemiluminescent NO_x monitor. The technique utilizes a dual flow system and dual channel NO_x monitor to correct positive interferences from NO_2 and peroxyacetylnitrate (PAN). The concentration of HNO_2 is determined by difference between the two measurements. Sensitivity of the method is a function of the ratio of sampling flow rate to carrier gas flow rate, which permits readily a highly sensitive measurement. This technique possesses a detection limit of about 0.05 to 7.1 μg/mL, which is considered to be very low and make this method accurate (13).

Another technique used in Nitrous acid research is Differential optical absorption spectroscopy (DOAS), which determines concentrations of trace gases by measuring their specific narrow band absorption structures in the UV and visible spectral region (18). It consists of a continuous light source (Xe-arc lamp) and an optical setup to send and receive the light through the atmosphere. The typical length of the light path ranges from several hundred meters to many kilometers. After its path through the atmosphere the light is spectrally analyzed and the concentrations are derived. In comparison to the chemiluminescent method the detection limit of DOAS is around 100 ppt depending on the path length.

Tuneable diode laser absorption spectroscopy (TDLAS) is yet another technique of determining the concentrations of different species in the atmosphere in their gas phases. A basic TDLAS setup consists of tuneable diode laser light source, transmitting optics, optically accessible absorbing medium, receiving optics and detectors. The emission wavelength of the tuneable diode laser is tuned over the characteristic absorption lines of a species in the gas in the path of the laser beam. The signal is then analyzed in tuneable laser absorption spectrometer to measure the concentration of the trace gases in the atmosphere. The detection limit of this method is even higher than in DOAS, 200-500 ppt, which puts TDLAS to be less accurate than DOAS in determination of concentrations of trace gases in the atmosphere and not suitable for specific and careful nitrous acid measurements (10).

The PF-LIF – Photofragmentation Laser induced fluorescence is a technique based on laser photolysis of molecules into less complex fluorescent fragments, from which the parent molecule can be detected. The measurements are performed using two different lasers in a pump-probe fashion. The first laser (pump) photo dissociates the parent molecule and produces fragment, whereas the second laser (probe) generates fluorescence from the fragments and this radiation is the signal to be detected. The detection limit of this technique is pretty low in the range of 10 ppt, and considered to be one of the most accurate measurement techniques (3).

Another apparatus and technique that is used for measurements of aerosols and trace gases such as HONO in the atmosphere is chemical ionization mass spectrometry (CIMS). This instrument consists of an electrostatic precipitator for collecting charged particles, an evaporation-ionization chamber and a triple quadrupole mass spectrometer equipped with a collision-induced dissociation chamber (CID). The CID chamber is used to strip clusters down to their core ion before their mass is analyzed (27). The system is equipped with bipolar charger and a nanometer aerosol differential mobility analyzer (nano-DMA) at the inlet to charge and select particles of a given size, and with a condensation particle counter at the outlet, which is used to quantify the collected aerosol mass. The detection limit of this instrument is around 60 ppt, which is suitable for determination of micro structured aerosol particle concentrations as well as trace gases contained in the atmosphere (24).

Cavity ring-down spectroscopy (CRDS) is an optical spectroscopic technique that enables measurement of absolute optical extinction by samples that scatter and absorb light that is used in studies of gases which absorb light at specific wavelengths and determination of their concentrations in part per trillion levels. This instrument consists of a laser to illuminate a highly concentrated optical cavity consisting of reflective mirrors, then due to the constructive interference of the laser beam in resonance; the intensity builds up in the cavity. When the laser is turned off the light starts to decay at a certain known rate, which in case of the presence of a light absorbing species will be higher. By measuring the rate of decaying light in the cavity the concentration and mole fraction of the gas can be measured. The detection limit of this technique is relatively high in the region of 1 ppb. Considering that Nitrous acid concentration in air are usually in the ranges of parts per trillion, this technique might not be very accurate in HONO measurements (17).

Proton-transfer-reaction mass spectrometry (PTR-MS) is a very sensitive method for monitoring of gaseous compounds in ambient air. It consists of an ion source connected to a drift tube and an analyzing system (Time-of-flight mass spectrometer). The detection limit of this technique is in the region of single digits parts per trillion, therefore making this technique suitable enough for monitoring nitrous acid concentration in the atmosphere (20).

2.2 LOPAP

The LOng Path Absorption Photometer (LOPAP) technique was introduced by Kleffmann study and research group at the University of Wuppertal, Germany (22). The absorption photometer using a UV Visible spectrometer measures the azo-dye that is formed through a series of reactions: The ions of NO2 that were scrubbed in the solution react with Sulfanilamide (SA) to form a diazonium ion, to which 1-napthylethylene-diamine (NED) is introduced to form the azo-dye – a highly light absorbing species. By analyzing the content of this azo-dye in the solution by spectrometer determines the amount of NO2 that reacted, therefore giving the intensity measurements into the software. The absorption measurements follow Beer's Law:

$ABS = \log (I_{background}/I_{abs}) = k_{\lambda} * l * c$ (Eq 1)

The measurements are performed in two channels simultaneously with readings for two wavelength 544 nm and 710 nm in each. The reason for the setup of two channels is the subtraction of interferences in Channel 2 from Channel 1, leaving the useful absorption present. The intensity measured at 710 nm wavelength is the light intensity with no absorber present in the solution ($I_{background}$) and the intensity at 544 nm corresponds to the light intensity with the presence of absorber (I_{abs}). Therefore, the light intensity at 710 nm wavelength is considered to be a reference, so there is no need in taking a blank measurement for comparison to the absorbing light intensity measurement. The k_{λ} in Beer's Law Equation represents the absorption coefficient of the azo dye and is equal to $5*10^{4}$ M^{-1} cm^{-1}, the L value is the pathlength that light travels though the absorber, which lowers the detection limit of the instrument with its higher value and C is the concentration of the species being measured (6). Judging from the Beer's Law equation the log of the ratio of the intensity readings is linearly dependent on the concentration of the absorber, and the slope of the graph represents the product of absorption coefficient k_{λ} which is wavelength dependent and the pathlength that light travels through the absorber (12).

Due to the simultaneously recorded readings for the wavelengths of both 544 and 710 nm, the blank readings that are usually needed when applying Beer's Law are not required, since the intensity at 710 nm wavelength acts as the reference and used when the absorption cross section is close to 0. Beer's Law equation is slightly changed by addition of a constant, due to the fact that the starting material from which the light absorbing azo dye is prepared, also absorb light at 544 nm wavelength, therefore the Beer's Law takes the form (12):

$ABS = \log (I_{background}/I_{abs}) = k_{\lambda} * l * c + \log(\text{Constant})$ (Eq 2)

The constant depends on the reagents SA and NED, therefore whenever the batches of these chemicals are renewed, a background measurement is needed.

The instrumental setup of the LOPAP instrument includes a sampling unit, where all of the reactions take place, and the detection unit, from which the measurements are recorded. The sampling unit consists of two glass coils of 17 cm long each for two channels connected in series, to which the prepared reagent solution of 0.06 M SA is pumped at a flow rate of 0.4 mL/min for all tubes for both channels. The roller ISMATEC pump is used for this purpose. Gases from air are pumped through the coils at a flow rate of 1 L/min. The liquid reagent with consistent air from the coil goes through a debubbler, in order for any bubbles in the tubes to be removed before they get into the detection unit. Almost all of the nitrous acid concentration is getting measured in channel 1, however all other species that are soluble are getting sampled in channel 2. The nitrous acid concentration is corrected by subtracting measurements in channel 2 from measurements in channel 1. The desired diazonium ion is formed in the reaction of SA with HONO, and the solution is then pumped through another debubbler after which the 0.2 mM concentration NED reagent is added to the solution to form the light absorbing azo dye, which is then transferred separately through each channel into the liquid core waveguide (LCW) (12).

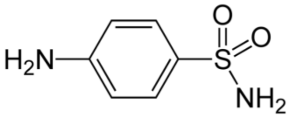
Detection unit of the LOPAP instrument consists of the LCW, spectrometer itself, computer and the software. As mentioned previously the detection limit can be decreased by increasing the pathlength that light travels through the absorber. The Liquid Core Waveguides (LCW) method is designed specifically for the purpose of increasing the sensitivity of the LOPAP instrument (11). The LCW consists of an optical fibre with a liquid core (hence the name), which in turn consists of the glass core and a cladding, and performs a function to generate a total internal reflection that follows Snell's Law (12). The idea behind generating a total internal reflection is based on the light traveling from one medium that retains a refractive index nc to another medium with refractive index of nf at an angle P. A Teflon AF2400 capillaries or coating in the glass tubing are used in this application of LCW in order to create a total internal reflection with an aqueous core, since the nc needs to be less than the core refractive index (value of 1.33) (11). In LCW method there is a critical angle at which the total internal reflection occurs, and in the case in which a Teflon AF is used, the angle is 14.1 degrees, which means that the total internal reflection occurs at all angles less than 14.1 degrees. One of the problems that the preceding research group has ran into is the adsorption of the azo dye to the surface of Teflon coating, which decreased the amount of transmitted light, which consequently reduced the sensitivity and stability of the instrument. The solution that was found to be feasible was to replace the current LCW's with Liquid Waveguide Capillary Cells, in which a quartz capillary is coated in Teflon AF. This resulted in cleaner Teflon and eased a cleaning procedure.

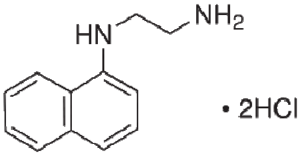
The spectrometer used for the measurements in LOPAP has an LS-1 tungsten halogen lamp as a light source. The light traveled into both LCW channels using a Y optical fibre and went in the output directed by two optical fibres into a mini-CCD Spectrometer S 2000. In order to convert the measurement into a readable computer data an ADC1000-USB analog-to-digital converter was used, which connected the spectrometer to the computer using a USB cable. The software in the computer used to generate the data from the measurements was Ocean Optics Spectrasuite 2000 (12).

2.3 Chemical Reactions and Schematic of LOPAP method

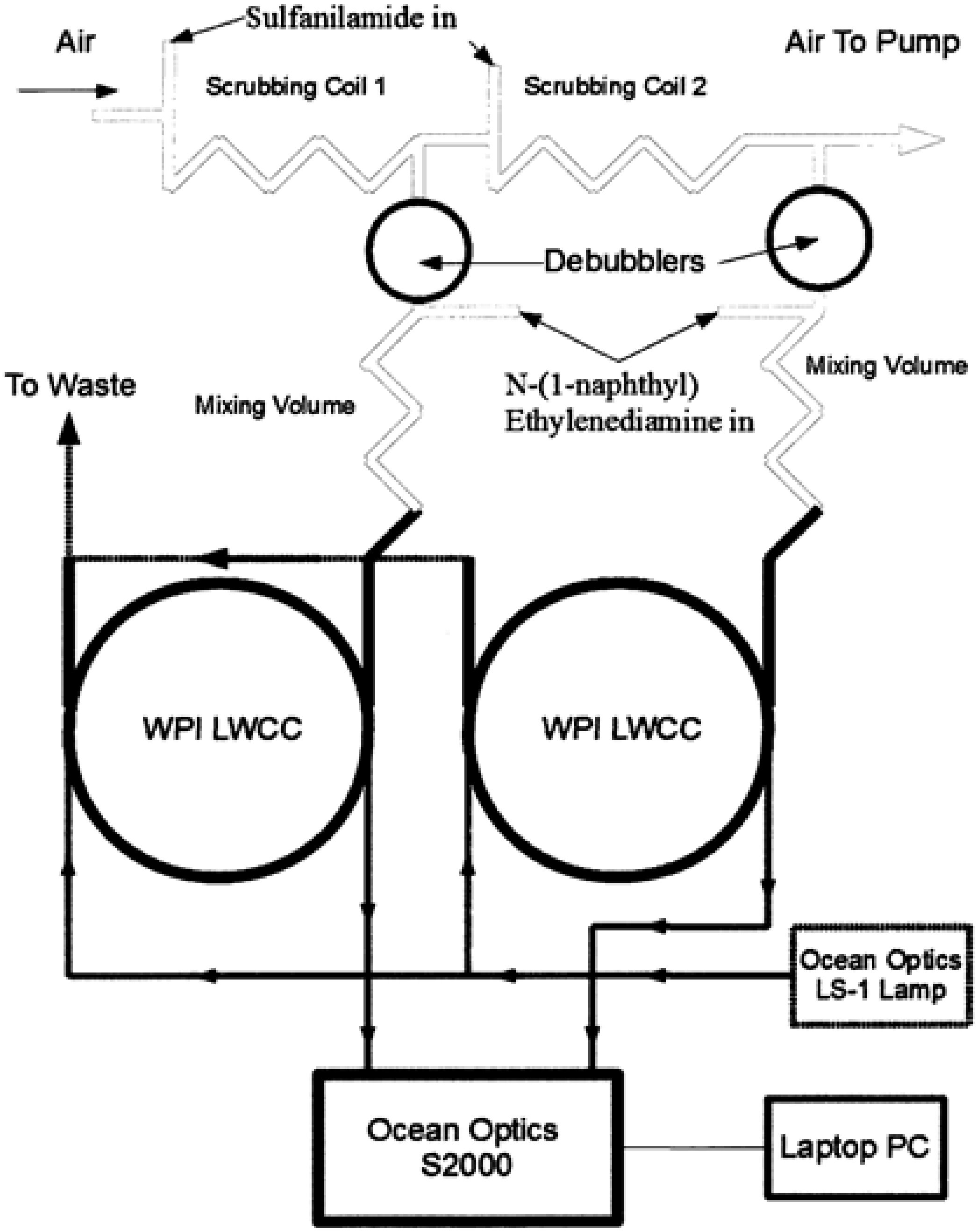
The following are the reactions that are happening in the LOPAP instrument converting the NO_2^- ion into azo dye for photometric evaluation:

1). $HONO + H^+ \rightleftharpoons NO^+ + H_2O$

2).  (SA) + $NO_2^- + 2H^+$ → Diazonium salt + H_2O

3).  (NED) + Diazonium salt → Azo Dye + HCl

The following is the schematic of the whole LOPAP instrument:



3.1 Calibration Procedure and data for LOPAP

The calibration of LOPAP can be performed by one of two methods: a nitrite standard solution of different concentrations or a source of HONO gas of known concentration. The second method includes a reaction of sodium nitrite with hydrochloric acid to produce HONO:

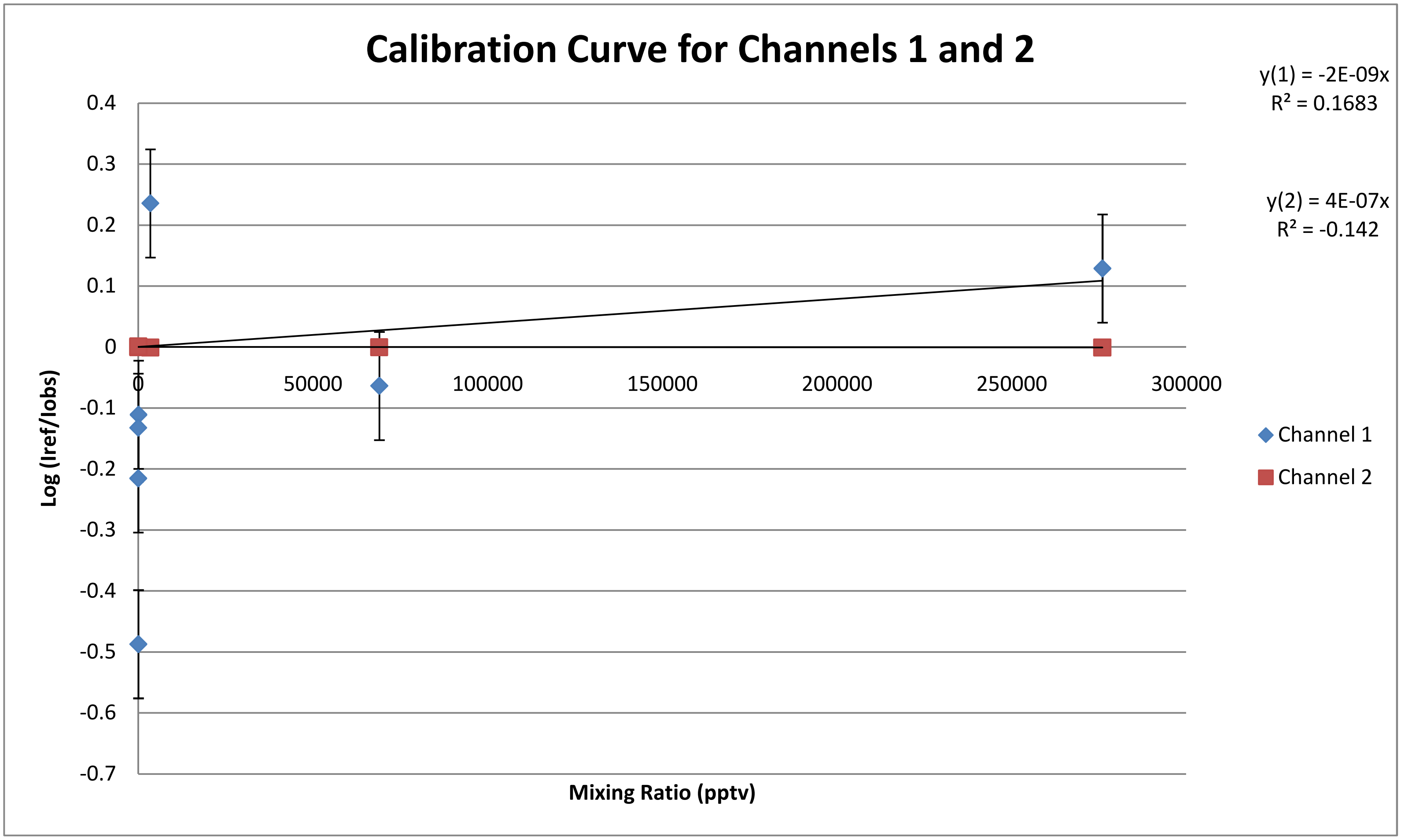
$HCl(g) + NaNO_2(s) \rightarrow NaCl(s) + HONO(g)$ (R9)

The gases are humidified in this reaction since it will not proceed in the absence of water vapour, due to the formation of sodium chloride on the sodium nitrite crystals. However, the humidity needs to be around 60%, since it can lead to deliquescence. Compared to the first calibration method by a nitrite standard solution, the second method is performed with rather sophisticated equipment, which cannot be used in the field. In comparison, both of these methods proved to be equally accurate and quantitative, in which the uncertainties from each of the channels include the uncertainties of the gas flow rate, liquid flow rate and the slope of the calibration curve, where the total uncertainty was calculated to be around 10%. The detection limit of LOPAP is calculated using three times the standard deviation of the measurement taken from the reagents and turned out to be around 5 ppt. Another measurement is also useful in terms of elimination of additional interferences is sampling of a zero air with no nitrous acid present. This measurement is performed in order to eliminate any absorption contribution coming from somewhat light absorbing reagents SA and NED used.

The reagent used in the calibration procedure by the method of liquid nitrite standards is prepared in series of different concentrations using $NaNO_2$ from Sigma-Aldrich. A sample of 0.6917 g of dry $NaNO_2$ in the form of a fine yellowish powder was put into a 1 L volumetric flask and diluted up to the mark with Milli-Q water to make 1 L of 10^{-2} M $NaNO_2$ solution. From this batch two more $NaNO_2$ solutions of 10^{-4} M and 10^{-6} M concentrations were made. Consequent dilutions were performed in 100 mL volumetric flasks in order to prepare standards for calibration measurements of the following concentrations: $4*10^{-7}$ M; 10^{-7} M; $5*10^{-8}$ M; 10^{-9} M; $5*10^{-10}$ M; 10^{-10} M and $5*10^{-11}$ M. The calibration measurements started with the lowest concentration up to the highest.

The SpectraSuite 2000 software parameters were specifically set the same way for both the calibration and the experimental measurements. Boxcar width parameter was set to 10 in order to make the curve smoother; Integration time was set to 10 micro seconds; the average number of scans varied with different experimental setup and depended on the saving mode of the measurements to be around 2500. The save mode in the software was set up for any measurement for every 10 minutes during the experiment for nitrous acid determination in air, however in the measurements of calibration the save mode was set up for every 1 minute, as well as the average number of scans was set up to the value of 1 in order for easier monitoring of the changes in the curve. Calibration connections and set up of all of the tubing in the LOPAP instrument was different from the set up for the actual measurement collection and was performed in the following order: Run Milli-Q water through the LOPAP to rinse the whole system at first; Run the lowest concentration of $NaNO_2$ solution for 10 minutes and record the data, which is done in triplicate; Between each run of the same concentration the system was rinsed with Milli-Q water for 10 minutes, as well as when changing the concentration of the solution. The following are the calibration curves that are created from the calibration procedure explained above and performed on October 23, 2011:

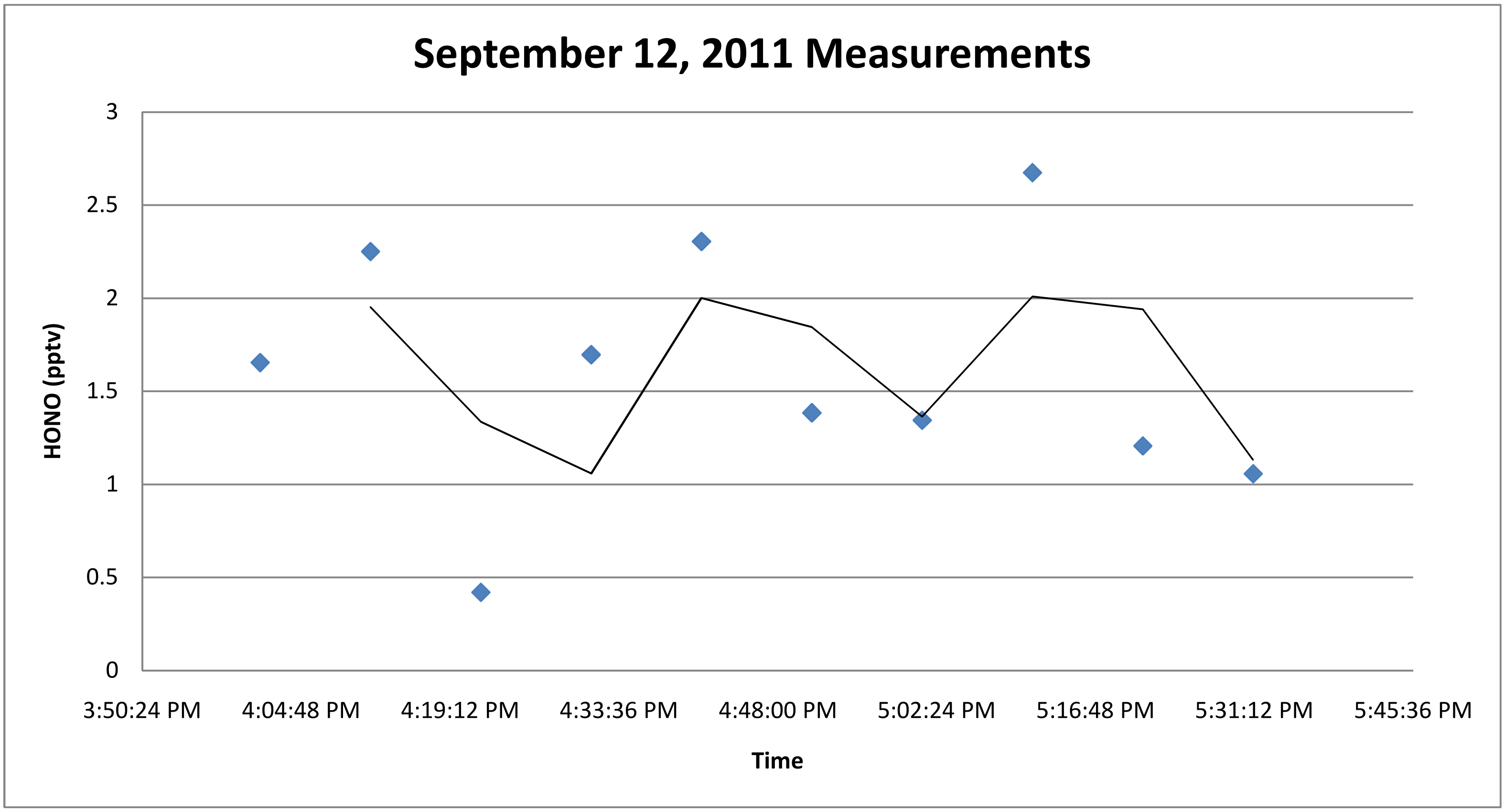
3.2 Calibration Curves and Analysis

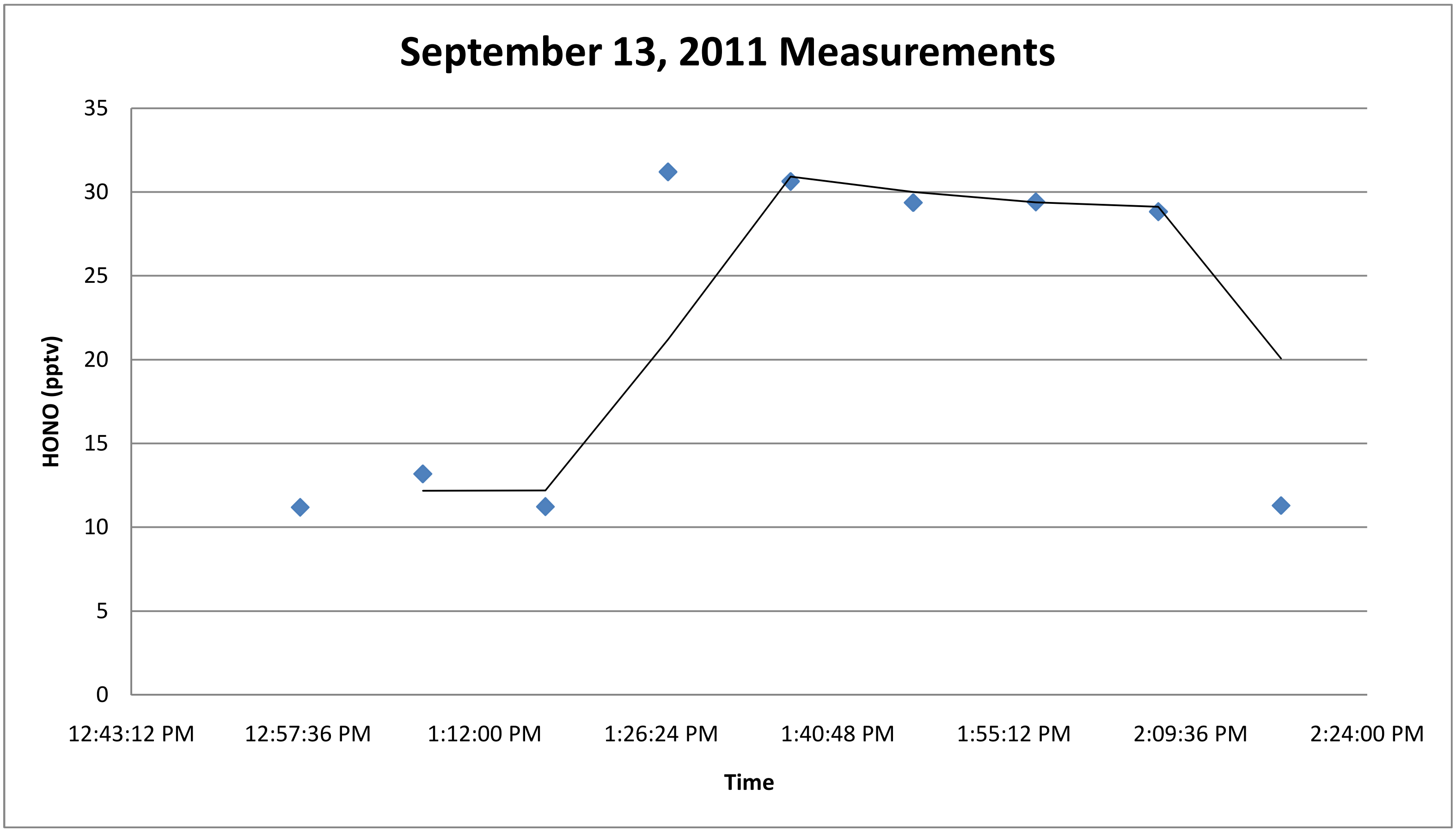


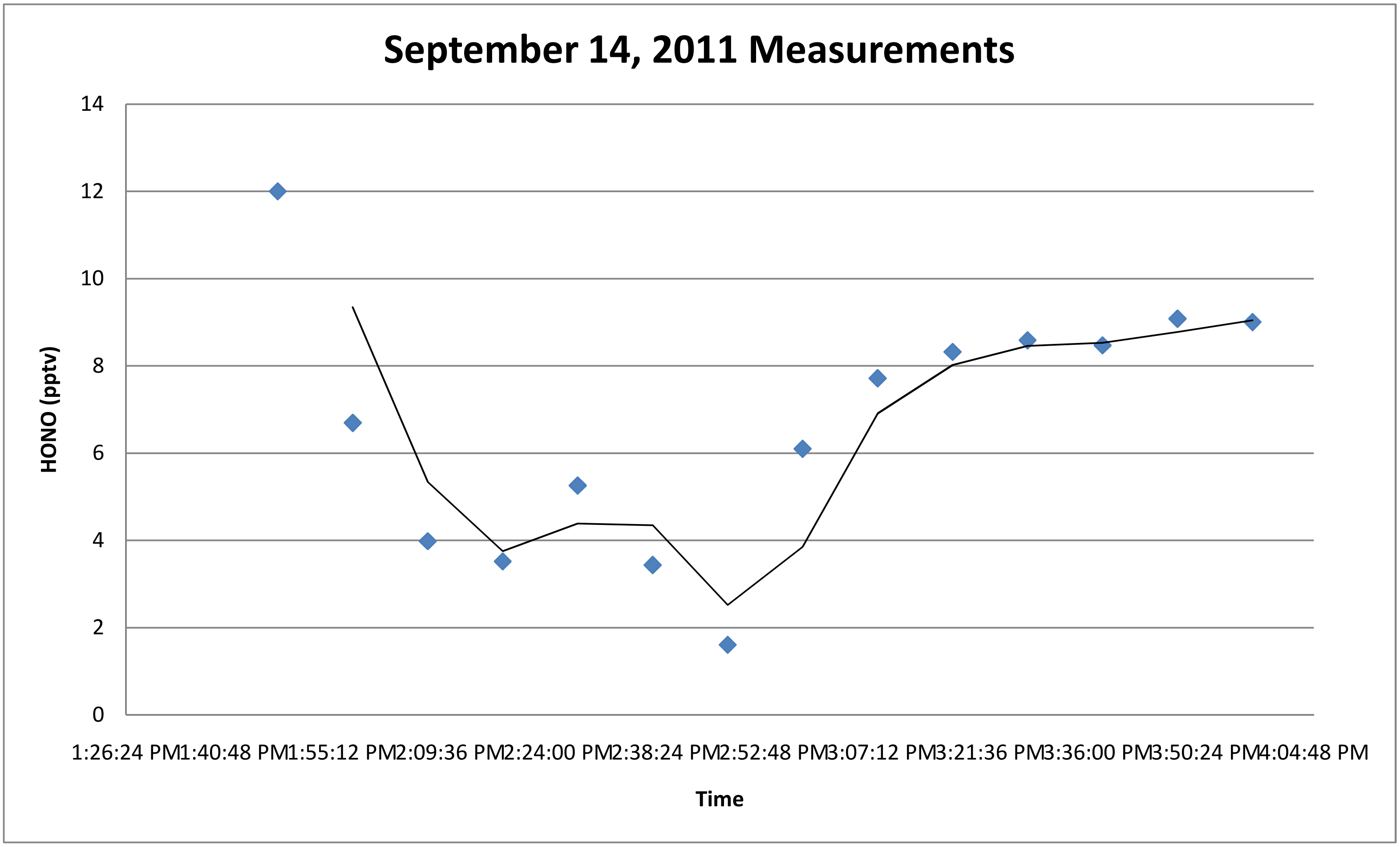
From the calibration curves performed on the LOPAP it can be seen that the calibration curve of channel 1 is relatively close to the expected, however the curve for channel 2 is very close to zero, which comes from very low concentrations of NO_2 ions coming towards the channel 2 absorption. Even though the expected trend is present, that the slope of channel 1 calibration curve is higher than of channel 2, the observed values cannot be correct. The possible reason for such results is either the malfunction of the spectrometer itself or the lack of flow into the channel 2 opening of the LCW. Another observation is towards the data from channel 1 made to the fact that there are negative values of the LOG of the ratio of the intensities, which is also not expected from the calibration curve. Even though the calibration values do not present a correct set of curves, the following actual experimental values of the nitrous acid measurements prove to be relatively close to the expected values. This comment goes towards the notion of the fact that the flow rates into both channels of LCW during the calibration procedure were drastically different.

4.1 Experimental Procedure and obtained data

Experimental procedure was performed in a "wet" laboratory and started with the preparation of the reagents SA and NED for the measurements to be taken. Both Sulfanilamide CAS 63-74-1 – minimum 99% and N-(1-Naphthyl) ethylenediamine dihydrochloride CAS 1456-25-4 were ordered from Sigma-Aldrich and were completely dried out of water in an oven at approximately 80 C temperature overnight. 10.3343 g of dry SA were weighed by difference was in the form of small shiny white crystals and were poured into the 1 L volumetric flask. To the same volumetric flask 0.083 L of 12 M HCl was added and diluted with Milli-Q water to prepare 1 L of 1 M HCl and therefore form a 0.06 M solution of Sulfanilamide. 0.1041 g of NED was weighed by difference and poured into a 2 L volumetric flask in the form of fine white powder. 0.167 L of 12 M HCl was added to the 2 L volumetric flask and diluted with Milli-Q water up to the mark, to make 2 L of 1 M HCl and consequently 0.2 mM of NED reagent. Both volumetric flasks were shaken carefully for the reagents to dissolve completely and were stored in the refrigerator when not in use. Since NED is light sensitive, the batch should be covered in aluminum foil. The actual experimental measurements were taken on the following dates: September 12, 13, 14, 2011 and October 9, 10, 11, 12, 2011. The following are the graphs of curves of the analyzed data:




September 13, 2011 Measurements
HONO (pptv)
0
5
10
15
20
25
30
35
12:43:12 PM
12:57:36 PM
1:12:00 PM
1:26:24 PM
1:40:48 PM
1:55:12 PM
2:09:36 PM
2:24:00 PM
Time


September 14, 2011 Measurements
HONO (pptv)
0
2
4
6
8
10
12
14
1:26:24 PM
1:40:48 PM
1:55:12 PM
2:09:36 PM
2:24:00 PM
2:38:24 PM
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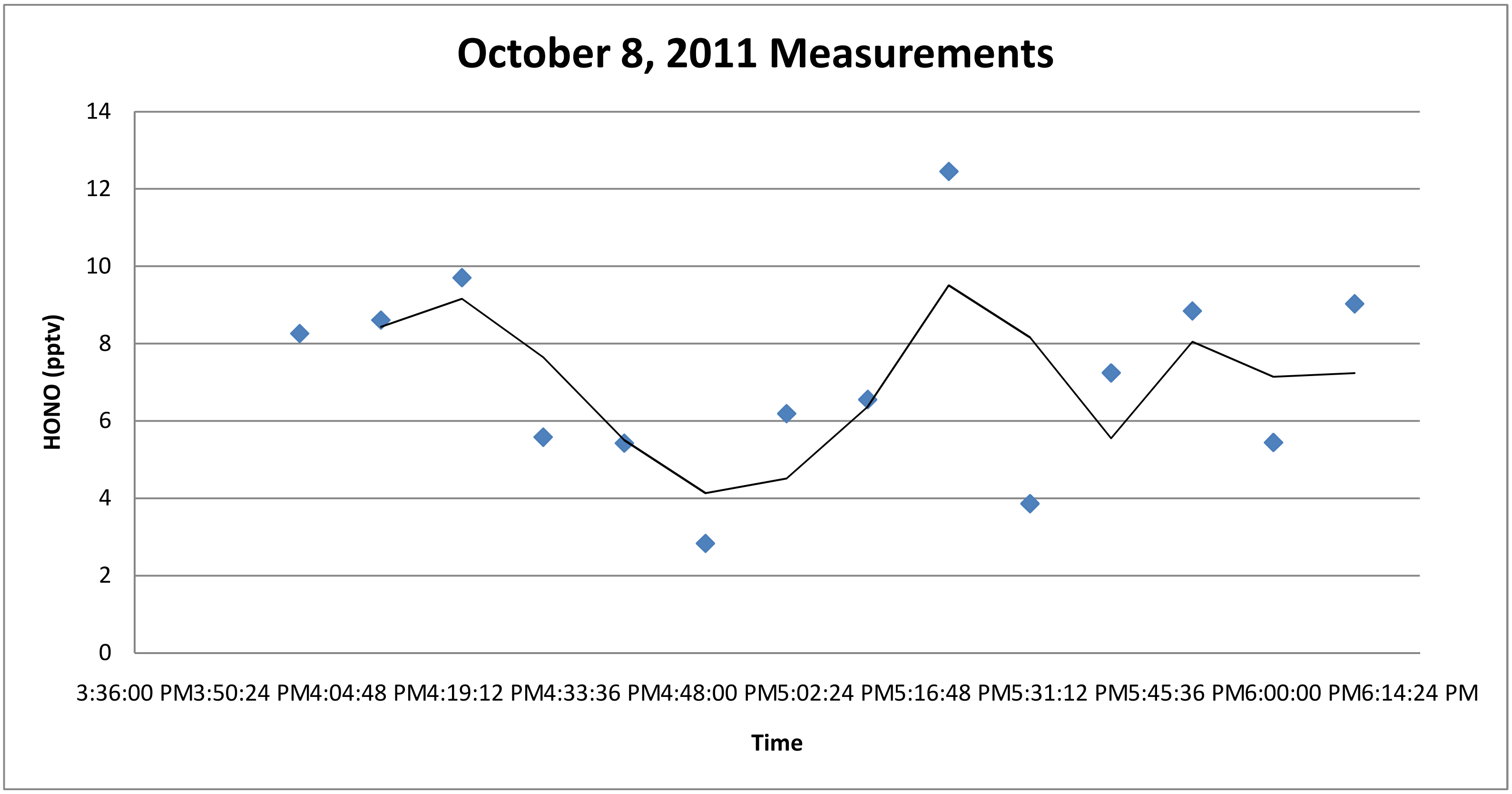
3:50:24 PM
4:04:48 PM
Time


October 8, 2011 Measurements
14
12
10
8
6
4
2
0
HONO (pptv)
3:36:00 PM
3:50:24 PM
4:04:48 PM
4:19:12 PM
4:33:36 PM
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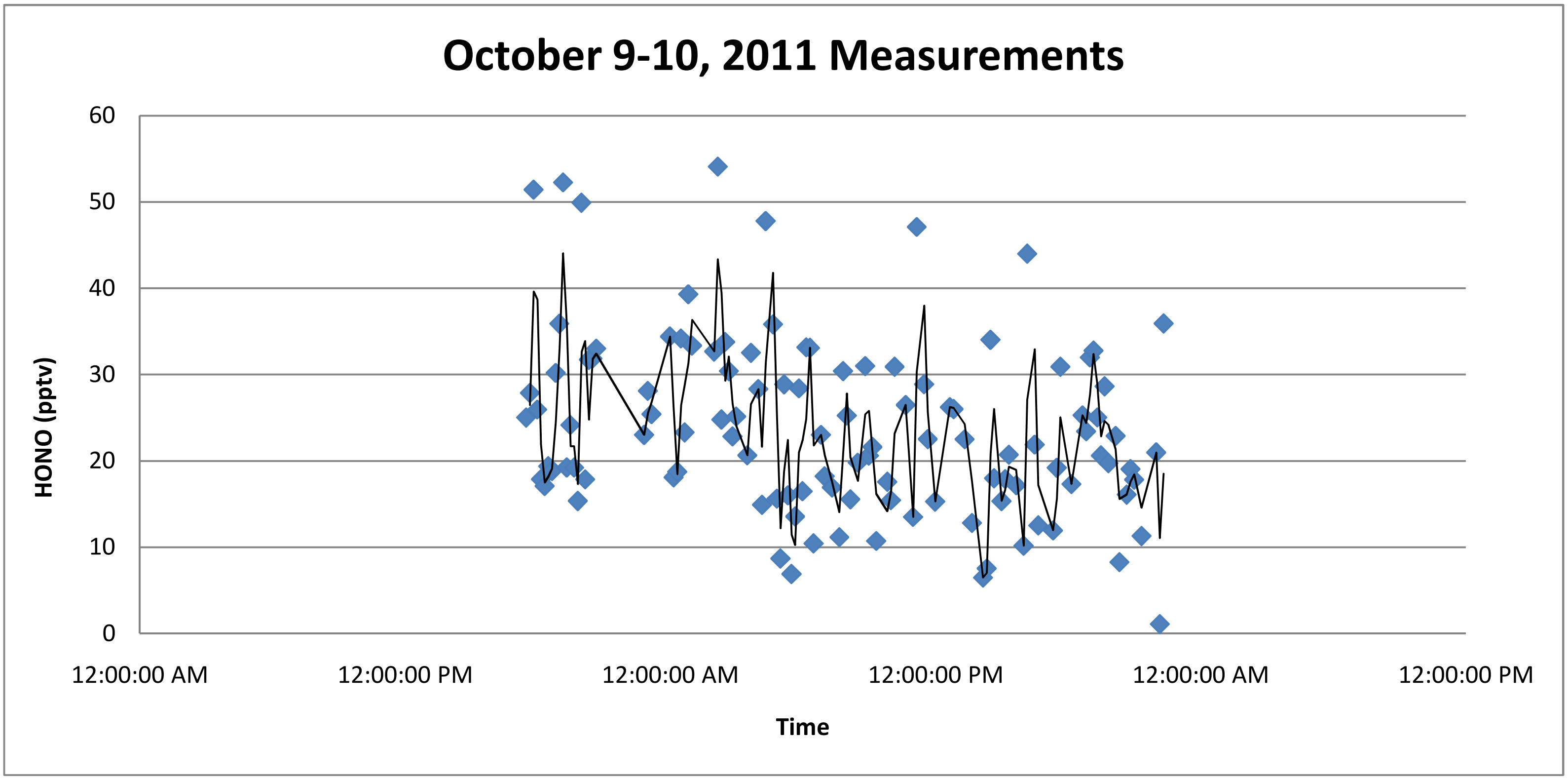
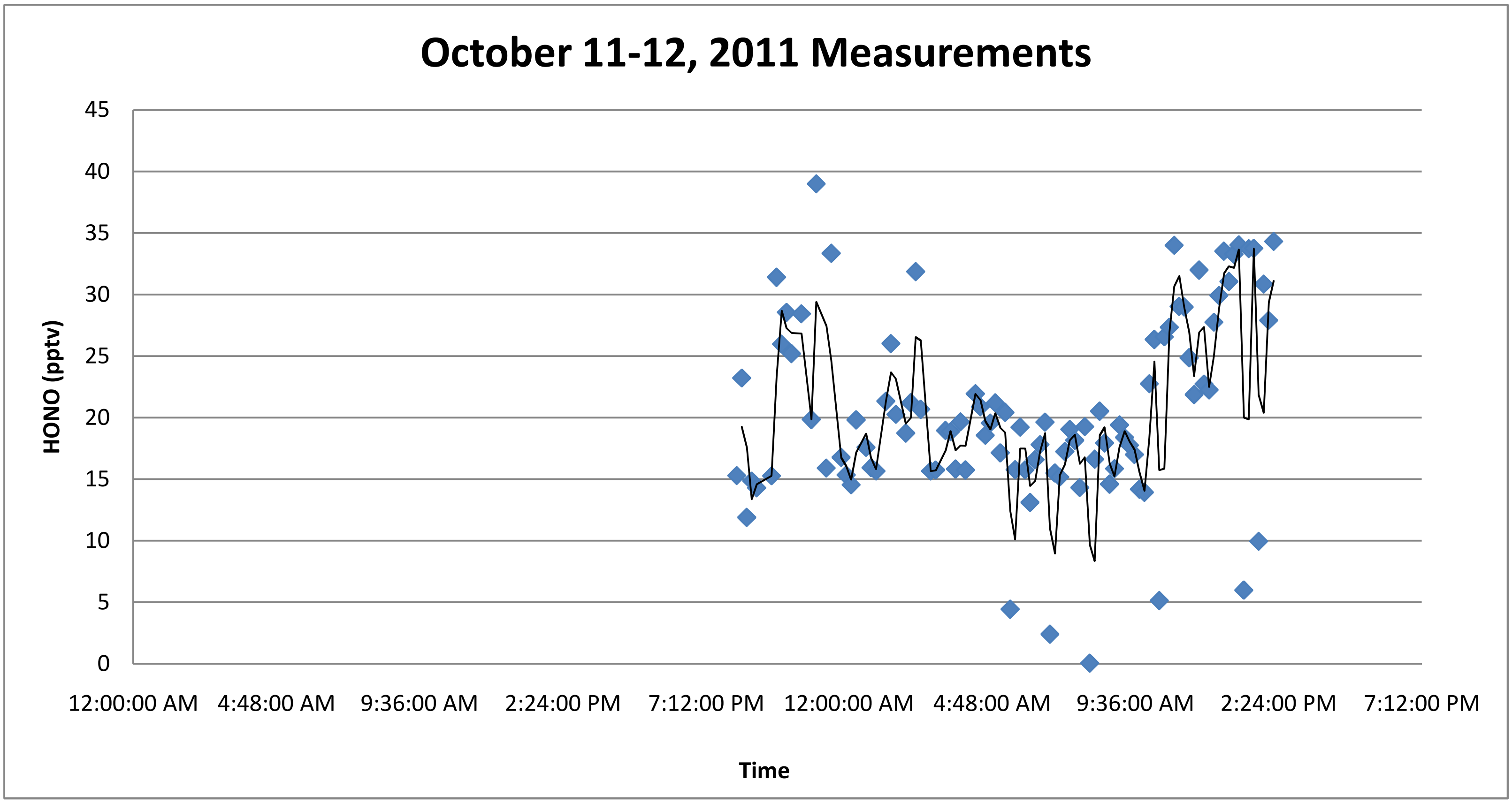
6:14:24 PM
Time


October 9-10, 2011 Measurements
60
50
40
30
20
10
0
HONO (pptv)
12:00:00 AM
12:00:00 PM
12:00:00 AM
12:00:00 PM
12:00:00 AM
12:00:00 PM
Time



4.2 Experimental Results Analysis

Judging from the obtained data taken on September 12, 2011 from 4 pm up to 5:30 pm the concentration of Nitrous acid in the atmosphere is relatively low in the region of 1 – 2.5 pptv, which seems to be reasonable keeping in mind the time of the day. Since the sun was still present in the sky, there would be no build-up of nitrous acid due to the photolysis reaction (R1). September 13, 2011 measurement graph shows the measurements taken from 1 pm to 2:30 pm with HONO ratios ranging from 10 – 30 pptv, which is a little less obvious, due to the fact that the sun was already in the sky for quite a long time and should have photolyzed most of the HONO in the troposphere. However, this can be explained by constant production of HONO from the vehicle emissions at the time of the measurements. Since the measurement station is located at the rooftop of Petrie Science and Engineering Building which is less than 500 m away from Steeles Avenue, the traffic at the time of those measurements could have been high enough to produce such results. In the graph for September 14, 2011 the area of the curve measured from 1:30 pm to about 3 pm shows a decrease of nitrous acid concentration and an increase in the area from 3 pm to about 4 pm, again possibly controlled by traffic conditions on Steeles Avenue during that time. The following measurements are taken on October 8, 2011 and show a relatively steady curve at times from 4 pm to about 6 pm on the average of 7-8 pptv of nitrous acid concentration. A continuous production and depletion of HONO in the troposphere can account for these variations. The next graph was produced from the measurements starting from 5:30 pm on October 9, 2011 and ending at 10:20 PM on October 10, 2011. In this graph the relative concentrations of HONO in the troposphere vary, however a closer look needs to be taken in analyzing the data. From 5:30 pm towards the evening up to about 8 pm the nitrous acid concentration varies from 20 to 40 pptv on average, which can be explained by the dusking sun, however from the point at 8:30 pm to about 5:30 am on October 10, the concentration is relatively stable at around 30 pptv and a slight increase trend can be noticed due to the night time build-up. As soon as the sun starts to dawn at about 6 am the concentration of HONO drops to the relative average values of 10 to 15 pptv which is explained by the photolysis (R1). Another jump in the concentration is observed towards the evening of October 10 around 5:30 pm, believed to be due to the traffic conditions at the observed time, which is followed by a drop in the HONO concentration at around 7 pm and a trend of increase from 7 pm up to 10 pm. This data shows a relative consistency in the theoretical assumptions of the reactions that are occurring in the troposphere during the whole day. The last graph is the analysis of the measurements taken from 8 pm October 11, 2011 to 2:30 pm October 12, 2011. The analysis here is similar to the analysis of the previous graph, except for the rapid increase of nitrous acid concentration towards the morning of October 12. The data shows a pretty reasonable trend of the HONO build-up on October 11 evening and depletion on October 12 at around 6:30 am, however at the time of 10:00 am and onwards to 2:30 pm the concentration holds at the average values of 25 - 35 pptv, which seems to be less obvious even keeping in mind the usual traffic conditions during the morning. Two possibilities are analyzed: either an instrument malfunction or another source of HONO is present which was not accounted for before. The second option is less likely in the area where the measurements taken, since there is no soil or other possible sources of nitrous acid on the rooftop of the building and in addition there was no rapid increase of nitrous acid concentration in the experimental data of the previous day. However, we cannot factor out the possibility of the wind gusting either towards or away from the instrument and from which direction. In the Weather Report for October 11, 2011 the wind direction at 10 am was eastbound, after which it changed to east-southeast and then southbound, with the speed of around 5.6 km/h. The Weather Report for October 12, 2011 shows a different wind conditions at 10 am: Southeast wind of speed of around 13 km/h. Judging from the geographical location of the Petrie Science and Engineering building and the location of the LOPAP scrubbing coil placed on the rooftop of the building a southeast wind could possibly bring an additional nitrous acid contribution from relatively forested area towards Black Creek Drive. Wind on October 11 was relatively similar to the wind on October 12 in terms of direction, however was 2.5 times less powerful and may have not been able to carry the HONO molecules towards the instrument. This observation if proven to be correct would contribute towards the theory of another possible source of nitrous acid located in rural areas and forested regions.

5.1 Conclusions

In conclusion, any measurements that are obtained from the LOng Path Absorption Photometry technique is but a part of a bigger research model, where many other instruments are gathering information on other chemicals that are present in the atmosphere. In order to better understand a bigger picture that is present at this point LOPAP, as well as other techniques are developed to measure species separately and then put together in a model. Since LOPAP instrument is very sensitive, a special care and maintenance is needed during an operation. Cleaning procedures are very important as well as making sure of all the proper connections at play and keeping track of the diameters of the tubing, which also make a difference and can contribute to the discrepancy in the obtained experimental data. The LOPAP instrument used in this research was mostly assembled by hand and therefore an even more care and caution needs to be taken when performing any experiments on it.

The observed data provided gives some idea of the variations in nitrous acid concentration in the troposphere. Even though the calibration curves suggest some LOPAP instrument malfunction, the experimental measurements are close to the theoretical assumptions values of HONO evolution and depletion in the atmosphere, and therefore can be included in the overall research model. Those theoretical assumptions include the photolysis reaction of HONO, vehicle emissions in producing NO_2 pollutant, as well as the source in rural and forested areas. A huge complication that the researchers run into when performing the measurements of nitrous acid concentrations in troposphere is the interference from other gaseous species contained in the atmosphere that absorb light at the similar wavelengths as nitrous acid, therefore throwing off the experimental data making the data less reliable. One of the suggestions to improve the already existing model is to continue with gathering experimental data to better quantify the diurnal cycle of nitrous acid in troposphere at this point, as well as performing measurements in forested areas to quantify any changes or variations in nitrous acid concentration and compare them to the existing measurements in urban areas. As another study was performed in Polar Regions, it was discovered of another possible source of nitrous acid emitted into the troposphere – the secondary reactions over the snow surfaces (22). It was observed that high concentrations of HONO evolve at the snow surfaces due to fulvic and humic acids that are contained in soils, reactions of which are much faster than already mentioned heterogeneous disproportionation of NO_2 with H_2O on humid surfaces (5). The kinetics of this reaction due to its fast rate and added to the model of the presence of organic compounds in polar regions give the insight of the help in explanation of the strong HONO formation and high $HONO/NO_x$ ratios that are observed in these regions. These measurements cannot be explained by laboratory measurements of Nitrate photolysis and need to be performed out in the field (21). In another research study performed, the observation suggested that dew water, abundantly available on ground surfaces, especially on canopy surfaces in forested regions, during summer and autumn nights, serves as a sink and a temporary reservoir of atmospheric HONO and as a source in the morning when the dew droplets evaporate, which is yet another branch of research that needs to be quantified as precisely as possible (14). There is a huge need in continuation of the research of the sources of nitrous acid in troposphere in order to evaluate and possibly avoid the evolution of this gaseous species, as it creates another atmospheric pollution problem around the world.

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