Aircraft-based Trace Gas Measurements in a Primary European Ship Corridor

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ABSTRACT: Aircraft measurements of gaseous ship emissions were performed in the vicinity of the heavily travelled ship lanes through the English Channel and in the exhaust trail of a major sea-going container ship. In the single ship plume experiment the concentration and dilution of major emissions (CO_2, NO, NO_y, SO_2) were measured up to a distance to the source ship and plume age of 25 km and 1650 s, respectively. Emission factors for NO_x and SO_2 were determined from individual plume encounters. The inferred NO_x emission indices compare well with calculated emission indices from the engine emission model of the manufacturer. The deduced SO_2 emission indices from the SO_2 enhancements in the plume are smaller than calculated emission indices bases on the analysed sulphur content in the fuel sample. However, the difference is still within the estimated error limits for the SO_2 emissions factor measurements. A survey flight in the ship corridor through the English Channel revealed the presence of a multitude of ship plumes aged between 0.5 and several hours. Many of the observed concentration enhancements in the ship corridor are due to the superposition of several plumes with different ages.

1 INTRODUCTION

Shipping represents a major element of international transportation. Combustion from ships produces gaseous species and aerosols that contribute to anthropogenic pollution and climate change (e.g. Corbett and Fischbeck, 1997, Lawrence and Crutzen, 1999, Endresen et al., 2003). A number of model studies have been performed to investigate the local, regional and global impact of gaseous ship emissions on photochemistry (Capaldo et al. 1999, Lawrence and Crutzen 1999, Kasibhatla et al. 2000, Davis et al. 2001, Glasow et al. 2002, Endresen et al. 2003, Song et al. 2003). These studies revealed that photochemical and heterogeneous processes in the ship exhaust plumes and the ship corridors are important but not well parameterized in the chemistry transport models. Experimental data to investigate these processes, however, are very sparse. Chen et al. (2005) performed aircraft measurements in the exhaust trail of two ships off the coast of California in 2002 and found that models underestimate NO_x and SO_2 losses and largely overestimate HNO_3 abundances in the plumes. Recently, Williams et al. (2005) reported observations in exhaust plumes of several small marine ships off the coast of New England performed on board the research vessel Ron Brown in summer 2004. Here we report on first aircraft measurements in a major European ship traffic corridor including detailed observations in the exhaust trail of a large container ship. The objectives of these investigations are to provide data for analysis of plume dilution and mixing, determination of ship emission factors, and validation of plume box and chemistry transport models. This paper presents the measurements of chemical compounds, observations of particulate ship emissions are described in the proceedings contribution of Petzold et al. (this issue).

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2 EXPERIMENT

The measurements were performed on 23 and 30 July 2004 as part of the DLR research program Transport and Environment. The DLR research aircraft Falcon was used based from Creil in northern France. The objective of the flight on 23 July 2004 was to survey the English Channel at the western exit and search for corridor effects of ship emissions. The English Channel is one of the most travelled ship corridors in the world. About 500 ships per day use the east- and westbound shipping lanes in the English Channel. The objective of the flight on 30 July 2004 was to sample the exhaust trail of a designated source ship, a very large container ship. The sampling of the container ship plume was performed off the coast of north-western France near 48.2°N/ 6,5°W. Information on the operating conditions of the ship and the engine as well as a sample of the fuel burnt were provided by the ship operator.

Measurements presented here include CO_2, NO, NO_y, O_3 and SO_2. A NDIR absorption spectrometer was used for fast CO_2 measurements (modified LI-COR 6262) with an accuracy of ±0.8 ppmv for a time resolution of 1 s. (Fischer et al., 2002). NO and NO_y were detected using chemiluminescence technique (Schlager et al., 1997, Ziereis et al., 1999). Individual NO_y compounds were catalytically reduced to NO on the surface of a heated gold converter with addition of CO. The inlet tube for air sampling was oriented rearward and heated to 30°C to avoid sampling of NO_y in particles and adsorption of nitric acid on the wall of the sampling tube, respectively. The accuracy of the NO and NO measurements is 8 and 15 % for a time resolution of 1 s. Detection of O_3 was by UV absorption technique (Thermo Electron Corporation, Model 49) with an accuracy of 5 % for a time resolution of 5 s. SO_2 was measured using an ion trap mass spectrometer and chemical ionization technique (Speidel et al. 2006).

3 RESULTS

3.1 *Individual plume measurements*

Figures 1 shows the route of the container ship and the Falcon flight track during the exhaust trail measurements on 30 July 2004. The detailed sampling of the plume was performed between 16.30 – 17.30 UTC at flight levels between 93 and 266 m asl. The wind direction was east/southeast with a mean wind velocity of 2.5 ms^{-1}. Besides the exhaust plume of the container ship additional plumes were present of other ships cruising west (downwind) of the container ship on similar routes.

Table 1 summarises the observations during ten successful plume penetrations. Given are the measured enhancements of mixing ratios of CO_2, NO, and NO_y in the plume. Also included is time, altitude, and estimated plume age for each encounter. NO and NO_y values are missing for the encounters at small plume ages due to concentrations in the plume outside the measurement range of the instruments. A device for dilution of the sample air prior to detection was not used during these first measurements of ship plumes.

Figure 2 (right panel) shows the measured peak mixing ratios of CO_2, NO, and NO_y for the plume encounters as a function of plume age. After a plume age of 1000 s the exhaust plume is diluted by a factor of $3.5 \cdot 10^{-5}$ considering the initial CO_2 mixing ratio at the engine exit of 40.000 ppmv. Observed $\Delta NO_y/\Delta CO_2$ ratios versus plume age are shown in the right panel of Figure 2. The $NO_y/\Delta CO_2$ ratios for the plume encounters #6 and #10 agree within error estimates with the initial NO_x/CO_2 ratio at the engine exit indicating no NO_y loss for plume ages up to 1300 s for the meteorological conditions in the boundary layer during the measurements. The $NO_y/\Delta CO_2$ ratio of plume encounter #3 is slightly smaller than the initial NO_x/CO_2 ratio at the engine exit suggesting onset of reactive nitrogen loss.

3.2 *Ship traffic corridor measurements*

Figure 3 depicts the Falcon flight track on 23 July 2004. The flight section in the ship corridor was from Brest (48.5°N, 4.2°W) to the northwest (50°N, 7°W) at a constant altitude of 200 m asl. Figure 4 shows observed mixing ratios of NO_y, NO, SO_2, and CO_2 along the Falcon flight track in the ship

corridor (right panel). Coincident enhancements in the mixing ratios of NO_y, NO and SO_2 were found caused by a multitude of ship exhaust plumes aged between about 0.5 and 5 hours. In many cases measured concentration peaks are due to superposition of several ship plumes. For some of the exhaust plumes enhancements of the CO_2 mixing ratios were also detected. An example is shown in the right panel of Figure 3. Observations in this multiple plume were used to infer emission factors for NO_x (see below).

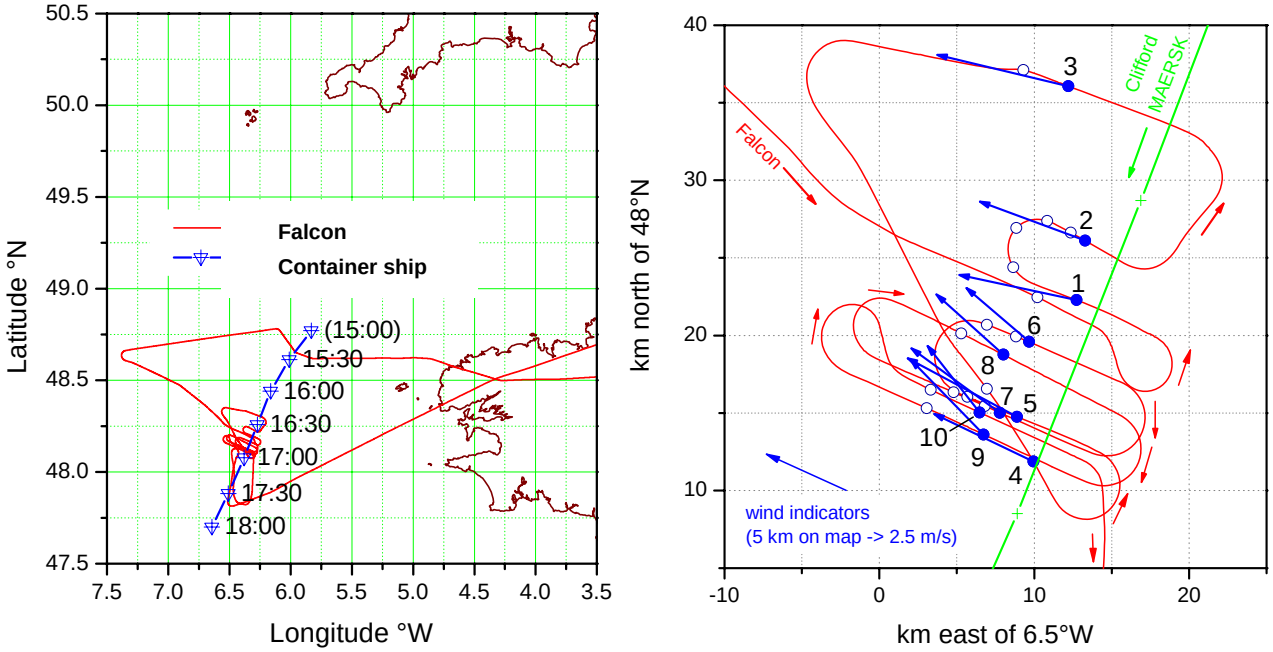

Figure 1. Sampling strategy of the exhaust plume of the large container ship. Routing of the Falcon and container ship (left panel). Falcon encounters (solid circles) of the container ship plume are labelled from 1-10 (right panel). The wind direction and velocity are also indicated. Plumes from other nearby ships were also penetrated (open circles).

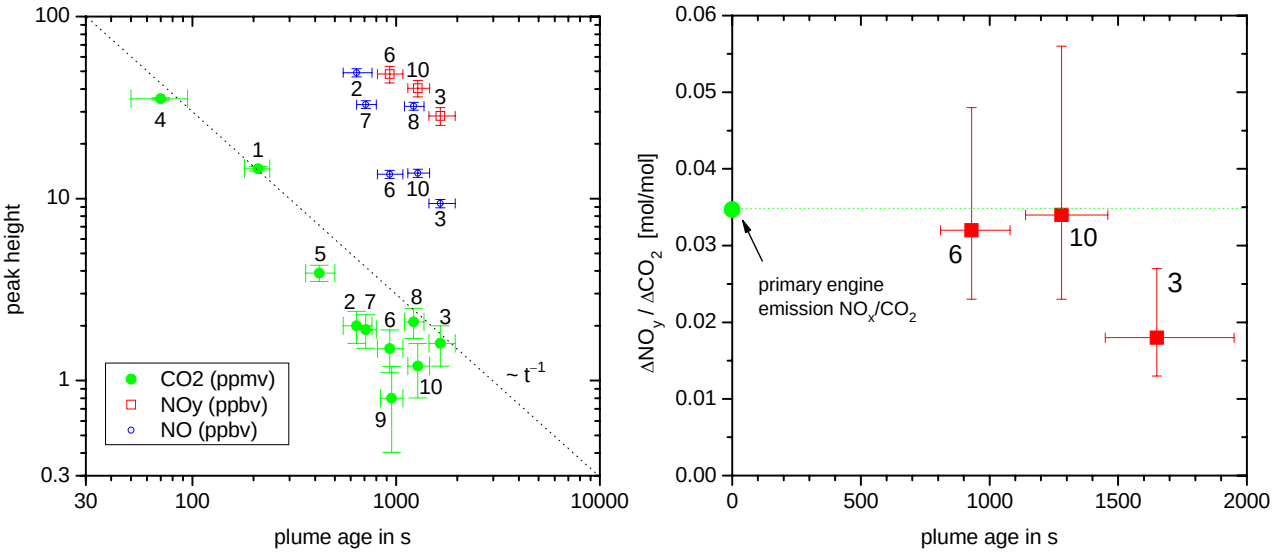

Figure 2. Observed peak concentrations of CO_2, NO_y, and NO for the container ship plume transects versus estimated plume age (left panel). Measured NO_y/CO_2 ratios of the plume encounters #3. #6, and #10. Also included is the initial emission NO_x/CO_2 ratio at the engine exit (right panel).

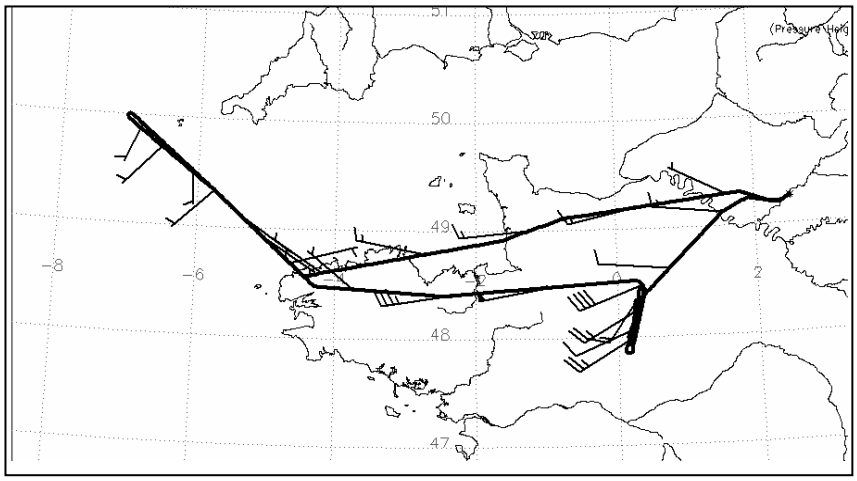

Figure 3. Falcon transect through the ship corridor at the exit of the English Channel at a constant altitude of 200 m asl on 23 July 2004.

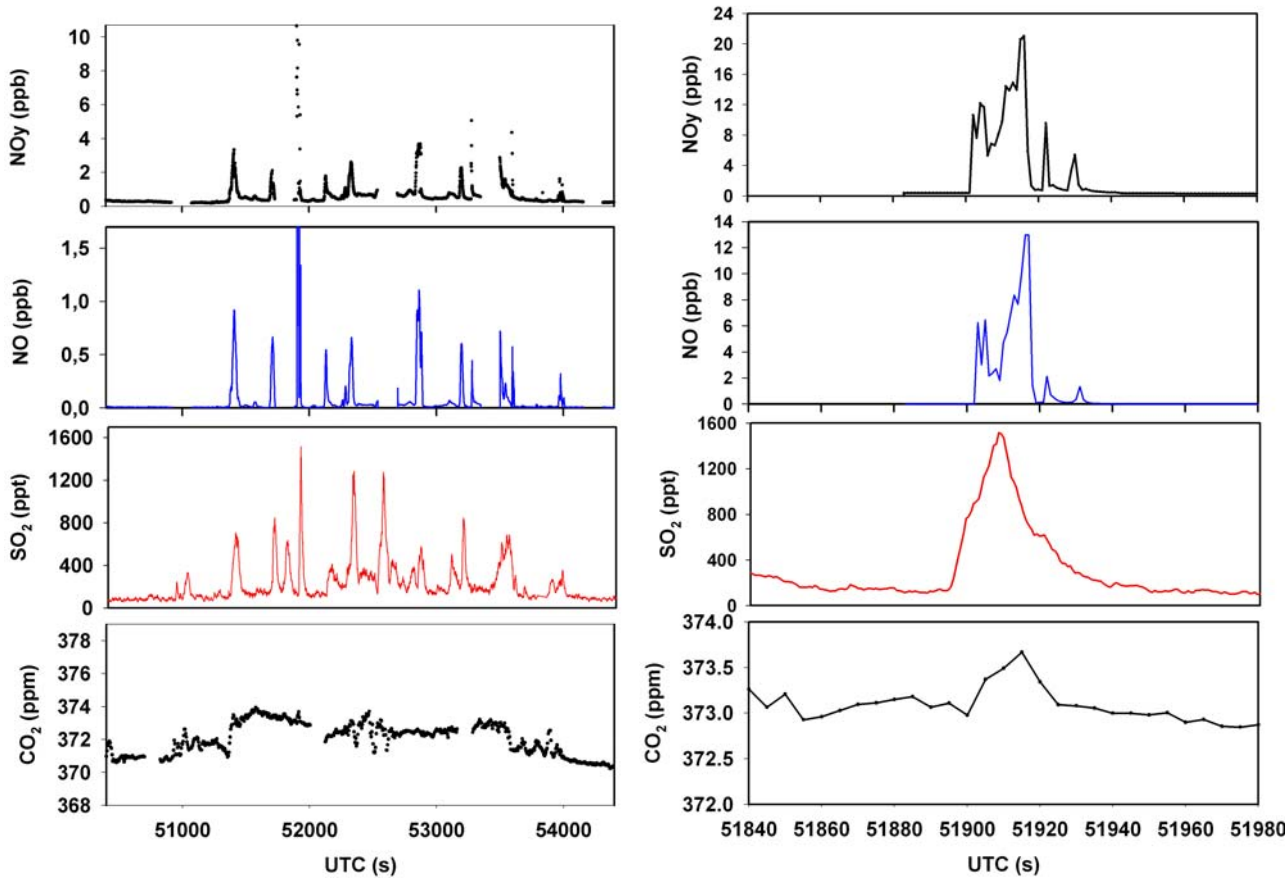

Figure 4. Time series of observed NO_y, NO, SO_2, and CO_2 for the ship corridor transect (left panels). Observed concentration enhancements in the multiple plume sampled at about 51910 s (UTC) in the ship corridor (right planels).

Table 1. Observed differences of trace gas mixing ratios for the individual plume encounters relative to ambient concentrations in the boundary layer. Plume ages are calculated using the wind measurements from the Falcon

#	UTC Sec	Alt m	plume age S		ΔCO2 µmol / mol	ΔNO nmol / mol	ΔNOy nmol / mol	ΔNOy / ΔCO2 mmol / mol
1	60194	134	210	±30	14.6±0.4	-	-	-
2	60307	105	640	-90/+120	2.0±0.4	49.2±2.5	-	-
3	60536	95	1650	-200/+300	1.6±0.4	9.4±0.5	28.4±3.2	18(-5/+9)
4	60977	93	70	-20/+25	35.3±0.5	-	-	-
5	61136	150	420	-60/+80	3.9±0.4	-	-	-
6	61274	149	930	-120/+150	1.5±0.4	13.6±0.7	48.3±5.1	32(-9+16)
7	61470	194	710	-70/+90	1.9±0.4	32.9±1.6	-	-
8	61689	195	1220	-120/+150	2.1±0.4	32.2±1.6	-	-
9	61903	263	950	-110/+130	0.8±0.4	-	-	-
10	62157	266	1280	-140/+180	1.2±0.4	13.8±0.7	40.4±4.2	34(-11/+22)

3.3 *Determination of emission factors*

Emission factors for NO_x were derived from the plume encounters #3, #6, and #10 during the flight on 30 July 2004 (see Table 1) and the multiple plume observed in the ship corridor during the flight on 23 July 2004 (Figure 3, right panel). Emission factors for SO_2 were inferred from the plume encounters #3 and #10. Emission indices (emitted mass per kg fuel burnt) for NO_x (as NO_2 mass) were calculated using (e.g. Schulte & Schlager, 1996)

$$EI(NO_x) = EI(CO_2)\ 46/44\ \Delta[NO_x]/\Delta[CO_2] \quad (1)$$

where $EI(CO_2)$ denotes the CO_2 emission index, 46 and 44 the mole masses of NO_2 and CO_2, respectively. $\Delta[NO_x]$ and $\Delta[CO_2]$ are the observed enhancements of the mixing ratios in the plumes relative to ambient background concentrations. For $\Delta[NO_x]$ we used the measured $\Delta[NO_y]$ and assumed no loss of reactive nitrogen in the plumes. The CO_2 emission index is known with high accuracy (3070 ± 20 g CO_2 / kg fuel) from the carbon mass fraction in ship fuel (85.1%) and the fraction of carbon that is converted to CO_2 for cruise conditions (98.5%). The calculated NO_x emission indices are given in Table 2.

Emission factors for SO_2 were derived from the ratios of the integrals of the corresponding plume enhancements

$$EI(SO_2) = EI(CO_2)\ \ 64/44\ \ \int[SO_2]/\int[CO_2]. \quad (2)$$

Integral ratios needed to be used because of the different time responses of the CO_2 and SO_2 measurements. The calculated SO_2 emission indices are also summarized in Table 2.

Table 2. Summary of emission indices derived from the plume observation. For comparison calculated values are also given.

Date, Plume encounter	$EI(NO_x)$ measured (g NO_2 / kg fuel)	$EI(NO_x)$ calculated (g NO_2/ kg fuel)	$EI(SO_2)$ observed (g SO_2/ kg fuel)	$EI(SO_2)$ calculated (g SO_2/ kg fuel)
30 July, #3	96 ± 14	112 (a)	46 ± 12	49 (c)
30 July, #6	103 ± 15	112 (a)	-	49 (c)
30 July, #10	109 ± 16	112 (a)	40 ± 10	49 (c)
23 July, corridor	98 ± 15	86 (b)	-	

(a) engine model of manufacturer for measurement conditions, (b) mean all cargo ships (Eyring et al. 2005), (c) from analysis of sulphur content in the fuel sample of the container ship (2.45% by mass), (d) from mean sulphur content of cargo ship fuel (Eyring et al., 2005).

The inferred $EI(NO_x)$ values compare well with calculated emission indices for the container ship using the engine emission model of the manufacturer and the known engine operating conditions during the measurements. The SO_2 emission factors derived from the integrals of the CO_2 and SO_2 enhancements observed in the plume are lower by 6% and 19% compared to the values calculated

from the known sulphur content in the fuel burnt by the container ship. Considering the estimated errors, however, the emissions factors are still consistent with the values derived from the analysis of the sulphur in the fuel.

4 CONCUSIONS

The measurements in the exhaust trail of a designated source ship and in the ship corridor revealed that aircraft-based observations in ship plumes are possible for plume ages up to about 5 hours. The inferred emission factors for NO_x are consistent with reported mean values for the fleet of large container ships. Observed SO_2 enhancements in the plumes relative to the CO_2 enhancements as a dilution tracer are smaller than calculated values from the known sulphur content in the fuel but still agree within error limits. In order to study SO_2 losses in the exhaust plumes further measurements with higher accuracy and for larger plume ages are needed. During the flight transects in the ship corridor very inhomogeneous concentration field were found for trace gasses related to ship emissions due to multiple aged plumes. Next year a large aircraft campaign on ship emission will be performed in the frame of the EC project QUANTIFY with an extended set of instruments.

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