

# DOAS observations over Borneo during the SHIVA aircraft campaign

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**ABSTRACT** Airborne spectroscopic measurements were carried out during the SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere) campaign at Miri, Malaysia in November and December 2011. The dataset was collected during 16 sorties of the DLR (Germany's national research center for aeronautics and space) research aircraft "Falcon" over Borneo comprising different flight profiles, which covered the boundary layer up to 12 km altitude. The measurements were performed using the well established Differential Optical Absorption Spectroscopy (DOAS) technique in limb geometry, which supports measurements of UV/visible absorbing species (e.g., O<sub>3</sub>, BrO, NO<sub>2</sub>, HCHO, CHOCHO, IO). During the sorties the frequent detection of CHOCHO and HCHO indicates elevated photochemical oxidation of isoprene and other volatile organic compounds (VOCs), which are mainly emitted by the tropical forests in Borneo. Furthermore, local air pollution of NO<sub>x</sub>, possibly due to fossil fuel combustion, biomass burning, oil rig and ship emissions, and from local traffic was detected. During dedicated flights near the shores of north-eastern Borneo, elevated amounts of IO occurred, indicating that iodine may play an important role in the photochemistry of the marine boundary layer. Furthermore, signatures of HCHO and CO (measured by the SPIRIT instrument) were detected in the outflow of convective clouds, indicating rapid transport of near surface air into the upper troposphere. The proceeding reports on these findings and presents preliminary conclusions on likely major photochemical processes in pristine marine and terrestrial air, polluted air, and air transported into the upper troposphere.

(**Keywords:** SHIVA, atmospheric trace gases, marine boundary layer)

## INTRODUCTION

The SHIVA aircraft campaign took place in Miri, Malaysia in November and December 2011 aiming to reduce uncertainties in the amount of naturally emitted halogen-containing ozone depleting substances reaching the stratosphere (<http://shiva.iup.uni-heidelberg.de/>, see the proceeding by Pfeilsticker et al.[1]). Airborne measurements were collected during 16 sorties of the DLR research aircraft "Falcon" over Borneo comprising different flight profiles, which covered the boundary layer up to 12 km altitude.

Specific objectives of the aircraft-borne DOAS [2] measurements during the field campaign were to study (a) the abundance of halogenated compounds in the marine boundary layer (MBL) via bromine (BrO) and iodine monoxide (IO) measurements, (b) the oxidation capacity of the atmosphere i.e., investigations of the

oxidation of volatile organic compounds (VOCs), leading to formaldehyde (HCHO) and glyoxal (CHOCHO), (c) regional air pollution, i.e., emissions by volcanoes, biomass burning, oil rigs, or anthropogenic combustion, and (d) the composition of air masses in convective outflows around thunderstorms. For the interpretation of the DOAS measurements, the measurements obtained from the other instruments on board the aircraft are used. The dataset includes e.g. in situ measurements of carbon monoxide (CO) (SPIRIT [3]), ozone (O<sub>3</sub> monitor [4]), and sulphur dioxide (SO<sub>2</sub>) (CI-ITMS [5]).

## INSTRUMENT DESCRIPTION

### DOAS instrument

The DOAS instrument [6] consists of a telescope unit to collect scattered skylight in limb direction, a housing

with two optical spectrometers ( $\lambda_{UV} = 320 - 400 \text{ nm}$ ,  $\lambda_{vis} = 409 - 530 \text{ nm}$ ) and a PC with a control unit. The limb scattered skylight spectra are analysed for the atmospheric absorption of  $O_3$ , BrO,  $NO_2$ , HCHO, CHOCHO, IO, BrO, HONO and  $O_4$ . The basic quantity received by the DOAS measurements is the differential slant column density (dSCD) which is the difference of a slant column density (SCD) and a reference spectrum. The SCD is defined as the concentration  $c$  of a specific absorber integrated along the light path  $L$  and is given in units of molec/cm<sup>2</sup>. Post-flight data analysis further involves radiative transfer calculations and mathematical inversion of the measurements, in order to infer absolute concentrations of the targeted gases from measured dSCDs. The telescope unit of the DOAS instrument was integrated into an aircraft window on the port side of the aircraft together with a webcam. The viewing direction is orthogonal to the heading direction of the aircraft.

**SPIRIT instrument**

The SPIRIT instrument [3] is a portable infrared laser absorption spectrometer for concentration measurements of different trace gases. It uses a continuous wave distributed feedback room temperature quantum cascade laser (QCL) and a patented new optical multi-pass cell to detect, e.g. CO.

**Ozone monitor**

The  $O_3$  mixing ratios were measured with a slightly modified commercial ozone monitor TE49 [4]. The measurement technique is based on the UV absorption at 254 nm according to the Lambert-Beer law.

**CI-ITMS instrument**

The CI-ITMS instrument [5] is a Chemical Ionization Ion Trap Mass Spectrometer to detect trace gas molecules as e.g.,  $SO_2$ .

**GOME-2 satellite instrument**

The GOME-2 instrument [7] is a nadir scanning spectrometer mounted on the MetOp satellite to detect atmospheric trace gases in the ultraviolet and visible wavelength range. The retrieval of the  $NO_2$  VCDs (and of other UV/vis absorbing gases) from the GOME-2 satellite instrument is based on the DOAS technique and the KNMI modelling approach (<http://www.temis.nl/airpollution/no2.html>) and the retrieval of HCHO VCDs is performed as described in [8] and [9]. The VCD is defined as the concentration  $c$  of a specific absorber integrated along the height  $z$  and is also given in units of molec/cm<sup>2</sup>.

**IDENTIFICATION OF DIFFERENT EMISSION SOURCES**

In order to identify the different emission sources, different trace gas species with different sources and loss processes have to be analysed. Table 1 summarises the different emission sources and their composition, e.g. if a biomass burning event occurs, an increase in CO,  $NO_2$  and HCHO is expected to be observed. In the following, two exemplary sorties (November 16, and 19, 2011) are discussed with regard to the different possible emission sources.

**Table 1.** Identifying different emission sources according to the composition of trace gas species.

Biomass burning	Volcanic emissions	Oil rigs	Ship emissions	Anthropogenic combustion	Convective outflow of thunderstorms
CO	-	CO?	CO	CO	CO
$NO_2$	-	$NO_2$	$NO_2$	$NO_2$	$NO_2$
HCHO	-	HCHO	HCHO	HCHO	HCHO
-	$SO_2$	$SO_2$	$SO_2$	$SO_2$	-
-	-	-	-	-	HONO
-	-	-	-	-	BrO?, IO?

### Sortie on November 16, 2011: marine boundary layer study

Figure 1 shows the flight track of the first sortie of the Falcon aircraft on November 16, 2011. The aircraft started in Miri and cruised southwestward along the coast of Borneo passing Bintulu to Kuching Bay on a constant flight altitude of 100 m. In Kuching Bay the aircraft turned and headed back towards Miri on the same way, however on different flight levels. Back over Miri, the aircraft climbed northward flying a loop with a maximum altitude of 12.8 km.

Figure 2 shows the main results of this sortie. Along the low level parts of the flight the NO<sub>2</sub> mixing ratios occasionally peaked in general at the same locations both for the forward and return track, cf. the NO<sub>2</sub> enhancement detected around 04:30 UTC (event 1a) is also seen on the return track around 06:00 UTC (event 1b), and at the same location HCHO, CO, O<sub>3</sub> and SO<sub>2</sub> were elevated too. According to the information provided in Table 1, this plume could be due to emissions either from oil rigs, ships, or anthropogenic combustion. At this particular location several ships crossed the flight route, heading

towards the industrial area near Bintulu (3.3°N/113.1°E). Furthermore, the air masses mainly originated from the south-western direction, where many oil rigs are located.

In Figure 2 another plume of NO<sub>2</sub>, HCHO, CO and SO<sub>2</sub> occurred at around 04:45 UTC (event 2a) and around 05:45 UTC (event 2b) again at the same location on the forward and return flight. This increase in pollutants can be linked to anthropogenic emissions from Sibul (2.3°N/111.8°E), and Mukah (2.9°N/112.1°E).

Figure 3 shows the 10-day average of NO<sub>2</sub> and HCHO VCDs derived from the GOME-2 satellite instrument, where increased VCDs of NO<sub>2</sub> and HCHO frequently occurred in the region near Bintulu.

### Sortie on November 19, 2011: A convective outflow study

The outflow of a meso-scale convective cell was investigated on the afternoon of November 19, 2011, when a large thunderstorm cloud north of Brunei was probed (see Figure 4).

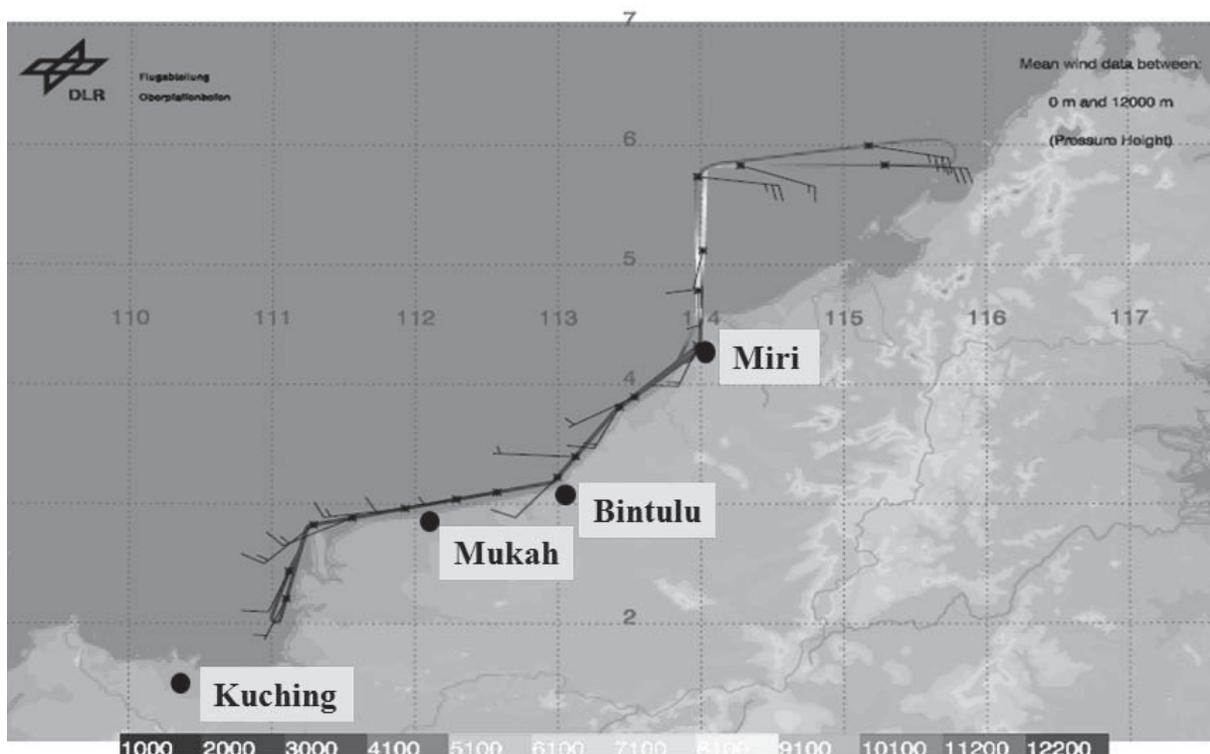
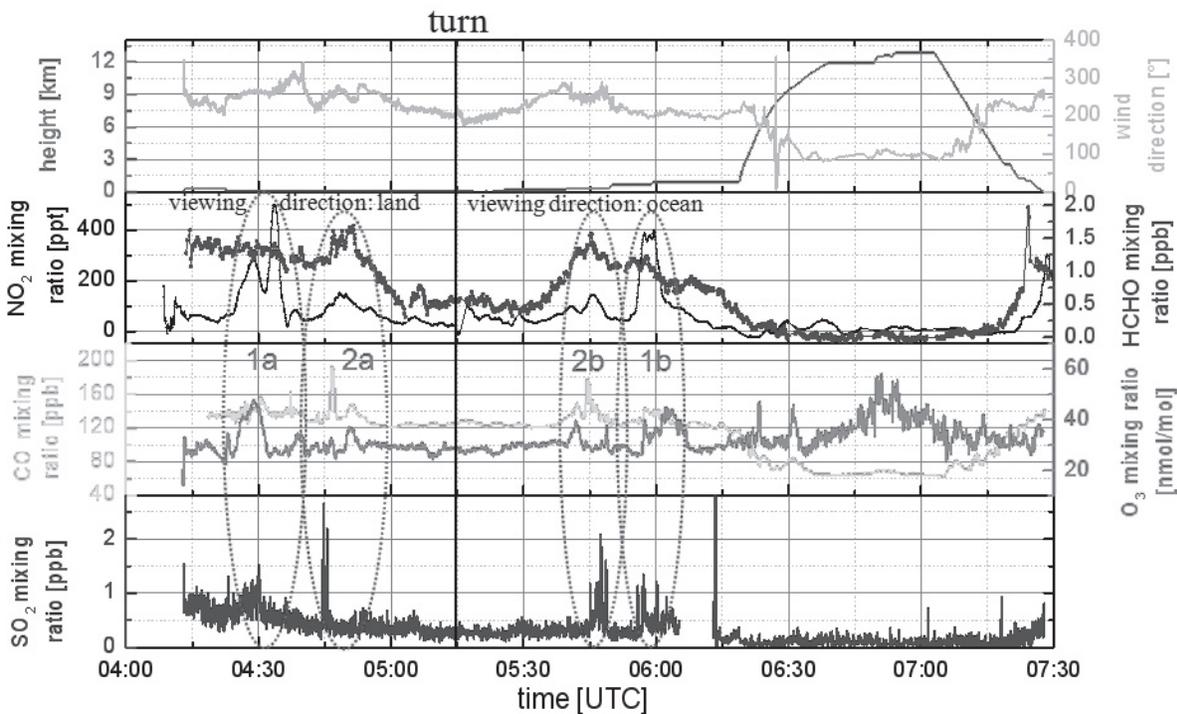
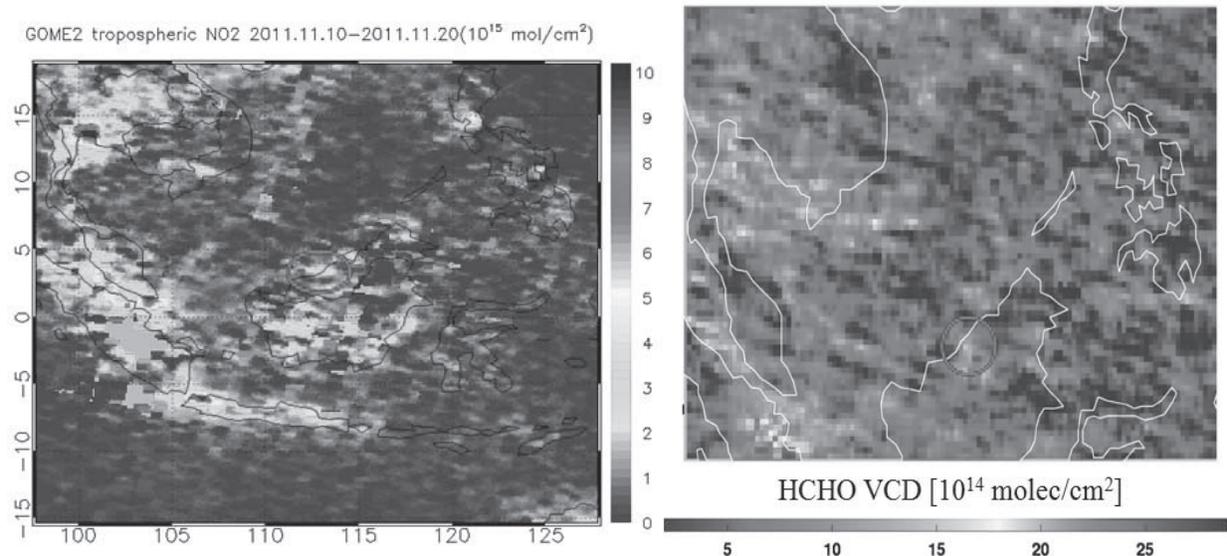


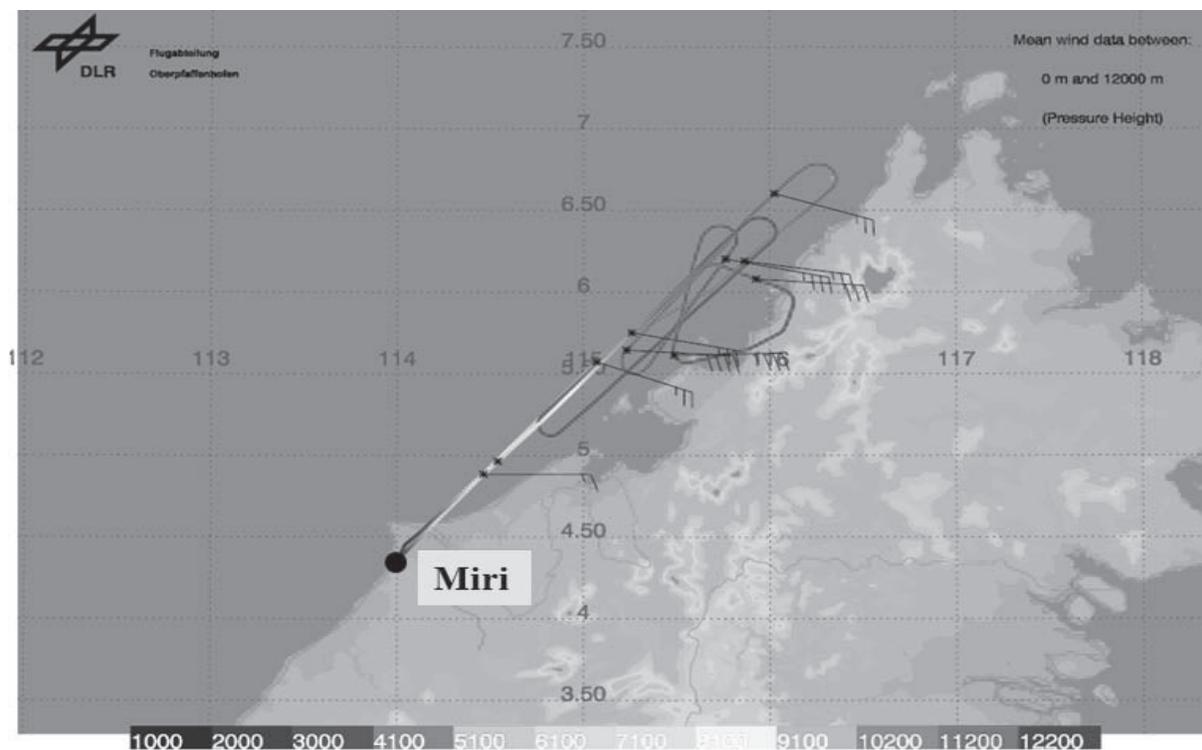
Figure 1. Flight track of the first sortie on November 16, 2011. The colour coding indicates the height in meters. Adopted from DLR, *Flugabteilung, Oberpfaffenhofen*.



**Figure 2.** Sortie of the Falcon aircraft on November 16, 2011: marine boundary layer study: height (red) and wind direction (grey) from the Falcon dataset, NO<sub>2</sub> (black) and HCHO (purple) mixing ratios from the mini-DOAS instrument, CO (green) mixing ratios from SPIRIT, O<sub>3</sub> (pink) mixing ratios from the ozone monitor and SO<sub>2</sub> (blue) mixing ratios from CI-ITMS. The turn in Kuching Bay is marked with a black bar. The different events (1a-b, 2a-b) are marked with a dotted red circle.



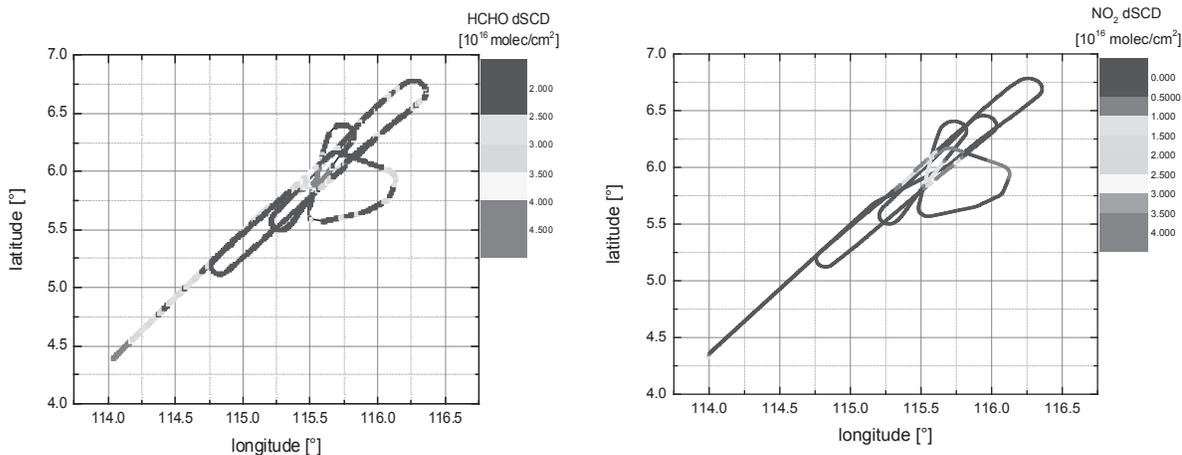
**Figure 3.** GOME-2 NO<sub>2</sub> VCD (left panel) and HCHO VCD (right panel): 10-day average (10 - 20.11.2011), cloud fraction < 40%. The red circles mark the regions with enhanced VCDs of NO<sub>2</sub> and HCHO.



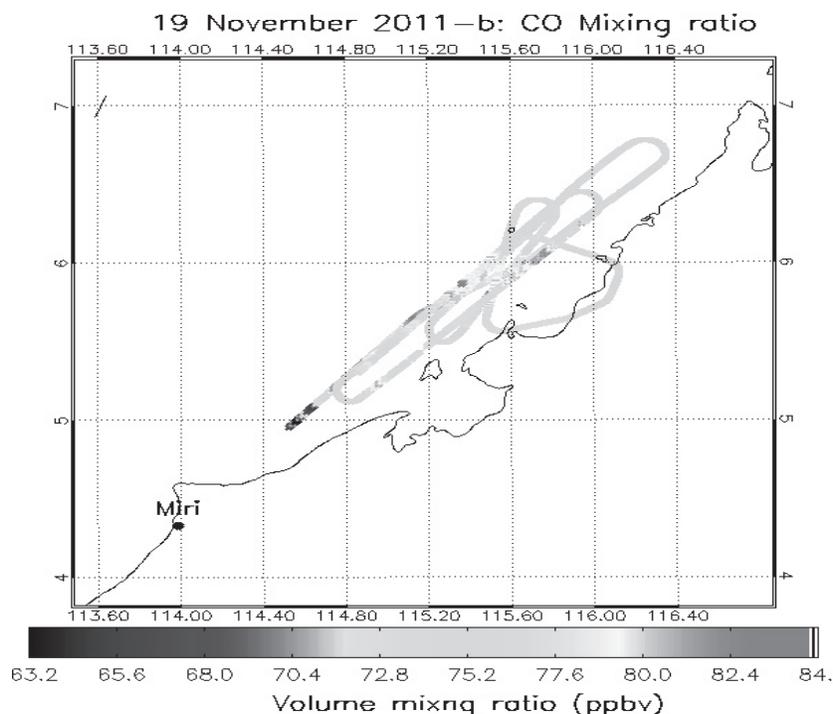
**Figure 4.** Flight track of the sortie on November 19, 2011. The colour coding indicates the height in meters (adopted from DLR, *Flugabteilung, Oberpfaffenhofen*).

Figure 5 shows the dSCDs of  $\text{NO}_2$  and HCHO measured along the flight track. Only dSCDs are shown, as the conversion from dSCDs to mixing ratios within and around a cloud is complex due to the changing light path. Not unexpected every time the Falcon aircraft penetrated

the outflow of the Cb cloud plume  $\text{CO}$ ,  $\text{NO}_2$  as well as HCHO were elevated as compared to background concentrations. The simultaneous enhancements of these gases clearly indicate a rapid uplift of polluted air originating from near the surface to the upper troposphere.



**Figure 5.** Sortie of the Falcon aircraft on November 19, 2011: HCHO dSCDs (left panel) and  $\text{NO}_2$  dSCDs (right panel) colour coded along the flight track.



**Figure 6.** Sortie of the Falcon aircraft on November 19, 2011: CO mixing ratios colour coded along the flight track.

### SUMMARY

During the SHIVA Falcon aircraft sorties from Miri/Borneo signs of emissions from natural and anthropogenic sources were detected. For example simultaneous enhancements of CO, SO<sub>2</sub>, NO<sub>2</sub> and HCHO can be ascribed to emissions of ships, oil rigs and anthropogenic combustion processes at the north-western coast of Borneo.

The atmospheric oxidation capacity was investigated via measurements of isoprene, CHOCHO, HCHO and CO. HCHO mixing ratios of up to 1.5 ppb were detected, whereas CHOCHO reached mixing ratios of approximately 50 - 100 ppt.

The composition of air masses in convective outflows around thunderstorms was also studied through simultaneous measurements of CO, HCHO and NO<sub>2</sub>. Within the outflow region of convective cells in the upper troposphere, the concentrations of these gases were simultaneously elevated indicating their origin from near the surface.

On several occasions IO could also be detected in small amounts of approximately 1 ppt around the north-eastern coast of Borneo (not shown here), but during all sorties BrO never exceeded the detection limit of approximately 3 ppt, thus likely limiting the role of halogens in tropospheric photochemistry to iodine.

### ACKNOWLEDGEMENTS

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### REFERENCES

1. Pfeilsticker, K., Dorf, M., Sturges, B., Oram, D., Engel, A., Rex, M., Bracher, A., Roozendaal, M., Hendrick, F., Theys, N., Krüger, K., Quack, B.,

- Wallace, D., Fueglistaler, S., Pyle, J., Marecal, V., Catoire, V., Pirre, M., Chipperfield, M., Heard, D., Stohl, A., Eckhardt, S., Sinnhuber, B-M., Rozanov, A., Wittrock, F., Schlager, H., Samah, A.A., Phang, S.M., Anton, A., Sentian, J., Po Teen Lim, Mujahid, A., Nur Aleesha Abdullah, Maznorizan, and Nor Aieni Binti Haji Mokhtar (2012): The SHIVA Western Pacific campaign in fall 2011, SCS Proceeding December 2012.
2. Platt, U. and Stutz, J. (2008): Differential Optical Absorption Spectroscopy: Principles and Applications, Physics of Earth and Space Environments, Springer Verlag, Berlin.
  3. Guimbaud, C., Catoire, V., Gogo, S., Robert, C., Chartier, M., Laggoun-Défarge, M., Grossel, M., Albéric, P., Pomathiod, L., Nicoullaud, B. and Richard, G. (2011): A portable infrared laser spectrometer for flux measurements of trace gases at the geosphere–atmosphere interface, *Meas. Sci. Technol.*, 22, 075601, doi:10.1088/0957-0233/22/7/075601
  4. Schlager, H., P. Konopka, P. Schulte, U. Schumann, H. Ziereis, F. Arnold, M. Klemm, D. E. Hagen, P. D. Whitefield, and J. Ovarlez (1997), In situ observations of air traffic emission signatures in the North Atlantic flight corridor, *J. Geophys. Res.*, 102(D9), 10,739–10,750, doi:10.1029/96JD03748
  5. Speidel, M., Nau, R., Arnold, F., Schlager, H., and Stohl, A.: Sulfur dioxide measurements in the lower, middle and upper troposphere: deployment of an aircraft-based chemical ionization mass spectrometer with permanent in-flight calibration, *Atmos. Environ.*, 41, 2427–2437, 2007.
  6. Prados-Roman, C., Butz, A., Deutschmann, T., Dorf, M., Kritten, L., Minikin, A., Platt, U., Schlager, H., Sihler, H., Theys, N., Van Roozendael, M., Wagner, T., and Pfeilsticker, K. (2011): Airborne DOAS limb measurements of tropospheric trace gas profiles: case studies on the profile retrieval of O<sub>4</sub> and BrO, *Atmos. Meas. Tech.*, 4, 1241-1260, doi:10.5194/amt-4-1241-2011
  7. Callies, J., Corpaccioli, E., Eisinger, M., Hahne, A., and Lefebvre, A. (2000), GOME-2- Metop's second-generation sensor for operational ozone monitoring, *ESA Bull.*, 102, 28–36
  8. De Smedt, I., Müller, J.-F., Stavrakou, T., van der A, R., Eskes, H., and Van Roozendael, M. (2008): Twelve years of global observations of formaldehyde in the troposphere using GOME and SCIAMACHY sensors, *Atmos. Chem. Phys.*, 8, 4947-4963, doi:10.5194/acp-8-4947-2008
  9. De Smedt, I., T. Stavrakou, J.-F. Müller, R. J. van der A, and M. Van Roozendael (2010), Trend detection in satellite observations of formaldehyde tropospheric columns, *Geophys. Res. Lett.*, 37, L18808, doi:10.1029/2010GL044245