



## TNA User Report

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Project title	Instrumental inter-comparison and kinetic study of halogen oxides and NOx instrumentation (HALOXCOMP)
Name of the accessed chamber	IASC
Number of users in the project	5
Project objectives (max 100 words)	<p>The first aim of the project was an instrument inter-comparison for the detection of NO<sub>2</sub>, IO and BrO. This inter-comparison is key for understanding the performance of the field instrument Mocamar, in particular for halogen oxide radicals. The campaign aimed at quantifying the transport of the radicals from the chamber into the measurement cell.</p> <p>The second objective was to perform kinetics experiments that are relevant for the polluted marine atmosphere. We were particularly interested in the reaction of I<sub>2</sub> + NO<sub>3</sub> under dark conditions, as well as I + NO<sub>x</sub> reaction with the chamber being illuminated.</p>
Description of work (max 100 words):	<ol style="list-style-type: none"> <li>1. Connection of the instrumentation to the chamber and optical re-alignment where necessary.</li> <li>2. Set-up and testing all the devices including the open-path instruments installed on the chamber. Check sensitivity and calibration of the spectrometers on NO<sub>2</sub> detection.</li> <li>3. Protocol development for controlled reagent introduction and photolysis. (NO<sub>2</sub>, O<sub>3</sub>, Br<sub>2</sub>, I<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>)</li> <li>4. Inter-comparison experiments under a range of conditions (including RH, aerosol loading, and other interfering species). The main target species detected were NO<sub>2</sub>, IO and BrO.</li> <li>5. Iodine/NOx kinetics experiments.</li> </ol>

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<sup>1</sup> Physics; Chemistry, Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

<sup>2</sup> UNI= University and Other Higher Education Organisation;

RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);

SME= Small and Medium Enterprise;

PRV= Other Industrial and/or Profit Private Organisation;

OTH= Other type of organization.

<sup>3</sup> UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher EXP= Engineer; ACA= Academic; TEC= Technician.

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The group of Ravi Varma from NITC in Calicut India also participate to the campaign. Anoop Sreevalsam and Arun Ramachandran were there during the first part of the campaign, and they will contribute to the analysis of the IBB-CEAS data.

## Trans-National Access (TNA) Scientific Report

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Figure 1. The participants of the HALOXCAMP campaign. Left to right: Dean Venables (UCC), Camille Blouzon (IGE-CNRS), Bryan P. Keary (UCC), Roberto Grilli (IGE-CNRS), Albane Barbero (IGE-CNRS), Meng Wang (USST), Albert A. Ruth (UCC), Jun Chen (USST). Missing on the photo: Anoop Sreevalsam and Arun Ramachandran (NITC).

### • Introduction and motivation

In-situ measurements of reactive species are a major challenge in atmospheric chemistry owing to their short lifetimes and thus generally low mean ambient mixing ratios. Halogen oxide radicals play an important role in the oxidative capacity at Polar Regions, where, even if very remote locations, they exhibit relatively high oxidative activity.<sup>1</sup> In Antarctica, OH radicals have been measured at levels higher than expected (between  $4 \times 10^5$  and  $2.5 \times 10^6$  molecules  $\text{cm}^{-3}$ ) both at the coast as well as in land.<sup>2,3</sup> These high levels of the hydroxyl radical may be explained through recycling reactions either in the presence of  $\text{NO}_x$  or XO.

$\text{NO}_x$  recycling reaction take place mainly in the plateau, with the snowpack being the main source of  $\text{NO}_x$ ,<sup>4</sup> while the recycling reaction with XO is more expected at coastal regions, where satellite

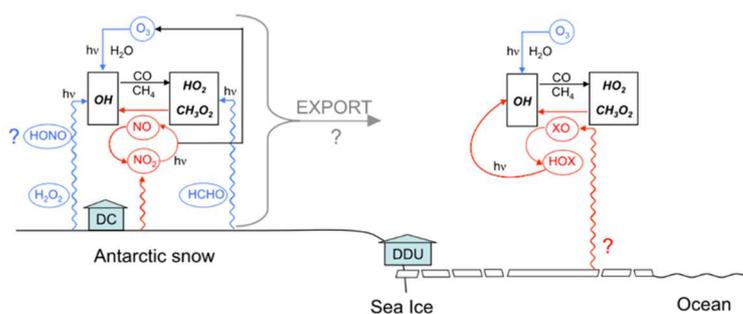


Figure 2. A schematic of different reaction schemes that may take place in Antarctica. In blue are primary sources leading to the production of OH radical, while in red are possible recycling reactions. In land, over the Antarctic snow, the main possible sources of OH are related to the chemistry of  $\text{NO}_x$ , while at the coast OH may be recycled either by the presence of XO or by the transport of  $\text{NO}_x$  from the main land.

measurements show a correlation between the presence of sea-ice and halogen oxide molecules (mainly BrO).<sup>5,6</sup> Measuring halogen oxide radicals at Polar Regions, and particularly at the coast and over the sea-ice is therefore crucial for understanding their sources, their role in particles formation and more in general in the oxidative capacity of the atmosphere (Fig. 2). In this context, HALOXCAMP allowed an instrumental inter-comparison under controlled conditions, with IBB-CEAS instruments directly installed at the chamber (which do not suffer from losses of radicals in the gas inlet) and extractive instruments such as Mocamar<sup>7,8</sup> and IBB-CEAS instruments connected to the chamber. After the inter-comparison, kinetic experiments were carried out to investigate the reaction between halogen molecules and  $\text{NO}_x$  species.

- Scientific objectives

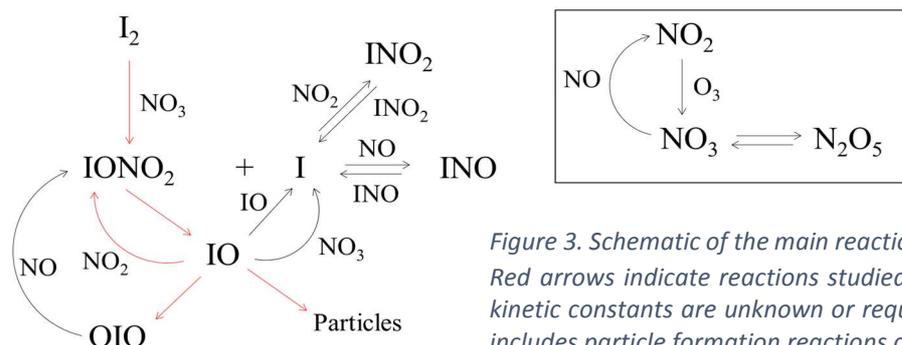


Figure 3. Schematic of the main reactions involving iodine and  $NO_x$ . Red arrows indicate reactions studied in this work and for which kinetic constants are unknown or require more investigation (This includes particle formation reactions and pathways).

The aim of the inter-comparison campaign consisted of testing the instruments on the  $NO_2$  and halogen oxide detection, and quantifying the transport of these reactive species into the measurement cell of the extractive instruments.  $NO_2$  detection allowed comparison of most instruments involved in the campaign, and their stability and detection limits to be determined. Afterwards, the comparison was repeated on the halogen oxide radicals (particularly IO, which is detected by Mocamar as well as by the broadband cavity operated at 427 nm in the chamber) in order to quantify inlet losses as a function of the residence time. Kinetics experiments aimed to better understand reactions taking place between halogen molecules and  $NO_x$ . A schematic of possible paths is reported in Figure 3, with red arrows showing reactions on which this work focussed.

- Reason for choosing the simulation chamber/ calibration facility

The facility was chosen for several reasons, including the CRAC group's experience in setting up open path optical cavity spectrometers across the cavity. This is a key capability because it precludes potential inlet losses that can influence extractive instrumentation. The CRAC group were also able to set up multiple optical cavity spectrometers, allowing measurement of BrO (UV), IO and  $NO_2$  (blue),  $I_2$ , OIO,  $NO_2$  (green), and  $NO_3$  (red), allowing a detailed exploration of halogen chemistry. Moreover, the CRAC team have significant experience in the preparation of reactive halogen species.

- Method and experimental set-up

Prior the campaign the chamber was equipped with four IBB-CEAS instruments, consisting in four cavities installed directly on the chamber for measuring in the UV (385 nm), blue (427 nm), green (530 nm) and red (662 nm) wavelength regions. Commercial instruments for  $O_3$ , NO,  $NO_2$  and particles were installed near by the chamber and were pumping air continuously (ca. 0.5 L/min per instrument).

The extractive instruments (Mocamar (IGE), IBB-CEAS (IGE) and IBB-CEAS (USST) instrument) were installed on Monday 16<sup>th</sup> on a table next to the chamber. Inlet ¼" PFA tubes of about 1.5, 2.5 and 2 m of length, were used, respectively.

Ozone was produced by flowing  $O_2$  through a discharge ozone generator. Pure  $NO_2$  was injected directly in the chamber using a micro-syringe in a septum while flushing with dry air.  $N_2O_5$  was synthesized by reaction of  $NO_2$  and  $O_3$  in a reaction tube and trapped with dry ice. It was then stored in the dark at liquid nitrogen temperature to prevent its degradation. Its injection into the chamber was performed by flushing the glass tube with  $N_2$ , while maintaining the tube at  $-70^\circ C$  using dry ice. For  $I_2$ , a weighted amount of  $I_2$  crystals were dissolved in methanol. The solution was then placed in a flushing tube using a micro-syringe, and dry air was flown over the iodine while heating the tube. Molecular bromine,  $Br_2$ , was taken from the headspace above liquid bromine using a gas tight syringe. This approach proved unsatisfactory, likely owing to adsorption of bromine to the syringe needle.

Better, though less quantitative, introduction of Br<sub>2</sub> into the chamber was achieved with a plastic syringe without the needle. This gas phase bromine was introduced into the chamber in a flowing stream of dry compressed air.

- Data description and preliminary results

Apart from the Mocamar and the commercial sensors (including the SMPS-CPC), the other instruments need post-data analysis. For this reason, the data description and the results are not finalised here. The first inter-comparison test was conducted for the detection of NO<sub>2</sub>. Concentrations ranging from few pptv up to 100 ppbv were inserted into the chamber. Large concentrations allowed the calibration

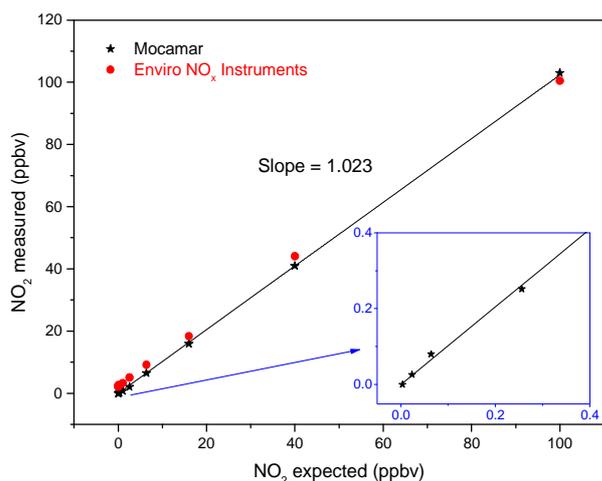


Figure 4. The calibration results for the NO<sub>2</sub> detection. The results from Mocamar and the commercial instrument ET Enviro was compared to the concentration expected from the amount of pure NO<sub>2</sub> injected and the total volume of the chamber. Good agreement was found, with a good linearity

was replaced by a higher spec rotary pump, capable of delivering a flow of up to 17 L/min into the Mocamar measurement cell. Experiments were then conducted at different flowrates in order to identify the residence time required for efficiently transporting radicals into the cavity. BrO was formed by adding Br<sub>2</sub> and O<sub>3</sub> inside the chamber and switching on the UV photolysis lights. Preliminary results are shown in Figure 4. Up to 400 pptv of BrO were measured by the Mocamar instrument at maximum flowrate. The decrease in concentration with time is due to dilution caused by continuous flushing of the chamber (60 L/min) to ensure that the chamber did not collapse during sampling. In the inset of Figure 5, raw data are shown (red dots). After every change in flowrate, a measurement at the maximum flowrate was taken in order to account for the dilution factor. The black line represents the evolution of concentration at maximum flow, and it is obtained by interpolation of the raw data. In the main graph, BrO losses (normalized by the concentration at the maximum flow) are plotted against the residence time. Even at 17 L/min (a residence time of  $t_r = 0.1$  sec) losses of BrO are still present, but they have not yet been quantified. This will be possible once all the data from the campaign are analysed, and concentrations of O<sub>3</sub>, Br<sub>2</sub> as well as the quantum yield for the photolysis in the chamber are available. Unfortunately, it was not possible to shorten the inlet or further decrease the cavity volume, so that additional data-points at shorter residence times could not be obtained. The same experiment was performed for IO. However, because IO can also be photolysed by the laser (at 436 nm) inside the cavity, a different procedure was used, which consisted of switching on and off the UV light for each flowrate. This allowed us to remove the contribution of the intra-cavity photolysis. The results obtained are in agreement with the ones reported for BrO. One more test was performed on the IO radical by gradually decreasing the intra-cavity laser power. This test showed that IO

of the UV, green and red broadband cavity instruments installed on the chamber against the other instrument measuring NO<sub>2</sub> in the blue region. From the amount injected and the chamber volume the expected concentration can be calculated and it was compared to the measurement of Mocamar and the commercial NO<sub>x</sub> instrument Enviro from ET. A good agreement was found for both instrument, with a better linearity (Slope = 1.023) for Mocamar (Figure 4). The measurements were used to calibrate the IBB-CEAS instruments.

Afterwards, tests related to the transport of halogen oxide radicals were conducted. It was found that, at the flowrate used by the Mocamar instrument (0.8 L/min), the transport of the radicals was inefficient. The membrane pump used for the instrument

concentrations seemingly decreased linearly with power, and by extrapolating the concentration at 'zero' laser power, the transported amount was quantified. This approach is in good agreement with the one outlined above.

Kinetic experiments were designed with the aim of taking advantage of the variety of instruments available at the same time at the IASC chamber facility. The experiments mainly focused on the reaction of iodine with  $\text{NO}_x$ . The table in the next page summarizes the experiments conducted. A first kinetic experiment was conducted by adding  $\text{I}_2$ ,  $\text{O}_3$  and  $\text{NO}_2$  in the chamber. When switching on the UV light, we observed formation of IO and a slow decrease of  $\text{NO}_2$  possibly highlighting formation of  $\text{IONO}_2$ . This experiment was accompanied with some particle production.

The second kinetic experiment was performed by adding  $\text{I}_2$  and  $\text{NO}_2$  in the chamber under dark conditions. When red lights (with a high-pass filter at 650 nm) were switched on, we observed a decrease in  $\text{NO}_2$ , possibly caused by simultaneous formation of  $\text{INO}_2$ . No particle formation was seen. In a third experiment,  $\text{N}_2\text{O}_5$  was added to the chamber which at room temperature and rapidly decomposed into  $\text{NO}_2$  and  $\text{NO}_3$ .  $\text{I}_2$  was then added in the dark, and red lights were switched on in the chamber. This cause a dramatic production of particles together with the formation of IO with very low levels of  $\text{O}_3$  (<1 ppbv, potentially below the detection limit of the commercial photometer). IO was measured by Mocamar in very small concentrations, < 1 pptv. We think that  $\text{O}_3$  formation is due to the presence of UV and visible light in the chamber coming from the four IBB-CEAS cavities, or that the reading is an artefact caused by  $\text{IONO}_2$  formed in the reaction, which absorbs strongly at 250 nm. A second experiment was attempted, where only the red cavity (which does not photolyse  $\text{NO}_3$ ) was left on. The aim was to see if particles were still formed and IO observed. This is an interesting and important result because it seems that particles are formed by the presence of  $\text{I}_2$  and  $\text{NO}_3$ , while almost no particles are formed if only  $\text{I}_2$  and  $\text{NO}_2$  are present. The relative humidity of the chamber was kept well below 1% (typically at ca. 0.1%) during all the kinetic experiments.

Finally, while working on the detection of BrO, the observation of OBrO was attempted.  $\text{NO}_2$  and  $\text{O}_3$  were injected in the chamber ( $\text{O}_3$  was added in large excess) and  $\text{NO}_3$  was formed in the dark. Afterwards  $\text{Br}_2$  was injected and UV light was switched on. Under these conditions BrO formation was not observed (with a detection limit 2 pptv) and there was no evidence for the presence of OBrO in the chamber. Further analysis is needed to confirm this result. All results outlined here are provisional interpretations of the data obtained. Further analysis is needed to confirm the findings and interpretations, and more experiments may also be required for quantitative conclusions.

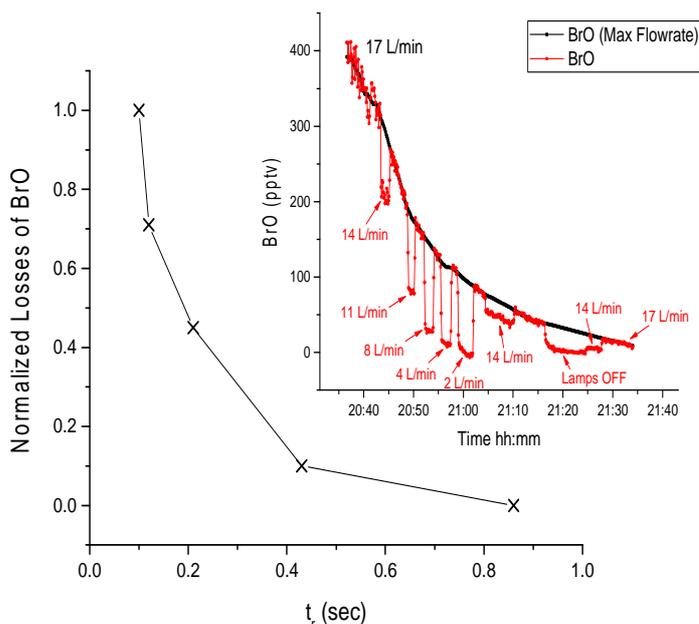


Figure 4. Measurement of the transport efficiency of BrO from the chamber into the Mocamar Cavity (preliminary data). The chamber was filled with  $\text{Br}_2$  and  $\text{O}_3$ , in the presence of UV light. BrO was formed in the chamber, and 400 pptv were transported to the cavity at a maximum flowrate of 17 L/min. The decrease in concentration over time is due to dilution of the reactants in the chamber due to continuous flushing. In the main plot, residence time,  $t_r$ , is plotted against the losses of BrO normalized with respect to the maximum achievable flow rate.

Precursors	Conditions	Observations
I <sub>2</sub> (~20 ppbv) O <sub>3</sub> (~100 ppbv) NO <sub>2</sub> (~20 ppbv)	-UV Light	- IO was formed - We probably see formation of IONO <sub>2</sub> (decrease in concentration of NO <sub>2</sub> while light is switched on - Very small particle formation
I <sub>2</sub> (~20 ppbv) NO <sub>2</sub> (~20 ppbv)	- Dark - Red light ( $\lambda > 650$ nm) - Absence of O <sub>3</sub>	- We probably see formation of INO <sub>2</sub> - No particles formation
I <sub>2</sub> (~20 ppbv) N <sub>2</sub> O <sub>5</sub> (~2 ppbv)	- Dark - Red light ( $\lambda > 650$ nm) - Absence of O <sub>3</sub>	- NO <sub>3</sub> formed at few hundreds of pptv - IO was only observed when small amount of O <sub>3</sub> were observed with the commercial photometer. This observation can be due to small amounts of UV in one of the cavities which leads to the gradual formation of O <sub>3</sub> , or it is an artefact of the photometer, since IONO <sub>2</sub> also absorbs strongly in the UV at around 250 nm (just like O <sub>3</sub> ) IO can also be formed through gradual dissociation of IONO <sub>2</sub> into IO and NO <sub>2</sub> . - Large particle formation was observed
NO <sub>2</sub> (~20 ppbv) O <sub>3</sub> (~700 ppbv) Br <sub>2</sub> (~8 ppbv)	Dark for NO <sub>3</sub> formation (NO <sub>2</sub> + O <sub>3</sub> ) UV Light after Br <sub>2</sub> injection	- Not Observation of BrO - OBrO detection was attempted. Further data analysis is needed

## • Conclusions

The campaign HALOXCAMP was a success. It allowed the IGE team to quantify for the first time the transport of halogen oxide radicals into the cavity measurement cell. The preliminary results indicate that a residence time of 0.1 s is insufficient for transport of the radicals. Thanks to these results, the Grenoble team will be able to work on the improvement of the inlet line of the Mocamar instrument. Alternatively, a LP-DOAS (long-path differential optical absorption spectroscopy) approach could be set up for IO and BrO detection, which does not require the gas to be transferred to a measurement cell. In fact, LP-DOAS measurements are performed in an open-path configuration, where the laser light is sent over a certain distance through the atmosphere (up to few km) and reflected back to be analysed by a spectrometer. This would remove all uncertainty concerning inlet losses. The preliminary results of the kinetic experiments are very promising. To our knowledge the rapid and rather efficient formation of inorganic particles from the reaction of I<sub>2</sub> with NO<sub>3</sub> has not been observed before. Again, further data analysis (and/or more experiments) are required to confirm the findings and corresponding hypotheses.

## • Outcome and future studies

This work could potentially lead to two/three manuscripts: a first one on the improvement of the Mocamar instrument for efficient transport of XO into the measurement cell and the corresponding precise characterisation. This will require a new design of the gas inlet capable of transporting the gas sample in the cell much faster than 0.1 second, followed by further study in the laboratory to quantify the transport efficiency. A second manuscript could focus on the results from the kinetic experiments of iodine/NO<sub>x</sub> chemistry. The formation of inorganic particles under dark conditions and in the presence of I<sub>2</sub> and NO<sub>3</sub> which has been observed for the first time. It could help to better explain the night time chemistry of the polluted marine boundary layer. A third manuscript could arise if, after the data analysis, we realized the formation of OBrO in the chamber. The valorisation proposed here, has to be confirmed after a complete analysis of the data.

Regarding future studies, the Mocamar instrument could be tested again at the chamber facility. In the future, other kinetic experiments related to the chemistry between halogen species and NO<sub>x</sub> can be conducted in collaboration between UCC, IGE and USST, which was revealed to be a productive team with high complementarity.

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**Chamber name and location:** IASC, UCC, Cork

**Campaign name and period:** HALOXCAMP, 16-27/07/2018

**Text:**

