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# Lagrangian analysis of low level anthropogenic plume processing across the North Atlantic

Low altitude anthropogenic plume processing

Real et al.

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## Abstract

The photochemical evolution of an anthropogenic plume from the New-York/Boston region during its transport at low altitudes over the North Atlantic to the European west coast has been studied using a Lagrangian framework. This plume, originally strongly polluted, was sampled by research aircraft just off the North American east coast on 3 successive days, and 3 days downwind off the west coast of Ireland where another aircraft re-sampled a weakly polluted plume. Changes in trace gas concentrations during transport were reproduced using a photochemical trajectory model including deposition and mixing effects. Chemical and wet deposition processing dominated the evolution of all pollutants in the plume. The mean net O<sub>3</sub> production was evaluated to be -5 ppbv/day leading to low values of O<sub>3</sub> by the time the plume reached Europe. Wet deposition of nitric acid was responsible for an 80% reduction in this O<sub>3</sub> production. If the plume had not encountered precipitation, it would have reached the Europe with O<sub>3</sub> levels up to 80-90 ppbv, and CO levels between 120 and 140 ppbv. Photochemical destruction also played a more important role than mixing in the evolution of plume CO due to high levels of both O<sub>3</sub> and water vapour showing that CO cannot always be used as a tracer for polluted air masses, especially for plumes transported at low altitudes. The results also show that, in this case, an important increase in the O<sub>3</sub>/CO slope can be attributed to chemical destruction of CO and not to photochemical O<sub>3</sub> production as is often assumed.

## 1 Introduction

It is recognised that emissions from large urban/industrial regions can have large-scale impacts on levels of O<sub>3</sub>, particles, and other trace constituents downwind from continents. These impacts are important because they may affect the ability of downwind countries to meet air quality standards, and because of the climate impacts of O<sub>3</sub> and particles through radiative forcing. Anthropogenic pollution occurs primarily in the

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boundary layer (BL) over continents. This pollution may then be transported at low levels directly impacting the BL of a downwind continent or may be exported from the BL into the mid and upper troposphere by frontal systems or convection and transported at higher altitudes (Li et al., 2005). Because of lower water vapour and temperature, loss processes are less active and pollutant lifetimes are longer in the upper troposphere. However, high altitude plumes are less likely to directly impact the BL composition of a downwind continent. Several modelling studies have already shown that long-range transport of pollutants from North America to Europe is one of the most important due to large emissions and relative proximity of the two continents (Wild and Akimoto, 2001; Stohl, 2001; Stohl et al., 2002). There is clear experimental and modelling evidence for such export from North America at both low and high altitudes. Polluted plumes have been sampled at remote surface sites such as Sable Island or Chebogue Point (Parrish et al., 1998; Millet et al., 2006), off the New England coast, and also downwind in the Azores (Parrish et al., 1998; Owen et al., 2006) in the mid Atlantic Ocean. Analysis of these polluted plumes showed that they were usually transported at low altitudes, below 3 km. Modelling studies suggest that one third of CO exported from North America occurs in the lowest 3 km (Li et al., 2005) and Owen et al. (2006) suggested that low level transport of North American pollution above the marine BL may provide an effective mechanism for long-range transport of anthropogenic pollution over the Atlantic ocean with a resulting impact on lower tropospheric O<sub>3</sub> in downwind regions.

Whilst there have been several measurements of polluted plumes with North American origins in the free troposphere over Europe (e.g. Huntrieser et al., 2005), there have been fewer detailed cases at low levels and the impact of such long-range transport on O<sub>3</sub> levels in the European BL is not well documented (Derwent et al., 1998). Ground-based sites on the west coast of Europe do occasionally observe such cases. For example, Li et al. (2002) reported several measurements of moderately polluted plumes at Mace Head (west coast of Ireland) with weak enhancements in CO and O<sub>3</sub>. Despite the relative lack of experimental evidence, global model simulations suggest that the impact of anthropogenic North American pollution on European BL O<sub>3</sub> is im-

portant. [Li et al. \(2002\)](#) and [Auvray and Bey \(2005\)](#) estimated an increase of 2 to 4 parts per billion by volume (ppbv) in European O<sub>3</sub> concentrations during summer, which could be responsible for 20% of the violation of the European Union threshold for O<sub>3</sub>. These studies suggest that half of the import of North American O<sub>3</sub> in the BL is due to transport at low altitudes with the remainder due to subsidence of high altitude plumes.

[Derwent et al. \(2004\)](#) suggested a higher value of 8 ppbv increase in the European BL using an O<sub>3</sub> tracer technique in a semi-Lagrangian global model. During high pollution events, under conditions typified by a strong Icelandic Low located between Iceland and the British Isles, [Auvray and Bey \(2005\)](#) simulated an increase of European O<sub>3</sub> due to North American pollution of more than than 10 ppbv. Several explanations have been proposed for the difference between the non-negligible impact of North American pollution on European O<sub>3</sub> simulated by models and the lack of experimental evidence. [Stohl et al. \(2002\)](#) suggested that North American pollution reaches the European BL primarily south of the Pyrenees where measurement sites are sparse, and also that North American plumes are generally older than 10 days when reaching Europe, and therefore, hard to accurately trace back to sources.

In this study we address these issues through the analysis of data collected in a pollution plume transported at low level over the North Atlantic as part of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) ([Fehsenfeld et al., 2006](#)) also encompassing the European Intercontinental Transport of Ozone and Precursors (ITOP) experiment, which took place in summer 2004. As part of this campaign, the International Transport and Chemical Transformation (ITCT)-Lagrangian 2K4-experiment (an IGAC task) executed a Lagrangian study of polluted air masses transported across the North Atlantic. Four research aircraft based in North America, the Azores and western Europe sampled the same air masses several times during long-range transport. Lagrangian experiments have been conducted previously, but this was the first time that a Lagrangian experiment was conducted in the free troposphere on intercontinental scales. The main advantage of this kind of study is that changes in a plume concentrations over several days can be estimated by compar-

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ing two Lagrangian samplings, and the processes leading to these changes can be evaluated with reduced uncertainty. After the campaign a detailed analysis using trajectories, a Lagrangian dispersion model, and in-situ measurements was performed by Methven et al. (2006), and showed that there were five cases where the same air mass had been sampled several time across the Atlantic.

The overall goal of this paper is to improve our understanding about low level long-range transport of anthropogenic plumes over the North Atlantic and their impact on O<sub>3</sub> and precursors levels over Europe. In particular, we analyse the evolution of a North American plume observed during the Lagrangian 2K4 experiment which was originally very polluted, and then transported at low levels over the North Atlantic toward Europe. The aim is also to determine the relative importance of processes influencing its chemical composition, and to explain why polluted North American plumes are not easily detected at surface measurement sites over Europe.

The Lagrangian plume in question originated from the New York-Boston conurbation and was sampled 3 times just off the New England coast on 3 successive days by the National Oceanic and Atmospheric Administration (NOAA) P3, and then, 2 days later off the west coast of Ireland, and 3 days later over the English Channel by the German Deutsches Zentrum fur Luft- und Raumfahrt (DLR) Falcon. First, the Lagrangian matches identified by Methven et al. (2006) are discussed in Sect. 2 together with the observed chemical evolution of pollutants during the plume transport. Cases where the Lagrangian matching is less good due to the influence of other processes such as mixing with local emissions are also identified. Next, to evaluate the relative contributions of chemical, physical and dynamical processes to changes in O<sub>3</sub> concentrations in the plume during transport, a photochemical trajectory model was used (Sect. 3). In Sect. 4, results are presented from model runs initialised with upwind data over New England, and compared to downwind data over Europe. The model was run along a trajectory representative of the mean plume transport pathway and giving the best match between plume samplings. The model was first run with chemistry only (Sect. 4.1), and then including wet and dry deposition (Sect. 4.2) as well as mixing with air masses in

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close proximity to the plume (Sect. 4.3). The ability of the model to simulate the contribution of photochemical processes to  $O_3$  changes in the plume was further tested by examining the evolution of trace gas correlations using multiple model runs initialised across the first plume sampling (Sect. 4.4). Conclusions are presented in Sect. 5.

## 2 Lagrangian case: measurements and analysis

### 2.1 Identification of Lagrangian matches

Methven et al. (2006) used a novel technique to identify Lagrangian matches between flight segments from different aircraft during the entire IGAC Lagrangian 2K4 campaign in July 2004. This technique combined trajectories, calculated using global meteorological analysis (European Center for Medium Range Weather Forecast 40 year Re-analysis; ERA-40), and hydrocarbon fingerprint analysis. A match was defined as an occasion when a pair of whole air samples (analysed for their hydrocarbon content) collected during different flights exhibited highly correlated hydrocarbon fingerprints (when such measurements were available), and the sample time windows were also connected by both backward and forward trajectories. Results from the Lagrangian particle dispersion model, FLEXPART, run with CO tracers (Stohl et al., 2004) were also used to confirm matches. Five clear Lagrangian cases covering a variety of situations were identified. Further details can be found in Methven et al. (2006).

In this paper, we build on the work of Real et al. (2007) which focused on the Lagrangian analysis of the forest fire case, also discussed by Methven et al. (2006), with the examination of the case of low level pollutant plume transport. An anthropogenic plume from New York-Boston was sampled first by the NOAA P3 over the Gulf of Maine and Nova Scotia on 3 successive days (20, 21, 22 July), and then by the DLR Falcon flying just off the coast of Ireland on 25 July and over the English Channel on 26 July 2004. The flight tracks of these 5 flights are shown in Fig. 1. The segments of the 3 flights identified as Lagrangian matches were labelled as Lagrangian case 3 by

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Methven et al. (2006). The same Lagrangian time windows are used in this study. The ability of the Methven et al. (2006) analysis to identify Lagrangian matches has been shown to work well in the free troposphere where transport is mainly driven by advection (Real et al., 2007). However at low altitudes, certain meteorological features are not well resolved by analysed winds, and can induce errors in the Lagrangian analysis. For example, Riddle et al. (2006) analysed the ability of trajectory models to represent air mass transport during the ICARTT campaign by using Lagrangian balloons. These balloons were launched close to the Lagrangian match of the NOAA-P3 aircraft on 20 July. On 21 July, the balloon location and aircraft Lagrangian match were very well co-located (less than 2 km apart) suggesting that the matching between these 2 samples is good. However, this is not the case for 22 July. Important differences were found between balloon and model trajectories between 21 and 22 July over the Newfoundland coast, maybe due to poor simulation of strong coastal winds in the ECMWF analyses. Moreover, the hydrocarbon match on 22 July was the least consistent. Therefore, it appears that Lagrangian match on 22 July is less good. The accuracy of the Lagrangian samplings is discussed further in the next section where the observations in the plume segments are discussed.

The meteorological situation during plume transport has been examined using the Geodetic Earth Orbiting Satellite GOES-1 and METEOSAT satellite images superimposed with surface pressure values (see Fig. 3). On 19 July, a cold front passed over the north-east coast of the United States (US). Behind this front, strong outflow took place below 3 km transporting air from the New York-Boston region on 20 July towards Newfoundland on 22 July. From the 22 to 25 July, strong winds established over the Atlantic Ocean between the Azores/Bermuda High and the Icelandic Low, particularly on 22 July, which transported the polluted plume to Europe. On 25 July the Icelandic Low moved northward allowing the air masses to reach the Irish coast. This low level export from the North American east coast in conjunction with a cold front is a classical feature of North American summertime meteorology, and has been shown by, for example, Li et al. (2005) to be an important factor driving summertime pollution export. Warm con-

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veyor belts associated with cold fronts lift pollution from the central and north-eastern US into the upper troposphere over Newfoundland, and strong north-eastward outflow takes places at low level behind the cold front. [Li et al. \(2005\)](#) evaluated the occurrence of such events to be 5 to 7 per month in summer. The transport over the North Atlantic towards Europe is then dependent on the Azores High/Icelandic Low position and strength. [Guerova et al. \(2006\)](#) reported that of the export events identified by [Li et al. \(2005\)](#), 3 reached central Europe, with about half at low levels. [Li et al. \(2002\)](#) evaluated a higher frequency of low level North American plumes reaching Europe during summer 1994 to 1997. The plume studied here is a case of this kind of pollutant export.

## 2.2 Chemical composition of the Lagrangian matches

Detailed information about the instrumentation on board the aircraft can be found in [Fehsenfeld et al. \(2006\)](#). Since measurements taken by the different aircraft will be used to infer the chemical evolution of the plume, it is important to compare these measurements. Several comparison flights were performed between the 4 aircrafts involved in the campaign. Overall, the comparison indicated that O<sub>3</sub> measurements agree within 2 ppbv and CO within 3 ppbv, for the aircraft used in this study. Comparison of hydrocarbons was more difficult but where possible, comparison showed good agreement. More details about the comparison flights can be found in [Methven et al. \(2006\)](#) and [Fehsenfeld et al. \(2006\)](#). The general behaviour of the plume evolution is first examined in terms of observed trace gas mean values and correlations. Observed concentrations of O<sub>3</sub>, NO and NO<sub>y</sub> with respect to CO in the 5 Lagrangian matches are shown in Fig. 2 with averaged values during the 5 match time windows reported in Table 1. Correlation coefficients,  $r$ , and slopes were also calculated and provide information about the dispersion of data around the correlation line, and therefore, the quality of the correlation. These results are given in Table 4 and are also discussed later in Sect. 4.4 when they are compared to model simulations.

The first interception of the plume by the P3 on 20 July showed a highly polluted

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plume with high values of CO (200 ppbv) very well correlated ( $r=0.91$ ) with high values of O<sub>3</sub> (90 ppbv), NO<sub>x</sub> (500 pptv) and very high levels of NO<sub>y</sub> (15 550 pptv). Here, NO<sub>y</sub> was mainly in the form of HNO<sub>3</sub> representing approximately 92% of total NO<sub>y</sub>. One day later, CO, O<sub>3</sub> and NO<sub>x</sub> levels slightly decreased, but remained elevated. HNO<sub>3</sub> concentrations showed the strongest decrease to only 32% of the initial value. O<sub>3</sub> and CO were still highly correlated with a similar slope (0.51) whereas the slope between NO and CO decreased strongly even though the two species were still very well correlated ( $r=0.85$ ). On 22 July, CO, NO<sub>x</sub>, PAN, HNO<sub>3</sub> and O<sub>3</sub> levels decreased and the species are not correlated anymore with value of  $r$  between 0.14 and 0.3. Moreover, concentrations of the main volatile organic compounds (VOCs) (C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>5</sub>H<sub>8</sub>, CH<sub>3</sub>OH, acetone) increased and are higher than on the first Lagrangian sampling. This lack of correlation as well as the increase in VOCs could be explained by very strong and inhomogeneous mixing with another air mass, or as previously discussed this match appears to be incorrect due to large uncertainties in the calculation of trajectories on this day. Therefore, although comparisons between model results and data on 22 July are shown, the uncertainty surrounding this match should be kept in mind

The 3 North American interceptions (20, 21 and 22 July) were made close to remote surface sites in New England (Sable Island, Chebogue Point and Appledore Island). Polluted plumes from the New York-Boston region are often encountered in this region, as shown by [Chen et al. \(2007\)](#) who estimated that these events occurred 15% of the time during summer 2004. Comparison of measurements in the Lagrangian match and those analysed by [Parrish et al. \(1998\)](#) at Sable Island and Chebogue Point between 1991–1994, shows that the mean O<sub>3</sub> and CO values as well as the O<sub>3</sub>/CO measured slopes are in the upper range of the surface observations. The aircraft observations were collected above the surface and were probably subject to less dry deposition of O<sub>3</sub>. Another factor that can explain the larger O<sub>3</sub>/CO slope is that the NO<sub>x</sub> to CO emission ratio in the US has changed since the early 1990s. Assuming that the production of O<sub>3</sub> is NO<sub>x</sub> limited, then steeper O<sub>3</sub>/CO relationships could be expected in 2004 as suggested by [Honrath et al. \(2004\)](#).

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After the plume crossed the North Atlantic it was intercepted on 25 July by the DLR Falcon aircraft off the west coast of Ireland. Lower concentrations of pollutants were measured with mean concentrations of 138 ppbv CO, 44 ppbv O<sub>3</sub>, and 175 pptv NO<sub>y</sub>, which represents only 2% of the initial NO<sub>y</sub> value. Correlation between species are now very low including the O<sub>3</sub>/CO slope (−0.03). Mean values and slopes can be compared with those measured in summer at Mace Head (53° N, 10° W), on the Irish west coast between 1994 to 1997 by Li et al. (2002). Indeed, using global model runs with and without North American sources, Li et al. (2002) estimated CO and O<sub>3</sub> levels in North American plumes reaching Mace Head. Mean values measured in the Lagrangian plume are typical of those evaluated by Li et al. (2002), but the O<sub>3</sub>/CO slope is much less than the typical values of 0.2 to 0.4 reported by Li et al. (2002). Reasons for the discrepancies between these measured slopes are analysed further in Sect. 4.4. Although these O<sub>3</sub> value are much less than on the first sampling of the plume, they still represent an increase compared to background for the remote marine environment where the measurements were taken, i.e. 10 to 20 ppbv above average for O<sub>3</sub> and 10 to 40 ppbv for CO.

According to Methven et al. (2006), the plume was intercepted a last time by the Falcon over the English Channel on 26 July with CO and O<sub>3</sub> levels slightly lower than the previous day and a negative O<sub>3</sub>/CO slope. As for NO and NO<sub>y</sub>, measured levels strongly increased compared to the previous match and NO and NO<sub>y</sub> levels were even higher than in the first match. This suggests that strong mixing with freshly polluted European air masses had taken place.

The evolution of the plume observed here seems fairly typical in terms of the reductions in pollutant levels during transport across the Atlantic and the transport pathway by cold front advection over the US followed by rapid transport towards Europe. Further analysis using a photochemical trajectory model and comparison with the observations in the Lagrangian match segments will provide an insight into the processes which are responsible for the observed plume evolution.

### 3 Modelling

The Lagrangian photochemical model, CiTTYCAT (Cambridge Tropospheric Trajectory model of Chemistry And Transport) has been used to examine the different processes influencing the evolution of trace gases within the plume, and in particular, O<sub>3</sub>, CO and NO<sub>y</sub>. CiTTYCAT has been used previously to examine the origin of polluted layers over the North Atlantic during past campaigns (Wild et al., 1996; Evans et al., 2000). This model also successfully captured the trace gas evolution in the forest fire Lagrangian plume transported over the North Atlantic during ICARTT (Real et al., 2007) and identified by Methven et al. (2006). The model is considered as an isolated air parcel, and run along trajectories calculated using large-scale meteorological analyses. Ninety chemical species are treated in the model including degradation of 14 hydrocarbons using chemical rate data from JPL (2003), and updates discussed in Arnold et al. (2006). The photolysis scheme used in the runs presented here is based on a 2-stream multiple scattering scheme (Hough, 1988).

#### 3.1 Chemical initialisation

The model was first used to try to reproduce the average evolution of average concentrations in the plume (Sects. 4.1, 4.2.1, 4.3). The model was initialised with concentrations measured in the plume on 20 July by the P3, and compared with average concentrations measured by the same aircraft on 21 and 22 July as well as by the Falcon on 25 and 26 July. These measured concentrations are indicated Table 1. The only species for which the initial value has not be taken from measurements is methane, with a typical value of 1.8 ppmv. In order to characterise the variability in plume concentrations, 3 simulations were carried out: one with mean concentrations measured during the plume match segment, and 2 others using the mean concentrations + (–) standard deviation (std). Note that all species are well correlated in the plume making this approach appropriate. Then, in order to extend the analysis the model was initialised across the full range of concentrations in each match segment

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and their inter-relationships (correlations) analysed (Sect. 4.4).

### 3.2 Trajectories

The model was run along a trajectory calculated with the FLEXTRA model (Stohl et al., 1995) using ECMWF ERA-40 wind fields. Position, temperature and water vapour used in CiTTYCAT were interpolated from the FLEXTRA trajectory at every CiTTYCAT time-step. All trajectories initialised in the P3 Lagrangian match on 20 July showed approximately the same transport, so the one initialised around 21:20 was chosen (see Fig. 1). This trajectory passes closest to the P3 Lagrangian matches on 21 and 22 July, and the Falcon matches on 25 and 26 July.

### 3.3 Representation of physical phenomenon

Wet and dry deposition as well as mixing can be included in the model. Dry deposition is simulated when the air parcel is in the BL using a velocity parameter which depends on surface type and on the height of the BL. The BL was defined climatologically from GEOS-1 meteorological data (Schubert et al., 1993). The original wet deposition scheme is a simple scheme using a lifetime for soluble species. More details about the model can be found in Wild et al. (1996) and Evans et al. (2000). The model was first run with only photochemical processes (Sect. 4.1). In order to study the chemical evolution of the plume in absence of other processes. Then, since the plume was transported at low altitudes, and sometimes in the BL, runs were made including dry deposition (Sect. 4.2.1). GEOS METEOSAT satellite images (see Fig. 3) indicate the presence of clouds, on certain occasions in the same location as the plume, especially over the North American coast. Moreover, the strong decrease in  $\text{HNO}_3$  measured in the plume is likely to be the result of wet deposition since  $\text{HNO}_3$  is highly soluble. For this reason, runs were also carried out including wet deposition. In addition, a new scheme was implemented based on precipitation rates from ECMWF (Sect. 4.2.2). Note that aerosol levels in the plume were high initially but dropped between the 20

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and 22 July from a number concentration of about  $5.5 \times 10^3 \text{ cm}^{-3}$  to  $3.0 \times 10^3 \text{ cm}^{-3}$ , which may also indicate that deposition was active, even if other mechanisms (i.e. dilution, coagulation) can also explain this decrease. Heterogeneous reactions, were not included in the simulations discussed here. One of the main impacts of heterogeneous reactions is to through the conversion of  $\text{NO}_x$  into  $\text{HNO}_3$  via the heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  at night. This process may be important for  $\text{NO}_x$  budget but the rate for conversion ( $\gamma$ ) is highly variable and may depend, in particular on the sulfate aerosol loading (Brown et al., 2006). Brown et al. (2006) evaluated a not negligible value of  $\gamma$  in the Newfoundland region during ICARTT, but less important than westward. It will be seen in Sect. 4.3 that  $\text{NO}_x$  levels in the plume are underestimated in the simulation, suggesting that the inclusion of heterogeneous  $\text{N}_2\text{O}_5$  hydrolysis would not give better results in this case. Finally, mixing between the plume and surrounding air masses was also considered (Sect. 4.3).

## 4 Results

### 4.1 Chemistry-only simulations

Simulated concentrations of  $\text{CO}$ ,  $\text{O}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$  and PAN for the model runs initialised with mean, mean +std and mean –std concentrations measured in the P3 Lagrangian match on 20 July are shown in Fig. 4 together with simulated  $\text{O}_3$  production and destruction terms. Water vapour and temperature data interpolated along the trajectory from ECMWF analyses are also shown. These results include only changes due to chemical processes in the model.

#### 4.1.1 Simulated plume characteristics

The modelled chemical evolution of the plume shows two interesting features. Firstly, despite high levels of water vapour, high concentrations of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$  and  $\text{O}_3$  are

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maintained in the plume whereas PAN levels decrease rapidly due to high temperatures. Analysis of  $O_3$  production and destruction terms shows that  $O_3$  destruction due to water vapour is important, but is almost balanced by the  $O_3$  production. Sensitivity tests will help to understand the origin of this high  $O_3$  production (see Sect. 4.1.3). The second interesting feature is the high oxidising capacity of the plume. In these chemistry only simulations, OH levels remain high during the entire run with mean values of  $4 \times 10^6$  molec.  $cm^{-3}$  and peaks around  $15 \times 10^6$  molec.  $cm^{-3}$  around noon. This can be mainly explained by high water vapour, due to the low altitude of the plume, and high levels of  $O_3$ .

One of the main impacts of this high oxidising capacity is the strong photochemical destruction of CO, which decreases by about 50 ppbv in 6 days. CO is often considered as a pollution tracer, not really affected by chemical loss over a period of 10 days or less and a strong decrease in CO levels is usually attributed to dilution and mixing. In this case, assuming no other loss processes, CO levels decreased by 25% solely as a result of chemical destruction. This would imply that for this plume, transported at low altitudes, the CO chemical lifetime is about 20 days. This value can be compared with a value of 30 days for the global mean CO lifetime during summer.

#### 4.1.2 Comparison of measured and simulated concentrations

The general evolution of measured PAN and CO values can be reproduced by chemical processing suggesting an important role for photochemistry in this case although CO is still overestimated after 6 days and PAN data were only available from the P3. Measured NO and  $NO_2$  values are generally overestimated by the mean simulations, and are more represented by the mean –std simulation.  $O_3$  values are overestimated by more than 40 ppbv after 5 days but the strongest difference is found between simulated and measured  $HNO_3$  with average modelled concentrations 13 ppbv higher after 3 days. These differences suggest that other processes such as deposition and mixing were also important. Unfortunately, measurements of other species like  $H_2O_2$  or HCHO for the three P3 flights were not available to provide further tests of the model

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results discussed in the next sections. Concerning OH, simulated values are the same order of magnitude as those calculated by [Warneke et al. \(2004\)](#) using a box model initialised with measurements from a research ship along the New England coast, i.e. in the same region as the Lagrangian plume during the first 3 days, albeit at a lower altitude. However, the peak noon values simulated here are higher than those measured, for example, in the Los Angeles basin by [George et al. \(1999\)](#) ( $7 \times 10^6$  molec $\cdot$ cm $^{-3}$ ), and by [Ehhalt and Roher \(2000\)](#) at a rural German site ( $12 \times 10^6$  molec $\cdot$ cm $^{-3}$ ). Measured  $\text{JO}^1\text{D}$  and  $\text{JNO}_2$  during the 3 first Lagrangian samplings are in good agreement with simulated values (not shown) but the model underestimates several VOCs:  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  are underestimated by 70, 140, 20, 110 and 90 pptv respectively on the 25 July. Concerning water vapour and temperature, the difference between measured values and those interpolated from ECMWF analyses along the trajectory is always less than 20% for water vapour and 4K for temperature. Therefore, in these runs which only take chemical processes into account, the overestimation in  $\text{O}_3$  is leading to an overestimation in OH and therefore other processes are also playing an important role as will be discussed in the following sections.

#### 4.1.3 Sensitivity tests

In order to better understand photochemical processing in the plume and possible reasons for the differences between simulated and observed  $\text{O}_3$ , two sensitivity tests were performed. Firstly, initial  $\text{HNO}_3$  concentrations were reduced to zero (S-no $\text{HNO}_3$ ) in order to study the role of  $\text{HNO}_3$  in the net production of  $\text{O}_3$  during transport. Secondly, a cloud with an optical depth of 5 (value of the mean cloud optical depth observed around the world by [Rossow and Schiffer, 1991](#)) was simulated just above the plume (S-CLOUD) in order to examine the maximum effect of a cloud layer on photolysis rates inside the plume. The S-CLOUD simulation is representative of a maximum effect because clouds were not present during the entire transport over the North Atlantic as shown by the GOES-METEOSAT satellite images. In particular, clouds were not present during the match periods when, as noted previously, modelled photolysis

rates agree well with the measurements. The chosen optical depth is also relatively high for non-convective clouds. In both cases simulations were initialised with mean values measured in the plume. Results of these sensitivity tests are shown in Fig. 5.

Results of the run S-noHNO<sub>3</sub> clearly show that the maintenance of high O<sub>3</sub> levels in the chemistry-only simulation is mainly due to HNO<sub>3</sub> photolysis. Indeed after 6 days, O<sub>3</sub> concentrations in the S-noHNO<sub>3</sub> simulation are lower than the reference simulation by about 35 ppbv, and the mean net O<sub>3</sub> production has decreased by 70%. One of the consequences of this is a reduction in the oxidising capacity of the plume (OH is reduced by 30%) leading to slightly higher simulated CO concentrations. It shows that when initial HNO<sub>3</sub> concentrations are high, the quantity of HNO<sub>3</sub> available for photolysis becomes non-negligible, and, in the absence of loss processes, HNO<sub>3</sub>, which acts initially as a reservoir, then releases NO<sub>2</sub> during long-range transport. Neuman et al. (2006) also measured high HNO<sub>3</sub> in several other plumes during the ICARTT campaign, some of them as far as 1000 km downwind from source regions and showed the importance of HNO<sub>3</sub> in the production of O<sub>3</sub> in plumes rich in HNO<sub>3</sub>. However, this strong role played by HNO<sub>3</sub> assumes a weak influence of wet deposition.

Concerning the S-CLOUD simulation, the presence of cloud above the plume is responsible for a reduction in photolysis rates (−9% for NO<sub>2</sub> rate and −7% for O<sub>3</sub> rate) in these runs. Since there are compensating effects both O<sub>3</sub> production and destruction are reduced and so the presence of cloud does not modify O<sub>3</sub> levels by much and cannot explain the difference in between observed and simulated O<sub>3</sub> values. Because of the O<sub>3</sub> photolysis reduction, the oxidising capacity of the plume is slightly reduced (by a few percent) and therefore CO destruction.

## 4.2 Chemistry and deposition simulations

### 4.2.1 Dry deposition

Results of model runs including photochemistry plus dry deposition are shown in Fig. 6 (orange lines). Dry deposition is simulated in the model when the plume is in the BL,

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i.e. about 15% of the time. The BL definition in the model is climatologically defined, and so, not specifically calculated for the days of the study. The modelled BL heights for the Lagrangian matches were checked by plotting vertical profiles of water vapour observed by the P3 aircraft around the Lagrangian matches. In the BL, air masses are mixed and the water vapour profile should be relatively homogeneous whereas outside the BL it should exhibit strong vertical gradients. The profiles in Fig. 7 show that every time the aircraft was over ocean (profiles a) and part of profile b), the BL height was less than 0.4 km and so the plume was above it, whereas over land, it was between 1 and 1.5 km and the plume was in the BL. This corresponds well to the model simulation with no dry deposition simulated for the 2 first Lagrangian sampling (over sea) whereas dry deposition is active on 22 July (over land). Inclusion of dry deposition in the simulations leads to decreases of 8 and 20% in  $O_3$  and  $HNO_3$ , respectively. However, it is clear that dry deposition alone cannot explain the observed decrease in either  $HNO_3$  or  $O_3$  in this plume. For a plume travelling at lower altitude and spending more time in the BL, a much more important impact of dry deposition could be expected. The results are also sensitive to the definition of the BL height and to positional errors in the trajectories as already discussed for 22 July in Sect. 2.

#### 4.2.2 Wet deposition

As noted already, satellite images and the strong decrease of  $HNO_3$  levels in the plume suggest that wet deposition was active during the transport of this plume away from source regions. In the basic model, wet deposition is parameterised using a local constant loss rate,  $r$  ( $s^{-1}$ ) (run S-WET1). In this study, two new schemes have also been implemented linking wet deposition to more realistic precipitation using column integrated precipitation rates,  $p$  ( $mm\ s^{-1}$ ) calculated from ECMWF. The first scheme (S-WET2) is based on Walton et al. (1988) who introduced a wet deposition coefficient,  $S$ , such that  $r=S \times p$ . For a very soluble gas, such as  $HNO_3$ , Penner et al. (1991) suggested values of  $S$  equal to  $2.4\ mm^{-1}$  for stratiform precipitation, and  $4.7\ mm^{-1}$  for convective precipitation. The second scheme (S-WET3) uses a classical formula

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for the simulation of wet loss of a very soluble species,  $r=p/L$  where  $L$  represents the quantity of condensed water integrated over the tropospheric column (mm). Wentz and Spencer (1998) estimated a value of  $L$  from a satellite study using  $0.18 \times (1 + (Hp)^{0.5})$ , where  $H$  is the rain column depth, taken as equal to 3 km at mid latitudes. In this formulation there is no distinction between convective and stratiform precipitation. These two formulations apply to very soluble gases like  $\text{HNO}_3$ . To evaluate  $r$  for other gases, results from Crutzen and Lawrence (2000) have been used. They determined a factor  $\alpha_{\text{spec}}$  that varies from 0 for insoluble gases to 1 for very soluble gases, and depends on the Henry's Law coefficient (see Table 2) in such way that the new local loss frequency,  $r^* = r \times \alpha_{\text{spec}}$  is calculated. Note that none of these wet deposition schemes make a distinction between precipitation within and below clouds. This information was not available from ECMWF analyses for this study.

Results from the runs including dry and wet deposition, S-WET1 (pink lines), S-WET2 (blue lines) and S-WET3 (green lines) are shown in Fig. 6 together with precipitation rates simulated by ECMWF along the trajectory. It can be noted that the Lagrangian matches correspond with very low precipitation which is coherent with the fact that modelled photolysis rates agree well with measured values in runs with no clouds.

In order to compare the rate of decrease of  $\text{HNO}_3$ , a parameter  $\tau_{1/2}$  can be defined as  $\tau_{1/2} = \log(2) \times \frac{1}{r_{\text{mean}}}$  where  $r_{\text{mean}}$  is the mean local loss frequency calculated along the trajectory. This parameter is the half-life of a trace gas corresponding to an exponential decrease in its concentration. It is equal to 19, 15 and 6 h, respectively, for simulations dry+S-WET1, dry+S-WET2 and dry+S-WET3. The run dry+S-WET3 underestimates  $\text{HNO}_3$  concentrations by about 2.5 ppbv compared to the measurements on 21 July. Results from the dry+S-WET1 and dry+S-WET2 simulations compare better with the data even if  $\text{HNO}_3$  is underestimated in the dry+S-WET2 run by about 1.5 ppbv on 21 July, and overestimated in the dry+S-WET1 run by the same order of magnitude.

Overall, results using ECMWF precipitation rates (S-WET2 and S-WET3) do not give better results than S-WET1 even if these schemes are more realistic. Here, and

in the following sections, results using wet deposition scheme, S-WET2, have been used because it gives better agreement with  $\text{HNO}_3$  measurements than S-WET3, and is more physically realistic than S-WET1. Since  $\text{NO}_y$  is mainly made up of  $\text{HNO}_3$ , the half-life of  $\text{HNO}_3$  with the S-WET2 scheme can be compared with the one estimated by [Stohl et al. \(2002\)](#) for  $\text{NO}_y$  during the 1997 NARE campaign also off the north-east coast of North America. In that study  $\tau_{1/2}$  was estimated to be around 40 h, a factor of 2 slower than in the case studied here. This can be partly explained by the fact that air masses selected by [Stohl et al. \(2002\)](#) were rapidly exported out of the BL by frontal warm conveyor belts, and so only subject to wet deposition. The plume studied here stayed in the BL during the first few days, and was therefore influenced by both wet and dry deposition.

Overall results from the chemistry and dry/wet deposition are closer to the measurements than the chemistry only run. The impact of wet deposition is also important for other species apart from  $\text{HNO}_3$ . Modelled  $\text{NO}_x$  is now almost equal to zero after 6 days due to the loss of  $\text{HNO}_3$ . This has an impact on  $\text{O}_3$  production rates which decrease by 60 % due to the wet removal of  $\text{HNO}_3$ . This leads to better agreement with the observations, although  $\text{O}_3$  is still overestimated slightly and  $\text{NO}$  slightly underestimated.  $\text{OH}$  is reduced by 27% when wet deposition is included leading to a slight increase in  $\text{CO}$  lifetime from 20 to 23 days.  $\text{CO}$  is still overestimated compared to the data suggesting that dilution and mixing were also important.

## 4.3 Role of mixing

### 4.3.1 Mixing parametrisation

In the previous simulations the plume was considered isolated from the background. In the real atmosphere, a plume is subject to stirring by large-scale winds followed by mixing by processes such as turbulence. This mixing process entrains surrounding air masses leading to changes in plume concentrations. In the model, the mixing scheme is a simple linear relaxation scheme ([Evans et al., 2000](#)) resulting in an exponential

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decay of plume concentrations toward background concentrations with a typical time scale,  $\tau$ -mix. Because of the Lagrangian aspect of this work, measurements made in the vicinity of the plume during the 5 match segments can be used to estimate background concentrations. This method has already been applied successfully to the Lagrangian forest fire plume case sampled during ICARTT (Real et al., 2007). The values used here are summarised in Table 3. During the first 3 days, the so-called background concentrations were typical of polluted air masses. Indeed, pollutant concentrations measured by the P3 on 20, 21 and 22 July between the ground and 2 km were always elevated over the Gulf of Maine and Nova Scotia. Between 22 and 25 July, the plume left the North American east coast, and travelled over the ocean. It can be considered that after leaving the coast, the plume was no longer surrounded by polluted air masses but by marine air masses. For this reason, air masses typical of marine air, measured in proximity to the plume on 25 July, were used to characterise background air masses during this transport. Finally, high levels of NO (up to 1.5 ppbv) and NO<sub>y</sub> (up to 6 ppbv) were measured on 26 July just after the sampling of the plume and so, higher levels of trace gases were used to define background values. These NO<sub>y</sub> rich air masses were relatively poor in CO and O<sub>3</sub> but rich in NO suggesting that they could be due to local ship emissions in the English Channel (Corbett and Koehler, 2003). However, back trajectories also show transport from southern England suggesting a possible urban source.

With regard to determination of  $\tau$ -mix, changes in CO concentration are often used since CO evolution is usually associated with strong dilution of polluted plumes (e.g. see Real et al., 2007). However, in this case, the decrease in CO is strongly influenced by photochemical processes, and so, is not a very good indicator of mixing. Arnold et al. (2006) evaluated a  $\tau$  of 10 days with a method based on hydrocarbon ratio changes, for plumes crossing the North Atlantic during the ICARTT campaign. The same  $\tau$  was used here except for the last day when a faster mixing rate was used ( $\tau=2$  days) as soon as the plume entered the European BL, to represent the strong increase in NO and NO<sub>y</sub> observed on the 26 July. It should be noted that the CO values mea-

sured on the 26 July in the vicinity of the plume are very close to the value in the plume itself. On this day, the plume was not easily distinguishable from the background based on CO or O<sub>3</sub> measurements alone. The mixing time-scale of 10 days, used during the first 5 days, implies slightly weaker mixing rates compared to previous studies (Real et al., 2007; Price et al., 2004). This could be related to the plume remaining relatively intact during transport due to strongly converging low level winds, and the fact that the plume was decoupled from the marine BL during transport making mixing and dilution less important in this case. However, the impact of the chosen value for the mixing rate is strongly dependent on the background mixing values used. For example, applying a stronger mixing rate during the first 3 days would not change results by much as the chosen background values are similar to those in the plume. The chosen mixing rates are therefore linked to a particular definition of the geographical limits of the plume, and should not therefore be taken as representative values for the lower atmosphere.

#### 4.3.2 Results: chemistry, deposition and mixing

Model results including chemistry, deposition and mixing processes are shown in Fig. 8. During the first 5 days, mixing does not change concentrations very much, mainly because of the low mixing rates used, and the fact that background concentrations used during the first 3 days are not much different from those in the plume. Overall, there is now good general agreement between the model simulations and the measurements for the entire period except for 22 July, which supports the hypothesis that this day is not a truly Lagrangian match. The agreement on the 21 is generally good although NO which is still slightly underestimated. There is good agreement with CO and O<sub>3</sub> data on 25 July, with further decreases of 13 and 6 ppbv, respectively, but NO is still underestimated. However, as the measured NO value is so low that it is close to the detection limit of the instrument it is hard to come to any conclusion on the overestimation or not by the model. Modelled concentrations are also closer to the data on the 26 July, especially for NO which was mixed with higher background values. These discrepancies are analysed further in the following section using O<sub>3</sub>/CO and NO<sub>y</sub>/CO

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correlations.

Concerning the modelled OH values, the runs including deposition and mixing lead to a reduction in OH of 25% with a mean values of  $3 \times 10^6$  molec.  $\text{cm}^{-3}$  over the period from the 21 to 25 July, with peak noon values around  $14 \times 10^6$  molec.  $\text{cm}^{-3}$ . These values are still slightly higher than measurements from [George et al. \(1999\)](#) in recent polluted plumes but in better agreements with the ones of [Ehhalt and Roher \(2000\)](#). Moreover, since the *J*-values and O<sub>3</sub> data agree well we can have some confidence in OH results.

It is also interesting to re-examine the comparison with measured VOCs. Whereas all VOCs measured on 25 July were underestimated in the run with chemistry only, the model results including deposition and mixing for the long lived VOCs are now in better agreement with the data mainly because of the decrease in modelled OH. For example, on 25 July, the comparisons are 1076 pptv, 159 pptv and 22 pptv for modelled C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>4</sub>H<sub>10</sub> against measured values of 1075 pptv, 169 pptv and 25 pptv, respectively. On the other hand, modelled values of C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> with shorter lifetimes of 2 and 0.8 days are almost zero when measurements show values around 100 pptv for this two species. It is possible that the plume was influenced by local oceanic or biogenic emissions of these species off the coast of Ireland. Such air masses with elevated emission of alkenes and low CO and O<sub>3</sub> values were measured in proximity to the Lagrangian plume by the Falcon.

Further light is shed on this in the next section comparing modelled and measured trace gas correlations (see Sect. 4.4).

#### 4.3.3 Influence of the different processes on pollutant levels in the plume

By analysing simulated O<sub>3</sub> production and destruction terms, the influence of chemical, deposition and mixing processes on O<sub>3</sub> can be evaluated. In the runs including all processes, and giving the best agreement with the data, a decrease of 42 ppbv in O<sub>3</sub> concentrations over 6 days is calculated. Of this decrease 75% is due to chemical destruction, including the effects of dry and wet deposition on O<sub>3</sub> production, which

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gives a mean net O<sub>3</sub> production of −5 ppbv/day. The remaining 25% is due to direct O<sub>3</sub> dry deposition (10%) and mixing (15%). Without both wet and dry deposition the net O<sub>3</sub> production is only −1.1 ppbv/day. This is mainly due to HNO<sub>3</sub> photolysis providing a source of NO<sub>x</sub> as discussed previously. Thus, these model results show that indirectly deposition processes were responsible for 80% of the impact of photochemistry on O<sub>3</sub>, with the large majority (78%) being due to wet deposition rather than dry deposition. Modelled CO decreases by 60 ppbv which is in good agreement with the observed evolution in the plume. Analysis of model results shows that 66% is due to chemical destruction and 34% due to mixing and dilution of the plume. Therefore, in this case, photochemical processes governed the evolution of both O<sub>3</sub> and CO in the plume. Whilst this has been shown previously to be the case for O<sub>3</sub>, this is the first time, to our knowledge, that photochemistry has been shown to be the dominant process governing CO evolution over a period of several days. If the plume had not been subject to deposition processes, it would have reached Europe with much higher levels of O<sub>3</sub> (80–90 ppbv), and lower levels of CO (120–140 ppbv). It can be envisaged, that plumes originating from North America with slightly lower CO values, would reach Europe with even lower CO values due to strong OH oxidation, and thus may not be detected using the methods often applied to diagnose pollutant plumes such as application of CO thresholds. This point is discussed further in the next section.

#### 4.4 Correlation study

Comparison of the full range of observed and simulated concentrations in the Lagrangian match samplings, and their interrelationships can provide useful additional information about the evolution of pollutant concentrations in a plume, than just comparison of means ±std. Observed correlations in the Lagrangian matches have already been discussed in Sect. 2. In this section, multiple runs are used in order to characterise the variability across the Lagrangian samplings in an attempt to reproduce the observed changes in the correlation between species. This method has already been used successfully to analyse the forest fire case sampled during ICARTT (Real et al.,

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2007).

The multiple model runs were initialised with P3 measurements averaged every 30s during 20 July Lagrangian match samplings. With this method, each run represents a different part of the initial correlation (black crosses in Fig. 9) observed by the P3.

5 Model results after 1 (green triangles), 2 (blue diamonds), 4 (pink squares) and 5 (violet stars) days are shown in Fig. 9 for 3 cases: chemistry-only simulations (case A), simulations with chemistry and wet plus dry deposition (case B), and simulations with chemistry, deposition and mixing (case C).  $O_3/CO$  and  $NO_y/CO$  correlations are shown for each case, and  $NO/CO$  correlations are shown for case C. The simulated slopes for the different cases are reported in Table 4.

10 It has already been seen in Sect. 4.1 that the chemistry-only runs were unable to reproduce the chemical evolution of the plume but, nevertheless, it is still interesting to examine the evolution of the slopes in the case without deposition or mixing. The  $O_3/CO$  and  $NO_y/CO$  simulated in case A are very different from those observed. The slopes increase with time whereas the data show an overall decrease. The modelled increase is not due to an increase in  $NO_y$  or  $O_3$  that remains nearly constant, but is due to the strong chemical destruction of CO in these runs. Therefore, in the run with chemistry only, an increase in the  $O_3/CO$  slope is the result of a decrease in CO, and not the result of photochemical  $O_3$  production as it is often stated (Andreae et al., 1994; Mauzerall et al., 1998). Along the same lines, Chin et al. (1994) showed that a decrease in  $O_3/CO$  slope could be due to the secondary production of CO by hydrocarbon oxidation in a fresh plume, and not only due to chemical destruction or deposition of  $O_3$ . When deposition processes are included (case B),  $NO_y/CO$  slopes show very good agreement with those observed on 21 and 25 July but not on 26 July. Modelled  $O_3/CO$  slopes now decrease but less than observed on the 25 July. Because mixing is simulated as a homogeneous process, modelled slopes change little between cases B and C due to small changes in  $O_3$  production. However, the correlation lines are shifted towards “background” concentrations, and the dispersion is reduced (see also discussion in Real et al., 2007). This leads to better overall agreement with the

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data in this correlation space although there are still some differences. The bad match between measurements and simulations on the 22 July has already been identified using mean concentrations analysis (Sect. 4.1) and is not discussed further.

Interestingly, this approach shows differences for the 25 July in measured and modelled  $O_3/CO$  slopes ( $-0.03$  and  $0.36$ , respectively) that were not apparent in the simulations using mean concentrations which agree well with the mean data. Further analysis based on the correlations suggests that the measurements in this Lagrangian match can be divided into 2 different parts, from 15:54 to 16:06 and 16:06 to 16:21, and 2 different air masses may have in fact been sampled. This distinction is shown in Fig. 10 based on the observed  $O_3/CO$  correlation. For the first segment, CO and  $O_3$  are not really correlated, with a slope of  $0.02$  whereas for the second segment, the slope is positive with a value of  $0.28$ , and a correlation coefficient of  $0.75$ . This slope is comparable to measured values at ground-based sites such as Mace Head (Li et al., 2002). It is also closer to the simulated slope ( $0.36$ ) whereas the weak slope in the first segment is not reproduced by the model runs initialised with measurements on 20 July. Therefore, it seems that the second segment represents the best match with the plume from 20 July whereas the first segment appears to have been influenced by inhomogeneous mixing in the edges of the plume, possibly with marine air masses, not reproduced by the model.

The last important difference is observed between modelled and measured NO/CO and  $NO_y/CO$  slopes between the 25 and 26 July. The data slopes are particularly strong on the 26 July, especially compared to the 25 July. In this case the Lagrangian plume appears to have been strongly dispersed when it reached Europe on the 26 July and “background” concentrations also included fresh emissions with very high levels of NO and  $NO_y$ , as noted previously. The model does not capture this variability since the plume is not mixed with the full range of concentrations in this local plume but only with its mean concentrations. Therefore, this last sampling cannot be really considered as Lagrangian because of the strong influence of fresh emissions.

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## 5 Conclusions

The case of an anthropogenic plume transported from North America (New York-Boston region) over the North Atlantic to Europe at low altitudes has been studied in a Lagrangian framework. This plume was initially strongly polluted with high concentrations of  $O_3$ , CO and  $NO_x$ , typical of North American polluted plumes, and also very high levels of  $HNO_3$ . During transport, all pollutant concentrations decreased, and the plume was much less polluted when it was intercepted off the west coast of Ireland several days later. A Lagrangian photochemical model (CiTTyCAT), has been used to assess the different processes influencing the evolution of pollutant levels in the plume during this long-range transport. Average concentrations and correlations between trace species ( $O_3/CO$  and  $NO_y/CO$ ) were examined, and compared to data collected in the Lagrangian match segments. Overall, the analysis shows that some of the links identified as Lagrangian by Methven et al. (2006) are not truly Lagrangian, in particular for 22 July because of probable errors in ECMWF coastal winds and 26 July due to the influence of local emissions. In addition the correlation analysis showed that part of the match on 25 July also appears not to be well linked to 20 July.

The evolution of the chemical composition in the plume (mean values and correlations lines) is best reproduced when photochemistry, dry/wet deposition and mixing with surrounding air masses are all included. Model results show that these changes were mainly driven by photochemical and deposition processes, especially wet deposition. Mixing with air masses in close proximity to the plume during transport did not have a strong impact on trace gas concentrations during the first 5 days due to strong and rapid transport by low level winds and isolation of the plume from the marine boundary layer over the Atlantic. Mixing with local pollution sources (from ships or London conurbation) appears to have been important on the 26 July.

Mean net  $O_3$  production in the plume was negative over the 6 day period at about  $-5$  ppbv/day leading to mean  $O_3$  plume level of 44 ppbv when it reached Europe. This value is low compared to European pollution over land but is significantly enhanced

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compare to the remote oceanic region where the plume was sampled. Plume O<sub>3</sub> was directly impacted by dry deposition, and indirectly by wet deposition through the strong scavenging of HNO<sub>3</sub>. For the plume studied here, this implies that wet deposition was responsible for an 80% reduction in net O<sub>3</sub> production. This study and the one from Neuman et al. (2006) show that because polluted plumes from the New-York/Boston region were very rich in HNO<sub>3</sub>, wet deposition can have a strong impact on O<sub>3</sub> levels. Runs with no wet deposition, showed that HNO<sub>3</sub> photolysis can maintain high O<sub>3</sub> levels during plume transport leading to much lower mean net loss (−1 ppbv/day). In that case, the plume would have reached Europe with much higher O<sub>3</sub> levels (between 80 and 90 ppbv) resulting in a strong import of O<sub>3</sub> directly in the European BL.

Another important result is the important influence of photochemistry on CO levels in the plume rather than mixing which is usually assumed to be the most important process over this time scale. In this case, photochemical destruction explains 66% of the CO decrease compared to only 34% for mixing. This is due to relatively high O<sub>3</sub> levels coupled with high water vapour levels leading to a high oxidising capacity in the plume, and therefore a reduction of CO chemical lifetime to 23 days. This has several consequences. Firstly, this means that CO cannot be always used as a tracer of North American pollution when the plume transport is at low altitudes. This may also explain the low levels of CO often observed in the European BL in plumes originating from North America. The latter does not imply that the plume was weakly polluted but that photochemistry was intense. Secondly, we have shown that an observed increase in the O<sub>3</sub>/CO correlation slope can result from CO chemical oxidation (destruction), and not photochemical production of O<sub>3</sub> as is often assumed.

Overall, these results show that O<sub>3</sub> import into downwind regions can be very sensitive to scavenging processes along route as well as photochemical processing and that CO levels can also be strongly influenced by photochemical loss. Whilst there are uncertainties related to the Lagrangian analysis including errors in trajectories, studies using this modelling framework are able to provide detailed analysis of the processes governing pollutant levels during long-range transport. They can also be used to eval-

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uated plume transport and processing in global models that typically have problems resolving such features.

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**Table 1.** Measurements taken during Lagrangian match windows as defined in Table 1 of Methven et al. (2006). Data for each window is shown as “mean (standard deviation) [number of measurement averaged]”.  $\text{NO}_y$  values indicated for the first 3 Lagrangian matches are simply the sum of measured  $\text{HNO}_3$ , PAN,  $\text{NO}_2$  and NO. All measurements indicated in the first column (20 July) are used to initialise the model, except for temperature, water vapour (ECMWF data are used) and aerosols (no aerosols in the model).

	P3-20/07 (25 mn)	P3-21/07 (6 mn)	P3-22/07 (23 mn)	Falcon-25/07 (27 mn)	Falcon-26/07 (9 mn)
CO (ppbv)	200 (30) [1427]	183 (12) [361]	181 (8) [755]	138 (12) [1621]	121 (1.8) [541]
$\text{O}_3$ (ppbv)	90 (15) [1501]	88 (6) [361]	57 (6) [781]	44 (2.9) [1621]	43 (1.5) [541]
NO (pptv)	63 (25) [1351]	46 (7) [361]	32 (10) [751]	10 (0.002) [1313]	47 (43) [389]
$\text{NO}_2$ (pptv)	441 (185) [1351]	210 (51) [361]	115 (35) [751]		
PAN (pptv)	649 (331) [650]	481 (134) [181]	268 (70) [215]		
$\text{HNO}_3$ (pptv)	14400 (9500) [1236]	4584 (1032) [361]	2229 (631) [646]		
$\text{NO}_y$ (pptv)	15553 (10360)	5307 (1383)	2644 (742)	175 (38)	940 (417)
$\text{C}_2\text{H}_4$ (pptv)	21 (9) [5]	30 [1]	83 [2]	100 [2]	113 [2]
$\text{C}_2\text{H}_6$ (pptv)	1291 (303) [5]	1170 [1]	1205 [2]	1075 [2]	988 [2]
$\text{C}_2\text{H}_2$ (pptv)	311 (153) [5]	310 [1]	266 [2]	169 [2]	174 [2]
$\text{C}_3\text{H}_6$ (pptv)	3 (1) [3]	5 [1]	26 [2]	93 [2]	81 [2]
$\text{C}_4\text{H}_{10}$ (pptv)	141 (75) [5]	103 [1]	209 [2]	25 [2]	62 [2]
$\text{C}_5\text{H}_8$ (pptv)	0.2 (0.055) [5]	0.4 [1]	318 [2]		
$\text{C}_5\text{H}_{12}$ (pptv)	77 (35) [5]	76 [1]	94 [2]		
$\text{C}_6\text{H}_6$ (pptv)	61 (41) [5]	58 [1]	46 [2]		
$\text{C}_7\text{H}_8$ (pptv)	61 (41) [5]	24 [1]	20 [2]		
Methanol (pptv)	2197 (303) [68]	2140 (218) [14]	3360 (513) [39]		
Acetaldehyde (pptv)	758 (162) [68]	632 (82) [14]	608 (70) [39]		
Acetone (pptv)	2946 (647) [68]	2641 (187) [14]	3099 (193) [39]		
Aerosols ( $\text{cm}^{-3}$ )	5474 (1646) [1501]	3627 (640) [361]	2989 (340) [751]		
Temp (K)	293 (0.2) [1501]	291 (0.3) [361]	295 (0.8) [781]	283 (0.9) [1320]	282 (0.4) [541]
$\text{H}_2\text{O}$ (g/kg)	11.8 (0.5) [1501]	10.8 (0.5) [361]	12.8 (0.5) [781]	9.2 (0.5) [1621]	7.8 (0.3) [541]

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**Table 2.**  $\alpha_{\text{spec}}$  values as a function of effective Henry's Law coefficient.

Hf	$\text{Hf} < 10^3$	$10^3 < \text{Hf} < 10^4$	$10^4 < \text{Hf} < 10^5$	$10^5 < \text{Hf} < 10^6$	$10^6 < \text{Hf} < 10^8$	$\text{Hf} > 10^8$
$\alpha_{\text{spec}}$	0	0.15	0.5	0.85	0.95	1

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**Table 3.** Measured concentrations in the vicinity of the Lagrangian plume used as background concentrations for the mixing simulations.

Time windows	CO (ppbv)	O <sub>3</sub> (ppbv)	NO <sub>y</sub> (pptv)	NO (pptv)
21:00, 20 July–12:00, 21 July	182	73	6109	120
21:00, 21 July–12:00, 22 July	184	78	4085	55
12:00, 22 July–12:00, 23 July	170	65	3502	42
12:00, 23 July–22:00, 25 July	90	30	150	10
22:00, 25 July–26, July	130	47	5910	1160

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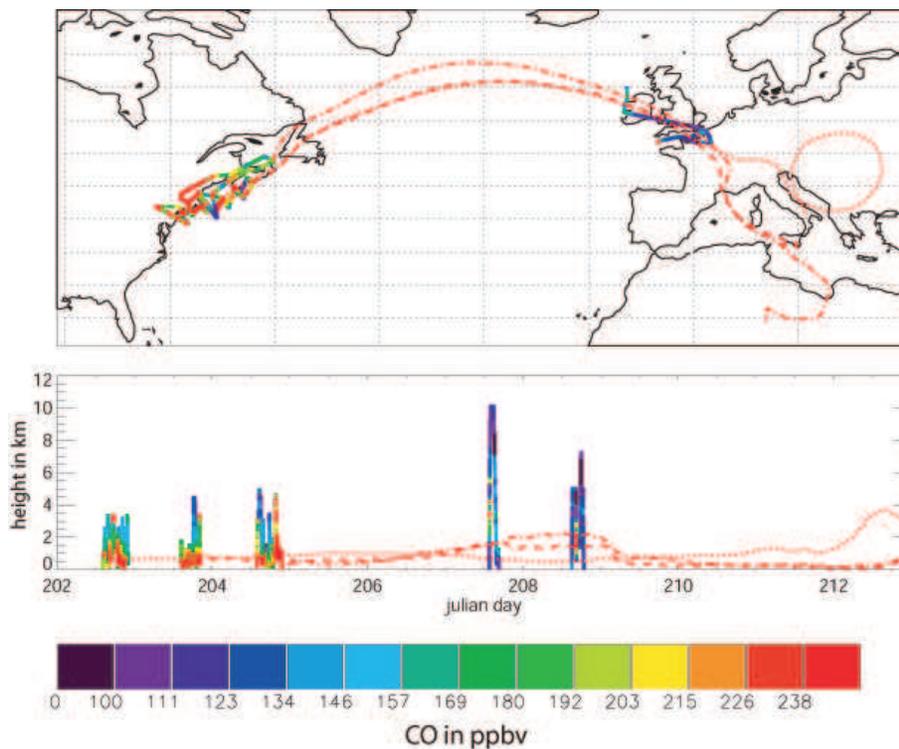
**Table 4.** Measured and simulated O<sub>3</sub>/CO correlation slopes with and without mixing and deposition. Measured correlation coefficients *r* are also reported in brackets.

	Measured slopes	Simulated without mixing or deposition (Case a)	Simulated with deposition (Case b)	Simulated with deposition and mixing (Case c)
P3–20 : O <sub>3</sub> /CO	0.47 (0.91)			
: NO <sub>y</sub> /CO	0.31 (0.85)			
: NO/CO	0.74 (0.89)			
P3–21 : O <sub>3</sub> /CO	0.51 (0.93)	0.52	0.46	0.46
: NO <sub>y</sub> /CO	0.09 (0.85)	0.27	0.09	0.09
: NO/CO	0.08 (0.14)	0.4	0.17	0.17
P3–22 : O <sub>3</sub> /CO	0.17 (0.21)	0.59	0.45	0.45
: NO <sub>y</sub> /CO	0.02 (0.3)	0.29	0.05	0.05
: NO/CO	0.16 (0.14)	0.41	0.09	0.09
Falcon 25 : O <sub>3</sub> /CO	−0.03 (−0.12)	0.69	0.36	0.37
: NO <sub>y</sub> /CO	0.001 (0.32)	0.3	0.0015	0.0015
: NO/CO	0.09 (0.043)	0.41	0.013	0.013
Falcon 26 : O <sub>3</sub> /CO	−0.31 (−0.35)	0.66	0.33	0.33
: NO <sub>y</sub> /CO	0.14 (0.7)	0.27	0.0011	0.0011
: NO/CO	15.5 (0.76)	0.23	0.009	0.009

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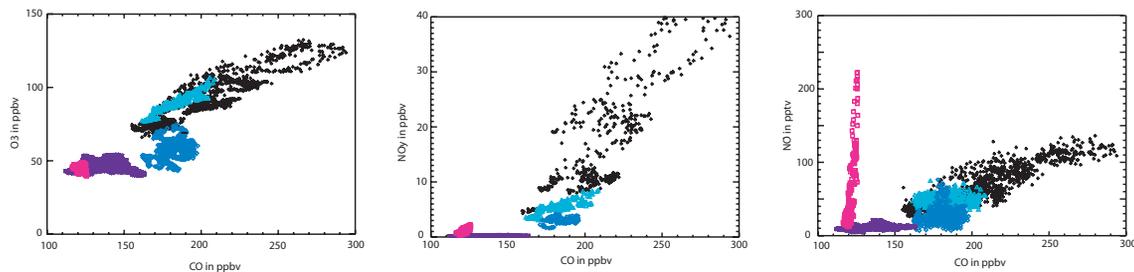


**Fig. 1.** Flight tracks of the P3 flights on the 20, 21, 22 July 2004 and Falcon flight on the 25 and 26 July 2004, coloured with measured CO. Three forward trajectories initialised in the 3 Lagrangian samplings of the P3 are also represented (respectively dotted, dashed and dashed-dotted lines on 20, 21 and 22 July 2004).

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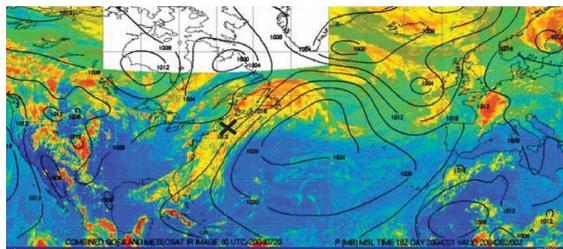
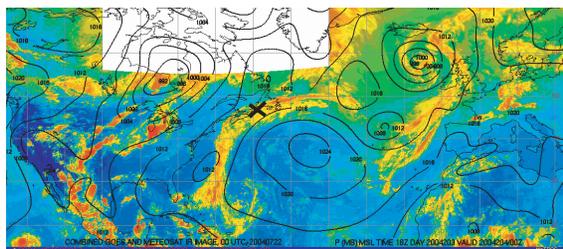
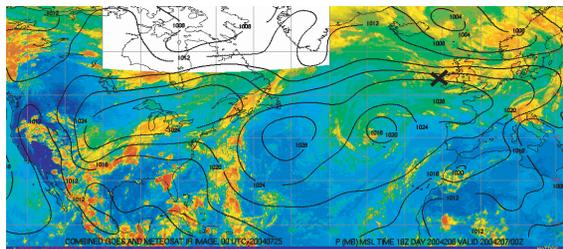
**Fig. 2.** Measured  $O_3$  and reactive nitrogen concentrations ( $NO, NO_y$ ) versus measured  $CO$  in the 5 Lagrangian match samplings. Black crosses represent measurements taken on 20 July and light blue triangles, dark blue diamonds, violet stars and pink squares the measurements taken on 21, 22, 25 and 26 July 2004, respectively.

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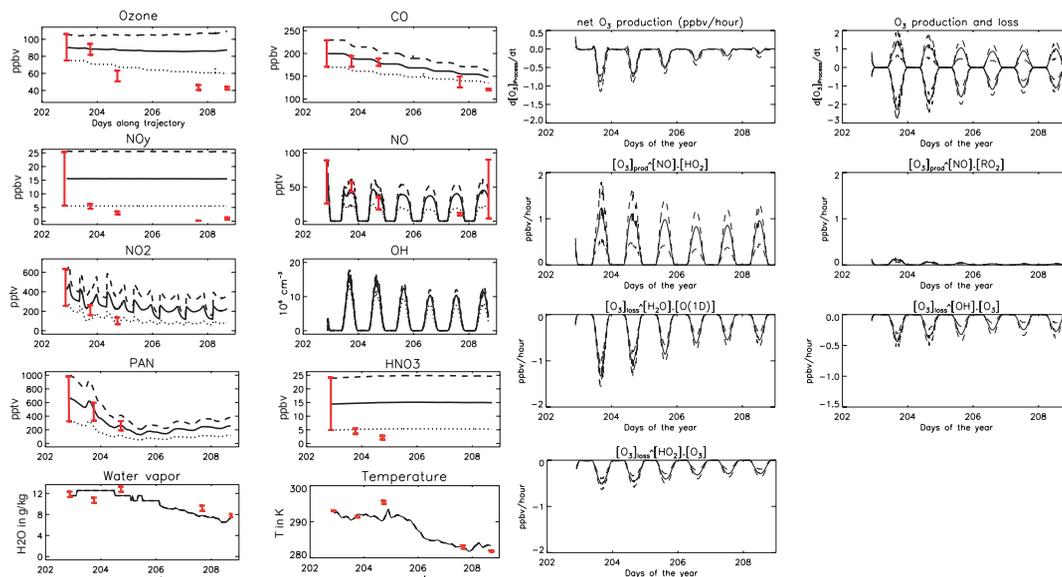
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20 July22 July25 July

**Fig. 3.** Infrared images combined from GEOS and METEOSAT for 20, 22 and 25 July 2004 taken from the NOAA products in support of ICARTT (Courtesy of O. Cooper, NOAA ESRL). Ground pressure values (black lines isobars) are also indicated. Black crosses represent the location of the Lagrangian matches on each day.

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(a) Concentrations, water vapour and temperature

(b) Hourly O<sub>3</sub> production and destruction terms

**Fig. 4.** Temporal evolution of (a) simulated concentrations, and (b) simulated O<sub>3</sub> production and destruction rates, initialised with mean (continuous lines), mean –std (dotted line) and mean +std (dashed lines) concentrations taken from the P3 measurements on 20 July. Downwind mean and std measurements taken in the plume are represented as red vertical lines (see text for details).

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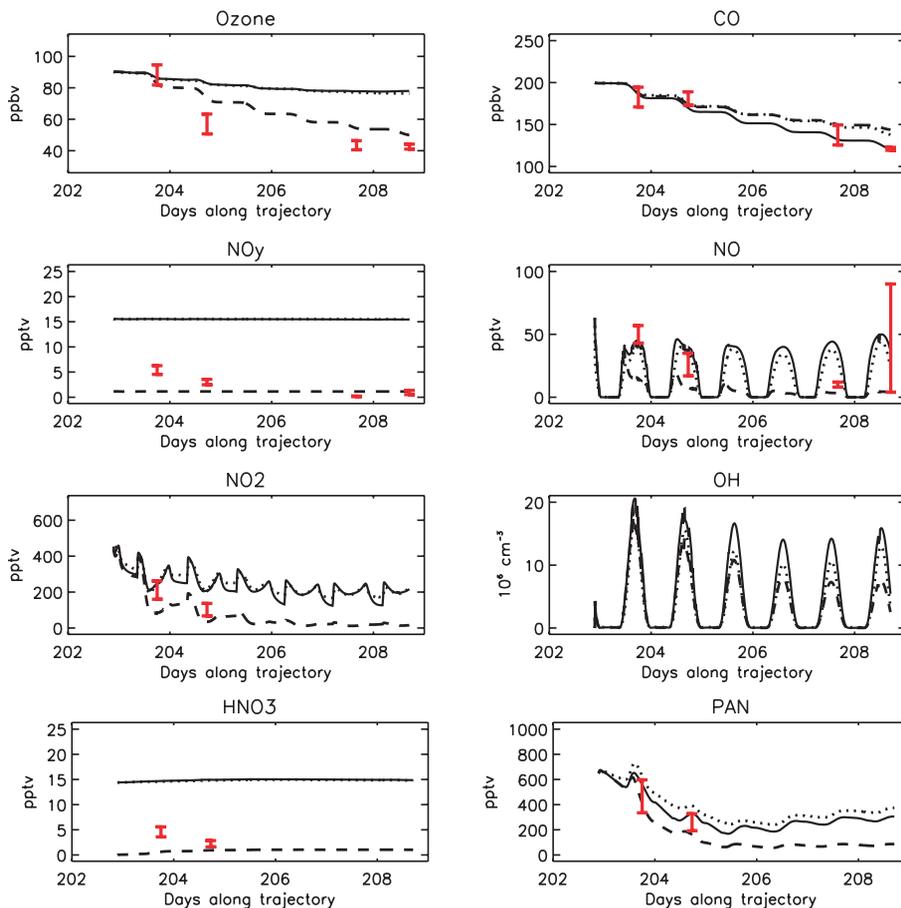
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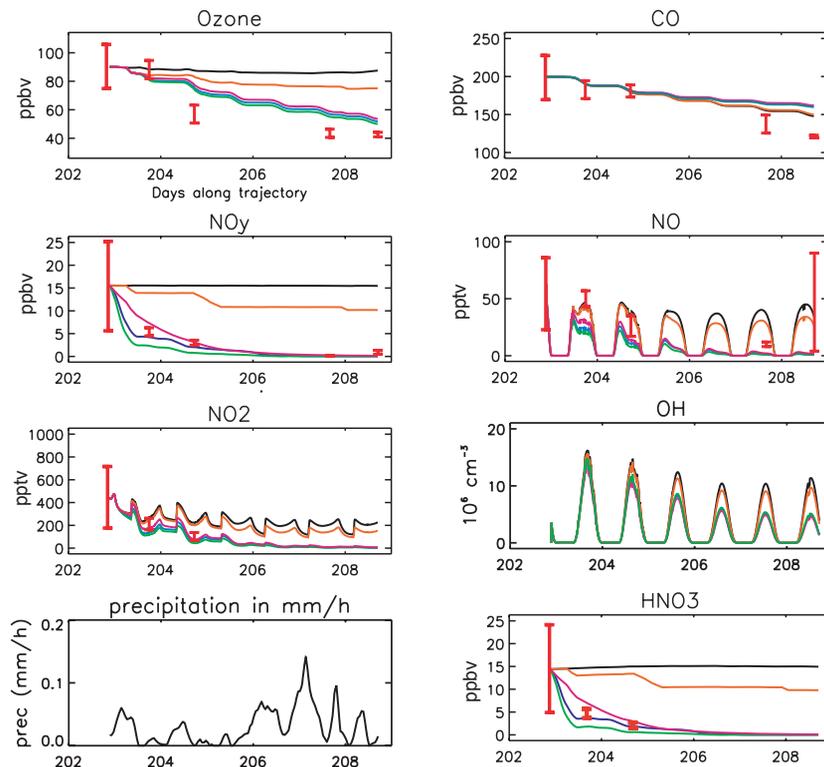
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**Fig. 5.** Reference simulation (continuous lines), S-noHNO<sub>3</sub> simulation (dashed lines) and S-CLOUD simulation (dotted lines) (see text for details).

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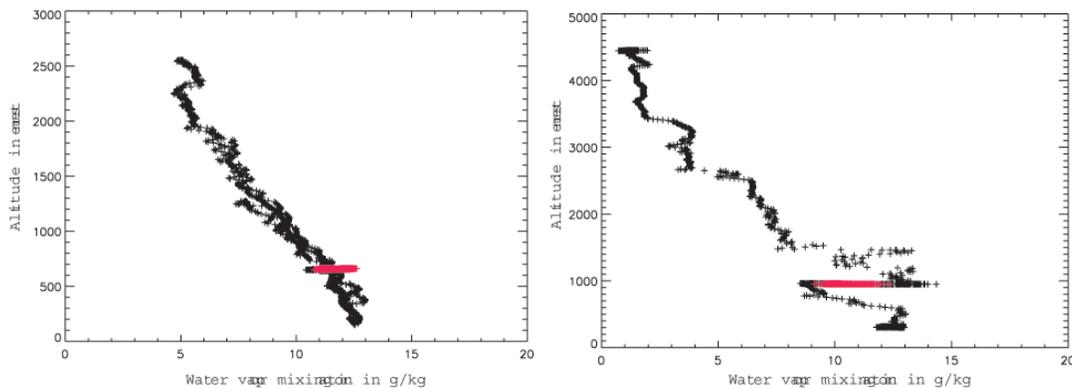


**Fig. 6.** Simulation without deposition (black lines), with dry deposition only (orange lines), with S-WET1 wet deposition+dry deposition (pink lines), with S-WET2 wet deposition+dry deposition (blue lines), and with S-WET3 wet deposition+dry deposition (green lines). Precipitation interpolated from ECMWF precipitation rates (sum over total column) are also shown.

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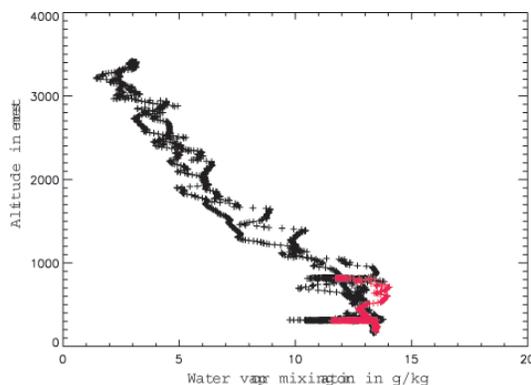
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(a) 20 July from 20:30 to 21:30

(b) 21 July from 07:30 to 18:30



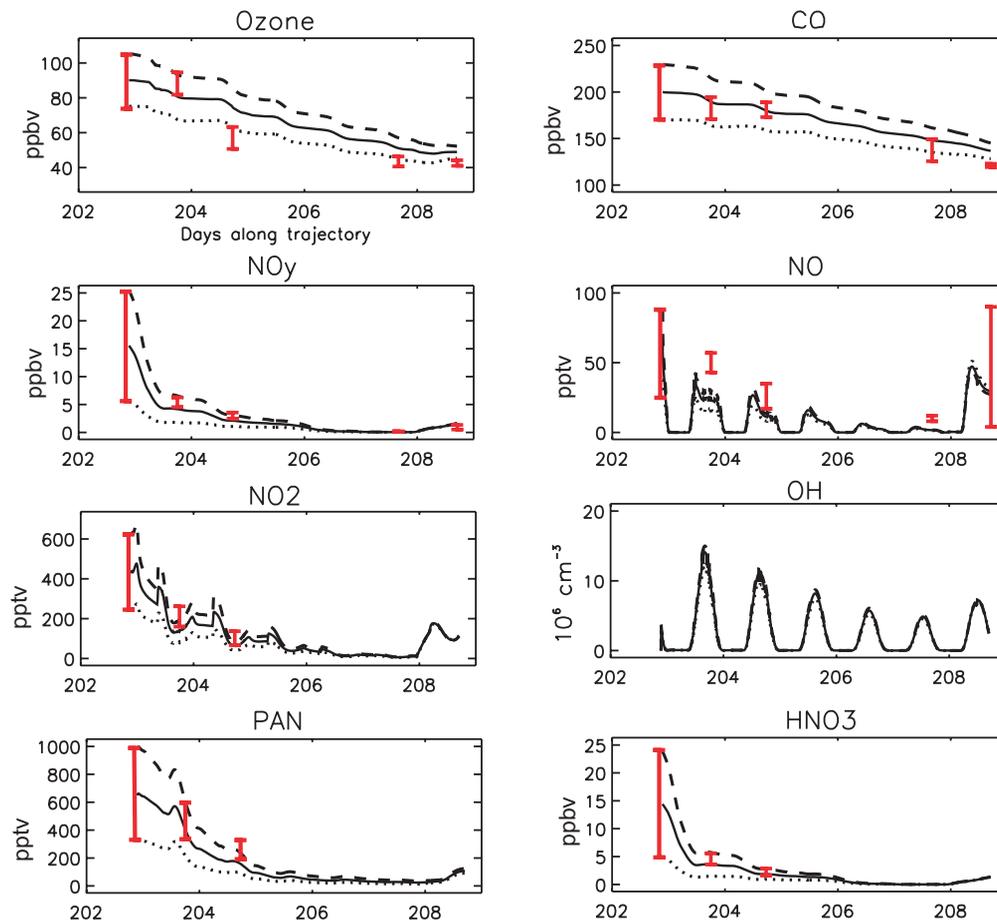
(c) 22 July from 17:00 to 18:00

**Fig. 7.** Vertical water vapour profiles measured by the P3 close to the Lagrangian matches on 20, 21 and 22 July. Measurements made in the Lagrangian matches are coloured in red.

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**Fig. 8.** Modelled concentrations for runs including chemical, deposition and mixing processes using mean  $\pm$  std concentrations (same as Fig. 4).

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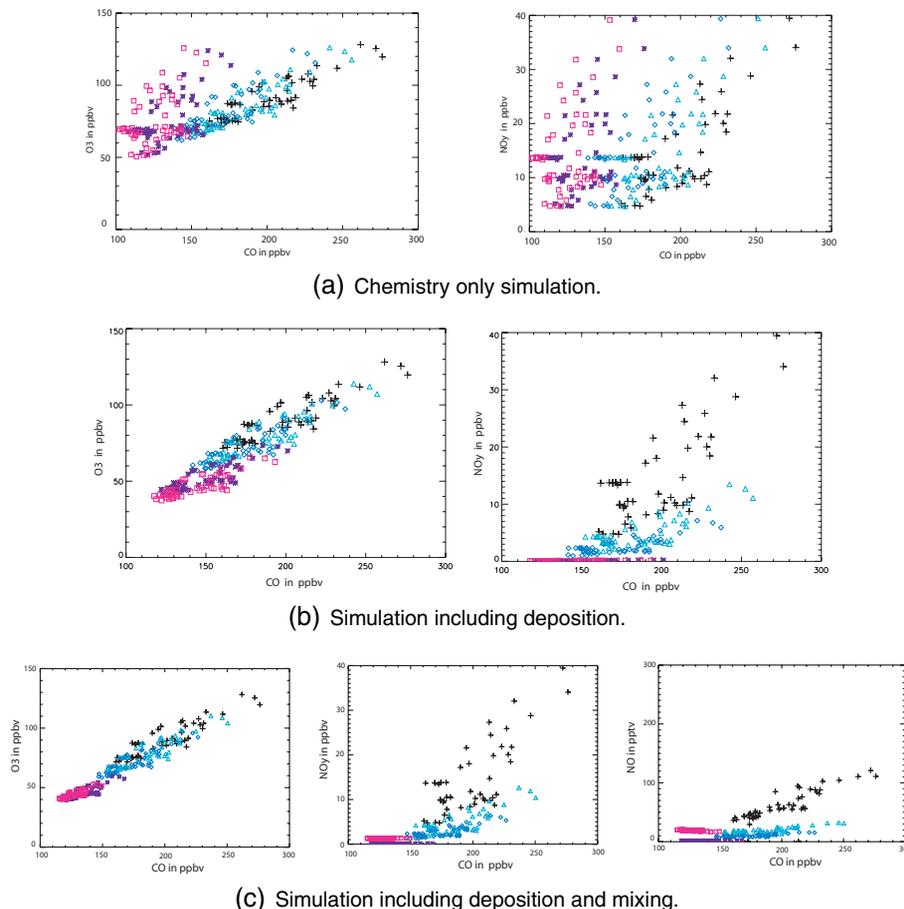
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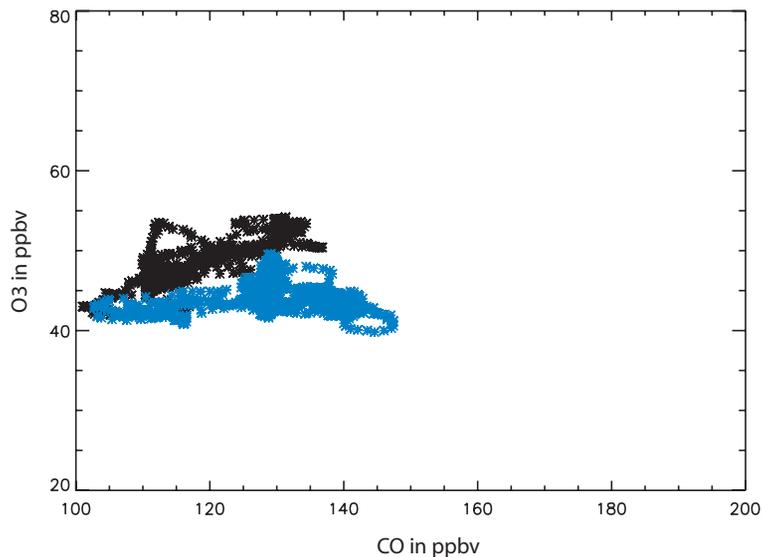
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**Fig. 9.** Simulated concentrations of  $O_3$ ,  $NO_y$  and  $NO$  versus simulated  $CO$  concentrations in the 5 Lagrangian samplings. Black crosses represent measurement in the 20 July Lagrangian match and green triangles, blue diamonds, pink squares and violet stars show the simulated concentrations on 21, 22, 25 and 26 Lagrangian samplings, respectively.

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**Fig. 10.** Measured O<sub>3</sub> concentrations versus CO concentrations in the 25 July Lagrangian match from 15:54 to 16:09 (blue crosses, part 1) and from 16:09 to 16:21 (black crosses, part 2).

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