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## What caused extreme ozone concentrations over Cotonou in December 2005?

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Extreme ozone over Cotonou in December 2005

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### Abstract

This paper reports the first record of extreme ozone measurement in Africa. As part of the AMMA program, the ozone vertical profile recorded on 20 December over Cotonou presents exceptionally high ozone concentrations with up to 295 ppbv at 1 km altitude.

- Retroplumes from the Flexpart model show that the air masses sampled at 1 km over Cotonou on this day come from the burning area situated north-east of Cotonou and pass over Lagos, Nigeria, which is highly impacted by urban pollution. We used the Master Mechanism box model to simulate the chemical composition of the plume during its transit.
- <sup>10</sup> We find that neither the biomass burning emissions of ozone precursors nor additional urban emissions from Lagos are high enough to simulate more than 120– 150 ppbv of ozone. The only way to reach almost 300 ppb of ozone within a few hours is to feed the air mass with large amounts of reactive VOCs as those recorded in the vicinity of petrochemical area. Sensitivity tests show that 250–600 ppbv of VOCs com-
- <sup>15</sup> bined with 35–80 ppb of NO<sub>x</sub> allow the ozone concentrations to be higher than 250 ppb. Nigeria is the first African country with gas extraction and petrochemical industries, and petrochemical explosions frequently happen in the vicinity of Lagos. The hypothesis of a petrochemical explosion in this area is the most likely scenario which explains the 295 ppbv ozone maximum measured over Cotonou, downwind of Lagos.

#### 20 **1** Introduction

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Tropospheric ozone is an important trace gas regarding its role in the oxidative capacity of the global atmosphere, its climate effect and its impact on air quality. Two main reasons make the tropical regions of interest regarding tropospheric ozone. Firstly, photochemistry and OH formation are more active in the tropics due to high UV radiation and humidity. Secondly, the tropics are important source regions of ozone precursors,

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especially through biomass burning (Andreae and Merlet, 2001; van der Werf et al.,

2006), biogenic (Guenther et al., 1995, 2006; Serça et al., 1998; Jaeglé et al., 2004, 2005; Aghedo et al., 2007) and lightning emissions (Moxim and Levy, 2000; Sauvage et al., 2007; Höller et al., 2009). In addition, some of the biggest cities in the world are situated in tropical regions (e.g. Lagos, Mexico city, Bangkok, Bombay, etc.). These
<sup>5</sup> cities are subject to increasing anthropogenic emissions and suffer air quality problems. Air quality in the megacities is quite recent issue in our scientific field. Lawrence et al. (2007) emphasized the role of megacities in controlling the pollution at regional scales. Butler et al. (2008) questioned the representation of the megacities emissions

in global models and pointed out large differences between available inventories.
 Several African campaigns from TROPOZ in 1987 to TRACE-A and SAFARI in 1992 and SAFARI in 2000 have highlighted the importance of the tropical region, and particularly Africa, as a source region of ozone precursors (e.g., Cros et al., 1992, 2000; Delmas et al., 1999; Jonquière et al., 1998; Jacob et al., 1996; Thompson et al., 1996; Swap et al., 2003). However, these programs did not specifically address air quality
 issues in African cities. Few studies were dedicated to this issue in Sub-Saharan cities. For example, Baumbach et al. (1995); Fanou et al. (2006); Linden et al. (2008) show

- exposure situations that exceed World Heath Organization (WHO) standards in Lagos (Nigeria), Cotonou (Benin) and Ouagadougou (Burkina Faso), respectively. More recently, the African Monsoon Multidisciplinary Analysis (AMMA) program is aimed at
- <sup>20</sup> documenting the chemical composition of the West African atmosphere and its variations linked to dynamics and climate. Indeed, Hopkins et al. (2009) presented a first analysis of in situ data recorded over the city of Lagos during an aircraft flight dedicated to anthropogenic pollution. In the frame of AMMA, an ozone sounding station was set up in Cotonou, Benin (6.21° N, 2.23° E) thanks to the IRD (Institut de Recherche et
- Développement) and the SMN/ASECNA (Service Météorologique National/Agence de securité et de navigation aérienne) people located there. These regular soundings were performed between December 2004 and January 2007 and aimed to better assess the seasonal and interannual variability of ozone vertical profiles in Equatorial Africa as described by (Thouret et al., 2009). They found that December 2005 was

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characterized by very high ozone concentrations throughout the troposphere compared to the rest of the sampled period (December 2004–January 2007). Also, the vertical profile obtained on 20 December 2005 that they presented shows exceptionally high ozone concentrations in the lower troposphere. Ozone concentrations almost reached

- <sup>5</sup> 300 ppb at around 1000 m altitude on this day. As far as we know, such extreme concentrations have never been recorded in the lower troposphere over Africa before. The highest ozone concentration ever reported in the literature has been measured in the metropolitan area of Mexico city with more than 300 ppb (West et al., 2004). Similar concentrations have also been recorded in pollution plumes originating from Beijing
- (286 ppbv, Wang et al., 2006), from Houston (238–251 ppbv, Berkowitz et al., 2004, Kleinman et al., 2002), from Mexico city (243–250 ppbv, deFoy et al., 2005; Tie et al., 2007; Molina et al., 2007) and from the Po valley in Italy (200 ppbv, Spirig et al., 2002). The lack of measurements dedicated to air quality or pollution episodes did not allow the exploration of such phenomenon in Africa. We report here the first extreme values
   of ozone concentrations ever measured in this Sub-Saharan region.
  - The objectives of this paper are to present the extreme ozone concentrations recorded on 20 December 2005 in the lower troposphere and to propose an hypothetic scenario, which explains how near 300 ppbv concentrations of ozone can be produced in the vicinity of Cotonou. The radiosounding data and the synoptic situation in Decem-
- <sup>20</sup> ber 2005 are presented in Sect. 2. The ozone anomaly is further detailed in Sect. 3. Section 4 presents the Master Mechanism (hereafter MM) box model we used for this analysis along with the possible scenario. The different hypothesis are discussed in Sect. 5 where we finally propose the most likely scenario.





#### 2 Data presentation and meteorological situation

### 2.1 Data acquisition

Three soundings have been launched in December 2005 (16th, 20th and 22nd around 10:00 UTC). The ozone measurements were made with balloon-borne ECC (Electrochemical Concentration Cell) ozonesondes coupled with a standard radiosonde including a sensor for relative humidity and temperature. We used the Vaisala manufactured RS80 radiosondes during the entire AMMA period. The air for the ozone measurements was sampled with a Science Pump 6A type. Further details on the entire data set along with quality and accuracy of ozone data can be found in Thouret et al. (2009).

#### 10 2.2 Synoptic situation

Cotonou, located on the coast of the Gulf of Guinea is the economic capital of Benin with a population of 1.2 mill. inhabitants (data from 2008). The city is situated 110 km east of Lagos (6.3° N, 3.2° E), which is the economic capital of Nigeria. The location of these two cities is shown on Fig. 6. Lagos is the most populated city in West Africa and one of the biggest cities in the world, with more than 13 million people over only 3577 km<sup>2</sup>. The biggest power plant of the northern hemisphere part of Africa is situated in Lagos. Also, Lagos hosts around 75% of the commercial and industrial activities of the country (Hopkins et al., communication AMMA), including petrochemical activities. At this time of the year (dry season), ozone vertical profiles over Cotonou and Lagos are characterized by enhanced ozone concentrations (up to 70 or 80 ppb on monthly average) in the Harmattan layer (between 1 and 3 km altitude) due to biomass burning occuring all over the Soudano Guinean band between 8 and 12° N (Sauvage et al., 2005; Thouret et al., 2009).

Ozone concentrations were measured at the ground based station of Djougou, about 400 km north of Cotonou as part of the AMMA program. Djougou is in the middle of the burning area and under the influence of Harmattan. This site is representative of the



Soudano Guinean region and the measurements made there give typical values of the chemical composition of the air masses impacted by biomass burning during the dry season. Figure 2 gives the time series of ozone concentrations recorded at Djougou in December 2005. Ozone concentrations greater than 100 ppb were measured several days in a row (14, 15, 16, 18, 19 and 26) with peaks at 123 and 120 ppb on the 15 and 16, respectively.

#### 3 Case study of 20 December

Figure 1 presents the three vertical profiles recorded in December 2005 over Cotonou. Only the tropospheric part (up to 17 km) is shown. Based on satellite and ozone soundings data, Thouret et al. (2009) has shown that December 2005 is characterized by relatively high ozone concentrations throughout the whole troposphere compared to the entire period of December 2004–January 2007. In the middle troposphere, the three profiles show similar ozone concentrations with values around 90 ppb between 6 and 10 km. The two profiles on the 20 and 22 December 2005 are very similar above 2 km
and both of them show concentrations close to 70 ppb at the surface. This value is the overall maximum of surface concentrations within the radiosounding data set. The most impressive feature of this figure is the ozone enhanced layer peaking at around

1 km altitude on the profiles of 20 December. This layer is about 1.5 km thick and ozone

concentrations are up to almost 300 ppb.

(i.e. 361 flights).

<sup>20</sup> Such high ozone concentrations have never been sampled before in this region. The MOZAIC program (Marenco et al., 1998, Sauvage et al., 2005) provide quite a large sampling of the ozone distribution over Lagos, Nigeria between 1997 and 2004. Figure 3 gives the scatter plot of all the MOZAIC measurements over Lagos during this period. The ozone concentrations in the MOZAIC data set maximizes at 120 ppb of ozone between 800 and 900 hPa. Concentrations as high as those recorded on 20 December over Cotonou have never been recorded during the seven years of operations

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To better assess how large the discrepancies are on 20 December 2005 compared to other sampled December months, we calculate the tropospheric column of ozone (TCO) as well as the contributions of the 0–2 km and 2–17 km layers. Table 1 gives these ozone amounts in Dobson unit for the three individual ozone profiles of December

- <sup>5</sup> 2005, the mean of December 2005 and the average of December 2004, December 2005 and December 2006. The TCO on 20 December 2005 is almost twice as large as a standard day (16 December 2005 for example). The 0–2 km layer accounts for almost 35% of the TCO on this day and is three to four times larger than usually observed at this altitude showing how exceptional the event is.
- Figures 4 and 5 give the wind direction and speed, respectively at 900 hPa between 5 and 10° N at the longitude of Cotonou for the month of December 2005. Data are computed from ECMWF analysis. Cotonou is 6.2° N latitude. The wind patterns are different between the 16 and the 20–22 December 2005. Around the 16, the Harmattan flow (wind direction between 30 and 80°) is well established . On the contrary, on
- <sup>15</sup> the 20 and 22 the monsoon flow (wind direction between 120 and 240°) still prevails, especially on the 20. Also, the 20 December 2005 as well as the 18 and 19 December are characterized by a particularly very slow southeastern wind, less than 1 or  $2 \text{ m s}^{-1}$ . This suggests that there can be an accumulation of pollutants in the stagnant air masses in the region of Cotonou and Lagos and indicates that an additional urban
- <sup>20</sup> source of ozone and ozone precursors from Lagos might interfere and favour ozone photochemical production during the travel between Lagos and Cotonou.

#### 4 Hypothetical scenario

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According to back trajectories analysis based on the FLEXPART lagrangian model (Stohl et al., 2005), the air masses in which very high ozone concentrations were measured on 20 December 2005 originate mainly from the northeast (Fig. 6). These air masses were over the burning area three days before as noted by Sauvage et al. (2005). The FLEXPART results show that the air masses have been rather stagnant

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between Lagos and Cotonou for more than one day (Fig. 6). The wind speed in the vicinity of Cotonou and Lagos was less than  $2 \,\mathrm{m \, s^{-1}}$ , meaning that air masses needed around 15 h to travel from Lagos to Cotonou and could be influenced by local pollution from Lagos.

- <sup>5</sup> We propose here a scenario that could explain this extreme and rare pollution event. As seen from the literature and from Figs. 3 and 4, ozone concentrations in biomass burning plumes seem to maximize around 120 ppb but not more in West Africa. To produce the additional 180 ppb to reach the 300 ppb, the air mass needs to be fed with fresh NO<sub>x</sub> and reactive precursors such as volatil organic compounds (VOCs). Table 3
- gives a non exhaustive overview of the possible ozone concentrations along with the ozone production rate and the associated gaseous pollutants measured in different urban areas known for episodes of high pollution. For example, ozone concentrations as high as 251 ppbv have been measured over Houston associated with high concentrations of ethene, propene and butene.
- The Master Mechanism zero-dimensional model (Madronich and Calvert, 1990) has been used to investigate the photochemical production of ozone in the region, one, two or three days before 20 December 2005. The Master Mechanism model consists of a detailed gas phase chemistry, with nearly 5000 reactions between nearly 2000 species. This model computes the time-dependent chemical evolution of an air par-
- <sup>20</sup> cel initialized with known composition, assuming no additional emissions, no dilution and no heterogeneous processes. This model cannot substitute a full 3-D Chemistry-Transport Model (CTM), but has the advantage of describing explicitly all intermediate chemical transformations (Madronich, 2006), which is necessary to describe such an extreme event. The calculated concentrations are not meant to be the exact values
- <sup>25</sup> recorded but rather to give an order of magnitude of the ozone amount that can be produced from various chemical mixtures. The meteorological forcing is taken from the sounding data in the altitude of the ozone enhanced layer. For example, temperature is set at 295 K, and is constant throughout the simulation. The ozone concentration in the air mass has been initialized at 50 ppb, which is the climatological background

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value at this time of the year in this region. For the simulations, we have used the time frame resulting from the back trajectories shown in Fig. 6. The air mass travels from the biomass burning area to the vicinity of Lagos during 24 to 48 h and afterwards takes about 15-18 h to reach Cotonou, where high ozone concentrations were measured.

- The first run is called "Biomass Burning" and gives the chemical composition of the 5 air mass after passing over a fire of biomass in West African savanna. Even though we set up the run to last for 42 h (beginning 12:00, end 06:00 LT, 2 days after) to be consistent with the back trajectories analysis (Fig. 6), Fig. 7a shows a 100 h lasting run in order to exhibit the leveling off at 120 ppbv of ozone. This run is initialized according to concentrations that are characteristic of a savanna fire as described by 10
- Poppe et al. (1998). Table 2 gives the amount of the total VOCs (which contain ethene, propene, ethane, benzene, propane, acetylene, butane, toluene), NO<sub>x</sub> (=NO+NO<sub>2</sub>), and carbonyl compounds (which contain formaldehyde, acetic acid, acetone and acetaldehyde) used for this Biomass Burning run. Figure 7 (top) presents the results
- from this first run and shows that NO<sub>x</sub> decreases from 40 ppb to a few ppt after 40 h 15 of simulation. CO concentrations remains constant at 1000 ppbv during the first day, then CO decreases by 20 ppbv per day. The ozone concentrations reach 90 ppb after the first 24 h and 120 ppb after two days which is what we expect to be typical of the biomass burning plumes in agreement with results from Djougou or from MOZAIC-Lagos (Figs. 2 and 3, respectively).

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The second run is called "Additional Lagos", and simulates the passing of the air mass already charged in biomass burning compounds over Lagos. It begins at 06:00 UTC local time and lasts for 3 days (72 h). CO and ozone concentrations at the beginning of this second simulation are those calculated in the "Biomass Burning"

run after 42 h. Other compounds are re-initialized. Additional fuel from Lagos urban 25 emissions provides fresh VOCs and NO<sub>x</sub>. We used the concentrations measured over Lagos on board the BAe-147 during the AMMA campaign (Hopkins et al., 2009). These concentrations are given in Table 2. Our case study is in December 2005 but we assume there is no significant seasonal variation for the anthropogenic emissions. This

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run shows that ozone concentrations reach 150 ppb after a few hours (Fig. 7b) and stay around this value for the rest of the simulation. These results show that anthropogenic emissions from urban pollution in Lagos is not sufficient to produce enough ozone downwind and explain the near 300 ppbv of ozone as measured in Cotonou.

- <sup>5</sup> Several studies have been conducted in the region of Houston, where petrochemical industries emit a large amount of VOCs and  $NO_x$  in the atmosphere (Kleinman et al., 2005; Berkowitz et al., 2004; Guangfeng and Fast, 2004), as well as in Asian petro-chemical complexes (Zhang et al., 2004; Hung-Lung et al., 2007). High ozone concentrations have been measured downwind petrochemical industrial facilities, where
- <sup>10</sup> highly elevated concentrations of NO<sub>x</sub> (much more elevated than in urban zones) and reactive VOCs are simultaneously present (Ryerson et al., 2003). Usual ozone concentrations in Houston reported in Ryerson et al. (2003) remain half the ones measured in Cotonou the 20 December 2005 though. To simulate similar values as observed on December 20th over Cotonou, we suggest that an exceptional release of VOCs and NO<sub>x</sub>
- took place near Lagos. A pipeline explosion due to a leak of hydrocarbons would emit large quantities of reactive hydrocarbons and NO<sub>x</sub>. Such a pipeline explosion actually occured on the morning of the 20 December 2005 in the vicinity of Port Harcourt in the Niger Delta river. The fire was not completely extinguished until 4 days later. The loss of gas has been estimated to be 7% of the daily production (Agence France Presse, 2006). Thus, it may be not surprising to have such accidents in the city of Lagos.

Therefore, we conduct a third run called "Additional petrochemical Accident" which simulates the passing of the air mass already charged in biomass burning over a hypothetical release of VOCs and  $NO_x$  from a petrochemical source. As with the second run, it begins at 06:00 local time and lasts for 3 days (72 h). This time we feed the biomass burning plume with 200 ppb of extra reactive VOCs and 55 ppb of NO<sub>x</sub> to rep-

<sup>25</sup> biomass burning plume with 200 ppb of extra reactive VOCs and 55 ppb of NO<sub>x</sub> to represent emissions of petrochemical compounds. Those values are based on different records from literature, which are detailed in Table 3 and are in the upper range of these values. As far as we know, very few measurements of ozone (and precursors) concentrations have been made during incidents or explosions in petrochemical indus-

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tries. As an example, reports on high VOCs emissions are available in Canada (in the region of Montreal), mentioning a probable industrial incident on 20 October 2003, with total VOCs concentration close to 1000 µg m<sup>-3</sup> (http://www.ec.gc.ca/cleanairairpur/caol/trackingbenzene/p4\_f.cfm#journees, in french), and among them, benzene s concentrations of 34 ppb (120  $\mu$ g m<sup>-3</sup>). Figure 7c shows the result of this last run. Ozone concentration increases by 170 ppb in  $\sim$ 5 h (around noon local time) and reach a maximum of 264 ppb. This gives an estimate of the ozone production rate of 34 ppb h<sup>-1</sup>, which is in the range of the ozone production rates calculated in the studies referenced in Table 3. The ozone concentration remains higher than 200 ppb for more than 3 days according to the model. The sounding recorded on 22 December 10 2005 shows that ozone concentrations were lower than those on 20 December 2005 down to 65–80 ppb but still higher than the ones recorded on the 16 December 2005 (40-70 ppb) as seen in Fig. 1. Either the sounding on the 22 December 2005 has not sampled the polluted plume or only its edge, or the concentrations have been diluted during these two days, which is not taken into account in the box model.

The run "Additional Petrochemical Accident" presented in Fig. 7c uses arbitrary values. To better assess the amounts of VOCs and  $NO_x$  that are necessary to produce ozone concentrations as high as observed on 20 December 2005 over Cotonou, we actually performed 49 sensitivity studies. In these test runs the  $NO_x$  concentrations vary from 6 to 78 ppbv and the VOCs amount from 55 to 555 ppb. Figure 8 shows the isopleths of the maximum ozone concentrations reached before the end of the simu-

- lation as a function of the initial NO<sub>x</sub> and VOCs amounts. The results of the first two simulations are recalled on this contour plot as the blue points on the left hand side. Figure 8 shows that a combination of 250–600 ppbv of VOCs and 35–80 ppb of NO<sub>x</sub>
- are necessary to produce more than 250 ppb of ozone. These ranges of concentrations do not correspond to biomass burning nor "regular" anthropogenic pollution but rather to emissions from a petrochemical accident.



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#### 5 Conclusions

As part of the AMMA program, ozone soundings over Cotonou were launched between December 2004 and January 2007. In December 2005, particularly high ozone concentrations have been recorded throughout the troposphere (Thouret et al., 2009).

<sup>5</sup> This paper focuses on the ozone vertical profile measured on 20 December 2005. This day is characterized by an exceptional ozone enhanced layer peaking at around 1 km altitude. This layer is about 1.5 km thick and ozone concentrations are up to almost 300 ppb within it. Such high concentrations were previously reported in China (Wang et al., 2006), in Mexico City (Molina et al., 2007) and close to petrochemical industries
 <sup>10</sup> near Houston in USA (Kleinman et al., 2002, 2005). However such event has never been reported over Africa and we reported here the first one of the region.

We have shown that the 294 ppbv of ozone measured on 20 December 2005 are far higher than the typical ozone concentrations recorded over West Africa provided by the MOZAIC and AMMA programs, which are lower than 120 ppbv. The wind pat-

- tern indicates that Cotonou is under the influence of the Harmattan flow at this time of the year and that its atmosphere is impacted by biomass burning pollution. We used Flexpart backward trajectories and a photochemical zero-dimensional model to built a scenario that explain how such high ozone concentrations could be produced in the vicinity of Cotonou. When the biomass burning emissions of VOCs and NO<sub>x</sub>
- are included in the model as initilization, the model simulates only up to 120 ppbv of ozone, which is in agreement with the typical ozone concentrations within biomass burning plumes. Adding urban emissions from the city of Lagos to the plume impacted by biomass burning does increase the ozone level but it remains below 150 ppb. To simulate ozone concentrations close to 300 ppb, we needed to assume that there was
- <sup>25</sup> a release of large quantities of VOCs and NO<sub>x</sub> as in a petrochemical accident. This kind of accident is known to happen frequently in Nigeria and in the vicinity of Lagos. Including these high emissions of VOCs and NO<sub>x</sub> in the box model allowed the model to produce up to 160 ppbv of ozone in a few hours and the ozone concentrations to

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reach 264 ppbv. Sensitivity tests showed that only 250–600 ppbv of VOCs combined with 35–80 ppb of NO<sub>x</sub> allow the ozone concentrations to be higher than 250 ppb.

Unfortunately, we did not find any proof of such petrochemical accident in the area of Lagos during this period (16–19 December 2005) using satellite data or daily news. However, this scenario is the most likely one. Such event has been probably very

<sup>5</sup> However, this scenario is the most likely one. Such event has been probably very limited in time and space but it should be remembered in future studies regarding air quality issue in this region as a non negligeable source of ozone and its impact.

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**Table 1.** Tropospheric columns of ozone from the surface up to 17 km and contributions of the 0-2 km and 2-17 km layers in Dobson Unit. These ozone amounts are calculated for the three individual soundings of December 2005 (16, 20, 22), the mean vertical profile of December 2005 and the mean vertical profile of December from years 2004, 2005 and 2006 (called mean AMMA).

Columns (DU)	16 Dec 2005	20 Dec 2005	22 Dec 2005	mean Dec 2005	mean AMMA
TCO (0–17 km)	52.5	94.9	70.7	66.3	50.3
0–2 km	8.0	32.1	11.9	9.3	8.2
2–17 km	44.5	62.8	58.8	57	42.0

**Table 2.** Ozone precursors concentrations used to initialized the three runs (Biomass burning, Additional Lagos and Additional petrochemical accident) performed with the Master Mechanism box model (Madronich and Calvert, 1990).

Compounds (ppb)	Biomass burning <sup>a</sup>	Additional Lagos <sup>b</sup>	Additional petrochemical accident <sup>c</sup>
Total COV	36.55	6.9	200–600
NO <sub>x</sub> (Nitrogen oxide)	40	6	55–80
CH₄ (methane)	1981		
CO (carbon monoxyde)	1000		
$SO_2$ (sulfur dioxide)	5		10
NH <sub>3</sub> (ammoniac)	5		10
Carbonyl compounds	2	10.1	40

<sup>a</sup> taken from Poppe et al. (1998)

<sup>b</sup> taken from Hopkins et al. (2009)

<sup>c</sup> Adapted from our sensitivity study (Fig. 8) and from the literature as presented in Table 3.

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**Table 3.** Non-exhaustive list of studies reporting events of high ozone concentrations. The ozone concentrations and production rates as well as the concentrations of some ozone precursors are given.

References	Region	Ozone (ppb)	Ozone prod. rate (ppb $h^{-1}$ )	gaseous pollutants (ppb)	
Wang et al. (2006)	Beijing metropolitan area	180–286	NC	CO (500–2000) NO <sub>y</sub> (12–60) SO <sub>2</sub> (4–60)	Extreme ozone over Cotonou in
Spirig et al. (2002)	Po Valley (Italia)	150–200	20–30	NO <sub>x</sub> (8–14) CO (500–600) C <sub>6</sub> H <sub>6</sub> (1.5–2.5) CH <sub>2</sub> O (5.2–10) NO <sub>y</sub> (37-47)	A. Minga et al.
Kleinman et al. (2005)	Houston area	151–211	25 - 140	NO (5–25) NO <sub>x</sub> gt 100 Isoprene (0.01–10.2)	Title Page
Kleinman et al. (2002)	Houston area	124–251	5 –45	NO <sub>x</sub> (1–40) Ethene (16) Propene (8) Butene (2.5)	AbstractIntroductionConclusionsReferences
Zhang et al. (2007)	Hong Kong area	120–203	NC	NO <sub>x</sub> (20–60) NO <sub>y</sub> (2–150) NO (0.01 – 100) SO <sub>2</sub> (1–70) CO (400 –3500) VOC (20–900) aromatic hydrocarbons (19–205)	Tables Figures
Berkowitz et al. (2004)	Houston area	205–238	NC	NO (122) NO <sub>y</sub> (59–146) CO (670–1100) HCHO (20–40) SO <sub>2</sub> (40–58) HNO <sub>3</sub> (3.7–8) PAN (3.6–15.9)	Back   Close     Full Screen / Esc
Guangfeng and Fast (2004)	Houston area	20–200	10–35	HCHO (1–34) Ethene (1–82) Toluene (1–5)	Printer-friendly Version Interactive Discussion
Hung-Lung et al. (2007)	Taiwan area	10–100	NC	52 VOC species (110–190)	

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(cc)



**Fig. 1.** Vertical profiles of ozone up to 17 km over Cotonou provided by the three soudings performed in December 2005: on 16 (red), 20 (black) and 22 (blue).

































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**Fig. 6.** Retroplumes calculated by the FLEXPART model for the first 24 h (top panel), between 24 and 48 h (bottom left), and between 48 and 60 h (bottom right) initialised over Cotonou in the ozone enhanced layers (between 800 and 1600 m) measured on the 20 December 2005. Black dots mark the position of Cotonou, Djougou and Lagos. Red crosses mark the position of active fires as detected by MODIS on the 16, 17, 18 and 19 December 2005.





**Fig. 7.** Time evolution of the ozone (black), CO (blue) and  $NO_x$  (red) concentrations simulated by the Master Mechansim box model for the three simulations: **(a)** biomass burning, **(b)** additional Lagos and **(c)** additional petrochemical accident.









