Investigation of NO_2 Pollutions on Board of Research Aircraft (Some Results of QUANTIFY and POLARCAT Field Campaigns)

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ABSTRACT: The results of investigation of NO_2 pollutions on board of research aircraft Falcon (DLR, Germany) are presented. The measurements have been carried out by chemiluminescent nitrogen dioxide analyzer developed in Central Aerological Observatory (Russia). The data of NO_2 distribution have been obtained during QUANTIFY (West Europe, July 2007) and POLARCAT (Greenland, July 2008) field campaigns. NO_2 measurements over Greenland during POLARCAT field campaign have been carried out using ACCENT support. Different sources of nitrogen oxides are investigated. Some aspects of nitrogen dioxide distribution and transport are considered. Chemical transformation of nitrogen oxides inside ship plumes is observed and analyzed.

1 INTRODUCTION

Aircraft measurements of NO_2 atmospheric pollutions have been carried out using chemiluminescent nitrogen dioxide analyzer developed in Central Aerological Observatory (Russia). They were performed on board of research aircraft "Falcon" (DLR, Germany) during Quantify (July 2007, Brest, France) and POLARCAT (June 2008, Greenland) field campaigns. First one was concerned to ship emission measurements in the major European ship corridor. Ship emission is very important component of anthropogenic environmental pollution which gives considerable impact of greenhouse gases, aerosols and another substances to atmosphere. There are some publications concerning experimental investigations and modeling studies of ship emission (Corbett and Fischbeck, 1997, Schlager et al. 2006, Petzold et.al. 2006). Chemical transport models parametrization needs detail information about chemical and photochemical reactions in atmosphere of polluted regions including exhaust plumes. Simultaneous measurements of different gas species permit to investigate chemical and photochemical processes in atmosphere including the processes inside individual exhaust plume. Specially developed cheniluminescent nitrogen dioxide analyzer has a high time (~0.2 sec) and space (~20m) resolution, which is important to make correct measurements of NO_2 distribution in small size ship emission plumes. Another experience of using this instrument on board of research aircraft "Falcon" was in POLARCAT field campaign in June 2008 in Greenland. The objectives of the campaign are to investigate the impact of urban and forest fire emissions in the Arctic troposphere, mechanisms of fire plume spreading (dispersion, mixing), chemical and photochemical transformations in the fire plumes, and impact of forest fire emission transported by pyroconvection into the lower stratosphere.

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2 METHOD AND INSTRUMENT

The instrument is based on chemiluminescent principle (Kinrade, 1991) that is interaction of NO_2 with luminol solution leads to light radiation in visible spectral range. The intensity of the light depends on the nitrogen dioxide concentration. This method is very fast and very sensitive to NO_2 but it has some interference in atmosphere. The highest interference is sensitivity to peroxiacetilnitrat (PAN), which is about 25% of NO_2 sensitivity. For correct NO_2 measurements it must be taken into account. Another interference is the sensitivity to ozone. It is not so high (less then 0.5% of NO_2 sensitivity) and it can be excluded by additional O_3 measurements or using special ozone scrubber. Special design of the instrument permits to take into account PAN influence. Ozone influence is excluded using "Falcon" ozone data.

The block diagram of the instrument is shown in Fig.1. Main sensor (Sitnikov et.al 2005) consists of liquid pump with special valve, reaction chamber and photoelectric multiplier (Fig.1a). Liquid pump for circulating the liquid is a syringe filled with a chemiluminescent solution. Its plunger is slowly displaced by a reduction motor. In order to exclude the possibility of the chemiluminescent solution boiling at low pressures and the appearance of flow-velocity instabilities, valve is connected to the pump outlet. This valve obstructs the chemiluminescent solution flow; as a result, the pressure inside the syringe during the movement of the plunger always exceeds atmospheric pressure. A nipple manufactured from such neutral materials as silicone, teflon, polyethylene, etc., can serve as a valve. This design of the pump completely excludes the possibility of bubble formation and ensures a constant liquid flow at external pressures of 1 to 1000 mbar. The consumption of the chemiluminescent solution is determined only by the velocity of the plunger's motion and amounts to 2.5 ml/h; i.e., 10 ml of the solution sustains the operation of the instrument for 4 hours that is for usual duration of "Falcon" flight. The pump supplies the solution into the reaction chamber and onto a porous substrate. The exhausted solution drains off into a vessel positioned below the reaction chamber.

The instrument includes two channels (main and auxiliary) with two chemiluminescent sensors (Fig.1b). One of them (auxiliary channel) has PAN-NO_2 converter (thermolytic cell) which is heated up to 200-250^oC. Thermolytic destruction of PAN provides increasing of NO_2 concentration:

$CH_3COO_2NO_2 \rightarrow CH_3COO_2 + NO_2$

This results in signal increasing in auxiliary channel because of different sensitivity to NO_2 and PAN. Simultaneous measurements in two channels permit to take into account the influence of PAN and increase the accuracy of NO_2 measurements. Ozone influence is corrected using the data of "Falcon" ozone measurements. Calibration of the instrument was performed in CAO and DLR. Fig.1c illustrates the process of measurements with correction taking into account PAN influence. Usually this correction was not high.

Air flow through the main and auxiliary channels (about 2 l/min) is provided by air pump with constant volume flow rate. The instrument is regulated by compact electronic block. It can operate in automatic regime. The data of measurements is recorded to internal flash memory. The instrument has RS232 interface for connection with computer or telemetry system.

Technical characteristics of the instrument:

The range of NO_2 measurements	0.05 – 100 ppbv;
Time resolution	0.2 s
Weight	5 kg;
Power	50 W.

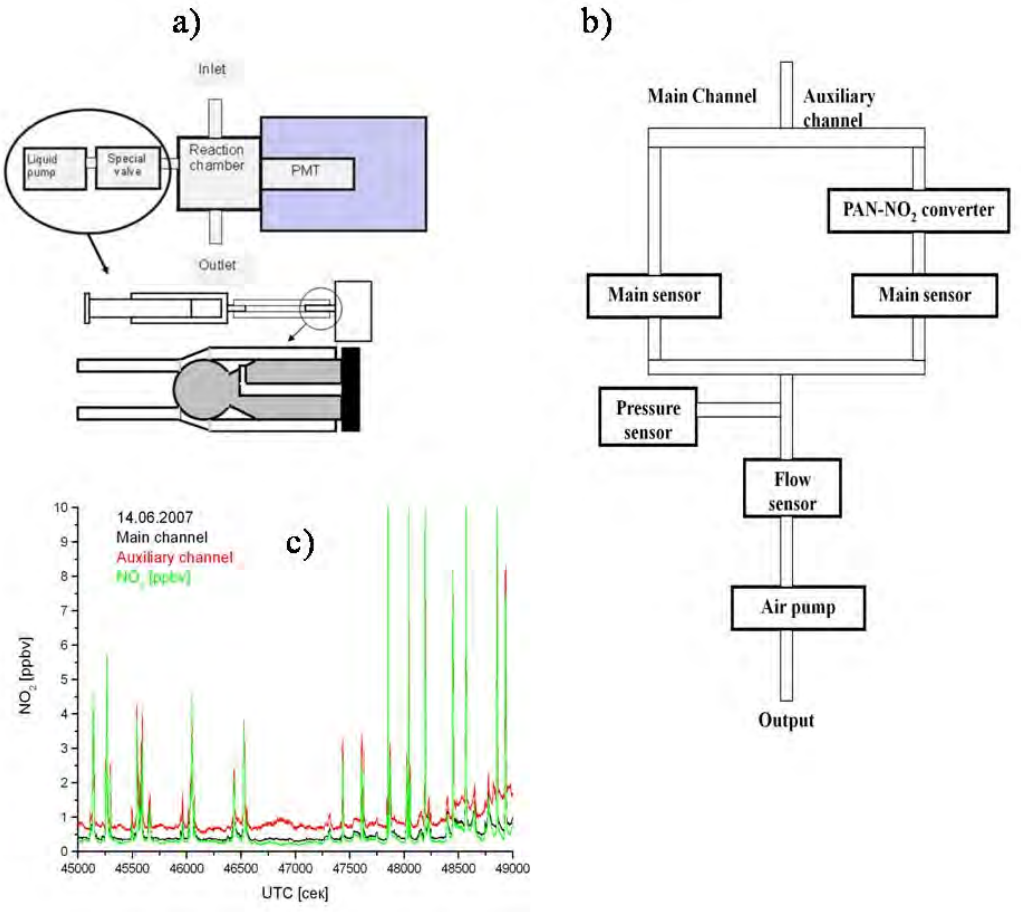

Fig.1. Block diagramm of the main chemiluminescent sensor (a) and chemiluminescent nitrogen dioxide analyzer (b) and time series of signals (in terms of NO_2 concentration) in main channel (black), auxiliary channel (red) and NO_2 concentration corrected taking into account PAN influence (green).

3 RESULTS AND DISCUSSIONS

Eight scientific flights were fulfilled in June 2007 during Quantify project field campaign by scientific aircraft Falcon in different routes. The altitudes changed from several hundred meters to several kilometers, the duration of flights was 3 – 3.5 hours. The measurements were made above the Atlantic Ocean as in non polluted areas as in sea transport corridor, the most polluted regions of Europe. Distribution of some atmospheric species such as nitrogen oxides, CO, CO_2, aerosols and others has been measured. NO_2 measurements were fulfilled by chemiluminescent nitrogen dioxide analyzer described above. Time response of the instrument was 0.2 sec. As the aircraft velocity was 100 m/sec, space resolution of NO_2 concentration measurements was about 20 m. Some results of nitrogen dioxide measurements are represented in Fig. 2-4.

The flight on 14th of June, 2007 was from Brest (France) to western coast of England as demonstrated in Fig.2. Different chemical components concentrations were measured in a dedicated exhaust plume of a large container ship (Atlantic Conveyor flight). During the flight the aircraft crossed the exhaust plume many times at different distances from the ship. Several trace species concentrations were measured for different life times of the exhaust plum (from 1 minute to several hours). Fig.2 represents NO and NO_2 concentrations measurements for the part of flight on the 14th of June, 2007. As the measurements were strictly synchronized we can determine dependence of NO_2 / NOx ratio from the life time of the exhaust plum. The results of the calculation are represented in Fig.2b. As figure shows initial NO_2/NOx ratio is very low (about 0.1). Then it increased up to 0.6 – 0.7 during some minutes. This increasing is connected with fast chemical reaction of NO with ozone, and after that variation of NO_2/NOx ratio was not high during some hours.

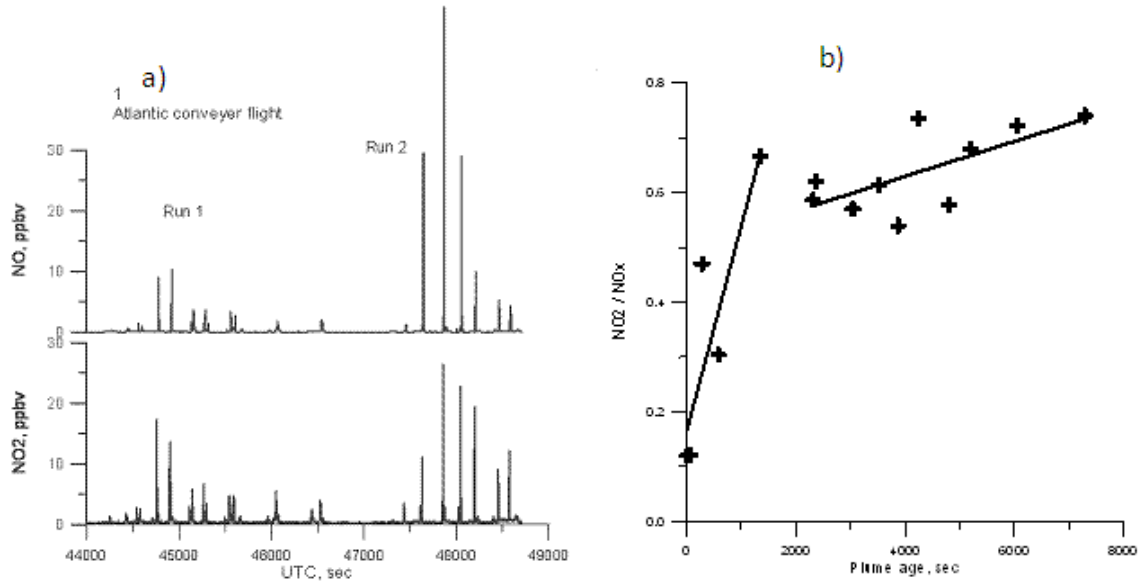

Fig.2. Time series of simultaneous NO and NO_2 measurements during Atlantic conveyor flight July 14, 2007 (a) and the ratio NO_2/NOx verses plume age calculated from this data (b).

On the 17th of June there were two flights along English Channel from Brest to Bremen (Fig.3a) and back to Brest (Fig.3b). The first flight from Brest to Bremen was started early in the morning. The second flight from Bremen to Brest was several hours later. NO_2/NOx ratios were calculated from the results of measurements in peaks of exhaust plumes of different ships. Fig.3c demonstrates the dependence of NO_2/NOx ratio from the day time for both flights on the 17th of June. Decrease of the ratio with time most likely associated with dependence of photochemical reactions rate from the Sun radiation intensity. Average NO_2/NOx ratio was 0.85 for the first flight and 0.64 for the second one. However NO_2/NOx ratio of every flight has spreading in its values. This spreading is probably connected with different plume ages or different weather conditions in different points of the route.

The measurements demonstrated that NO_2 distribution in a major ship corridor near Western coast of Europe highly inhomogeneous. Background NO_2 concentrations were less than 0.5 ppbv. Local maximums which caused by ship emission were found about several tens of ppbv, sometimes more than 100 ppbv. Such concentrations were measured at altitudes less than 500 meters. At altitudes above 500 meters as a rule background NO_2 concentrations were measured.

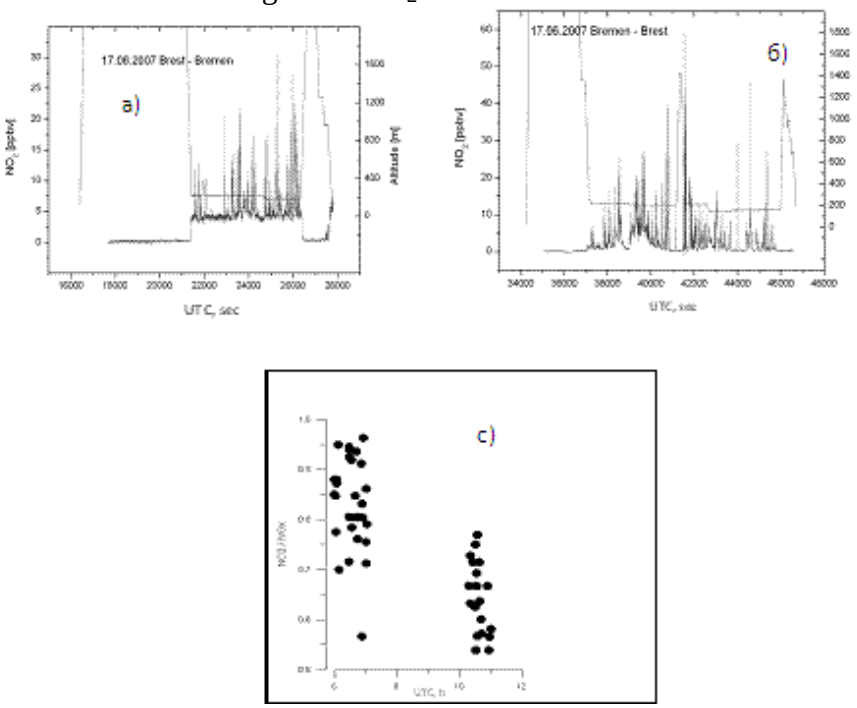

Fig.3. Time series of NO_2 concentration in ship corridor which is measured 17.06.2007 during the flights Brest-Bremen (a) and Bremen-Brest (b) and NO_2/NOx ratio verses day time (c) calculated from NO_2 and NO local maxima.

Another experience of using nitrogen dioxide analyzer on board of research aircraft was during POLARCAT field campaign in June 2008. The campaign is based in Kangerlussuaq (Greenland). There were some flights with different routes to make measurements of atmospheric species from urban and forest fire emissions of North America and Siberia. In most of flights the measurements show very low NO_2 concentrations. There were nearly or lower the detection limit of the instrument (some tens of pptv). Maximal NO_2 concentration (about 200 pptv) has been observed during the flight of July 10, 2008. (Fig.4b) The flight was performed over the Greenland in North direction (Fig.4a) mainly in stratosphere. Fig.4c shows 10 days backward trajectories from initial points with increased NO_2 concentration. Considered air masses with increased NO_2 concentration have different origin. As trajectory analysis shows the origin of air masses with increased (in comparison with phone concentrations) NO_2 concentration is not connected with lower troposphere.

Then according to completed measurements, the considerable increasing of NO_2 concentration in Arctic connected with forest fire is not observed during POLARCT field campaign.

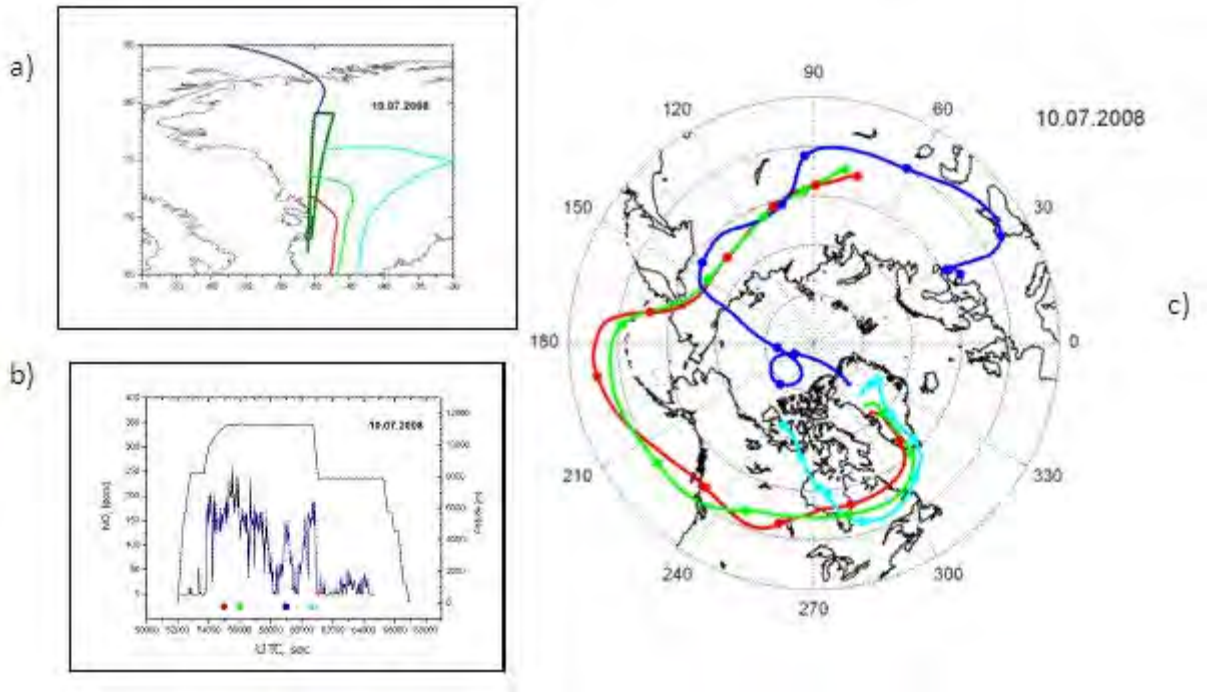

Fig.4. The route of research aircraft “Falcon” flight 10.07.2008 (a), time series of NO_2 measurements during this flight (b), 10 days backward trajectories of air masses plotted from initial points with maximal NO_2 concentration (c).

4 CONCLUSIONS

In the frame of European project QUANTIFY in Central Aerological Observatory Chemiluminescent Nitrogen Dioxide Analyzer for research aircraft have been developed and manufactured. NO2 measurements on board of research aircraft “Falcon” during QUANTIFY (June 2007) and POLARCAT (July 2008) field campaigns have been carried out using developed instrument. NO2 measurements in European ship corridor during QUANTIFY field campaign showed very inhomogeneous NO2 distribution from concentrations < 0.5 ppbv up to 100 ppbv connected with ship emission. Data analysis of the of simultaneous NO and NO2 measurements shows nitrogen oxides chemical transformation inside the individual exhaust plume.

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