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Hydro Aluminium AS

Measurements of CF_4 and C_2F_6 emissions from Hydro Aluminium's smelter at Husnes, Norway

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ABSTRACT

NILU and Hydro Aluminium performed a test campaign for measurements of CF_4 and C_2F6 for stack emissions at Husnes Aluminium Smelter. Time-integrated samples were taken with evacuated canisters combined with low-flow restrictors for continuous sampling periods as long as 6 weeks. The samples were analyzed at NILU with a Medusa preconcentration method combined with GC-MS SIM. As a main conclusion, time integrated sampling together with Medusa GC-MS methodology is a very precise alternative to the traditional attempts to quantify PFC-emission.

NORWEGIAN TITLE

Målinger av CF_4 og C_2F_6 emissioner fra Hydro Aluminium Husnes

KEYWORDS

CF_4 and C_2F_6 emissions | Aluminium industry | GC-MS Medusa

ABSTRACT (in Norwegian)

NILU og Hydro Aluminium utførte en testkampanje for målinger av CF_4 og C_2F_6 fra skorsteinsemisjoner ved Husnes Aluminium. Tidsintegrerte prøver ble tatt ved hjelp av evakuerte stålbeholdere kombinert med gass-fløde restriksjoner over tidsperioder på opptil 6 uker. Prøvene ble analysert på NILU med en Medusa oppkonsentreringsenhet som er koblet til en GC-MS i SIM modus. Metoden viser seg til å være et godt alternativ til de tradisjonelle emisjonsberegninger.

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1 Introduction

Tetrafluoromethane, CF_4, and hexafluoroethane, C_2F_6, are the two most abundant PFCs in the atmosphere and are both potent greenhouse gases with long atmospheric lifetimes, currently estimated at 50,000 and 10,000 years, and global warming potentials of 6,630 and 11,100 over a 100-year timescale. Emissions from the aluminium industries and the semiconductor industries are the main sources for the increasing atmospheric background levels of these gases.

In 2009- at Hydro Australia's smelter Kurri Kurri - CSIRO performed measurements of perfluorocarbons (PFC) with canister-sampling followed by off-line analysis with Medusa GC-MS (Fraser 2013). The Kurri Kurri study showed that this method was very cost effective and more precise than FTIR or TDL measurements and very suitable for long-time sampling.

Hydro Aluminium Norway contacted NILU in late 2019 to investigate the possibilities to establish a system for precise time-integrated PFC-measurements for both stack emissions, diffusive emissions and measurements at cell outflow-ducts.

NILU has long experience with PFC-measurements and is equipped with the most sophisticated instruments for PFC-measurements – the Medusa GC-MS. NILU also has long experience with time-integrated sampling into stainless steel canisters followed by off-line Medusa GC-MS analysis.

PFC-emissions from the aluminium industry are reported to national authorities according to detailed protocols prepared and recommended by the International Aluminium Institute (IAI) in close cooperation with national authorities like the U.S. Environmental Protection Agency, as well as IPCCs three-tiered PFC inventory approach. These very detailed protocols are based on campaigns with short-duration measurements using FTIR or QCL-lasers and calculations based on relationships between logged anode effect process parameters – either anode effect minutes per cell day or overvoltage.

Estimates from global atmospheric measurements are suggesting periods of both over-accounted emissions (nearly 40 % between 1996 and 2002) and under-accounted emissions (about 40% between 2003 and 2010) (Wong 2015). Despite significant progress from the aluminium industry in understanding and reducing their emissions over the last three decades, the global model emissions for CF_4 and C_2F_6 - using atmospheric measurements as input - continue to rise and are significantly larger than those currently reported by industry and governments. There is still strong evidence for unaccounted PFC-emissions from the aluminium industry as a whole, but also quite large regional discrepancies with special focus on East Asia. Environmental legislation of PFC-emissions may in the near future move towards online-emission monitoring or time-integrated sampling methods in combination with precise off-line measurement techniques.

As the main goal of this first project, Hydro Aluminium and NILU agreed to validate and further elucidate to what extent canister time-integrated sampling together with Medusa GC-MS methodology can be used and further improved as an alternative to the traditional attempts to quantify PFC-emission. Another important reason for this project was that Hydro Aluminium wanted to perform measurements at Husnes during the restart phase of hall B in 2020.

2 Background

2.1 Time-integrated sampling

“Time-integrated sampling or concentration representative sampling is when a sample is taken over a period of time, in which the concentration of a species is equal to the averaged concentration of an imaginary or real continuous analysis of the same species over the same time period”.

Using evacuated canisters together with a restrictor with linear flow properties will give representative air samples. PFC’s are very long lived and stable compounds as well as very volatile – making them ideal to be sampled into canisters and stored without analytical drawbacks.

2.2 Measurements with Medusa GC-MS

The **A**dvanced **G**lobal **A**tmospheric **G**ases **E**xperiment (AGAGE) has been measuring the composition of global atmosphere since 1978, www.https://agage.mit.edu/

AGAGE’s latest measurement upgrade is a preconcentration system called Medusa. For details like flow schemes, temperature settings, pressure regimes, adsorbent and columns (see Miller 2008). At the heart of the Medusa is a cold plate which maintains a temperature of - 175° C which cool two traps to about - 165° C. Each trap can be independently heated resistively from - 165° C to +200° C. The use of two traps with wide programmable temperatures ranges, coupled with the development of appropriate trap absorbents, permits the desired analytes from 2-liter air samples to be effectively separated from more-abundant gases that would otherwise interfere with chromatographic separation or mass spectrometric detection, such as N_2, O_2, Ar, H_2O, CO_2, CH_4, Kr and Xe. Importantly, the dual traps also permit the analytes to be purified of interfering compounds by fractional distillation and re-focusing from the larger first-stage trap (T1) onto a smaller trap (T2) (Figure 2) at very low temperatures, so that the resulting injections to the Agilent 5973 GC-MS are sharp and reproducible. A Linux operating system runs both the Medusa "front end" and the GC-MS in selective ion mode (SIM). This software includes the mass/charge ratio as a variable, as well as the many control and diagnostic parameters of the Medusa. Blanks and instrument linearities are measured routinely. An important advance in the Medusa is its ability to check its linearity by injecting a wide range of standard gas volumes. Such linearity and composition-independence are critical to accurate calibration, especially when propagating synthetic primary standards or when measuring samples spanning wide concentration ranges. The Medusa system uses a high precision integrating mass flow controller (MFC) for improved measurement of sample volumes. The Medusa systems are producing exceptional routine precisions. The practice of alternating ambient air and calibration gas analyses obtain the highest precision measurements. By using quantifier (target) and qualifier ions for each measured species, the Medusa also offers improved peak identification and reduced susceptibility to interference by co-eluting species.

Because of the high rate of standard gas consumption (24 litres/day), a quaternary level of whole-air calibration gas is added to the normal tertiary level of calibration. The quaternary working gases are calibrated over the course of their use in the field by analyses against the tertiary standards sent from Scripps Institution of Oceanography La Jolla, California, USA (SIO) for use with the Medusas. SIO has maintained the Central Laboratory for standards of halogenated gases within AGAGE for the last 4 decades and their scale together with the scale of NOAA (National Oceanic and Atmospheric Administration) are those scales which are used for reporting global atmospheric background concentrations.

Medusa measurements of the global atmospheric background concentrations of halogenated gases are very precise – usually within less than 1 % - and can deal with concentrations levels far lower than FTIR og QCL instrumentation.

3 Project milestones, progress and achieved results

3.1 First site visit

First site visit to examine suitable sampling spots, examine the technical assistance on site and to take preliminary test samples in order to gain first experience with concentration levels, sample amount, necessary dilution steps, possible interferences with co-emitting compounds like water, particles, SO_2, CO_2 or other halocarbons or hydrocarbons.

The first site visit was done in august 17th and 18th 2020 – Morten Isaksen from Hydro Aluminium hosted the visit of Ove Hermansen and Norbert Schmidbauer at Husnes Aluminium smelter. During the visit suitable sampling spots were identified but no samples were taken. The technical staff at the site was introduced to the sampling procedures and 10 samples were taken one month later on 18th September 2020. Those samples were taken without any use of a flow-restrictor - only a particle filter on each side of a HF-scrubber filled with gamma alumina smelter grade. The sampling time was 20 minutes and the canisters were still about 250 mbar under ambient pressure after sampling.

NILU investigated the integrity and stability of the PFC levels in the canisters over longer time periods. The samples were also analyzed for the whole AGAGE range of more than 40 additional halogenated compounds, C2-C9 hydrocarbons and some sulfur containing compounds (H_2S , COS and CS_2) as well as CO_2 , CO and Methane levels using a Picarro G2401 Laser Analyzer.

Overall - the samples did not cause any problems to the Medusa-preconcentration unit. No contamination issues due to high loads of compounds – no problems with the dilution of the canisters with zero air – no interferences with the target compounds. The linearity range was so wide that it did not pose any problem to find the right sample size for the final analysis of PFC-14 (CF_4) and PFC-116 (C_2F_6).
Results of the preliminary sampling exercise are shown in Table 1 :

Table 1: Husnes 18th September 2020.

Sample no.	Location	Time period	CF_4 pptv	C_2F_6 pptv
1	Outside, ground level east of Hall A	09:15 - 09:35	86.68	4.73
2	Outside, ground level between Hall A and B	08:50 - 09:10	86.07	4.88
3	Roof pos. 1	10:05 - 10:25	89.04	5.29
4	Roof pos. 2	10:25 - 10:45	106.85	8.49
5	Roof pos. 3	10:47 - 11:07	98.09	6.63
6	Roof pos. 4	11:10 - 11:30	91.22	5.55
7	Ra1a Stack north (1A)	12:37 - 12:57	957.19	79.73
8	Ra1b Stack south (1B)	12:59 - 13:20	924.70	73.66
9	Ra1a Duct pre scrubber	13:35 - 13:55	1333.19	73.85
10	Ra1b Duct pre scrubber	13:55 - 14:15	1552.48	91.91

Short interpretation of those test results:

Sample 1 and 2 showed real atmospheric background concentrations – very close to AGAGE background concentration for the northern hemisphere for September 2020 for both CF_4 and C_2F_6 – those samples were taken at ground level close to Hall A and at ground level between Hall A and Hall B.

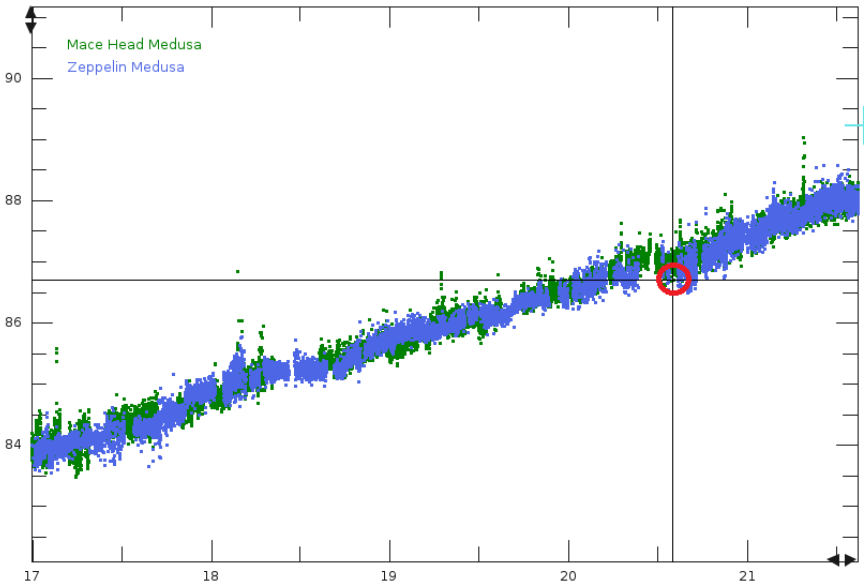

Figure 1 Atmospheric background concentration of CF_4 measured at Mace Head, Ireland and Zeppelin, Ny-Ålesund from 2017 to 2022 – the red dot is marking the 18th September 2020 and the concentration measured at ground level at Husnes at that date.

Samples 3, 4, 5 and 6 were taken at the roof of Hall A with an extension tube down into the roof lamellae. The results show slightly increased levels of both CF_4 and C_2F_6 . Those are short-time measurements and thus not representative – but showing small variations of the concentrations. Those emissions would be undetected with FTIR or QCL instrumentation.

Sample 7 and 8 were samples taken in the stack of hall A north and south and showed mixing ratios of about 950 ppt for CF_4 and about 70 ppt for C_2F_6 .

Sample 9 and 10 were raw-gas taken in the pipe before entering the seawater-scrubber. The mixing ratios are somewhat higher, but those samples were taken one hour later at that day. The exhaust before the wet-scrubber is much richer in Sulphur compounds, particles and HF than after the wet-scrubber towards the end-stack. Since the analysis of the PFCs was not affected by this – sampling at this spot instead of the stack would be a good alternative. The exhaust in the stack is saturated with water which can cause problems to both on-line instruments as off-line sampling.
All results show a mass ratio C_2F_6 / CF_4 within the limits of those reported by IAI , AGAGE or the Kurri Kurri smelter 0.1 +/- 0.01.

3.2 Test of CSIRO's sampling equipment

Test of CSIRO's sampling equipment that has been successfully used in sampling and measurement campaigns at the Kurri Kurri aluminium smelter in Hunter Valley, NSW, Australia and comparing it with NILUs own equipment.

NILU rented four sets of 30 litre stainless steel canisters from CSIRO together with flow restrictors (0.004"ID tube 1,2 m length) and 4 pressure loggers for the real sample flow. The linearity of all four canisters was tested and confirmed at the laboratory – all four canisters had an inflow rate that would allow more than one month of time-integrated linear inflow.

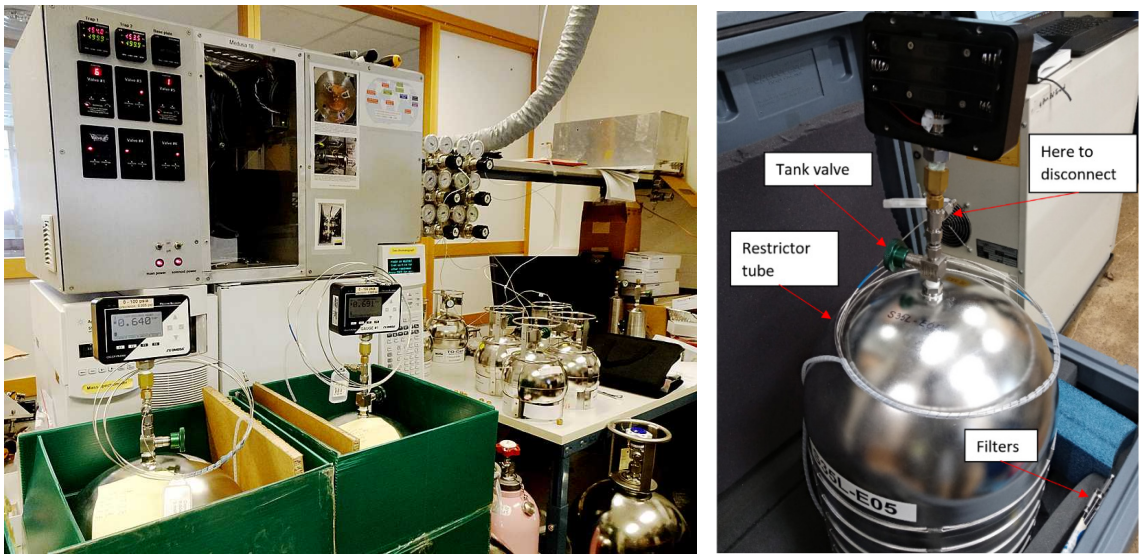

Figure 2 The 2 photos above showing the 30 litre canisters from CSIRO connected to the Medusa at NILU, Kjeller.

3.3 Methods for short time sampling

Establishing procedures for time-integrated canister sampling for short time periods like 1 to 8 hours and long-time periods of up to one month - for both chimney measurements as well as cell outflow measurements and roof-top fugitive emissions.

NILU has long experience with time-integrated sampling into canisters. Unlike CSIRO, NILU is using critical orifices with particle filters at both in and outlet. When using 3-liter canisters the linear sampling range is from vacuum to 0.85 bar - giving a total sample volume of 2550 ml. Use of 4 ml/min orifices will allow a time-integrated sampling time of more than 10 hours, while 10 ml /min orifices will allow 4 hours of integrated sampling and orifices of 80 ml/min can be used for 30-minute short time sampling. All three types were used at Husnes Alu smelter in June 2021 for measurements at cell-outflow experiments. NILU prefers those type of flow restriction over capillary based solutions which tend to be more prone to malfunctions like clogging (caused by condensation of water or other gases) or unintentional bending.

Figure 3 NILUs 3 litre canisters with critical orifice and pressure manometer

3.4 Medusa measurements

Establishing measurement and calibration procedures for concentrations levels far higher than atmospheric background concentrations of PFCs and other halogenated compounds at the Medusa GC-MS at NILU – including dilution procedures, calibration procedures, quality control measures, precision calculations, linearity tests.

All in all, 20 samples were taken during two campaigns. 4 samples with CSIRO's 30-liter canisters and 16 with NILU's 3-liter canisters. The canisters are still at sub-ambient pressure after ended sampling. At the laboratory the pressure is measured, and the canisters are pressurized with Zero-air to a pressure which allows multiple analyses of its content. The end pressure after Zero-air addition will give the dilution factor for the sample. Usually - the canisters were pressurized to an end pressure which allowed several consecutive runs at the Medusa. For samples from the roof top or samples from cell-outflow without anode effects low dilution was chosen – for samples from the chimney or from cell outflow with anode effects higher dilution was chosen. The sampling volume introduced to the Medusa preconcentration unit varied from one millilitre to up to two litres of sample. High-precision loops of 1 ml and 10 ml volume were used when high concentrations were expected. The content of the loop was then flushed to the Medusa with a Zero-air stream – the sampling time of the Medusa was set to 20 minutes – so multiple loop injections could be done within those 20 minutes – allowing sample volumes from 1 to 100 ml with 1- or 10 - ml steps. In that way, a volume could be chosen to best match the concentrations of the standard runs which are performed before and after each sample run.

Observations during the experiments showed that compounds like F-11, F-12 and SF_6 (and many other halocarbons) can be used as conservative tracers – their concentrations levels were identical to the real background levels and can therefore be used as a true measure for the accuracy of the dilution steps.

3.5 Canister cleaning

Testing the cleaning of the canisters before re-use in the next sampling campaign.

Cleaning of the canisters before and after use was done with a turbomolecular high vacuum pump at 10^{-5} mbar for 12 hours at 60 ° C – the canisters did not show any measurable levels of PFCs when refilled with Zero air.

3.6 Support by the technical staff

The staff at the facility has all the technical skills to perform the sampling by themselves without NILU personnel at the site.

3.7 First measurement campaign

First measurement campaign took place at Husnes on June 9th and 10th 2021 with Morten Isaksen and Henrik Åsheim from Hydro Aluminium and Ove Hermansen and Norbert Schmidbauer from NILU.

6 samples were taken directly from the duct of several dual-cell outflows at June 9th and 10th using different flow restrictors and averaging times of 30 min up to 12 hours. The results of those samples are not shown within the frame of this report.

Furthermore 4 stack samples were taken at the roof of Hall A using CSIRO's sampling equipment (30-liter canisters, 0.004" tubing as flow restrictor, pressure logger) with particle filter and HF-scrubber from NILU.

The samples were taken at each of the 4 stacks – but there was some doubt about the positioning of the capillary within the stack – should it face up-wards or down-wards? As a result - two were mounted with the sampling capillary facing upwards – while two were mounted facing downwards.

The two samples with the capillary facing upward clogged due to water – while the two other did perform linear sampling during one month of sampling.

Table 2: Husnes June-July 2021: Results in ppt_{vol}.

Stack	Run	CF_4	C_2F_6
Stack 1A (E05)	Run 1	189 140.29	12 642.01
-	Run 2	189 086.29	12 482.97
Stack 1B (E08)	Run 1	161 829.52	10 158.66
-	Run 2	161 825.06	10 428.91

The samples were analyzed twice as a 10 ml loop injection from the 30-liter canisters with an initial dilution of about 10.

The mass ratio C_2F_6 / CF_4 is 0,101 and 0.103 fits very well within the range of 0.1 +/- 0.01- which is measured and /or calculated for emissions from aluminium smelters by IAI , AGAGE or the Kurri Kurri smelter.

Figure 4 Stack sampling with 30 litre canister

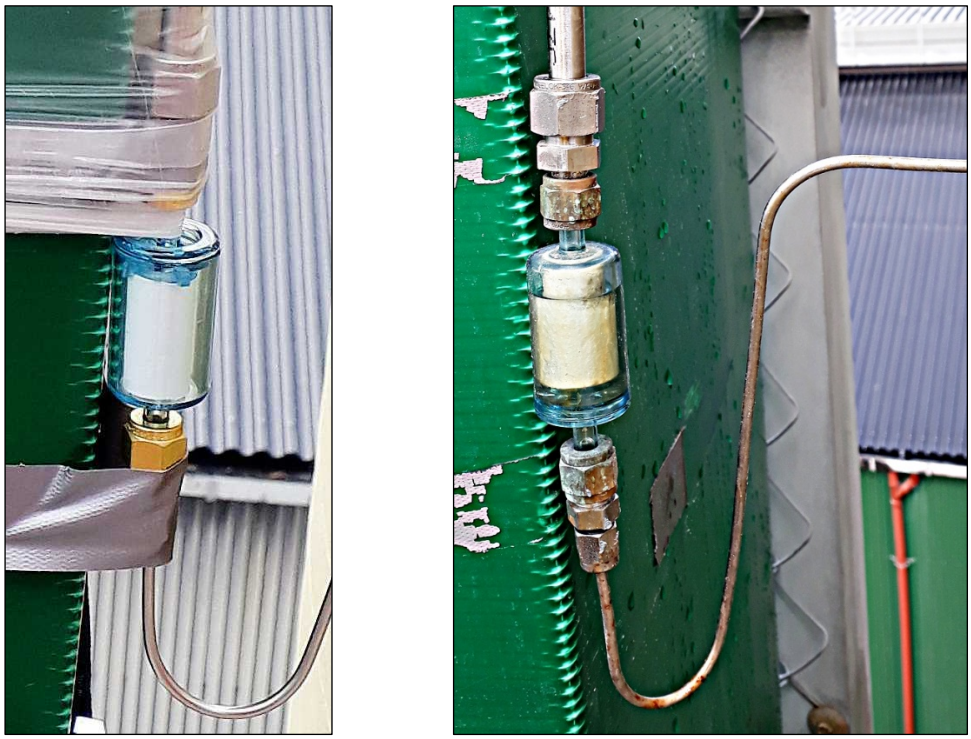

Figure 5 The 2 photos above: Particle filter after 30 days of sampling – one without any signs of water clogging – the other filled with water.

The samples taken with a down facing inlet tube inside the stack did not clog while the two samples taken with the capillary facing upwards were filled with water.

Figures 6 and 7 showing the tank-pressure in two tanks during 6 weeks of sampling. Small fluctuations in the pressure profile correlate with temperature change. Flask volume changes due to diurnal temperature show diurnal variations in pressure readings. Overall the sampling rate is close to linear sampling but should be corrected with some mathematical fit – CSIRO has done quadratic fit corrections for most of their flow restrictors.

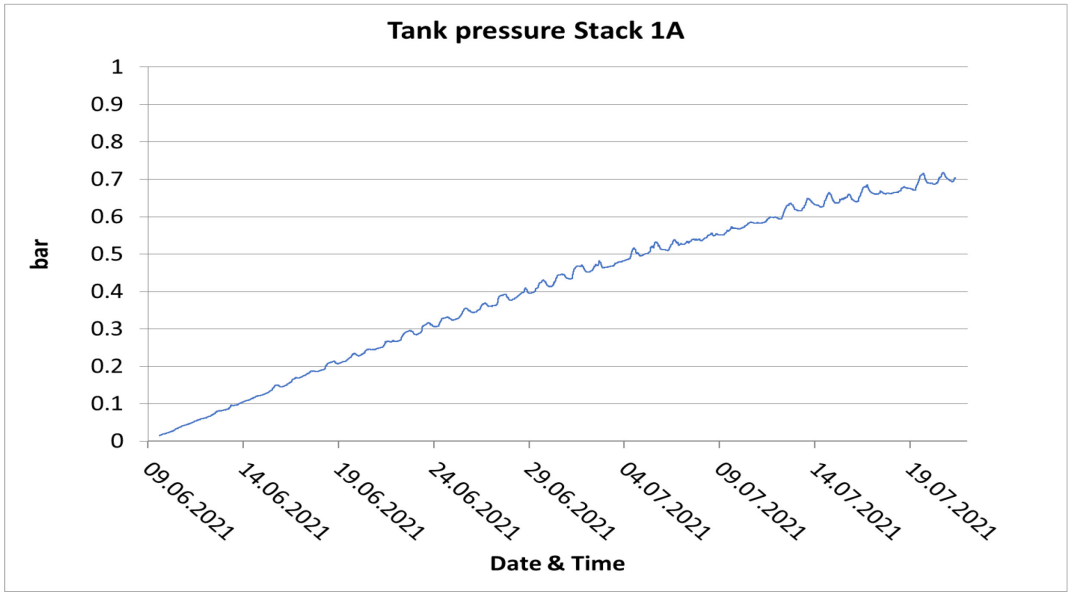

Figure 6 Tank pressure during 6 weeks sampling stack 1A

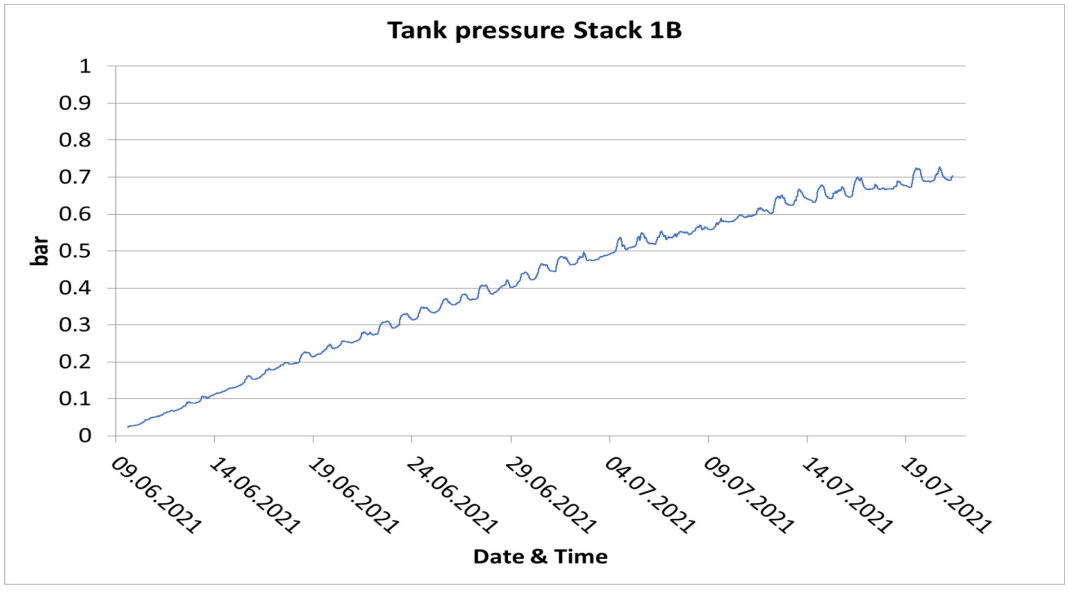

Figure 7 Tank pressure during 6 weeks sampling stack 1B

4 Outlook

Overall, the results of the project are very encouraging. The methods for time-integrated sampling and off-line Medusa GC-MS analysis are promising. There are still some issues to work on – like the prevention of clogging the air flow during stack sampling due to high water content and the final decision on size and design of the HF-scrubber and the pipes within the stack. Sampling at other sites than the stack, for example on the roof top or at cell level, did not reveal any problems.

NILU is confident in finding good solutions for those issues and that "true" emission values could be obtained from long-time-integrated stack-sampling combined with offline analysis. Time periods of one month could be sampled with a canister size of about 30L and a flow rate of 0.5 ml/min - after that period an aliquot of this sample is transferred to a smaller evacuated 3L canisters and shipped to the laboratory for analysis. The 30L canisters are then evacuated again (which could be done within some few minutes on site) and would be ready for another month of sampling - and so further.

The monthly means from the 3-liter canisters could be analysed every month or even be merged to one single yearly average later on at the laboratory.

Measurements at individual cell outflow can be performed with short time-integrated sampling ranging from minutes to several hours in order to monitor PFC emissions from conventional High Voltage Anode Effects (HVAE) (>8 V or 10 V) or Low-Voltage Anode Effects (LVAE)

Time-integrated sampling of airflows leaving the top of the halls will give a good indication of the diffusive emissions within the halls. Those emissions will vary in time, but will all in all be much closer to atmospheric background levels over long time periods. For those mixing ratios, FTIR or Quantum Cascade Lasers are not suitable. Offline sampling and GC-MS would be far superior and cheaper compared to quite insensitive online measurements.

The total cost of sampling and off-line analysis will be very competitive compared to long-time online measurements using FTIR or QCL. The sampling could be performed by the staff – not involving expensive site visits by NILU personnel. Such measurements could be done at all stacks at the same time and over the same time periods. Compared to that, a scenario with multiple online equipment seems very unrealistic.

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