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Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer.

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30 **Abstract**

31

32 Ozone holds a certain fascination in atmospheric science. It is ubiquitous in the atmosphere, central
33 to tropospheric oxidation chemistry, yet harmful to human and ecosystem health as well as being an
34 important greenhouse gas. It is not emitted into the atmosphere but is a by-product of the very
35 oxidation chemistry it largely initiates. Much effort is focussed on the reduction of surface levels of
36 ozone owing to its health and vegetation impacts but recent efforts to achieve reductions in
37 exposure at a country scale have proved difficult to achieve owing to increases in background ozone
38 at the zonal hemispheric scale. There is also a growing realisation that the role of ozone as a short-
39 lived climate pollutant could be important in integrated air quality climate-change mitigation. This
40 review examines current understanding of the processes regulating tropospheric ozone at global to
41 local scales from both measurements and models. It takes the view that knowledge across the scales
42 is important for dealing with air quality and climate change in a synergistic manner. The review
43 shows that there remain a number of clear challenges for ozone such as explaining surface trends,
44 incorporating new chemical understanding, ozone-climate coupling as well as a better assessment of
45 impacts. There is a clear and present need to treat ozone across the range of scales, a transboundary
46 issue, but with an emphasis on the hemispheric scales. New observational opportunities are offered
47 both by satellites and small sensors that bridge the scales.

48

1. Introduction

49
50

51 Ozone is central to the chemistry of the troposphere owing to its role in the initiation of
52 photochemical oxidation processes *via* direct reaction, photolysis and the subsequent reactions of
53 the photoproducts to form the hydroxyl radical (Monks, 2005). Tropospheric ozone is also
54 recognised to be a threat to human health (WHO, 2003;Lim et al., 2012), to have a deleterious
55 impact on vegetation (Fowler et al., 2009) and, through plant damage it impedes the uptake of
56 carbon into the biosphere (Sitch et al., 2007) as well as impacting built infrastructure (Kumar and
57 Imam, 2013). It is also an important tropospheric greenhouse gas (IPCC, 2007;Stevenson et al., 2013)
58 and is referred to as a short-lived climate pollutant (Shindell et al., 2012).

59 Ozone-related deaths are estimated to make up about 5-20% of all those related to air pollution e.g.
60 (Silva et al., 2013;Anenberg et al., 2009;Lim et al., 2012;Brauer et al., 2012). The OECD (OECD, 2012)
61 have stated that “without new policies, by 2050, air pollution is set to become the world’s top
62 environmental cause of premature mortality.” The report goes on to state that “Because of their
63 ageing and urbanised populations, OECD countries are likely to have one of the highest premature
64 death rates from ground-level ozone”.

65 While ozone has a relatively short atmospheric lifetime, typically hours, in polluted urban regions
66 where concentrations of its precursors are high, its lifetime in the free troposphere is of the order of
67 several weeks (Stevenson et al., 2006;Young et al., 2013), sufficiently long for it to be transported
68 over intercontinental scales. Thus in addition to its role as a priority pollutant on an urban scale, it
69 may influence air quality on a hemispheric scale (Akimoto, 2003;HTAP, 2010). There is little doubt
70 that ozone is a multifarious molecule. Recently, Simpson et al (Simpson et al., 2014) described ozone
71 as the “persistent menace”. Figure 1 shows some of the key interactions that drive ozone
72 concentrations in the troposphere and some of the feedbacks.

73

74 This review examines current understanding of the processes regulating tropospheric ozone at global
75 to local scales from both measurements and models. It takes the view that knowledge across the
76 scales is important for dealing with air quality and climate change in a synergistic manner. It would
77 be a herculean task to review all the literature on ozone, therefore much of the focus of this review is
78 on the recent findings and discoveries relating to tropospheric ozone. It builds on earlier integrative
79 reviews such as Brasseur et al (Brasseur et al., 2003) and the ACCENT reviews (Fowler et al.,
80 2009;Isaksen et al., 2009;Monks et al., 2009;Laj et al., 2009).

81 The review has four major sections. The first reviews the control of ozone across the scales, looking
82 at the interplay of chemistry, transport and deposition, and includes a brief climatological picture of
83 ozone. The second major section details the major impact of ozone with respect to health,
84 ecosystems and climate, while the third section highlights several current topics in relation to ozone
85 in the troposphere. The final section briefly overviews some of the policy context and issues in
86 relation to tropospheric ozone. In the conclusion, some future directions and issues with relation to
87 ozone are discussed.

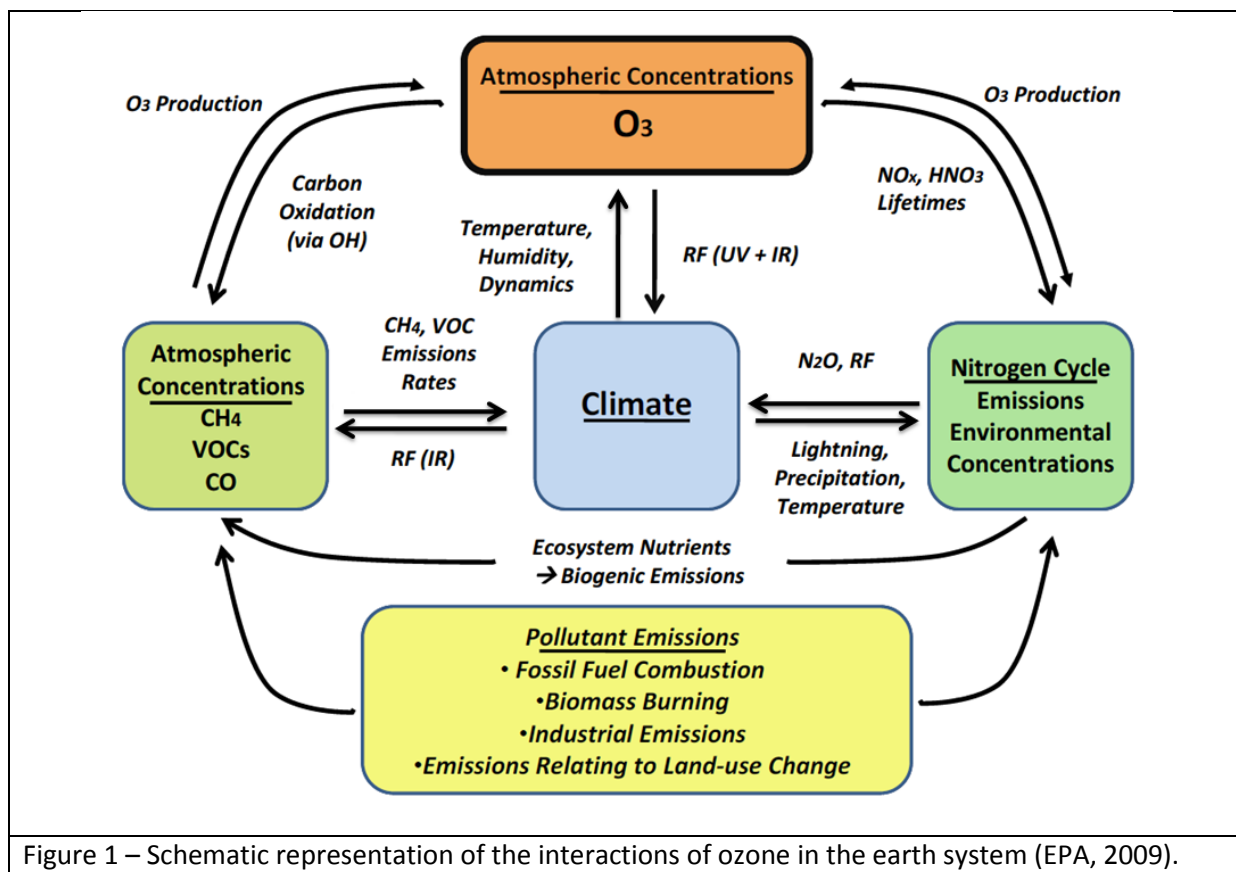


Figure 1 – Schematic representation of the interactions of ozone in the earth system (EPA, 2009).

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89 2 Ozone – control, precursors and climatology

90 2.1 What controls ozone?

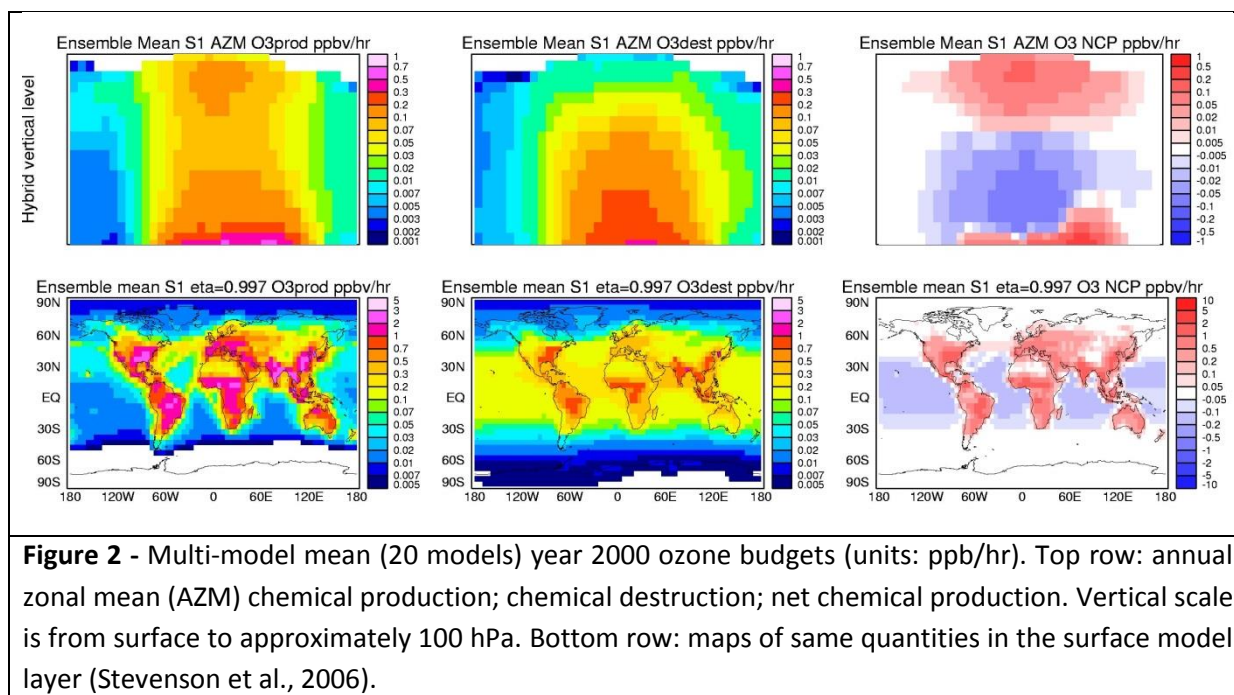
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92 The annual variation in ozone concentration at any given spatial scale depends on a number of
 93 factors, such as the proximity to large sources of ozone precursors, geographical location and the
 94 prevailing meteorological conditions (Logan, 1985). The tropospheric ozone budget at a given
 95 location is dependent on both photochemical processes and physical processes, including
 96 photochemical production and destruction of ozone, transport from upwind sources and removal at
 97 the Earth's surface (Monks, 2000;Lelieveld and Dentener, 2000).

98

99 Given the substantial stratospheric ozone concentrations, transport from the stratosphere was long
 100 thought to be the dominant source of ozone in the troposphere (Danielsen, 1968;Junge, 1962;Fabian
 101 and Pruchniewicz, 1977;Chatfield and Harrison, 1976). Photochemical mechanisms for the
 102 generation of ozone were first identified in work carried out in California in the 1950s (Haagen-Smit,
 103 1952) and until the 1970's high ozone was thought to be a local phenomenon associated with air
 104 pollution (Leighton, 1961). Early in the 1970's Crutzen (Crutzen, 1973) and Chameides and Walker
 105 (Chameides and Walker, 1973) suggested that tropospheric ozone originated mainly from production
 106 within the troposphere by photochemical oxidation of CO and hydrocarbons catalysed by HO_x and
 107 NO_x. Since then, improved understanding of the importance of both natural and anthropogenic
 108 sources of ozone precursors has highlighted the dominance of this ozone source, and recent model
 109 assessments suggest that chemical production contributes about 5000 Tg/yr to global tropospheric
 110 ozone (Stevenson et al., 2006;Young et al., 2013). In contrast, the net global source of ozone from

111 stratosphere-troposphere exchange (STE) is estimated to be about 550 ± 140 Tg/yr based on
 112 observational constraints (Olson et al., 2001; McLinden et al., 2000). The removal of ozone through
 113 dry deposition to vegetation and other surfaces at ground level remains poorly constrained on the
 114 global scale, although model assessments driven by observed ecosystem fluxes, vegetation types and
 115 meteorology suggest net removal of about 1000 ± 200 Tg/yr (Stevenson et al., 2006). Balancing the
 116 global tropospheric ozone budget therefore requires that there is net chemical production of about
 117 450 ± 300 Tg/yr (Stevenson et al., 2006). Note that this term is constrained by the estimated STE and
 118 deposition terms and by the global tropospheric ozone burden of about 335 ± 10 Tg, and that
 119 uncertainty in the absolute magnitude of gross ozone chemical production and destruction remains
 120 relatively large (Wild, 2007; Wu et al., 2007).
 121



122
 123 These global budgets mask substantial regional variation (see Figure 2) which spans the wide range
 124 of chemical environments present in the troposphere. Troposphere-wide chemical production of
 125 ozone from long-lived hydrocarbons such as methane is greatest in the tropical lower troposphere
 126 where OH radical concentrations are high (Bloss et al., 2005) and in continental regions and parts of
 127 the free troposphere with fresh NO_x emissions. Chemical destruction of ozone is largest in the lower
 128 troposphere where water vapour concentrations are high and in highly polluted regions where there
 129 is direct removal by reaction with NO. This latter condition is commonly referred to as chemical
 130 titration of ozone, and is typically short-lived as the NO₂ formed subsequently catalyses further
 131 ozone formation once it has been transported into cleaner environments. Localised halogen-
 132 catalysed ozone destruction may also affect surface ozone in Polar-regions during spring time (see
 133 Halogens section). Consequently, net chemical production occurs over most of the continental
 134 boundary layer where precursor concentrations are high and in the upper troposphere, where
 135 destruction is slow (Wild and Palmer, 2008; von Kuhlmann et al., 2003b, a). Net chemical destruction
 136 occurs in the mid-troposphere and marine boundary layer where precursor concentrations are low
 137 and in localised urban and Polar Regions under *titration* (via reaction with NO) and halogen
 138 destruction conditions, respectively. Despite large changes in the emissions of ozone precursors and

139 in net chemical production, the general location of these net production and loss regimes is thought
140 to have changed little since preindustrial times (Wild and Palmer, 2008). However, spatial
141 heterogeneity of anthropogenic precursor emissions and of biogenic hydrocarbons (Zare et al.,
142 2014), along with strong diurnal variability in chemical processes, deposition and meteorology,
143 suggests that local ozone production and loss regimes in the boundary layer may be much more
144 diverse than indicated by these coarse, regional-scale assessments.

145

146 *2.1.1 Role of Chemistry*

147

148 The basic chemistry that leads to the production and destruction of ozone has been detailed
149 elsewhere (Monks, 2005; Ehhalt, 1999; Jenkin and Clemitshaw, 2000). Ozone (O₃) photochemical
150 production in the troposphere occurs by hydroxyl radical oxidation of carbon monoxide (CO),
151 methane (CH₄), and non-methane hydrocarbons (generally referred to as NMHC) in the presence of
152 nitrogen oxides (NO_x). The mechanism of ozone formation in the troposphere, although very well
153 understood, remains a challenge in practice that will, no doubt, require many more years of research
154 to fully unravel. Typical photochemical timescales in the atmosphere are quite short (in the order of
155 seconds to tens of minutes) (Seinfeld and Pandis, 2006). In brief, the production of ozone in the
156 troposphere relies, fundamentally, on the photolysis of NO₂ (reaction R1) and the subsequent
157 association of the photoproduct O(³P) (the ground electronic state oxygen atom) with O₂ *via* reaction
158 2 through a termolecular reaction with a third body (M being used to represent any third co-reactant
159 i.e. N₂):



162 The difficulty with understanding the production of O₃ in the troposphere comes about through the
163 manifold ways in which NO and NO₂ are interconverted. The rapid interconversion between the two
164 compounds allows them to be treated as a chemical family – NO_x. (NB photolysis of NO₂ is fast, and
165 approximately altitude independent – $j_1 \approx 10^{-2} \text{ s}^{-1}$). For example, the reactions



168 both convert NO into NO₂. Considering reactions 1,2 and 4 one can derive a ratio of [NO]/[NO₂] that
169 depends on the local concentration of O₃ and the rate coefficients for reaction (4) and the photolysis
170 frequency for reaction (1) (at the surface the pseudo first order rate constant k_2' ($k_2 \cdot [\text{O}_2] \cdot [\text{M}]$) is
171 sufficiently fast that it is not a rate limiting step). This ratio is termed the Leighton ratio (Leighton,
172 1961) and also allows for an expression to be derived for the equilibrium concentration of O₃. Whilst
173 this chemistry is important, particularly in urban areas, it does not represent a mechanism for the net
174 production of O₃ in the troposphere. With the addition of volatile organic compounds, such as CO *viz*



176 It is possible to write a mechanism for the formation of O₃ that is propagated *via* VOC (Volatile
 177 Organic Compound) and NO_x (reactions (5), (3), (2) and (1)). In this series of reactions O₃ is used as a
 178 source of the hydroxyl radical (OH) through:



181 where O(¹D) is the electronic excited state atomic oxygen formed through photolysis at wavelengths
 182 <320 nm. However, the presence of VOC (CO) and NO_x, allow OH to be regenerated (R3) and
 183 promote formation of O₃ through NO₂ photolysis. The production of O₃ in the troposphere, mediated
 184 through the reactions involving VOC (CH₄) and NO_x can be shown schematically in Figure 3 and in
 185 relationship to changing precursor concentrations in Figure 4.

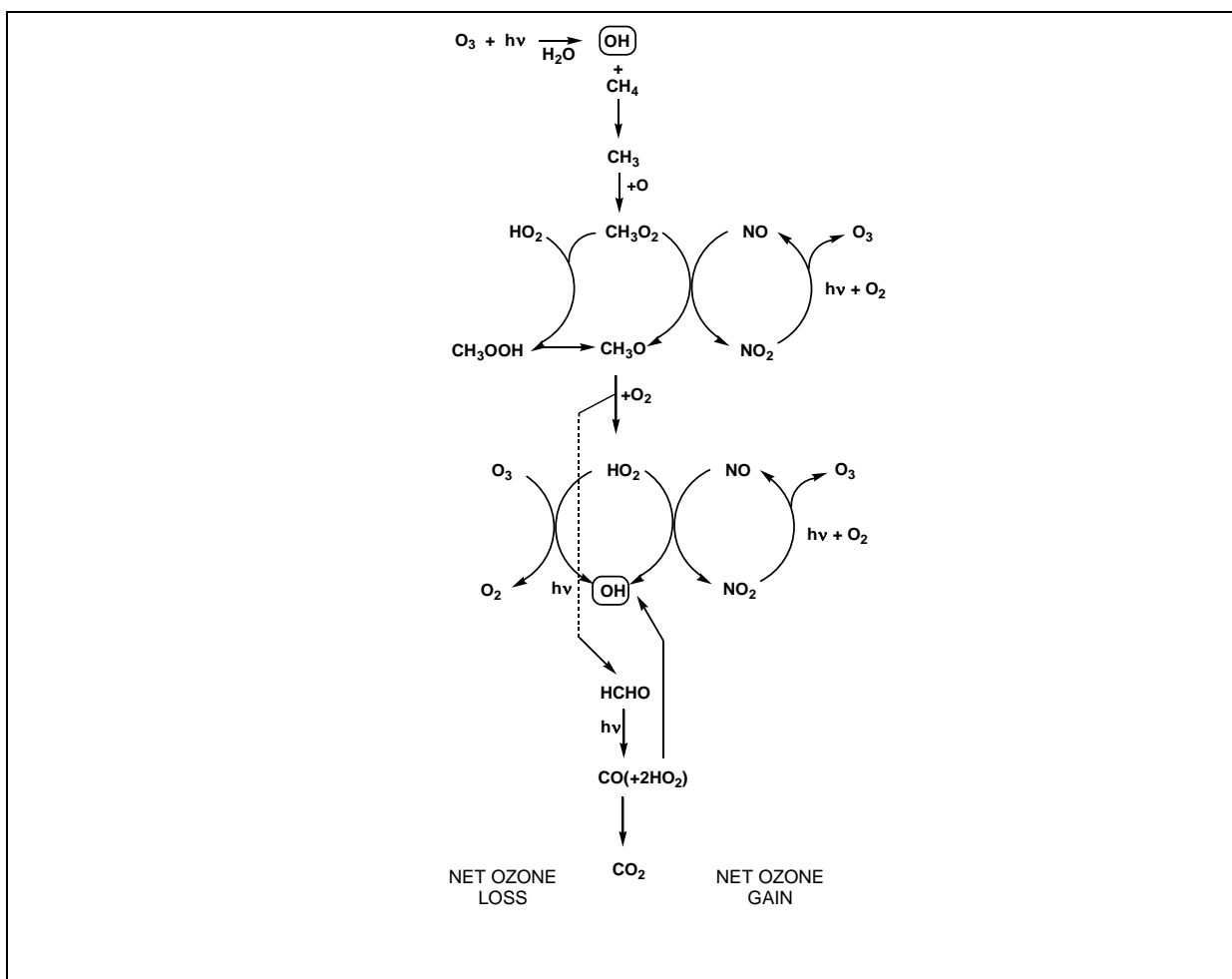


Figure 3 - Simplified mechanism for the photochemical oxidation of CH₄ in the troposphere (Lightfoot et al., 1992)

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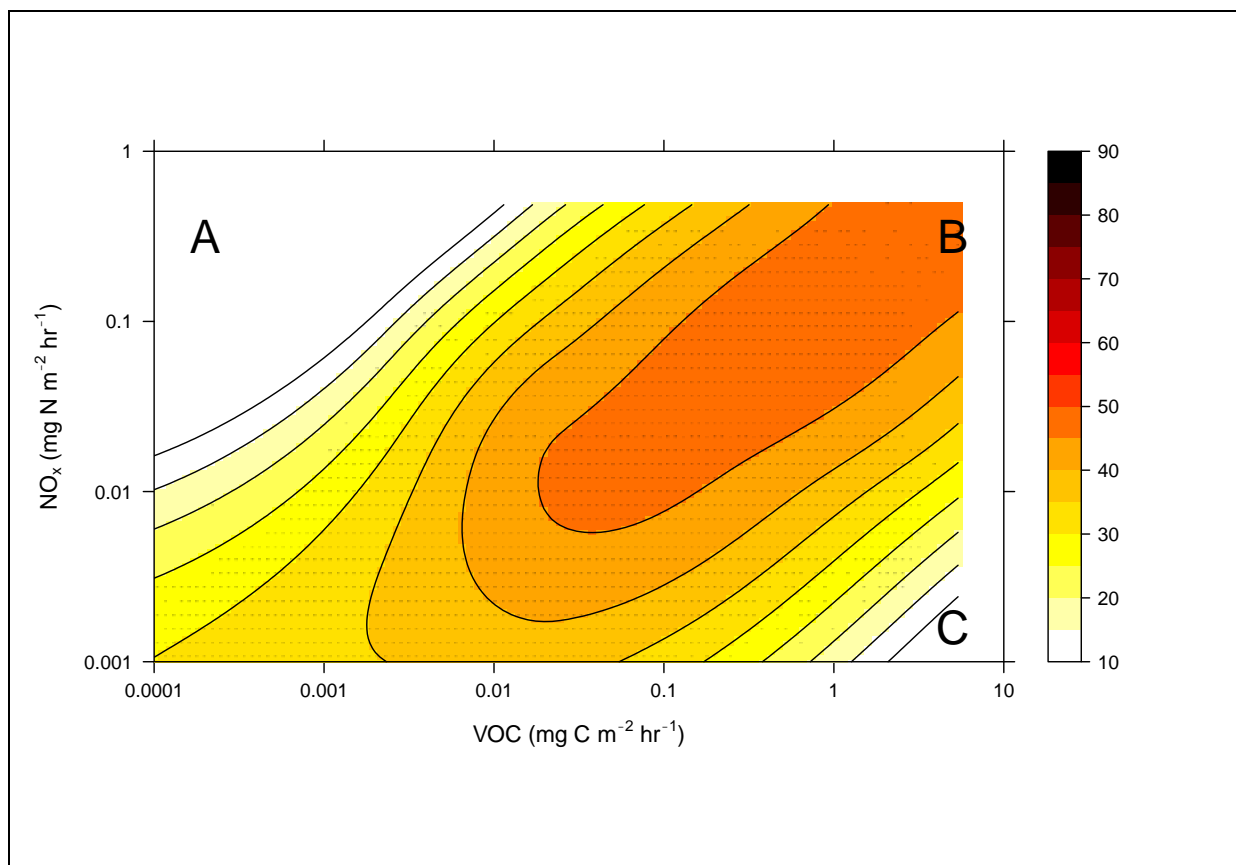


Figure 4 - O₃ mixing ratios (ppb) as a function of VOC and NO_x emissions as computed using the UKCA model of atmospheric chemistry (Archibald et al., 2011). Three main regions are identified. Top left corner (A): region of NO_x saturation and O₃ titration. Bottom right corner (C): region of VOC saturation and O₃ destruction. Diagonal elements (A-C, B-C): efficient conversion of NO-NO₂ and hence O₃ production increasing with increasing VOC and NO_x emissions (NB log₁₀ scales for emissions).

187

188 Figure 4 highlights the non-linearity of the O₃-VOC-NO_x system. The O₃ mixing ratios presented in
 189 Figure 4 are generated from photochemical modelling output generated using the UKCA model
 190 (O'Connor et al., 2014; Archibald et al., 2011). Regions in Figure 4 where there is net O₃ destruction
 191 (top left (A) and bottom right corners (C)) are typically referred to as the VOC limited and NO_x limited
 192 regimes. VOC limited refers to the fact that the production of O₃ is limited by the input of VOC (see
 193 e.g. (Zhou et al., 2014)). This can be rationalized by moving from point A to point B along a line of
 194 constant NO_x emissions and increasing VOC emissions. Moving in this direction it is evident from
 195 Figure 4 that O₃ production increases. A similar case applies for the NO_x limited regime where this
 196 time moving from point C to point B requires increasing NO_x emissions and results in increasing O₃
 197 mixing ratios.

198 This general mechanism of OH initiated O₃ formation can be extended to more complex VOC such as
 199 alkanes:



202 Where $C_2H_5O_2$ represents a member of a group of radicals termed organic peroxy radicals (RO_2 –
203 where R is used to represent alkyl, ally, or aryl groups), all of which possess the ability to convert NO
204 to NO_2 . The fate of the alkyl oxy radical (C_2H_5O) is more complex and can result in the formation of
205 HO_2 and other VOCs. It is the organic atmospheric chemistry of RO_2 that remains the great challenge
206 to our full understanding of the production of O_3 in the troposphere. Recent advances in our
207 understanding of the fate of RO_2 in the atmosphere are reviewed in section 4.10.

208 There are added complexities to the chemistry outlined above owing to the variety of sources of OH
209 e.g. from the photolysis of HONO (Kim et al., 2014), HCHO and the reaction of ozone with alkenes.
210 The Monks et al review (Monks et al., 2009) looked at much of the variety of ozone photochemistry
211 in more detail.

212 *2.1.2 Role of Deposition*

213

214 The concentration of ozone in the surface boundary layer is regulated by three processes:
215 atmospheric transport, chemical production/destruction and losses to surface by dry deposition.
216 Ozone is physically transported to the surface by atmospheric turbulence which can be readily
217 measured or modelled using well established methods. The rate of ozone removal at the surface
218 strongly influences the exposure of vegetation and the human population to ozone and is responsible
219 for much of the nocturnal decline in surface ozone in rural areas as deposition to the surface
220 consumes ozone beneath a nocturnal temperature inversion. During the day, vertical transport of
221 ozone to the surface layers is generally sufficient to maintain mixing ratios within 10% of the
222 boundary layer mean values, except in urban areas or near major roads, where local nitric oxide
223 sources remove ozone by titration (Colette et al., 2011). Thus the interplay between dry deposition
224 of ozone in the surface layers and mixing from higher levels in the atmosphere plays a major role in
225 regulating ozone exposure of ecosystem and the human population. The mixing in surface layers is
226 largely driven by wind and its interaction with frictional drag at the surface. The large diurnal
227 variability in ozone mixing ratios in rural areas and its variability with altitude has been used to
228 quantify the spatial variability in ozone exposure at the surface.

229
230 Ozone dry deposition has been widely measured using micrometeorological methods, which average
231 the flux to the surface at the field to landscape scale, over typically (10^4 - 10^6 m^2) (Fowler et al., 2009).
232 The controlling processes in ozone deposition are generally simulated numerically using a resistance
233 analogy (Erisman et al., 1994), as illustrated in Figure 5. Correct parameterisation in models is critical
234 to the determination of ozone budgets (Val Martin et al., 2014).

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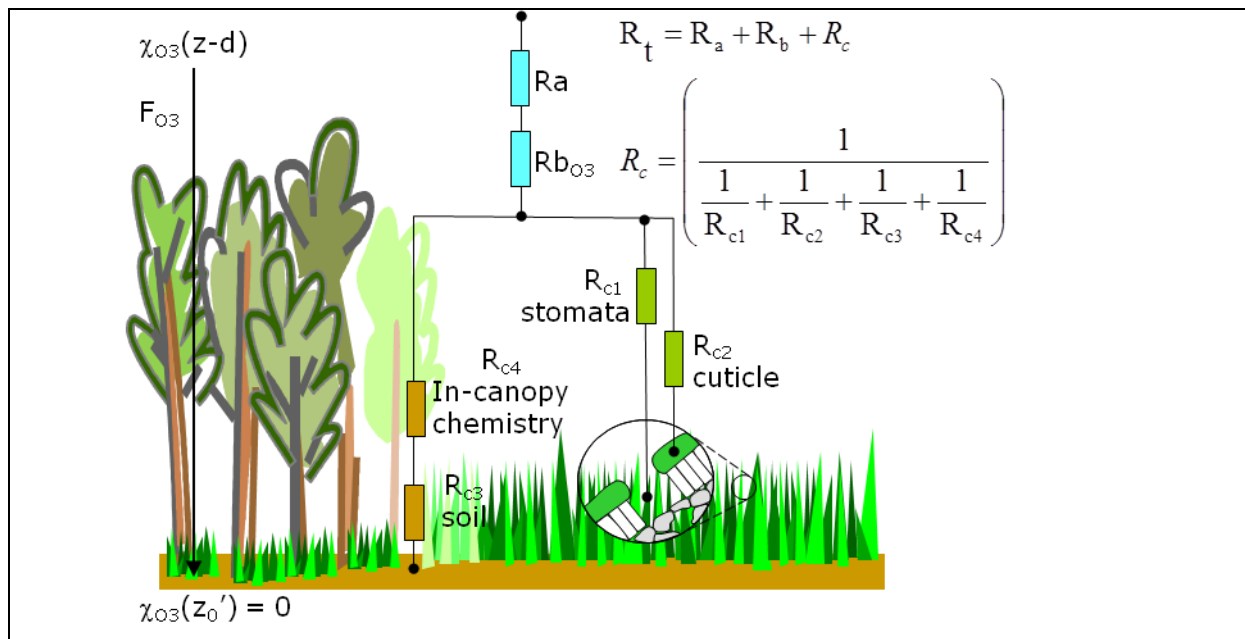


Figure 5 - The resistance analogy for ozone deposition to vegetation and soil (for details of nomenclature see text).

236

237 Ozone is a reactive gas and deposits readily on most surfaces simply by oxidative reactions (Grontoft,
 238 2004). Many studies have concluded that stomatal uptake is the main factor regulating surface
 239 fluxes, but as stomata are usually open during daylight hours, the smaller rates of deposition to non-
 240 stomatal surfaces are often a dominant component of the annual deposition to the surface (Fowler
 241 et al., 2009).

242 Considering the main sinks for ozone deposition at the surface in turn:

243 a) Stomatal Uptake

244 Plants open their stomata to take up CO₂ for photosynthesis and regulate stomatal opening to
 245 minimise water loss by transpiration (Farquhar et al., 1980). This also allows the uptake of other
 246 gases that may not benefit the plant, including ozone, which as a powerful oxidant, generates free
 247 radicals within the apoplast and cell fluids and is responsible for damage to cell metabolism (Mills et
 248 al., 2011a). Stomatal opening is controlled by water pressure in the guard cells which the plant
 249 regulates depending on: light, in general stomata open during the day and close at night; carbon
 250 dioxide concentration, with increasing CO₂ above current ambient inducing partial closure; soil water
 251 content, with stomata closing in drier soils to reduce water loss; temperature, with an increase in
 252 temperature increasing stomatal opening up to a species-specific maxima above which stomatal
 253 closing is induced; humidity, with greatest stomatal opening under low vapour pressure deficits and
 254 stomatal closing occurring at high vapour pressure deficits to conserve plant water; and phenology
 255 with stomatal conductance reducing as plants age. An example of the range of stomatal responses
 256 to these environmental and plant controls can be found for wheat in Grünhage et al. (Grünhage et
 257 al., 2012). Other factors can affect stomatal opening although not as directly as those listed above,
 258 for example, aerosols can damage the guard cells or block stomata and surface water can also block
 259 stomata.

260

261 The diffusion pathway through stomata as with atmospheric fluxes, can be quantified using a
 262 resistance analogy as illustrated in Fig. 4. The inverse of stomatal resistance is stomatal conductance
 263 (g_s) and is widely used by plant scientists to quantify stomatal exchanges of CO_2 and H_2O , and has
 264 also been used to develop stomatal flux-based risk assessments for ozone (Emberson et al.,
 265 2000; Mills et al., 2011b). The processes responsible for controlling stomatal function have been
 266 extensively studied in the field and laboratory leading to a variety of instruments and models to
 267 quantify stomatal resistance, R_{c1} , or conductance, g_s .

268
 269 b) Non-Stomatal Uptake

270 The reaction of ozone with external surfaces of vegetation is referred to as non-stomatal uptake. In
 271 controlled conditions in the laboratory, the flux may be measured quite straightforwardly by treating
 272 the vegetation in order to fully close the stomata. In the field, there is the complication that multiple
 273 sinks are present (leaf surfaces, senescent vegetation, soil and water) as well as stomatal opening.
 274 The usual approach to quantify non-stomatal deposition is by the difference between the total
 275 deposition flux and the stomatal flux, choosing surfaces to minimise the soil and senescent
 276 vegetation components. With reference to Figure 5, once R_{c1} has been determined from
 277 measurements or by modelling the sum of R_{c2} , R_{c3} and R_{c4} (non-stomatal, R_{ns}) can be calculated as the
 278 residual term:

279
$$R_{ns} = \left(\frac{1}{R_c} - \frac{1}{R_{c1}} \right)^{-1} \quad (1)$$

280 Whether it is possible to separate the components of R_{ns} (R_{c2} – external surfaces, R_{c3} – soil, R_{c4} – in-
 281 canopy chemistry) depends on the nature of the measurement site and canopy and there are some
 282 models available based on measurements over bare soil, senescent vegetation and in-canopy
 283 chemistry (Launiainen et al., 2013; Fares et al., 2013b; Fares et al., 2012; Bueker et al., 2012; Tuzet et
 284 al., 2011; Stella et al., 2011). Many research groups have taken this approach and Table 1 provides a
 285 summary of some of the different estimates of the values for R_{ns} in the literature.

Table 1 - Selected estimates of the non-stomatal resistance for ozone to snow, water, soil and plant surfaces from measurements.

Reference	Type	Surface	R_{ns} , s m^{-1}
(Chang et al., 2002)	Chamber	Agricultural soil (no data on moisture content)	ca 625 ca 475
(Wesely et al., 1981)	Field μmet	Wet bare soil	1000 \pm 100 (370 – 2100)
		Snow -11°C	2000 \pm 200
		-5°C	3500 \pm 200
		-1 to 2 °C	3300 \pm 300
		Lake water	9000 \pm 300
(Sanchez et al., 1997)	Field μmet	Semi-arid steppe (wet and dry)	Dry 275 Wet 437
(Rondon et al., 1993)	Field chambers	Coniferous trees	200 – 330
(Granat and Richter, 1995)	Field chambers	Pine	500 – 2500
(Coe et al., 1995)	Field μmet	Sitka spruce	ca 133
(Fowler et al., 2001)	Field μmet	Dry moorland	200 – 400
(Grantz et al., 1995)	Field μmet	Wet and dry grape	Dry 1020 Wet 292 ^a

(Grantz et al., 1997)	Field μmet	Wet and dry cotton	Dry 770 Wet 3030
(Zhang et al., 2002) ^b	Field μmet	Wet and dry: Mixed forest Deciduous forest Corn Soybean Pasture	244 – 970 397 – 1831 308 – 1332 137 – 735 571 – 879
(Gerosa et al., 2005) (Gerosa et al., 2009)	Field μmet	Mediterranean Oak (<i>Quercus ilex</i>)	Dry 249 Wet 177 Avg 67 – 204
(McKay et al., 1992) and references therein	Laboratory chambers and field	Sea water & saline solutions	650 – 6600
(Gallagher et al., 2001)	Field μmet	Coastal waters	950 \pm 70
(Coyle et al., 2009)	Field μmet	Potatoes Wet canopy Dry canopy	276
(Neiryck et al., 2012)	Field μmet	Temperate Forest	136

a from data reported in (Grantz et al., 1997)

b data derived from references therein

286

287 The literature reviewed in Table 1 reports estimates of R_{ns} , although few examine the controlling
 288 factors. In some of the studies, surface factors affecting ozone deposition, other than stomatal
 289 uptake, have been considered. For example, surface water has been found to both enhance and
 290 reduce deposition rates. The remainder of studies have considered solar radiation or surface
 291 temperature and found deposition rates increased with both variables, as well as in-canopy
 292 chemistry.

293 c) Solar Radiation and Surface Temperature

294 Given its reactive nature it is not unreasonable to find effects of surface temperature on R_{ns} and
 295 indications of such an effect were first reported by Rondon et al (Rondon et al., 1993). In their
 296 measurements of ozone deposition to a coniferous forest they found that the surface resistance to
 297 ozone was much lower than that predicted by stomatal conductance alone and the residual term
 298 (R_{ns}) varied with air temperature, radiation and stomatal conductance. It was proposed that this
 299 effect was due to temperature increasing the reaction rates of ozone with organic compounds on the
 300 canopy surface. Coyle et al (Coyle et al., 2009) found similar results in measurements for ozone
 301 uptake by potatoes, while also showing that surface wetness could enhance or reduce non-stomatal
 302 uptake depending on the initial status of the cuticles. While (Fowler et al., 2001) showed a clear
 303 reduction in R_{ns} with increasing total solar radiation and temperature. Cape et al (Cape et al., 2009)
 304 examined deposition to metals and artificial leaf surfaces and found a strong temperature response,
 305 which yielded activation energies for the reaction of $\sim 30 \text{ kJ mol}^{-1}$, similar to that found by Fowler *et*
 306 *al* (Fowler et al., 2001) for moorland of 36 kJ mol^{-1} and from other unpublished studies (Coyle et al.,
 307 2009). The simplest explanation of non-stomatal ozone deposition is that it represents the thermal
 308 decomposition of ozone at the surface, which increases with surface temperature. Other, more
 309 complex processes have been suggested including rapid reactions with very reactive hydrocarbon
 310 compounds (Hogg et al., 2007).

311 d) In-canopy chemistry

312 The reaction of ozone with nitric oxide (NO) is an important cause of reduced ozone concentrations
313 in urban areas. The same reaction also reduces ozone concentrations close to the surface where soil
314 emissions of NO are large. Some types of vegetation such as coniferous forests also emit highly
315 reactive volatile organic compounds (Di Carlo et al., 2004) which can rapidly deplete ozone
316 concentrations immediately above the canopy (Neiryneck et al., 2012;Stjernberg et al., 2012;Kurpius
317 and Goldstein, 2003). Over some forest canopies the major non-stomatal sink has been attributed to
318 these reactions although the compound(s) responsible have not been identified. Other transient
319 events such as grass cutting, which releases very reactive hydrocarbons (Davison et al., 2008) can
320 also lead to enhanced ozone deposition as a result (Coyle, 2005).

321 e) Deposition to Water

322 It has often been assumed that ozone deposition rates to water will be small and relatively constant
323 as ozone has a low solubility in water. The resistance of a water layer to the uptake of ozone by
324 dissolving and diffusing the gas is very large and values of 3×10^5 to $8 \times 10^5 \text{ s m}^{-1}$ have been suggested
325 (Wesely et al., 1981). They concluded that the far lower values found in their measurements (Table
326 1) resulted from surface chemical reactions, which has been supported by further work since then.
327 However measurements have shown that over vegetated surfaces deposition can be either
328 enhanced or suppressed by the presence of water films ((Fuentes et al., 1992)), (Padro, 1994)),
329 (Grantz et al., 1995;Grantz et al., 1997), (Pleijel et al., 1995)), (Coyle et al., 2009)) while over open
330 water deposition varies with water chemistry, turbidity and agitation. The deposition velocity of
331 ozone to open water is generally small, ~ 0.001 to 0.04 cm s^{-1} (Wesely et al., 1981;Chang et al., 2004)
332 and increases in deposition velocities to sea water have been observed with disturbance to the
333 surface. McKay et al (McKay et al., 1992) showed that increasing concentrations of chemical
334 surfactants in the seawater also enhanced deposition (see Table 1 for typical resistance values).
335 These results show that although deposition rates to water are generally small they can be significant
336 if other reactive compounds are present in the water, a conclusion also supported by measurements
337 to wet vegetated canopies. Research into ozone reactivity and solubility for the ozone water
338 treatment industry has highlighted the role of pH. Ganzeveld et al have explored the impact of dry
339 deposition of ozone over oceans (Ganzeveld et al., 2009). On a global scale, model studies indicate
340 that deposition to the ocean constitutes almost 40% of the total annual surface dry deposition of
341 ozone, far larger than that from any other land cover class (Hardacre et al., 2014).

342 *2.1.3 Transport and mixing processes*

343

344 a) Long-range transport

345

346 Research over the past two decades has clearly shown that ozone and ozone precursors are regularly
347 exported from their emission source, or point of production, to receptor regions far downwind on
348 the regional, intercontinental and even hemispheric scale (see reviews by Stohl and Eckhardt (Stohl
349 and Eckhardt, 2004), Monks et al. (Monks et al., 2009), National Research Council (Council, 2009b)
350 and (HTAP, 2010)). These transport pathways are predominantly from west to east at mid-latitudes
351 with in situ and satellite-based observations showing that pollution plumes (anthropogenic and
352 biomass burning) not only travel from North America to Europe, or from East Asia to North America,

353 but can also circle the globe (Jacob et al., 1999;Jaffe and et al., 1999;Lewis et al., 2007;Wild et al.,
354 2004).

355
356 The scientific community has a very good understanding of the meteorological mechanisms that
357 export pollution from the boundary layer of a source region (warm conveyor belts, deep convection,
358 and horizontal advection) and then transport these plumes through the free troposphere towards
359 the downwind receptor region. The most recent development is the conceptualization of
360 intercontinental transport within an isentropic framework that illustrates how transport of pollution
361 plumes from East Asia are constrained by the thermal structure of the atmosphere, preferentially
362 impacting the high elevation terrain of the western USA rather than the relatively low-lying eastern
363 USA (Brown-Steiner and Hess, 2011). The major uncertainty concerning long-range transport is
364 estimating the contribution of the imported pollution to the total quantity of pollution at the surface
365 of the receptor region. Some unique chemical tracers of upwind pollution sources do exist, for
366 example, stable lead isotopes can indicate events when Asian particulate matter reaches the surface
367 of California (Ewing et al., 2010). However, at present there are no routine and widespread
368 monitoring methods that can distinguish ozone and ozone precursors produced in a receptor region,
369 such as California, from the same species produced in an upwind region, such as East Asia.

370
371 The only feasible method for quantifying the impact of imported pollution at the surface of a
372 receptor region is to use chemical transport models or chemistry-climate models. Such models have
373 been used for this purpose since the 1990s but until recently their effectiveness has been limited by
374 their coarse horizontal resolution, typically 2x2 degrees (HTAP, 2010). Such large grid cells artificially
375 dilute the imported pollution plumes as well as local emissions of ozone precursors in the receptor
376 region, and also smooth the topography of the receptor region, removing the influence of terrain-
377 driven transport mechanisms that affect the mixing of imported pollution down to the surface.
378 However, recent model studies have used finer scale grids to avoid the problems associated with
379 coarse resolution models (Lin et al., 2012b;Huang et al., 2013;Zhang et al., 2014;Choi et al., 2014).
380 Because these finer resolution models provide more realistic simulations of observed pollution
381 plumes scientists have greater confidence in their quantification of the contribution of imported
382 pollution at the surface of a receptor region. Despite the improvements afforded by finer resolution,
383 a recent study of the quantity of background ozone advected into western North America shows
384 monthly mean differences as great as 10 ppbv between models, with the discrepancy attributed to
385 differences in the way that the models handle lightning NO_x, biogenic isoprene emissions and
386 chemistry, wildfires, and stratosphere-to-troposphere transport (Fiore et al., 2014).

387
388 Future climate change may affect the contribution of long-range transport downwind effects
389 (Glotfelty et al., 2014;Doherty et al., 2013). HTAP (2010) suggests “changes in climate will affect
390 meteorological transport processes as well as the chemical environment and lifetime of the
391 transported pollutants and hence the concentrations of pollutants arriving at downwind continents.”
392 Glotfelty et al. (2014) suggest a larger impact on the US from East Asian Emissions and Doherty et al.
393 (2013) showed stronger chemistry than transport positive climate feedbacks on increased ozone.

394
395

396 b) Stratosphere-troposphere exchange

397
398 The tropospheric ozone burden varies seasonally as measured by the remotely sensed AURA
399 OMI/MLS tropospheric column product (Ziemke et al., 2006). The region of the Earth with the
400 strongest seasonal ozone variation is the northern mid-latitudes where the ozone burden is at a
401 minimum in October and November and then increases by 30% through winter and spring until it
402 reaches a maximum in June (Cooper et al., 2014). Much of this seasonal variability can be explained
403 by the flux of ozone from the stratosphere to the troposphere with a Northern Hemisphere peak flux
404 in May and a minimum flux in November occurring predominantly in mid-latitudes (Hsu and Prather,
405 2009). Until recently ozone transport from the stratosphere to the troposphere was believed to be
406 dominated by processes such as tropopause folds and gravity wave breaking, with little attribution
407 given to deep convection (Stohl et al., 2003). However, a new model-based estimate that accounts
408 for deep convection penetrating the lowermost stratosphere increases the Northern Hemisphere
409 peak stratosphere-to-troposphere ozone flux by 19% and shifts the peak month from May to June
410 (Tang et al., 2011). Sudden STE events are well known to influence ground-based ozone
411 measurements over a short period (see e.g. (Dempsey, 2014;Zanis et al., 2003)).

412
413 While the tropospheric ozone burden responds seasonally to the flux from the stratosphere the
414 response is not uniform with altitude or latitude. Terao et al. (Terao et al., 2008) using a chemical
415 transport model calculated the stratospheric contribution to monthly mean ozone above four
416 ozonesonde sites between 75° N and 36° N. At 500 hPa the stratospheric contribution to ozone is
417 ~40% during spring and 25% in autumn at high latitudes, and 35-40% during spring and 10-15%
418 during autumn at mid latitudes. At 800 hPa these values are slightly less on a percent scale but much
419 less on an absolute scale, being ~20 ppbv during spring and 5-7 ppbv during autumn with relatively
420 little latitudinal gradient. Model estimates of the stratospheric contribution to surface ozone are
421 smaller than those for 800 hPa but the estimates vary greatly depending on the model used and the
422 region under consideration. For example, Lamarque et al. (Lamarque et al., 2005) estimated that the
423 monthly mean stratospheric contribution to a range of sites in the mid-latitudes and tropics of both
424 hemispheres is always less than 5 ppbv, regardless of season. In contrast, a study using a different
425 model estimated the stratospheric contribution to US surface ozone during late spring 2010 as being
426 < 5 ppbv along the Gulf coast, 8-13 ppbv across the eastern US, and 10-20 ppbv across the high
427 elevations of the western USA (Lin et al., 2012a). More recently Hess et al have claimed that that a
428 large portion of the measured ozone change in the sub-tropical NH are not due to changes in
429 emissions, but can be traced to changes in large-scale modes of ozone variability (Hess et al.,
430 2014).this

431 c) Seasonal transport patterns e.g. summer monsoons

432
433 In addition to the seasonal influence of stratosphere-troposphere exchange, ozone varies seasonally
434 at most sites around the world (Oltmans et al., 2013) simply due to shifting wind patterns associated
435 with migratory mid-latitude cyclone tracks or the transition between winter and summer monsoons.
436 For example, Mauna Loa Observatory, Hawaii in the northern tropics is influenced by westerly air
437 masses from Asia in the spring when it is located beneath the subtropical jet stream. But in autumn
438 the subtropical jet stream is far to the north leaving the site well within the tropical belt which
439 reduces transport from Asia resulting in 25% decrease in monthly median ozone (Lin et al., 2014b).

440 Similarly, Bermuda in the subtropical North Atlantic Ocean receives westerly transport from North
441 America during winter and spring, but during summer the westward and northward expansion of the
442 Azores-Bermuda High advects tropical air masses to Bermuda reducing ozone mixing ratios by 50%
443 (Moody et al., 1995). The North American Summer Monsoon becomes established above central
444 North America during July and August producing a stationary upper tropospheric anticyclone that
445 traps ozone precursors lofted from the surface as well as large quantities of lightning NO_x (Cooper et
446 al., 2009). Over several days the ozone precursors enhance tropospheric ozone within the
447 anticyclone by as much as 30-40 ppbv compared to sites upwind of the anticyclone (Cooper et al.,
448 2007). Ozonesondes launched from Ahmedabad, western India indicate that an upper tropospheric
449 ozone enhancement does not occur during the Asian Summer Monsoon despite the presence of an
450 anticyclonic recirculation similar to that found above North America during its summer monsoon.
451 Instead, an abrupt decrease in tropospheric column ozone is observed above Ahmedabad with the
452 onset of the Asian Summer Monsoon, with decreases occurring at all levels of the troposphere (Ojha
453 et al., 2014).

454

455 d) Climate variability

456

457 While mean climatic conditions are typically established over a 30-year period, climate variability
458 occurs on much shorter time scales of one to several years. Short-term climate variability modifies
459 the long-range transport pathways that channel ozone plumes on regional and intercontinental
460 scales, and also impacts regional-scale ozone photochemistry by modifying cloud cover. The impact
461 of climate variability on ozone transport and chemistry is a relatively new field of study that has
462 explored the effects of such phenomena as El Niño/Southern Oscillation (ENSO), the Pacific-North
463 American (PNA) pattern and the North Atlantic Oscillation (NAO). "The influence on ozone of low
464 frequency climate variability on time scales longer than 30 years has not yet been assessed due to
465 continuous ozone data sets being limited to durations shorter than 30-40 years."

466

467 ENSO has been shown to modulate the tropospheric ozone burden across the tropical Pacific Ocean
468 with lower tropospheric column ozone corresponding to the cloudiest regions (Ziemke and Chandra,
469 2003; Sekiya and Sudo, 2014). Zeng and Pyle (Zeng and Pyle, 2005) calculated an anomalously large
470 increase of stratosphere-troposphere exchange following a typical El Niño year, increasing the global
471 tropospheric ozone burden. In addition, changes in emissions, especially biomass burning,
472 associated with ENSO affect the ozone burden across the tropics (Doherty et al., 2006). ENSO has
473 also been linked to column ozone changes above Europe with positive anomalies of tropospheric
474 ozone column and surface ozone occurring in the spring following an El Niño year, for a variety of
475 reasons including changes in STE, biomass burning emissions and pollution transport pathways from
476 Asia and North America (Koumoutsaris et al., 2008). Voulgarakis *et al.* (Voulgarakis et al., 2010) used
477 a global chemical transport model to determine the interannual variability of the global tropospheric
478 ozone burden for the period 1996-2000 which included the strong El Niño event of 1997-1998. They
479 found that 79% of the interannual variability was due to changes in meteorology (mostly
480 stratosphere-troposphere exchange) and only 11% was due to changes in emissions. Changes in
481 cloudiness contributed a small but non-negligible amount (6%) to the interannual variability. ENSO
482 and the Pacific-North American (PNA) pattern also control the transport of ozone from East Asia to
483 Mauna Loa, Hawaii. A springtime decrease in transport from Asia to Mauna Loa over the period

484 1980-2011 has resulted in no significant ozone trend, while an increase in transport during autumn
485 has produced a very strong ozone trend of 3.5 ± 1.4 ppb decade⁻¹ (Lin et al., 2014b).

486
487 The transport of ozone and other pollutants across the North Atlantic Ocean and the Arctic is heavily
488 influenced by the NAO. During the high phase of the NAO, wintertime pollutant transport into the
489 Arctic is enhanced by 70% compared to times dominated by the low phase, with the major source
490 region being Europe, followed by North America (Eckhardt et al., 2003). The NAO has also been
491 shown to modulate ozone at the high elevation site of Izaña in the subtropical North Atlantic Ocean
492 (Cuevas et al., 2013), with a relaxation of the predominantly high positive phase of the NAO since the
493 mid-1990s allowing increased ozone transport from North America and the lower stratosphere to
494 Izaña in more recent years. Across Europe surface ozone observations tend to correlate positively
495 with the NAO (Pausata et al., 2012).

496
497 While transport of ozone from the stratosphere to the troposphere has a strong seasonal cycle,
498 recent work has also explored changes in the stratosphere-to-troposphere ozone flux and its impact
499 on the tropospheric ozone budget. Several modelling studies have given evidence for such a link
500 (Young et al., 2013; Kawase et al., 2011; Hess and Zbinden, 2013; Voulgarakis et al., 2011; Oman et al.,
501 2013), even demonstrating that the Mount Pinatubo eruption of 1991 reduced the flux of ozone
502 from the stratosphere to the troposphere until 1995 (Tang et al., 2013). According to a model-based
503 analysis, the interannual variability of the ozone mass flux from the stratosphere to the troposphere
504 is on the order of 15% for the Northern Hemisphere and 6% for the Southern Hemisphere (Olsen et
505 al., 2013). Correlations between remotely sensed ozone in the lowermost stratosphere and mid-
506 troposphere indicate that 16% of the northern hemisphere mid-latitude tropospheric interannual
507 ozone variability is controlled by the flux from the stratosphere (Neu et al., 2014). Ordoñez et al.
508 (Ordonez et al., 2007) showed that the positive ozone trends and anomalies in the lower free
509 troposphere over Europe during the 1990s were probably due to enhanced stratospheric ozone
510 contributions (dominated by changes in lower stratospheric ozone concentrations rather than by
511 variations of cross-tropopause air mass transport), particularly in winter–spring. Similarly, Tarasick et
512 al. (Tarasick et al., 2005) using the ozonesonde network over Canada, and Terao et al. (Terao et al.,
513 2008) using a global model for the northern extratropics found positive correlations between ozone
514 in the troposphere and the lowermost stratosphere. Using the same data as Ordoñez et al. (2007) for
515 the lowermost stratosphere, Logan et al. (Logan et al., 2012) found no trends in ozone for the
516 decades 1978-1989, 1990-1999, 2000-2009, except for a marginally significant decrease in winter for
517 1978-1989, driven by very low values in early 1989 and an increase in winter and spring for 1990-
518 1999. They found no evidence in the time series for the lowermost stratosphere from either
519 ozonesondes over North America (Tarasick et al., 2005) or from satellite data (McPeters et al., 2007)
520 to suggest that changes in stratospheric input can explain the increase in ozone over Europe in the
521 1980s. However, increases in stratospheric ozone after 1993 may have contributed to the increase in
522 tropospheric ozone in the 1990s.

523

524 **2.2 Changing ozone – a brief history**

525

526 The German chemist C.F. Schönbein is credited with the discovery of ozone in 1839 (Schönbein,
527 1843) and its presence in the atmosphere was one of his earliest concerns (Braslavsky and Rubin,

528 2011). Early work by Hartley identified its UV spectrum and its role as a UV filter in the atmosphere
529 (Hartley, 1881).

530
531 Modelling studies coupled to limited surface measurements from the late 1800s and early 1900s
532 indicate that ozone concentrations have changed across all scales of the troposphere during the
533 modern era due to enhanced emissions of precursors from industrialisation. A recent assessment
534 (Cooper et al., 2014) of the most reliable historical ozone records (reliable due to the quantitative
535 measurement methods employed), indicates that surface tropospheric ozone levels in western
536 Europe increased by a factor of 3-5 between the late 1800s and late 1900s, and by a factor of 2
537 between the 1950s and 1990s (Wilson et al., 2012; Parrish et al., 2012; Marenco et al., 1994; Staehelin
538 et al., 1994; Volz and Kley, 1988). Many locations around the world monitored ozone in the late
539 1800s and early 1900s using the semi-quantitative Schönbein ozonoscope (Marenco et al.,
540 1994; Bojkov, 1986). These estimates indicate that surface ozone was much lower in those days
541 compared to modern times, but the uncertainty of the measurements is so great that no accurate
542 estimate can be made of the absolute increase in ozone (see the review by (Cooper et al., 2014)).

543
544 Recent modelling studies (Young et al., 2013; Lamarque et al., 2005) suggest that the tropospheric
545 ozone burden in 1850 was 30% lower than the present day (see Figure 6), with the largest
546 contribution to the change coming from the northern hemisphere extratropics. Most current global
547 models are still unable to reproduce the low surface ozone concentrations reliably observed at
548 Montsouris near Paris at the end of the 19th century (Young et al., 2013; Hauglustaine and Brasseur,
549 2001), despite the models having more detailed chemistry schemes, improved emissions estimates
550 and finer spatial resolution (e.g. (Lamarque et al., 2010)). This suggests either problems with
551 interpretation of the original observations and their context, or weaknesses in our assessment of
552 precursor emissions or in our current understanding of atmospheric processes (Mickley et al., 2001).
553 However, the inclusion of bromine chemistry can help models to approach the low ozone values
554 measured at Montsouris in the late 1800s (Parrella et al., 2012).

555

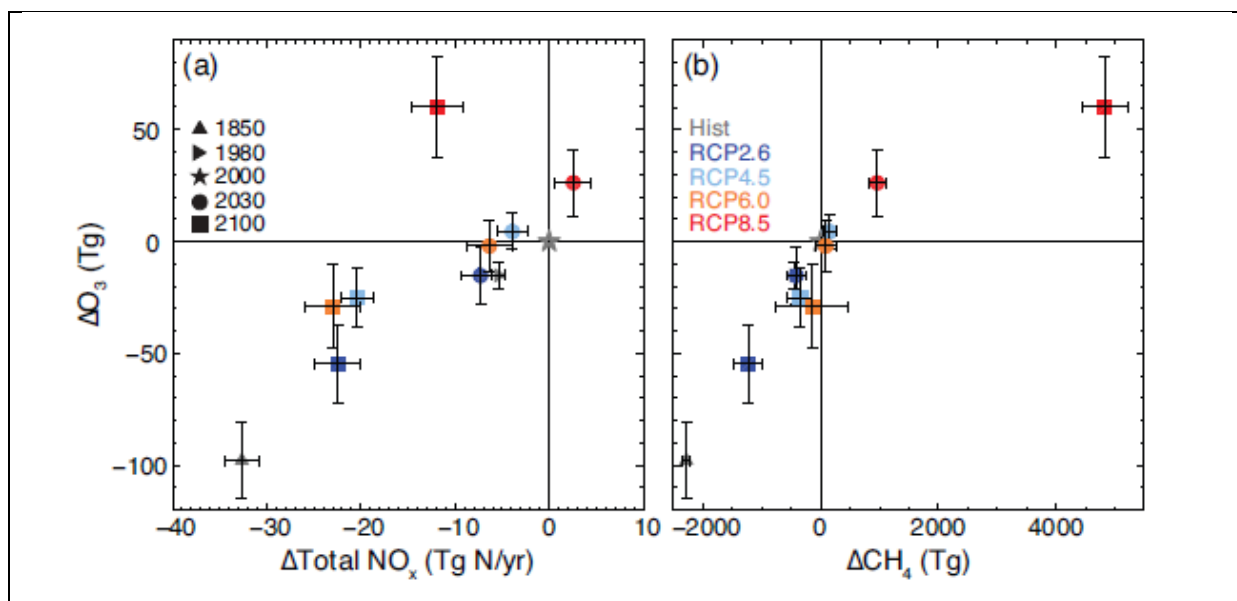


Figure 6 - Ensemble mean change in the tropospheric ozone burden compared to the year 2000 simulation as a function of (a) changes in total NO_x emissions and (b) changes in the tropospheric methane burden. Error bars indicate ± 1 std. dev. of the changes in ozone, NO_x emissions and

methane burdens, calculated from the spread of the models. Different colours represent the different scenarios, whereas different symbols represent the different time slices. (Young et al., 2013)

556

557 Establishing quantitative ozone trends from observations is important for testing our understanding
558 of the processes affecting ozone in the troposphere and for the attribution of these ozone changes to
559 changes in precursor emissions, removal processes and meteorology. It is also important from an air
560 quality perspective for determining the effect of emission controls and for identifying the extent to
561 which surface ozone is locally or regionally controllable. Observed ozone trends are a challenge to
562 interpret as there are a number of factors that may be responsible (Cape, 2008) including (a) changes
563 in anthropogenic emissions of precursors (local, regional and global), (b) effects of biomass burning
564 (both regional and global), (c) changes in Stratosphere-Troposphere exchange, (d) changes in
565 geographical emission patterns, (e) changes in land cover and (f) changes in meteorology e.g.
566 transport patterns, rain, radiation, temperature etc. Long time series of high quality measurement
567 data are required in order to detect the trend above the large inter-annual variation (Staehelin,
568 2003; Weatherhead et al., 1998; Weatherhead et al., 2002) and the sensitivity of the extracted trends
569 to location necessitates that this is done at a range of sites to ensure representativeness and permit
570 attribution of the observed changes. Jonson et al. (Jonson et al., 2006) have discussed some of these
571 effects in relation to ozone trends.

572

573 Global tropospheric ozone trends were recently assessed by the Intergovernmental Panel on Climate
574 Change (IPCC, 2013), and by Cooper et al. (2014) who provided an expanded discussion and update
575 to the IPCC assessment. Following is a summary of the findings from Cooper et al. (2014). Prior to
576 the 1970s, the only rural or remote quantitative ozone measurements outside of western Europe
577 were some short-term observations from Antarctica (Wexler et al., 1960) and Mauna Loa, Hawaii
578 (Junge, 1962) during the late 1950s. By the early and mid-1970s quantitative and continuous ozone
579 measurements were made at several rural and remote locations around the world for the purposes
580 of detecting long-term changes in the global composition of the atmosphere. Continuous records in
581 southern Germany began at the rural hilltop site of Hohenpeissenberg in 1971 and the mountaintop
582 site of Zugspitze (2670 m) in 1978, and measurements began at the summit of Whiteface Mountain
583 in upstate New York in 1973. Ozone measurements at remote sites were established by the U.S.
584 National Oceanic and Atmospheric Administration at its baseline observatories of Mauna Loa, Hawaii
585 (1973), Barrow, Alaska (1973), the South Pole (1975), and American Samoa (1976) (Oltmans et al.,
586 2013). Routine ozonesonde profiles became available in Germany, the US, Japan and Antarctica in
587 the early 1970s (Oltmans et al., 2013) and ship-borne monitoring of the marine boundary layer of the
588 North and South Atlantic Oceans began in the late 1970s (Lelieveld et al., 2004). The number of
589 urban rural and remote monitoring sites has continued to grow from the 1970s to the present day.

590

591 All available northern hemisphere surface monitoring sites indicate increasing ozone from 1950-1979
592 until 2000-2010, with 11 of 13 sites having statistically significant trends of 1-5 ppbv decade⁻¹,
593 corresponding to >100% ozone increases since the 1950s, and 9-55% ozone increases since the
594 1970s. In the southern hemisphere only 6 sites are available since the 1970s, all indicating increasing
595 ozone with 3 having statistically significant trends of 2 ppbv decade⁻¹. Ozone monitoring in the free
596 troposphere since the 1970s is even more limited than at the surface. Significant positive trends
597 since 1971 have been observed using ozonesondes above Western Europe, Japan and coastal

598 Antarctica (rates of increase range from 1-3 ppbv decade⁻¹), but not at all levels. In addition, aircraft
599 have measured significant upper tropospheric trends in one or more seasons above the north-
600 eastern USA, the North Atlantic Ocean, Europe, the Middle East, northern India, southern China and
601 Japan. Notably, no site or region has shown a significant negative ozone trend in the free
602 troposphere since the 1970s. From 1990 until 2010, surface ozone trends have varied by region.
603 Western Europe showed increasing ozone in the 1990s followed by a levelling off, or decrease since
604 2000. In the eastern US rural surface ozone has decreased strongly in summer, is largely unchanged
605 in spring, and has increased in winter. In contrast, few rural sites in the western US indicate
606 decreasing ozone, with half of all rural sites showing a significant increase in spring. The decrease in
607 ozone in Europe and the eastern USA is consistent with the decrease in ozone precursors in those
608 regions. Meanwhile in East Asia surface ozone is generally increasing where ozone precursor
609 emissions are growing.

610
611 Parrish et al. (Parrish et al., 2013) demonstrate that another manifestation of changes in
612 tropospheric O₃ is a shift of the seasonal cycle at northern mid-latitudes so that the observed peak
613 concentrations now appear earlier in the year than they did in previous decades (see Figure 7). The
614 rate of this shift has been about 3 to 6 days per decade since the 1970s. Parrish et al. (2013) put
615 forward an untested hypothesis that this shift may be due to changes in atmospheric transport
616 patterns combined with spatial and temporal changes in emissions. This study relied on three long
617 term (> 20 years) rural datasets in western Europe and one in the western USA. Cooper et al.
618 (Cooper et al., 2014) also explored this topic using 21-year data sets from one additional site in
619 western Europe and 5 additional sites in the USA, all in rural locations but more heavily influenced by
620 regional ozone precursor emissions than those examined by Parrish et al. (2013). Of these 6 sites
621 only three showed an earlier seasonal ozone peak, therefore the seasonal shift in the ozone cycle is
622 not universal for time periods of 21 years or less. Similar shifts in the ozone seasonal cycle have been
623 observed in the continental USA (Clifton et al., 2014; Simon et al., 2015; Bloomer et al., 2010).
624

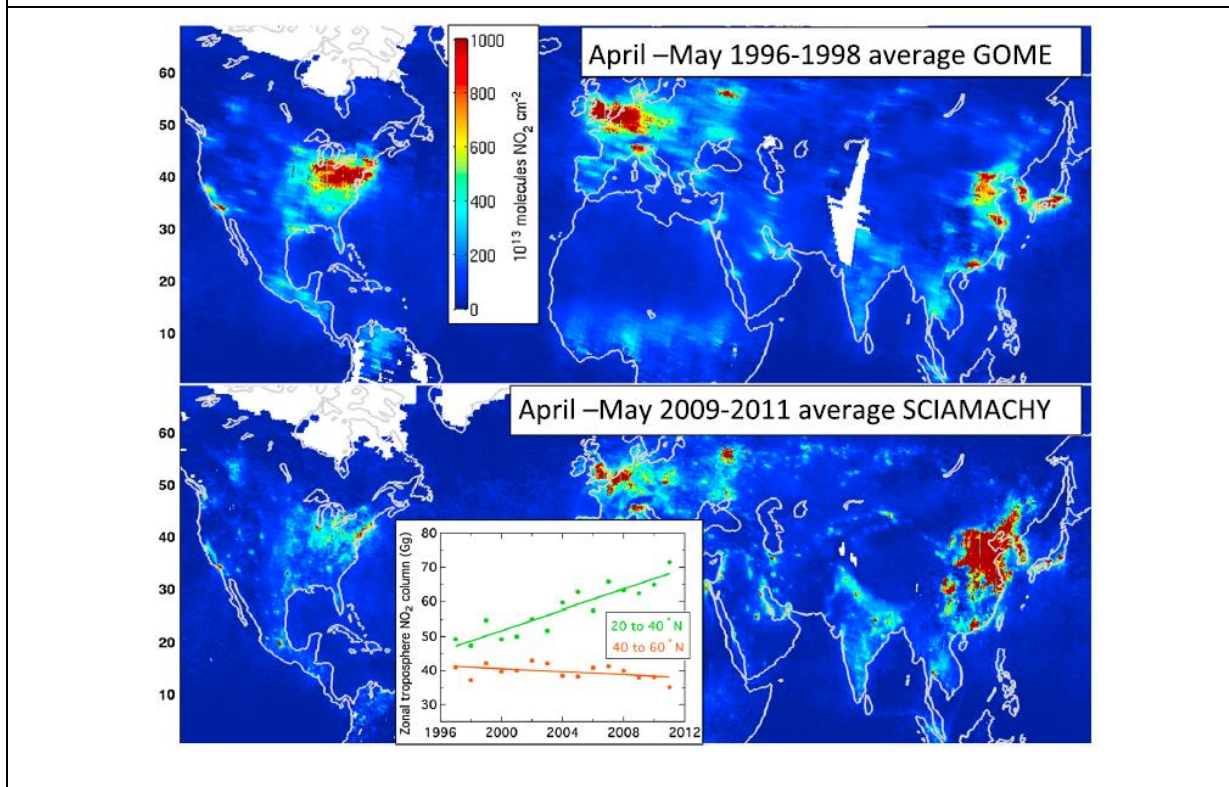
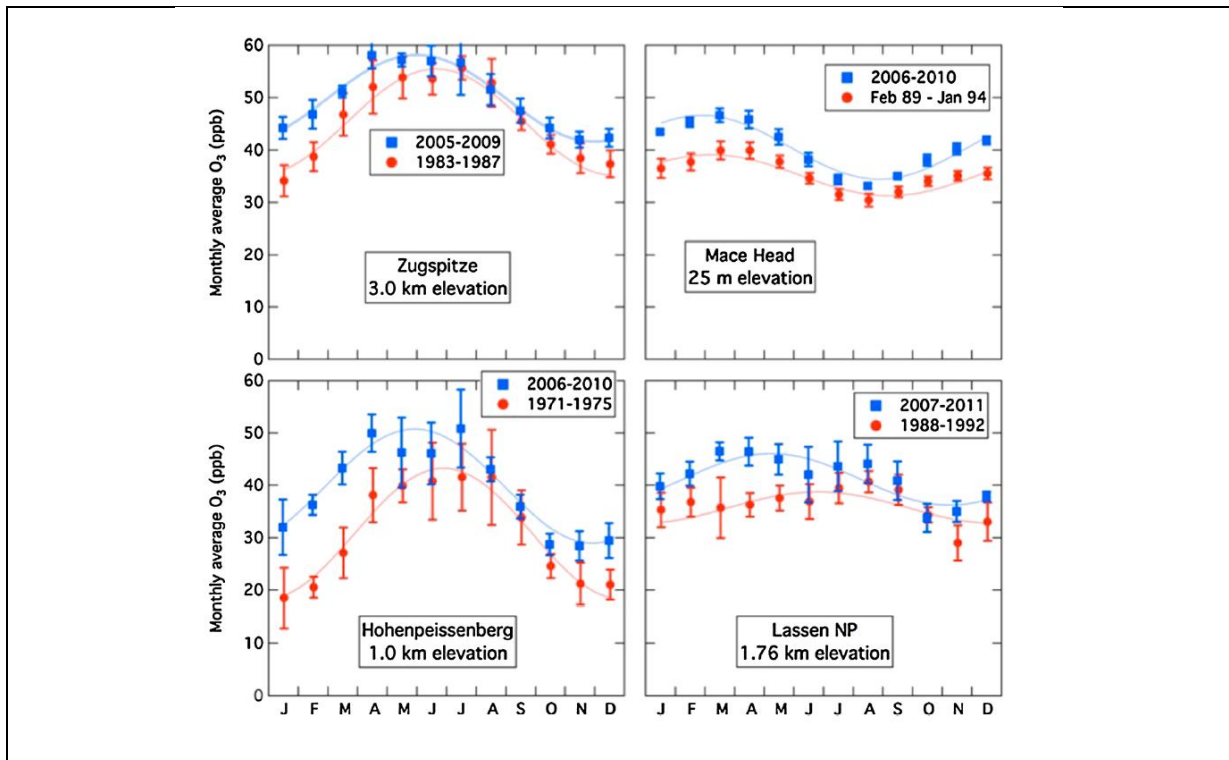


Figure 7 – a) Comparison of O₃ seasonal cycles at three European and one North American site for two periods separated by 17 to 35 years. The data points and error bars indicate 5 year averages and standard deviations of monthly averaged data for the indicated time periods. The curves of the respective colours are sine function fits to the data. b) Comparison of satellite measured springtime tropospheric NO₂ columns during two time periods separated by 13 years. The inset shows the temporal change in the total zonal troposphere NO₂ column for two Northern Hemisphere Latitude bands. (Parrish et al., 2013).

626

627 Episodic peak ozone levels in rural areas of Europe have been declining during the last three
628 decades due to regional pollution emission controls applied to the VOC and NO_x emissions from fossil
629 fuel combustion associated with motor vehicles and power plants (Jonson et al., 2006; Jenkin,
630 2008; Derwent et al., 2010). Long-term downward trends have been observed at many long-running
631 rural monitoring stations in the EMEP ozone monitoring network and appear to be more pronounced
632 at those stations where initial episodic peak levels were highest and insignificant at those stations
633 where initial levels were lowest (Derwent and Hjellbrekke, 2013). This behaviour has been
634 interpreted as resulting from the combined effect of regional pollution controls since 1990 (Vautard
635 et al., 2006) and increasing hemispheric ozone levels (Derwent and Hjellbrekke, 2013). In contrast,
636 episodic ozone levels in the high NO_x environments of major European towns and cities are now
637 rising towards the levels found in the rural areas surrounding them, as exhaust gas catalysts fitted to
638 petrol and diesel motor vehicles reduce the scavenging of ozone by chemical reaction with emitted
639 nitric oxide (Wilson et al., 2012; Colette et al., 2011).

640

641 Whereas the vast majority of the scientific literature on ozone trends relies on rural
642 supersites dedicated to the assessment of long term atmospheric change, the records of regulatory
643 monitoring networks are becoming progressively long enough to complete such assessments. In the
644 1990s European air quality legislation began to include some targets with regards to the ozone
645 monitoring network, so that the network now includes several thousand sites, a few hundred of
646 which have records longer than 10 years. The size and diversity of the data gathered in the Airbase
647 repository (maintained by EEA) offers an unprecedented view into air quality trends in Europe,
648 provided that (1) 10-yr records can be considered long-enough to assess trends, and (2) the station
649 representativeness of thousands of urban and rural background sites can be compared to the
650 handful of supersites used elsewhere. Colette et al (Colette et al., 2011) and Wilson et al. (2012)
651 (Wilson et al., 2012) propose such assessments and conclude that the dominating picture is towards
652 an increase of ozone in urban areas or non-significance of the rural background trends. They both
653 report that the fraction of sites with an increasing trend is smaller when looking at peaks compared
654 to daily means, but their findings suggest that the earlier reports of opposite signs of trends (Vautard
655 et al., 2006) does not hold for this more recent period using this alternate monitoring dataset. By
656 including urban stations in their analysis, Colette et al. (2011) also find an enhanced contribution of
657 upwards trends, hence consolidating the results of Derwent and Hjellbrekke (Derwent and
658 Hjellbrekke, 2013) regarding the fact that urban areas are gradually becoming closer to rural levels.

659

660 The anthropogenic contributions to the observed trends are difficult to extract from the
661 measurements, and reflect changes in both the magnitude and distribution of precursor emissions.
662 While global average ozone responds to changes in global precursor emissions, trends at a given
663 location are influenced by local, regional and global emission changes that may offset each other.
664 Multi-model ensemble studies of the contribution of regional anthropogenic emission changes to
665 regional and global surface ozone conducted under the LRTAP task force on Hemispheric Transport
666 of Air Pollution, HTAP, (Fiore et al., 2009; HTAP, 2010) have been used to assess the relative
667 contributions of long range transport and regional emission changes to regional ozone (Wild et al.,
668 2012). These show annual mean surface ozone increases of nearly 0.3 ppb/yr at northern mid-
669 latitudes between 1960-1980, similar to observed changes (e.g., (Parrish et al., 2012)), but small net

670 decreases in surface ozone over Europe and North America since 1990 when anthropogenic
671 emissions over these regions are believed to have peaked. A recent comparison between ozone
672 observations at northern mid-latitudes and output from three current chemistry-climate models
673 shows that the models (1) overestimate ozone mixing ratios, on average by ~5 to 17 ppbv in the year
674 2000, (2) capture only ~50% of ozone changes observed over the past five to six decades, and little of
675 observed seasonal differences, and (3) capture ~25 to 45% of the rate of change of the long-term
676 changes (Parrish et al., 2014). These differences may reflect poor representation of emission
677 changes or ozone changes due to natural sources, or they may reflect more fundamental weaknesses
678 in resolving key chemical, dynamical processes or climate variability over continental regions. Further
679 detailed analysis of the spatial and seasonal variability of local and regional ozone trends should
680 provide a more critical test of our current understanding of the processes affecting ozone as
681 represented in current models.

682

683 2.3 Ozone precursors

684

685 The spatial and temporal distribution of ozone and its precursors are in large part driven by the
686 distribution of their emissions. An accurate knowledge of the surface emissions and of their
687 evolution with time is therefore essential to support the analysis and modelling of air quality and
688 climate change interactions. Up-to-date and consistent emissions are moreover required for the
689 forecasting of the atmospheric composition (Frost et al., 2012).

690 Gridded global, regional, and national emission estimates exist for many of the pollutants that are
691 important for understanding and analysing the distribution of ozone and its precursors, i.e. NO_x, CO,
692 CH₄ and volatile organic compounds (VOCs). Some of these inventories are publicly available,
693 whereas others are developed by individual research groups or government agencies to study
694 specific aspects of emissions or atmospheric processes and are not always easy to access. In this
695 paper, we will focus only on publicly available datasets.

696 Some inventories provide global coverage with relatively coarse spatial resolution, while others focus
697 only on a specific region for selected species, and provide information at a very high spatial
698 resolution; other inventories consider only specific sectors (such as traffic, shipping, etc.)

699 Over the past few years, several inventories providing the distribution of surface emissions of
700 gaseous and particulate species were developed, at both the global and regional scales. This section
701 will review the main advances during the past few years concerning surface emissions having the
702 potential to impact ozone distributions and trends. The section will also discuss the current
703 information on emissions uncertainties and we will briefly review the most recent studies using
704 inverse modelling techniques to evaluate and optimize emission inventories.

705 2.3.1 Quantification of global emissions of ozone precursors during the past decades

706 Most anthropogenic emissions estimates are developed using the same methodology, based on the
707 product of estimates for activity data for different sectors and emission factors (mass emitted per
708 activity unit). Activity data are obtained from records provided by different countries or from

709 international organizations such as the International Energy Agency or the United Nations. This leads
710 to a country-based quantification of emissions, which are then gridded using different types of
711 proxies such as population, traffic, ship routes or location of power plants/factories. The quality of
712 the gridding depends on the quality and availability of the proxies, and therefore varies strongly
713 among the different regions of the world.

714 The data used for the quantification of emissions are not always consistent and many inventory
715 developers adjust these data based on expert judgment. *A priori* emission factors are not always
716 available or reported for all countries and for the differing emission sectors. They depend on
717 different factors such as the level of economic development and the type of technology used in each
718 region.

719 The emissions inventories developed in the past years cover both global and regional scales. Some of
720 these inventories provide emissions at the country level; some provide emissions for a few species or
721 for a larger number of species, and some provide emissions for one year, a few years or a few
722 decades. The main inventories providing emissions of gaseous and particulate compounds currently
723 used in global modelling or analysis of the atmospheric composition at the global scale and its
724 evolution are: ACCMIP (1850-2000 on a decadal time scale; (Lamarque et al., 2010)) and its extension
725 MACCity (monthly averages for the 1980-2010 period; (Granier et al., 2011)); EDGARv4.2 (1970-2008;
726 (Janssens-Maenhout et al., 2011)) and HTAPv2 (2008 and 2010;(Janssens-Maenhout et al., 2012));
727 ECLIPSE (2005-2050; (Klimont et al., 2013b)); RETRO (1960-2000;(Schultz et al., 2007a)); HYDE (1890-
728 1990; (van Aardenne et al., 2001)); POET (1990 and 2000;(Granier et al., 2005)); EDGAR3.2 (year
729 2000; (Olivier et al., 2005)).

730 Several inventories also provide emissions at the regional scale for different regions of the world.
731 Among these inventories, the TNO-MACC (Kuenen et al., 2011) and TNO-MACCII (Kuenen et al.,
732 2014) provide emissions for Europe at a high spatial resolution ($1/8^{\text{th}} \times 1/6^{\text{th}}$ degree), based on the
733 EMEP (Droge et al., 2010) emissions reported by the European countries. In North America, the US
734 Environmental Protection Agency (EPA) provides emissions since 1980 for the USA (available at
735 <http://www.epa.gov/ttnchie1/>), and Environment Canada provides non-gridded emissions for
736 Canada since 1985 (available at: <http://www.ec.gc.ca>). Inventories are provided for Asia by the REAS-
737 v1 (0.5x0.5 degree spatial resolution; (Ohara et al., 2007)) and REAS-v2 (0.25x0.25 degree spatial
738 resolution; (Kurokawa et al., 2013b)). The MEIC dataset (available at meicmodel.org) also provides
739 emissions for China, at a 0.25x0.25 degree resolution, and Sahu et al (Sahu et al., 2012) provide
740 emissions at a 1x1 degree resolution for India, as well as Garg et al. ((Garg et al., 2006) not gridded
741 emissions). Recently, an inventory was also developed for Africa by Lioussse et al. (Lioussse et al.,
742 2014) at a 0.25x0.25 degree spatial resolution.

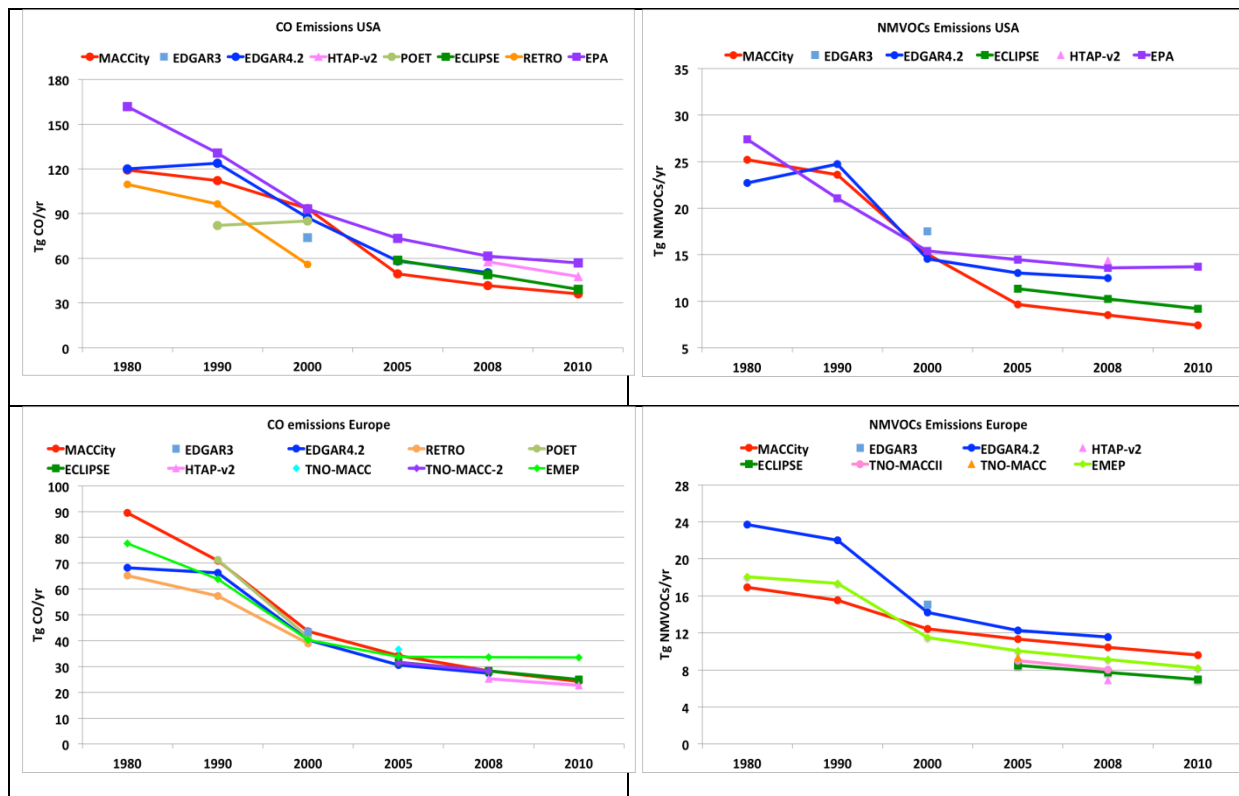
743 2.3.3 Evolution of emissions in different regions since the 1980s

744 During the past three decades and the past few years, surface anthropogenic emissions have shown
745 large changes in a few regions of the world. This section will focus on changes in emissions in Europe,
746 North America and Asia. There is still little information on emissions changes in other areas of the
747 world, and no detailed evaluation of the trends in emissions in these other regions can be made.

748 a. Emissions in Europe and North America

749 The implementation of emissions policies reductions in Europe and in North America over the past

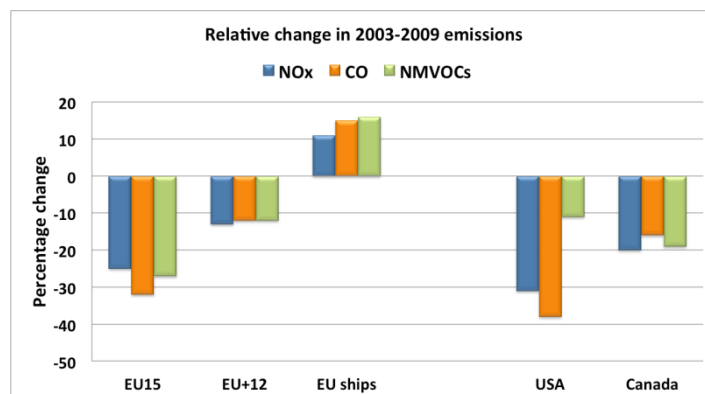
750 few decades has led to significant decreases in the emissions of ozone precursors. The agreement
 751 between available global and regional inventories is rather good among these inventories providing
 752 emissions of CO and NO_x for Europe and of NO_x for North America, with differences of 20-30%
 753 between the lowest and highest proposed values. However, larger differences are obtained between
 754 inventories providing CO in the USA and NMVOCs in all regions, as shown in Figure 8.



755 **Figure 8-** Emissions of CO and NMVOCs in the USA and Europe (Western and Central Europe) from
 756 various emission inventories.

757 A detailed analysis of the changes in emissions of ozone precursors in Europe between 2003 and
 758 2009 has been performed by Kuenen et al (Kuenen et al., 2014). This analysis has been extended in
 759 Figure 9 by adding emissions for USA and in Canada for the same period. These data highlight the
 760 significant decrease in the emissions of NO_x, CO and NMVOC over the European and North American
 761 continental regions. The changes in Figure 9 include shipping activities around Europe and the
 762 European seas. In contrast to industrial activities and to transportation in continental areas of
 763 Europe and North America, policies leading to the reduction of emissions from shipping have not yet
 764 been defined or implemented, resulting in significant increases in these emissions.

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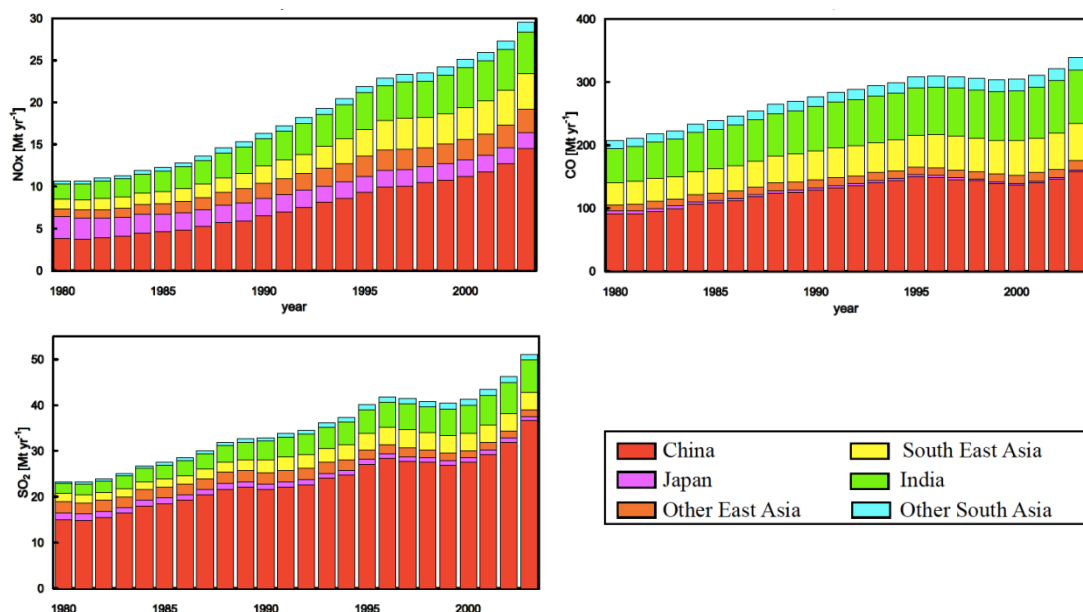
767 **Figure 9** - Relative change in NO_x, CO and NMVOCs emissions from 2003 to 2009 (from Kuenen et
 768 al., 2014), per country group: EU15 includes the EU Member States in 1995 as well as Norway and
 769 Switzerland, EU+12 includes the 12 New Member States, EU ships refers to all European sea regions
 770 combined. USA emissions are from the USA Environmental Protection Agency (EPA) and data for
 771 Canada are from Environment Canada.

772

773 b. Emissions in Asia

774 Emissions in Asia have shown dramatic increases over the past few years, which are now well
 775 documented, more particularly for China. Figure 10 shows the changes in the emissions of NO_x, CO
 776 and SO₂ for different Asian regions since 1980: the data in Figure 10 highlight the very large increase
 777 in NO_x emissions in China over the past few years. The main reason for these emissions changes are
 778 increases in coal use for energy generation and industrial activities, as well as a large increase in the
 779 number of vehicles (Kurokawa et al., 2013a). Zhao et al. (Zhao et al., 2013) have examined the
 780 impact of anthropogenic emissions control in China and have shown that these control measures
 781 have led to a decrease in the emissions factors and emissions for most compounds, except for
 782 nitrogen oxides.

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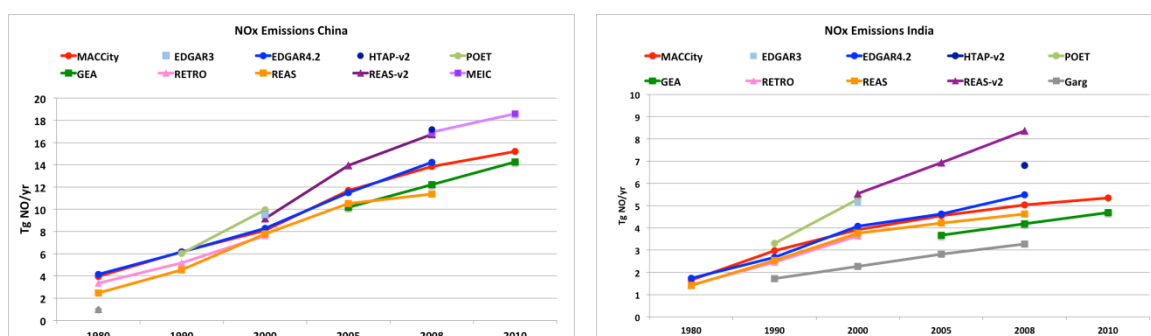
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786 **Figure 10** - Evolution of surface emissions of CO, NO_x and SO₂ for each Asian region (from
 787 Kurokawa et al., 2013).

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Comparisons between the regional and global inventories show significant differences, as shown in Figure 11 (Granier et al., in preparation, 2014): these figures show the total anthropogenic emissions of NO_x in China and India from 1980 to 2010, based on the data provided by the inventories mentioned in Section 2.3.1. All the inventories show an increase in the emissions over the years of the NO_x emissions, but the magnitude of the emissions and the rate of increase differ significantly between the datasets. There is a difference of about 50% between the lowest and highest total emissions in China. For India, the range of values proposed by the different groups is even larger, with a factor of about 2.5 between the lowest and highest emissions. Since NO_x concentration levels are a key factor in the production of ozone (see Section 2.1), such large differences in the emissions could make the analysis of ozone concentrations and their trends rather difficult to achieve. It should be noted that Figures 8 and 11 does not display any evaluation of the uncertainties on the inventories: since the data used for developing the inventories (activity data, emission factors) are not provided with estimates of the uncertainties, no estimation of the uncertainties on the emissions can be made.



804

805 **Figure 11** - Evolution of NO_x emissions in China and India from 1980 to 2010 provided by different
806 global and regional inventories (Units are Tg NO/year)

807 c) Shipping

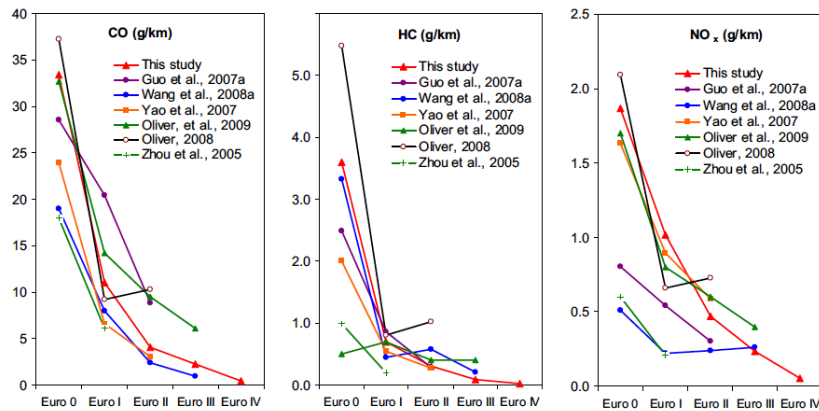
808 It is worth noting that nearly 70% of ship emissions occur within 400 km of coastlines, causing air
809 quality problems through the formation of ground-level ozone, sulphur emissions and particulate
810 matter in coastal areas and harbours with heavy traffic (Eyring et al., 2010). Offshore shipping
811 sources of NO_x may become significant as land based-emissions decline (Eyring et al., 2010; Jonson et
812 al., 2009; Dalsøren et al., 2010). The impact of ship emissions on tropospheric oxidants is mainly
813 caused by the relatively large fraction of NO_x in ship exhaust. Dalsoren et al (Dalsøren et al., 2010)
814 have shown that typical increases in yearly average surface ozone concentrations in the most
815 impacted areas from shipping emissions are 0.5–2.5 ppbV. Transport emissions are predicted to be a
816 significant contributor to US and European ozone by 2050 (Hauglustaine and Koffi, 2012).

817

818 **2.3.4 Uncertainties in anthropogenic emissions in different regions**

819 As indicated in the previous section, most emission datasets are provided without any information
820 on uncertainties on the data used for quantifying the emissions. Several sources of uncertainties
821 have been identified, which will be summarized in this section.

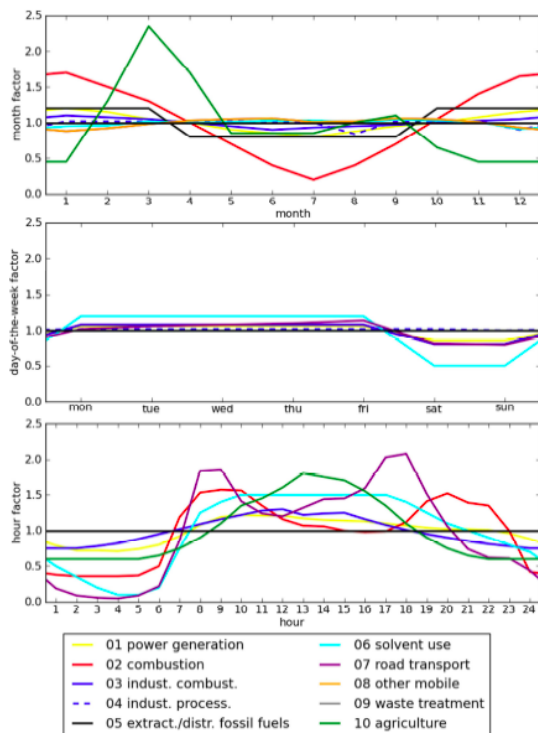
822 Activity data and emission factors are generally provided without any information on their
 823 uncertainties. Emission factors are empirical functional relations between pollutant emissions and
 824 the activity that causes them: a comparison of emission factors is shown on Figure 12, which displays
 825 measurements of emission factors in Chinese cities from different studies (Huo et al., 2012). This
 826 study has shown that the differences between emission factors are larger for older vehicles than for
 827 newer vehicles, which could be an indication of varying deterioration of emissions as vehicles get
 828 older.



829
 830 **Figure 12** - Comparison of emission factors of the LDGVs (light-duty goods vehicles) under real world
 831 driving conditions from different studies showing the greater variation for older vehicles. Note that
 832 the emission measurement technologies are different among these studies (from (Huo et al., 2012)).

833 The seasonal, weekly and daily variations of the emissions are generally not provided with
 834 inventories, and are not well characterized. Simple temporal profiles have been developed to
 835 describe the changes in emissions over a day, a week and a season, as shown in Figure 13 for the
 836 European LOTOS-EUROS model (Kuenen et al., 2011). These profiles depend on the emission sectors.
 837 The same diurnal profiles are applied for all days of the week and to every country in the model
 838 domain for all periods, without taking into account differences in the way of living in different
 839 countries and its change with time. Similar profiles are not available for most countries of the world,
 840 leading to large uncertainties in the temporal profiles of the emissions.

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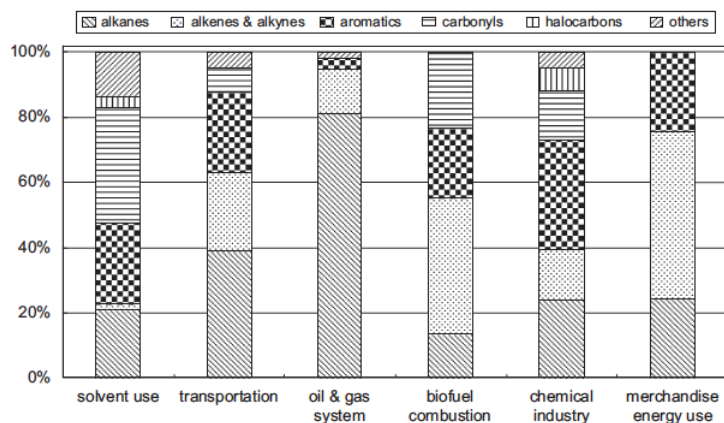


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843 **Figure 13** - Monthly (top), weekly (middle) and hourly (bottom) time profiles applied to
 844 anthropogenic emissions in Europe for different sectors (from Kuenen et al., 2011).

845

846 Good speciation of the NMVOCs lumped species is important for inventories. The translation of
 847 speciation into global and sometimes regional models chemical schemes is generally poor: a gridded
 848 speciated dataset has been developed as part of the RETRO inventory (Schultz et al., 2007a), and has
 849 not been revised or updated since. This speciation is currently applied to most global inventories, for
 850 all the past and future decades. In different regions, VOC speciated inventories have been developed
 851 for specific emission sectors often based on a few individual measurements that are extrapolated
 852 with dubious reliability to related unmeasured emission sources. An example of such a speciation is
 853 shown in Figure 14 for China (Wei et al., 2008). Li et al. (Li et al., 2014a) have developed a speciation
 854 for Asia, which provides emissions of a large set of VOCs for different model chemical schemes, for
 855 individual VOCs and lumped species.



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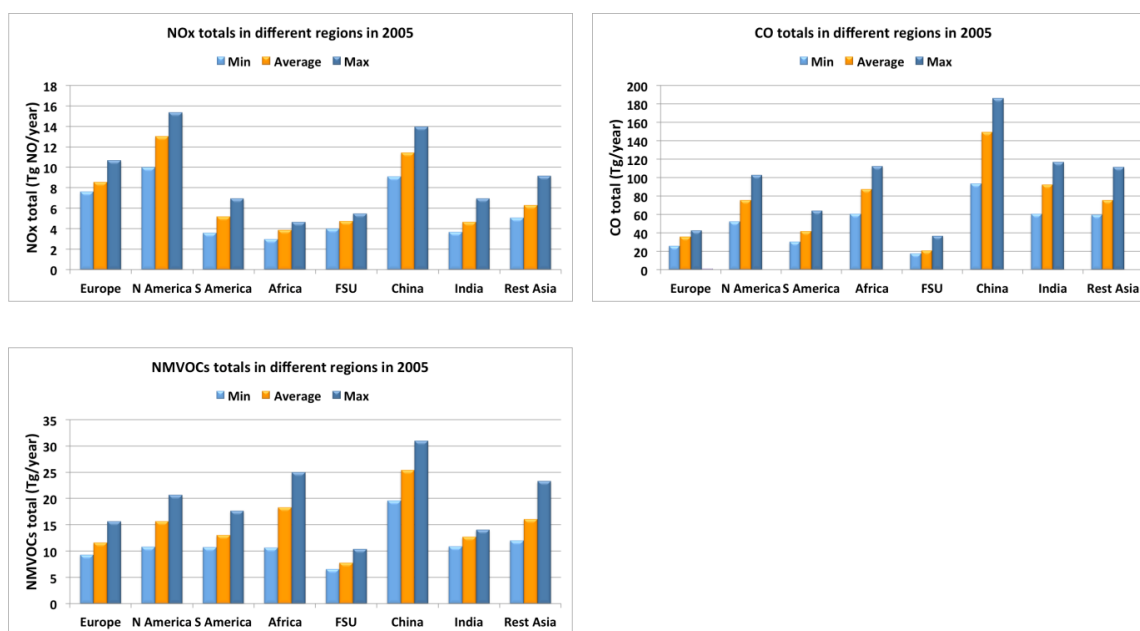
857 **Figure 14** - Chemical speciation for various emission sectors in China (Wei et al., 2008) showing the
 858 wide variation of VOCs with source that need to be represented in emission inventories.

859 Detailed information on the proxies used for the determination of the distribution in space of the
 860 emissions, i.e. on the proxies used for gridding emissions are also lacking. Other large uncertainties in
 861 the emissions are linked with resources (oil and gas) extraction and flaring, and to inland and
 862 international shipping. Emissions from agricultural practices (cattle, fertilizers, agriculture waste
 863 burning) are also very uncertain.

864 In order to summarize the uncertainties on anthropogenic emissions, we have calculated, for all the
 865 inventories mentioned in Section 2.3.1 the minimum, average and maximum values of the emissions
 866 for different world regions for NO_x, CO and NMVOCs emissions in 2005. The ranges shown in Figure
 867 15 cannot be considered as a quantification of uncertainties, but they provide information on the
 868 differences between currently available datasets. Detailed evaluations of the uncertainties on
 869 anthropogenic emissions have started: for example, a methodology applying Monte Carlo
 870 simulations to quantify the uncertainties, represented as probability distributions, for the emissions
 871 of several compounds in China was proposed by Zhao et al. (Zhao et al., 2011).

872 Figure 15 also highlights the emissions in Africa and the rest of Asia (all Asian regions except China
 873 and India), regions where more detailed information is required for a better analysis and modelling
 874 of the global atmospheric composition.

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 879 **Figure 15** - Minimum, average and maximum emissions taken from various inventories of NO_x, CO
 880 and NMVOCs for different regions of the world in 2005. The emissions of NO_x are reported in Tg
 881 NO/year.

882 **2.3.5 Emissions from fires**

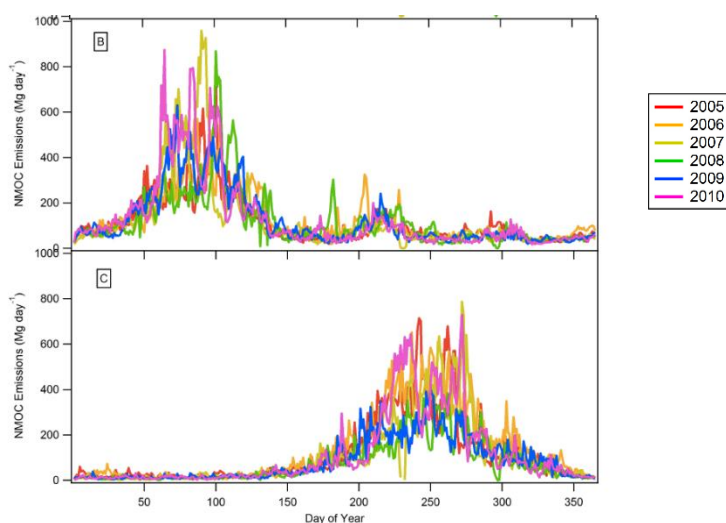
883 In the last few decades biomass burning has been recognized as an important source of ozone
 884 precursors (Hao and Liu, 1994;Schultz et al., 2008;Turquety et al., 2007). Since wildfires are strongly

885 dependent on meteorological conditions, drought episodes and human behaviour, they have a large
886 interannual variability (Duncan et al., 2003) and the resulting emissions are very variable in time and
887 space. It is therefore important to accurately characterize fire emissions, since they will partly drive
888 the short-term variability of ozone precursors and ozone (Parrington et al., 2012). A review of the
889 impact of biomass burning emissions on ozone was published by Jaffe and Wigder (Jaffe and Wigder,
890 2012).

891 The first inventories relied on data reported by forest services, observations from the ground and
892 from aircraft. Since the late 1990s, several inventories providing emissions from fires have been
893 developed based on observation of active fires and burnt areas by satellites, and more recently of
894 fire radiative energy. Other inventories have also been developed, through the representation of
895 fires in biogeochemical models. The most recent global datasets providing a spatial distribution of
896 the emissions of ozone precursors from fires are: MACCity (monthly, 1960-2008, 0.5x0.5 degree
897 resolution; (Granier et al., 2011)), GFAS (daily, 2003 to present, 0.5x0.5 degree resolution; (Kaiser et
898 al., 2012)), GFEDv2 (monthly, 1997-2010, 0.5x0.5 degree resolution) and GFEDv3 (monthly, 1997-
899 2010, 0.5x0.5 degree resolution) (van der Werf et al., 2006; van der Werf et al., 2010), IS4FIRES (daily,
900 2000-2013, 0.1x0.1 degree resolution, (Sofiev et al., 2009)), FINN (daily, 2002-current, 1x1 km
901 resolution, (Wiedinmyer et al., 2011)), GUESS-ES (monthly, 1970-2009, 1x1 degree resolution, (Knorr
902 et al., 2012)), GICC (monthly, 1900-2005, 0.5x0.5 degree resolution, (Mieville et al., 2010)), Kloster
903 (monthly, 1900-2004, 1.9x2.5 degree resolution, (Kloster et al., 2010)), RETRO (monthly, 1980-2000;
904 0.5x0.5 degree resolution, (Schultz et al., 2008)).

905 The inventories providing daily emissions have highlighted the very large variability of emissions from
906 fires in the different regions of the world. Only datasets providing emissions at a high temporal
907 resolution are able to provide information on short and intense fire episodes, which happen often in
908 different regions of the world, as a result of specific weather conditions or human-ignited fires. An
909 example of this variability is shown on Figure 16, from the FINN datasets (Wiedinmyer et al., 2011),
910 which also highlights the large number of high fire episodes in each hemisphere.

911

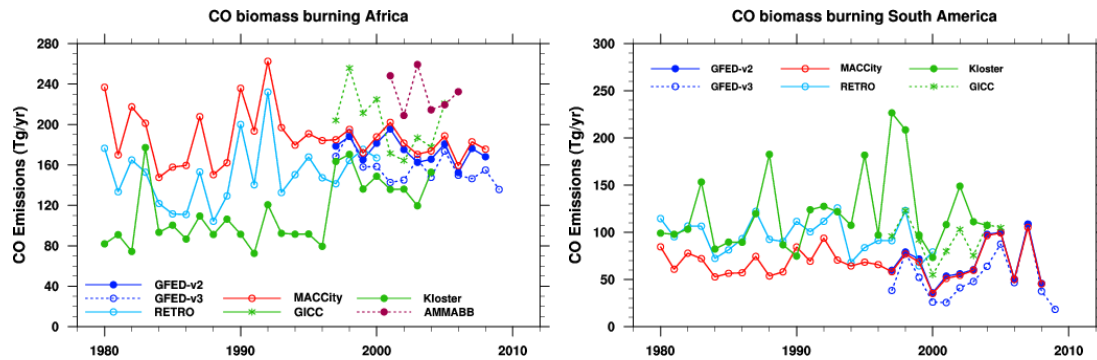


912

913 **Figure 16** - Daily emissions of NMVOC from fires for 2005 through 2010 for the Northern Hemisphere
914 (top) and the Southern Hemisphere (bottom) as represented in the FINN dataset (Wiedinmyer et al.,
915 2011).

916 Several studies have evaluated the differences between estimates of fire inventories, and have
 917 highlighted the large differences remaining between available datasets in different regions. Figure 17
 918 displays a comparison of several of the datasets previously detailed, for carbon monoxide in Africa
 919 and South America (from (Granier et al., 2011)). Differences in the emissions for each year, as well as
 920 in the interannual variability of the emissions are very large. It should be noted that the AMMA
 921 inventory for Africa, which includes the use of satellite observations as well as local information on
 922 the fires provides significantly larger emissions than the other inventories, which are based either on
 923 satellite data only, or on fires modelling.

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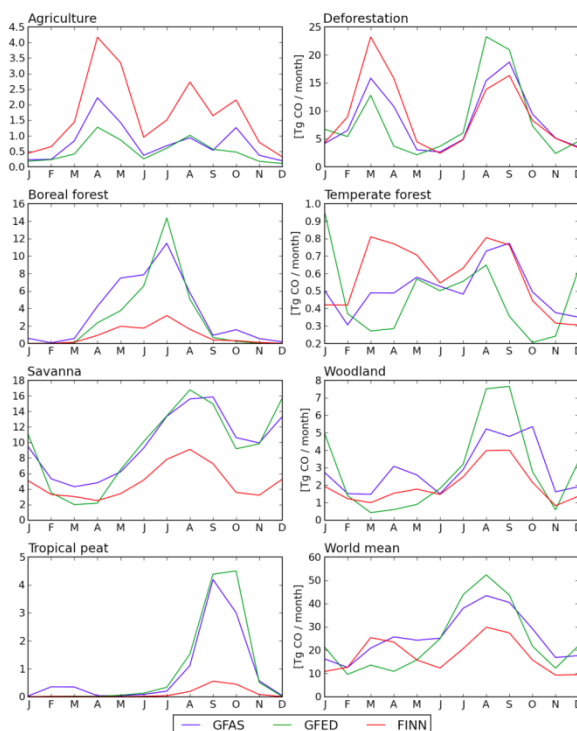


925

926 **Figure 17** - Emissions of CO in Africa (left column) and South America (right column) from 1980 to
 927 2009; from (Granier et al., 2011).

928 Another view of the differences between datasets is provided in Figure 18, where CO emissions from
 929 different estimates are reported for different biomes (from (Kaiser et al., 2013)). The largest
 930 differences are reports for peat and savannah fires. The seasonal variation shown in these datasets is
 931 relatively consistent, except for temperate forests, where the consistency is very low.

932



933

934 **Figure 18** - Mean seasonal CO emissions for 7 biomes associated with dominant fire type in GFED
935 (see Figure 17) and the world for 2003 until 2011. Emissions are shown for three different fire
936 emission inventories: GFAS, GFED and FINN (Kaiser et al., 2013).

937 The differences shown in Figure 18 demonstrate a limit to the accuracy of emissions resulting from
938 biomass burning. In turn, these impact on the distribution of ozone precursors and ozone through
939 uncertainties on burned area, fuel load, emission factors and injection heights.

940 Data on burned areas from long-term monitoring have become available only recently, i.e. after
941 1995, and these data have been evaluated only for a few regions. The satellite data provide good
942 information on spatial and temporal patterns of fire occurrence, but so far they have not provided
943 quantitative information with high accuracy (e.g., (Giglio and Kendall, 2004)). These data
944 complement data on fires in the mid-latitude regions, which are well monitored in many countries.
945 However, monitoring by tropical countries is still scattered and scarce, owing to limited resources at
946 the local level for records and accessibility. The effect of temporal resolution of fire emissions on
947 models has been recently explored (Marlier et al., 2014).

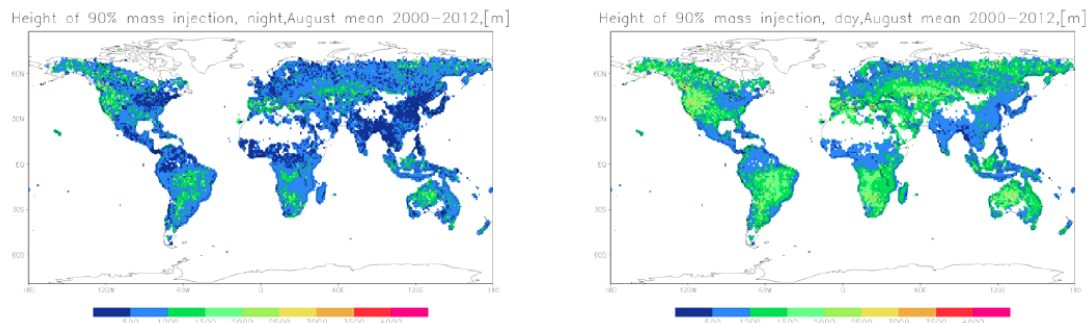
948 The amount of fuel load and the combustion factors are calculated either from ecosystem models or
949 through empirical formulas: these quantities depend on the fire severity, the fuel characteristics
950 (foliage and biomass density, moisture, vegetation type, organic content and moisture of the soil)
951 and the rate of spreading. These factors are highly variable and different studies have shown that
952 large uncertainties still remain in the spatial and temporal variation of this quantity. A study by Knorr
953 et al. (Knorr et al., 2012) has shown that the choice of the burned area dataset has by far the largest
954 impact on interannual variability of simulated emissions, and that for the quantification of the total
955 global emissions, burned area and combustion completeness have the largest impact on emissions
956 for most species.

957 Emissions factors for the different species are generally taken as constant for each type of ecosystem
958 in different countries. However, emissions from a fire depend on the fuel type and fire
959 characteristics, and they are often poorly determined. Most inventories currently use the emission
960 factors compiled by Akagi et al. (Akagi et al., 2011) or the Andreae and Merlet (Andreae and Merlet,
961 2001) compilation and following updates. Results from different studies nevertheless stress that
962 more complete combustion, as in flaming fires, would lead to a larger fraction of highly oxidized
963 species (e.g., CO₂, NO_x), while smouldering fires release more material in reduced form (e.g., CO, NH₃
964 and NMVOC species), which indicates that emission factors may vary with season, and that fire
965 characteristics can be very different from one fire to another even within the same geographical
966 location. Emissions factors from peat fires are not well quantified with different studies reporting a
967 wide range of values (Akagi et al., 2011).

968 The lifetime of the species released from fires depends on chemical processes in fire plumes and
969 therefore on the vertical distribution of the plumes. The plume injection height can be critical in the
970 impact of biomass burning (Leung et al., 2007). Several studies have proposed plume models or
971 parameterization of the top height of the plumes, based on empirical methods or on the use of
972 satellite observations (Tosca et al., 2011; Martin et al., 2010). A determination of the vertical profiles
973 of fires emissions at the global scale was proposed by Sofiev et al. (Sofiev et al., 2013), based on
974 satellite observations and semi-empirical formulas. An example is shown in Figure 19, which
975 highlights the importance of meteorology in the day-night variation of the height of fire plumes. It is

976 worth noting that the diurnal variation of the injection height is significant such that one can
977 practically consider two independent datasets, one for daytime and one for nighttime, with
978 transition during morning and evening (Sofiev et al., 2013). The influence on ozone can be a
979 combination of injection height and frequency (Williams et al., 2012).

980



981

982 **Figure 19** - Injection height (in m) for 90% of the mass injection for night (left) and day (right) for
983 August from biomass burning (Sofiev et al., 2013).

984 2.3.7 Natural emissions

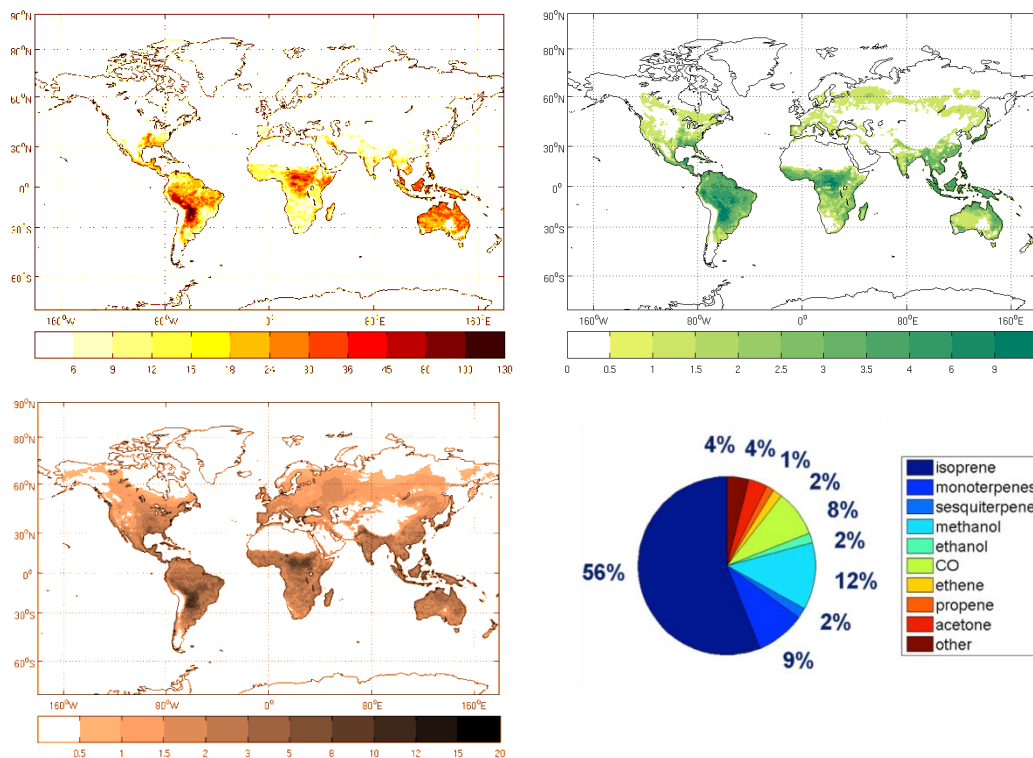
985 Natural processes in the atmosphere, vegetation and oceans lead to the emissions of a wide range of
986 compounds (Granier et al., 2004). Emissions resulting from lightning are discussed in Section 4.7.
987 This section only focuses on emissions of hydrocarbons from vegetation, since they can have a large
988 impact on the distribution of ozone and its precursors and because terrestrial vegetation is the
989 dominant source of atmospheric VOCs (Guenther et al., 1995). The emissions of isoprene and
990 monoterpenes are the largest, but many other compounds are also emitted. Many studies
991 performed during the past few years have used MEGAN (Model of Emissions of Gases and Aerosols
992 from Nature) to quantify the emissions of biogenic VOCs to the atmosphere. MEGAN is a model
993 system calculating temporal and spatial rates of emission of chemical compounds from terrestrial
994 ecosystems to the atmosphere under varying environmental conditions. It was first introduced by
995 Guenther et al. (Guenther et al., 1995; Guenther et al., 2006; Guenther et al., 2003; Guenther et al.,
996 1993). The most recent version of the model, MEGAN v2.1 was introduced in Guenther et al.
997 (Guenther et al., 2012). The current algorithm takes into account the impact of past and present
998 temperature, light (sun-lit and sun-shaded leaves), leaf age, CO₂ inhibition of isoprene emissions and
999 losses of primary emissions in the canopy and soil moisture.

1000

1001 Examples of emissions of isoprene, monoterpenes and methanol in 2003 are shown in Figure 20,
1002 together with the relative contribution of the different biogenic VOCs to the total amount emitted.
1003 Isoprene emissions account for 56% of the total, which indicates that the emissions of the other
1004 BVOCs and their chemical oxidation schemes (see section 4.3 and 4.10) also need to be taken into
1005 account when simulating the atmospheric composition of the atmosphere.

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1007



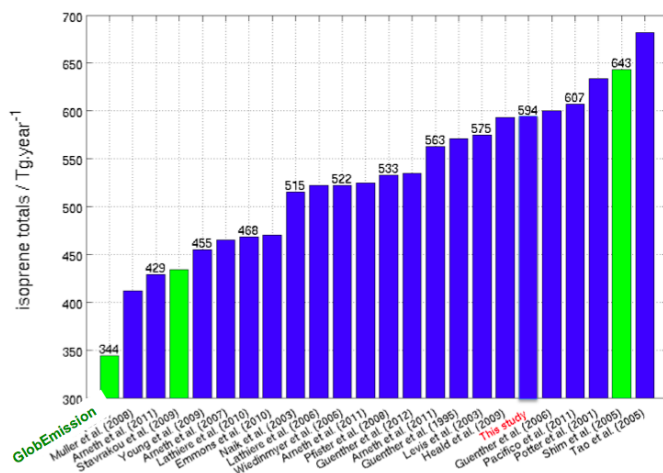
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1009 **Figure 20** - Mean annual emissions (in $\text{mg}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$) of isoprene (top left), monoterpenes (top
1010 right), methanol (bottom left), and contribution of each BVOCs to the annual global total average
1011 (bottom right) (Sindelarova et al., 2014).

1012 Previous studies show significant differences between the total amount of BVOCs emitted by
1013 vegetation (Sindelarova et al., 2014). These differences are related to the large uncertainties of
1014 different factors driving BVOCs emissions, such as radiation amount, leaf temperature, and
1015 parameterization of the soil moisture factor or the representation of canopy processes. There are
1016 also large differences in the vegetation types and in the distribution of plant functional types used in
1017 different models and/or their assignment with BVOCs emission activity.

1018 Other methods have been used to calculate the emissions of BVOCs by the vegetation. Arneth et al.
1019 (2007) (Arneth et al., 2007) have for example calculated the emissions using a dynamic global
1020 vegetation model (LPJ-GUESS, (Sitch et al., 2003)) and a physiological BVOCs emission algorithm.
1021 Studies conducted using the LPJ-GUESS model (Arneth et al., 2011) have shown that variations of
1022 driving input data such as meteorology and vegetation description among different models might
1023 lead to substantially different emission estimates.

1024 Figure 21 shows the differences between previous estimates of global total isoprene emissions: the
1025 difference between the lowest and highest estimate is 65%. In Figure 21, the three values indicated
1026 by green bars correspond to an optimization of isoprene emissions using inverse modeling
1027 techniques and formaldehyde satellite observations (see next section). The difference between the
1028 highest and lowest value is about a factor of two, which highlights the large uncertainties on the
1029 determination of isoprene emissions.



1030

1031 **Figure 21** - Isoprene global total estimated from different studies. Studies highlighted in green used
 1032 formaldehyde satellite data and an inversion modeling technique to constrain isoprene emissions
 1033 (Sindelarova et al., 2014).

1034

1035 [2.3.8 Evaluation and optimization of emissions using inverse modelling techniques](#)

1036 Inverse modelling techniques have been widely used during the past few years to optimize surface
 1037 emissions so that simulated atmospheric concentrations can reproduce observed concentrations.
 1038 Most recent studies either minimize the weighted distance between model and observations
 1039 (variational approach) or minimize the error variance of the estimated parameters (Kalman Filter
 1040 techniques) (Saide et al., 2011). Differences between the distributions provided by the models and
 1041 the observations are not only due to inaccuracies on the quantification of emissions, errors in the
 1042 model data (meteorological fields for example), but also in the representation of physical and
 1043 chemical processes in the models: all these factors need to be taken into account in inverse systems
 1044 (Elbern et al., 2007). Estimates of emissions using inverse techniques also depend on the *a-priori*
 1045 emission dataset used, on the meteorological fields used to drive the models used that infer
 1046 emissions (Arellano and Hess, 2006), and on the data used in the optimization of the emissions
 1047 (Hooghiemstra et al., 2012). A review of the current capabilities of inverse techniques to better
 1048 quantify surface emissions in North America using satellite observations was published by Streets et
 1049 al., 2013 (Streets et al., 2013).

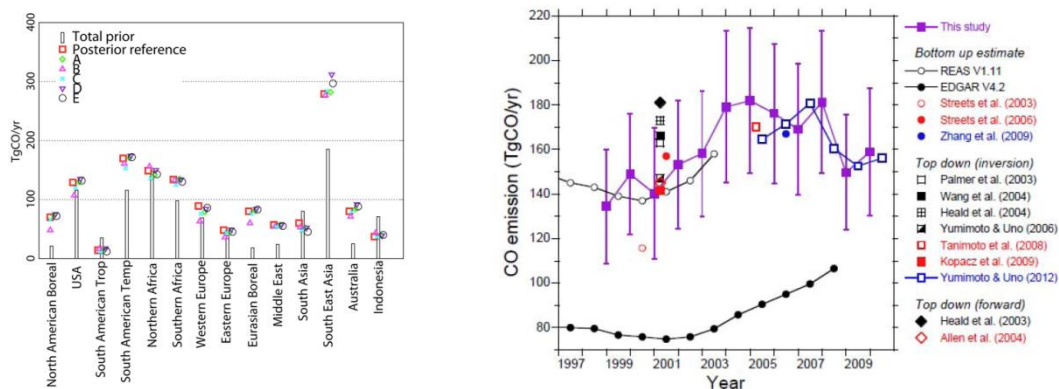
1050 These techniques have been mostly applied to the species for which observations from satellite are
 1051 available or for the optimization of local/regional emissions when comprehensive observation
 1052 datasets exist. Therefore, most studies have discussed the optimization of greenhouse gases (CO₂
 1053 and CH₄), of ozone precursors CO and NO₂, of aerosols and their precursors (see (Fuzzi et al., 2015)
 1054 companion paper), and of biogenic emissions using satellite observations of formaldehyde.

1055

1056 Several studies have applied inverse modelling techniques to the optimization of CO emissions using
 1057 observations from surface networks (Petron et al., 2004) as well as observations from the MOPITT
 1058 and IASI satellite instruments. Most of these studies using satellite data have concluded that the *a-*
 1059 *priori* anthropogenic emissions of CO might be underestimated as indicated in Figure 22a (Fortems-

1060 Cheiney et al., 2011) and 22b (Tohjima et al., 2014), more particularly at mid-latitudes of the
 1061 northern hemisphere in winter (Kopacz et al., 2010; Stein et al., 2014). However, an analysis of
 1062 satellite and aircraft observations has also shown that emissions inventories in North America might
 1063 provide overestimated values (Miller et al., 2008). Emissions resulting from fires have also been
 1064 optimized, and showed that current surface inventories might underestimate fires in boreal regions
 1065 (Pfister et al., 2005). Inverse techniques have also provided information on the seasonal cycles of
 1066 emissions from fires, for example in Africa as shown by Chevallier et al. (Chevallier et al., 2009).

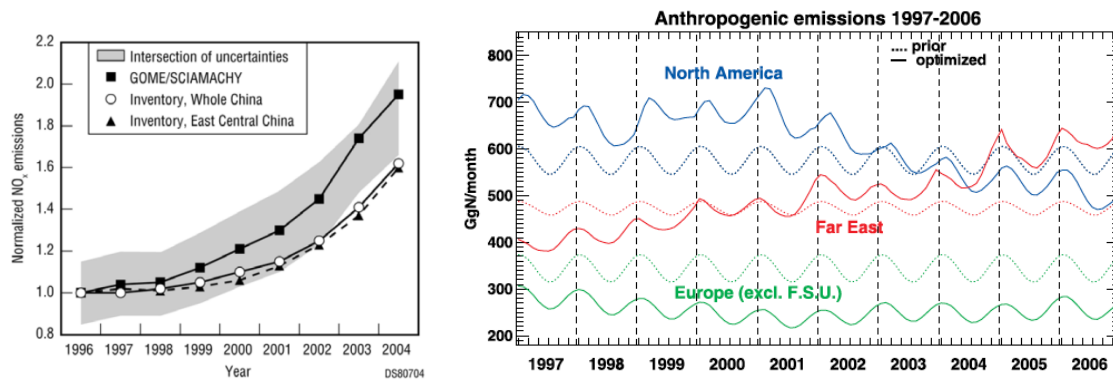
1067
 1068



1069
 1070 **Figure 22** - (a, left): Annual total posterior CO emissions per region for year 2004 compared to the a
 1071 priori reference : the different cases correspond to tests on different errors in the model (Fortems-
 1072 Cheiney et al., 2011). (b, right) : Comparison of estimated CO annual emissions in China from
 1073 inventories and inverse studies; the “This Study” refers to a top down estimate (Tohjima et al., 2014).

1074 Several studies have used satellite NO₂ column observations to constrain nitrogen oxide emission
 1075 inventories through inverse or forward modeling (Martin et al., 2004; Kim et al., 2009; Lamsal et al.,
 1076 2011; Wang et al., 2012). These studies exploited the relatively short lifetime of tropospheric
 1077 nitrogen oxides, which ranges from several hours to a few days. As a result, NO₂ has its largest
 1078 concentrations in the boundary layer close to emission sources, making measurements of NO₂
 1079 columns well suited to improving our knowledge of the emissions of NO_x. Two examples of
 1080 optimizations of NO_x emissions using satellite observations are given in Figure 23. Figure 23a shows a
 1081 quantification of emissions trends in China as provided by an inventory and optimized using the
 1082 SCIAMACHY/GOME observation for the 1996-2004 period is shown in Figure 23 (Zhang et al., 2007).
 1083 From 1996 to 2004, NO_x emissions over East Central China region increased by 61% according to the
 1084 inventory, while a 95% increase in the NO₂ columns was obtained from the satellite observations
 1085 during the same period. Stavrou et al. (Stavrou et al., 2008) have evaluated the changes in the
 1086 emissions in different regions of the world from 1997 to 2006 using an inverse method and found
 1087 larger increases in the optimized emissions when compared to prior emissions in the Far East region,
 1088 and emissions decreasing faster than in the inventories in North America.

1089



1090

1091 **Figure 23** - Temporal evolution of NO_x emissions over China from the Zhang et al. (2007) inventory
 1092 and inverse method using satellite observations. All data are normalized to the year 1996 (Zhang et
 1093 al., 2007).

1094

1095 Optimization of the emissions of several other compounds have also been evaluated through inverse
 1096 methods constrained by satellite observations, such as isoprene, methanol or formaldehyde
 1097 (Stavrakou et al., 2011;Stavrakou et al., 2009;Palmer et al., 2003;Wells et al., 2014;Barkley et al.,
 1098 2013) and other studies have focused on the optimizations of the emissions from different sectors,
 1099 such as ships ((de Ruyter de Wildt et al., 2012;Vinken et al., 2014).

1100

1101 2.4 A climatological view of ozone/linkages across the scales

1102

1103 The available observations show that tropospheric ozone is highly variable both in space and time, on
 1104 long and short scales. Over the remote oceans, observations show low ozone amounts within the
 1105 tropical Hadley circulation with little or no vertical gradient in mole fraction, then higher
 1106 concentrations at mid latitudes, with an increase with height, corresponding to the additional source
 1107 of tropospheric ozone from STE as well as in-situ chemistry (See Figures 24 and 25). Over the
 1108 continents and nearby oceans in the lower troposphere different behaviour is observed depending
 1109 on the level of the ozone precursors. Analysis of the seasonal-diurnal variations allows separating the
 1110 following types of ozone variations in the extra-tropics (Tarasova et al., 2007): clean background,
 1111 rural, semi-polluted non-elevated, semi-polluted semi-elevated, elevated and Polar/remote marine.
 1112 For the “clean background” regime in the Northern hemisphere the seasonal maximum is observed
 1113 in March-April, both for night and day. For those sites with a double maximum or a wide spring-
 1114 summer maximum, the spring maximum appears both for day and night, while the summer
 1115 maximum is more pronounced for daytime and hence can be attributed to photochemical processes.
 1116 There is much debate as to the origin on the spring maximum likely a combination of
 1117 dynamical/transport processes and photochemistry (Monks, 2000).

1118 In July, northern summer, major regions of elevated lower troposphere ozone are observed over
 1119 USA, Europe and East Asia from urban/industrial activities and regions of elevated ozone over the
 1120 tropics due to both biomass burning and other human activities. Satellite observations of
 1121 tropospheric ozone have revealed much detail about the spatial distribution including the discovery
 1122 of the regional tropospheric ozone maximum off southwest Africa over the Atlantic Ocean (Figure 24)
 1123 and the oscillation of tropospheric ozone over the Indonesian Archipelago in synchronicity with El

1124 Niño (Ziemke et al., 2010). In highly dynamic regions such as the Mediterranean basin (Lelieveld et
1125 al., 2002;Lelieveld et al., 2009), the strength of the meteorological systems (Azores anticyclone and
1126 Middle Eastern depression) are key factors in explaining both the variability and the anomalies of
1127 ozone in the lower troposphere in this region (Doche et al., 2014). Recent observations have
1128 suggested there is a summertime free tropospheric ozone pool over the Mediterranean (Zanis et al.,
1129 2014;Kalabokas et al., 2013).

1130

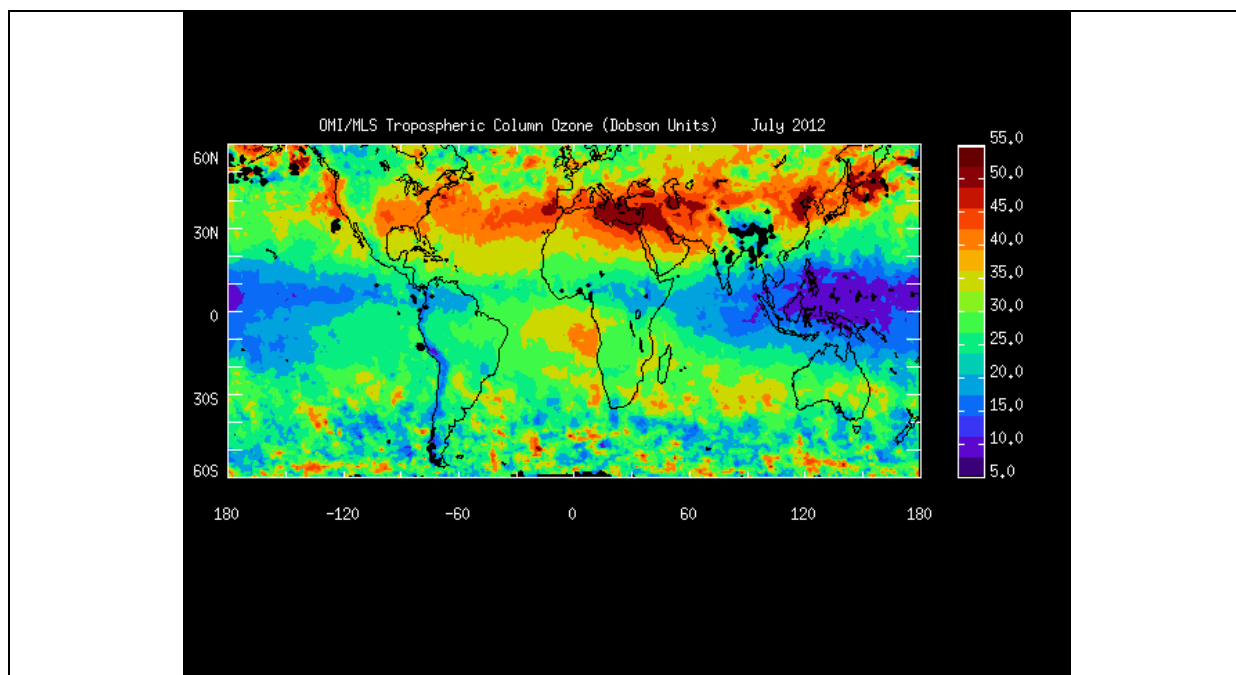


Figure 24 - Tropospheric ozone columns determined by residual from OMI observations of total column O_3 and MLS observations of stratospheric O_3 (Ziemke et al., 2006). Plots retrieved from http://acd-ext.gsfc.nasa.gov/Data_services/cloud_slice/index.html#nd

1131

1132 The data in Figure 24 clearly highlights the benefits offered by satellite data for investigating the
1133 global distribution of tropospheric ozone. However, it should be kept in mind that such data give an
1134 incomplete picture (Monks and Bierle, 2011) which requires complementary observing systems (Laj
1135 et al., 2009). It is worth noting that there are direct tropospheric ozone retrievals from satellite data
1136 (Liu et al., 2006). The AMMA campaign (Redelsperger et al., 2006) and associated analysis performed
1137 with the in-situ MOZAIC (Sauvage et al., 2005) and SHADOZ data (Thompson et al., 2003a;Thompson
1138 et al., 2003b) have revealed a somewhat different feature of ozone distribution (both in terms of
1139 amount of the tropospheric columns and in the location of the maxima) over Western and Southern
1140 Africa including the adjacent Atlantic Ocean. In July, when biomass burning mainly occurs over the
1141 southern tropical part of Africa, the tropospheric ozone column is about 45 DU over the continent
1142 (Thompson et al., 2014;Sauvage et al., 2005;Sauvage et al., 2006). Export of polluted air masses is
1143 observed throughout the Gulf of Guinea up to the coast of West Africa in the northern hemisphere.
1144 Reeves et al. (Reeves et al., 2010) provide a clear characterisation of the ozone distribution
1145 throughout the troposphere over West Africa during the monsoon period. Owing to previous analysis
1146 based on MOZAIC data (Sauvage et al., 2007a;Sauvage et al., 2005) and the regular ozone soundings
1147 over Cotonou over 2 years (Thouret et al., 2009), it has been shown that the biomass burning
1148 seasons in both hemispheres impact the tropospheric ozone profiles in both hemispheres as well. As

1149 a consequence, a picture like the so-called “Ozone paradox” (Thompson and Hudson, 1999) was
1150 shown to be no longer valid (Sauvage et al., 2006) owing to the insight provided by additional in-situ
1151 observations. Recent work has shown evidence for the removal of ozone in Saharan dust plumes
1152 (Andrey et al., 2014) which is correlated with both dust loading and total amount of water present.

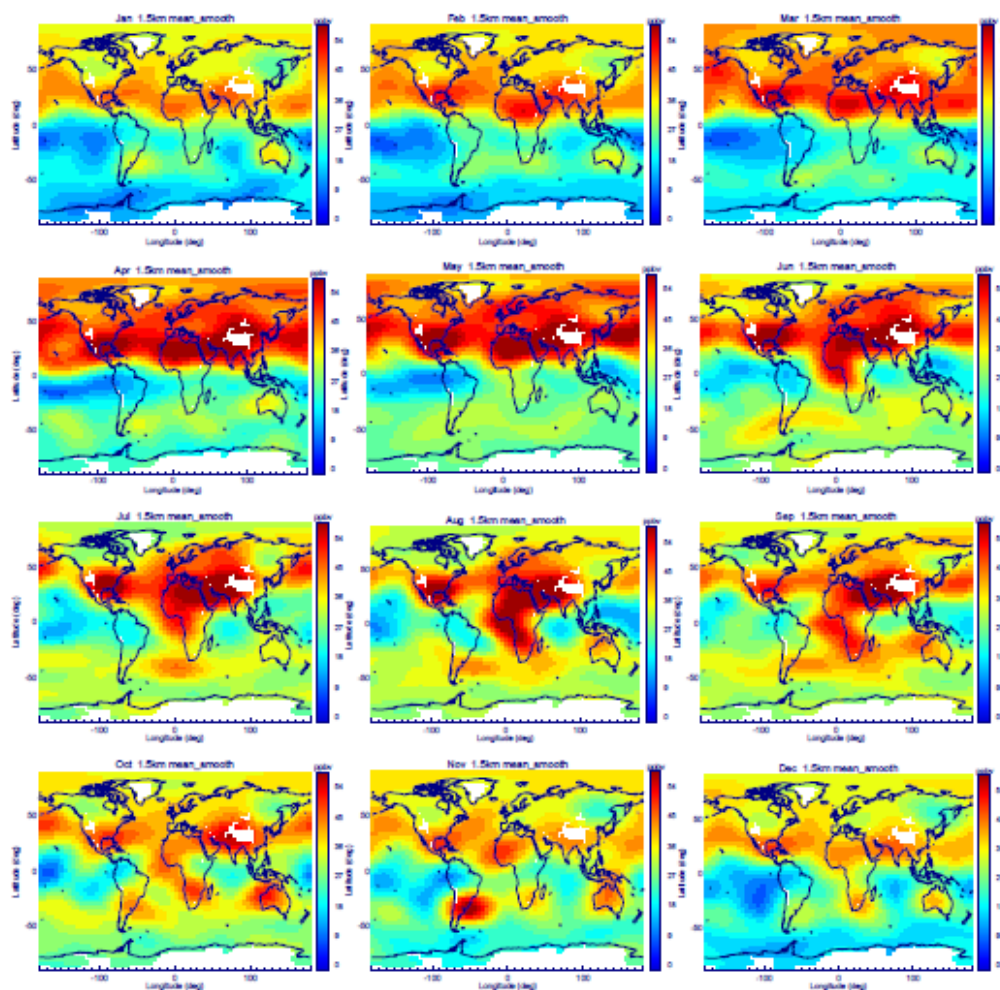


Figure 25 – Monthly global ozone distributions at 1.5 km a.s.l from trajectory mapped ozone soundings (Liu et al., 2013a).

1153
1154 At coastal or island sites in the tropics diurnal variation in ozone generally show a minimum during
1155 the daytime. Occasional air transport events from the mid-latitudes bring in higher ozone
1156 concentrations (Lawrence and Lelieveld, 2010). The mole fractions are low, typically 5 – 20 ppb, and
1157 the annual maximum occurs in June to September, southern winter, a characteristic of ozone in the
1158 southern hemisphere troposphere. For more continental tropical regional sources of ozone due to
1159 precursor emissions from such activities as biomass burning (e.g. (Ojha et al., 2014; Cristofanelli et al.,
1160 2010)), land clearing, agriculture and human settlements may cause occasional elevated ozone
1161 concentrations (Jacob et al., 1996). The seasonal ozone variation may be affected by these activities
1162 which can be influenced by seasonal meteorological conditions such as the occurrence of a wet/dry
1163 seasons (Valks et al., 2014; Rama Gopal et al., 2014; Cristofanelli et al., 2010; Sinha et al., 2014). Under
1164 stable conditions, ozone depletion due to ozone deposition and NO titration will occur. The diurnal
1165 variation of ozone will generally be characterized by lower concentrations at night and higher

1166 concentrations during the daytime (see e.g. (Rama Gopal et al., 2014)). Vegetation cover plays an
 1167 important role together with local meteorology in (natural) trace gas emissions. For example, tropical
 1168 forests and plantations are among the greatest emitters of isoprene, a reactive hydrocarbon species
 1169 which is involved in the photochemical cycle of tropospheric ozone (see section 4.3). Replacement of
 1170 tropical forest by agriculture (e.g. palm trees) may cause potential future elevated ozone levels
 1171 (Hewitt et al., 2009;MacKenzie et al., 2011) (see Figure 26).

1172

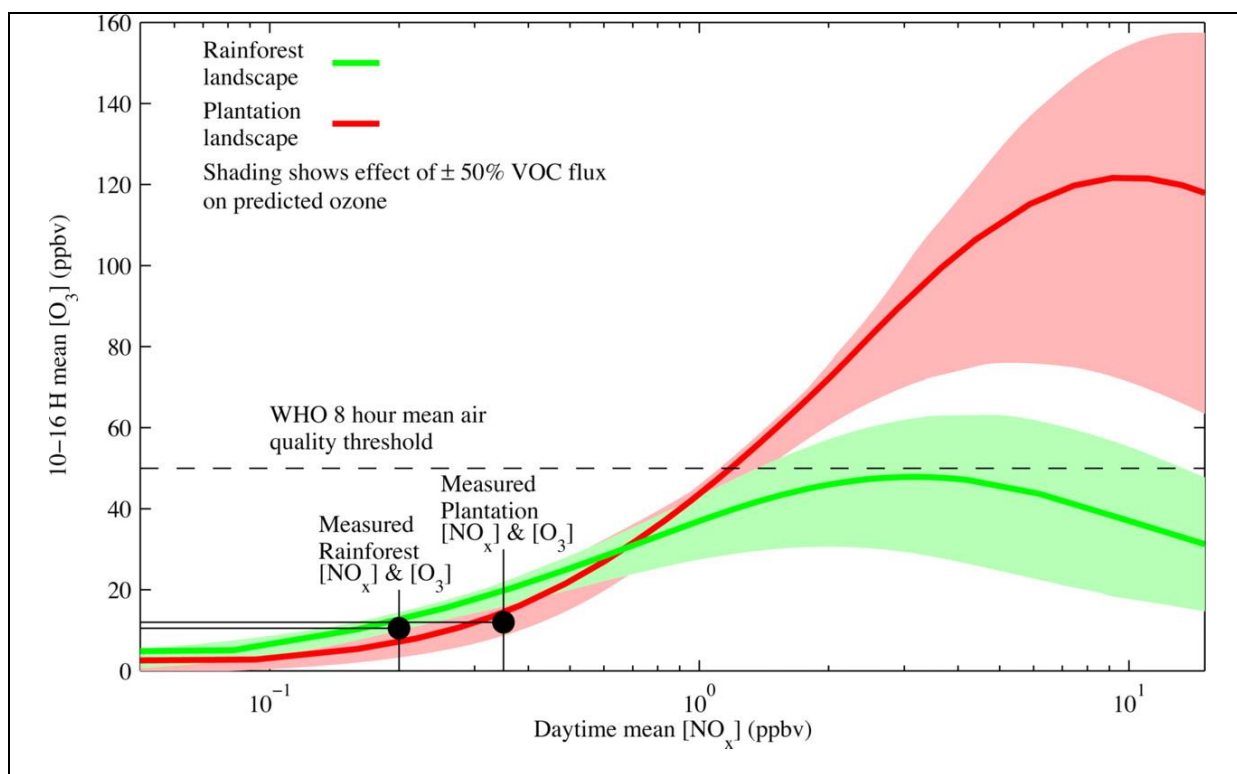


Figure 26 – Sensitivity of daytime (10.00-16.00 h) average ozone concentrations to [NO_x] in the boundary layer for isoprene and monoterpene emission rates measured in a rainforest and palm oil landscape (Hewitt et al., 2009).

1173

1174 High latitude sites may be influenced by the near continuous presence of snow or ice cover (Helmig
 1175 et al., 2007). Polar sites may have wind directions that remain relatively constant for months. Coastal
 1176 sites may have ozone depletion events, which are related to halogen chemistry (Simpson et al.,
 1177 2007), and which is evident for example at Barrow during northern spring, March to May (Oltmans et
 1178 al., 2012). The high reflectivity of snow and ice influences the photochemical reaction rates, because
 1179 more UV radiation is available than would be expected for these latitudes if one assumes a global
 1180 average value for the surface UV albedo. In stable conditions with bright sunlight, local
 1181 photochemical production has been observed due to NO_x emission from the snow (Helmig et al.,
 1182 2008a;Helmig et al., 2008b) and this is evident at the South Pole during November to February,
 1183 centred on southern summer. The ozone concentrations in background air at the South Pole peak in
 1184 winter/spring and fall to a minimum in summer/autumn as with other southern hemisphere sites.

1185 Moving to the urban scale the local coupling of NO_x and O₃ is important in that reductions in NO can
 1186 contribute to increases in ozone (Kley et al., 1994). In areas of high NO_x, as is often observed in
 1187 urban areas, ozone levels can be suppressed through the following reaction:



1189 This phenomenon, sometimes dubbed ‘NO_x titration’, thereby leads to the counter-intuitive effect
 1190 that reducing NO_x (NO) reduces the amount of ozone being suppressed and actually increases ozone
 1191 (Heal et al., 2013a; Sicard et al., 2013). The spatial variability of ozone in larger urban areas can be
 1192 very much driven by “titration” (Escudero et al., 2014). Figure 27 shows the gradual increase in
 1193 urban ozone, moving towards background levels, driven by reducing NO_x emissions over the last
 1194 couple of decades in the UK, decreasing the suppression of ozone. Figure 28 shows the “titration” in
 1195 urban areas across Europe from modelling studies, showing the widespread nature of this effect and
 1196 the need to couple the regional and hemispheric picture to the urban. In a sense there is an urban
 1197 decrement driven by this process. Conversely, there has been some work looking at megacity
 1198 impacts on regional ozone (Tie et al., 2013; Beirle et al., 2011; Guttikunda et al., 2005) (see also
 1199 Section 4.1).

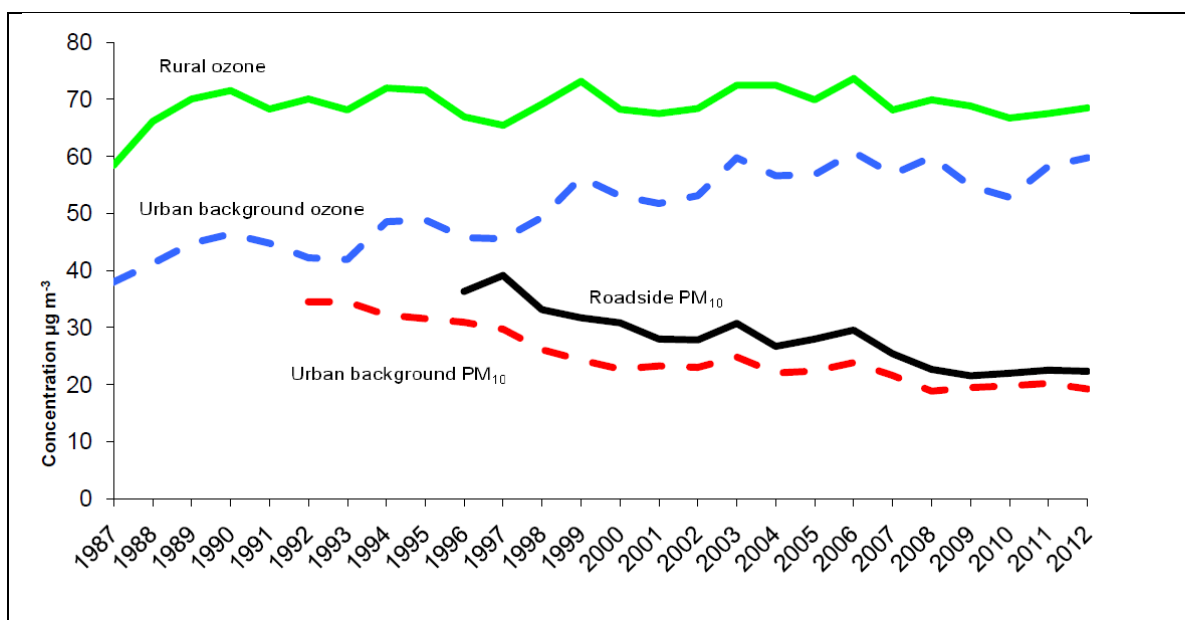


Figure 27: Annual levels of ozone (and PM₁₀) in the UK 1987-2012 (Defra, 2013) showing the rise of urban ozone concentrations towards the rural ones and the relatively flat rural concentrations over the last decade.

1200

1201 Given the strong NO_x-O₃ (sometimes referred to as O_x (Zlatev et al., 1992; Yu et al., 2008), see also
 1202 Figure 28) couple at the urban scale there are a number of issues around the role of an increase in
 1203 the NO₂:NO emission ratio caused by an increase in the share of diesel vehicles in Europe and the
 1204 role that may play in ozone formation (Weiss et al., 2012; Carslaw et al., 2011; Carslaw, 2005). Further
 1205 there are questions as to what extent spatially (along roadsides, across urban areas, regionally)
 1206 primary NO₂ emissions affect ozone concentrations (see e.g. (Yu et al., 2014)). Meteorology also
 1207 plays a large role in local scale ozone concentration affecting deposition and transport (e.g. (Vieno et
 1208 al., 2010; Francis et al., 2011)) alongside transport and dispersion in urban landscapes such as street

1209 canyons etc. (see e.g. (Baker et al., 2004;Zhong et al., 2014;Kwak and Baik, 2014)). Urban areas are
1210 dynamic regions in terms of emmision of ozone precursors that have seen strong changes owing to
1211 emmision reduction measures (see e.g. (vonSchneidemesser et al., 2011;vonSchneidemesser et al.,
1212 2010;McMeeking et al., 2012;Warneke et al., 2012;Vijayaraghavan et al., 2014)).

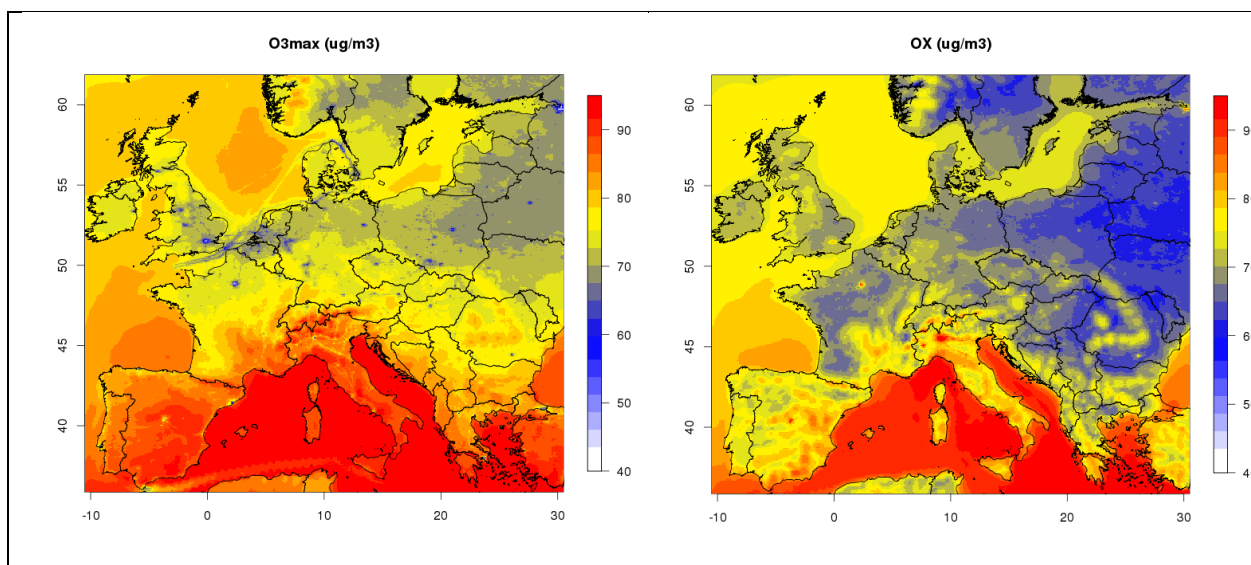


Figure 28 - In a continental chemistry transport simulation with the CHIMERE model at a resolution of 8 km, major urban centres in Northern and Central Europe highlight the NO_x titration process (left: summertime average of daily maximum ozone) while the total oxidant level (right: O_x as NO₂ + O₃, annual mean) is high in most European cities (adapted from (Terrenoire et al., 2013)).

1213

1214 3 Impacts

1215

1216 Surface level ozone has multiple impacts. As an oxidant it can induce respiratory problems and has
1217 been associated with premature human mortality (Bell et al., 2006;Gryparis et al., 2004). Further it
1218 can cause tree/vegetation damage (Krupa and Manning, 1988), reduce photosynthesis and growth
1219 (Reich and Amundson, 1985) and therefore crop yields (Fiscus et al., 2005) (see also (Felzer et al.,
1220 2007;Ashmore, 2005) for recent reviews). Ozone is also an important greenhouse gas (IPCC, 2013).

1221 3.1 Health

1222

1223 Ozone has long been known to cause adverse effects on health (Bates, 2005). The gas is a powerful
1224 oxidant and short-term inhalation induces inflammation of the entire respiratory tract, although the
1225 nasal cavity and the zone between the conducting and gas-exchange airways are potentially more
1226 susceptible. Significant inflammation can be detected at ambient levels of ozone in controlled human
1227 exposure studies, and although there is some degree of adaptation after repeated exposures,
1228 pulmonary inflammation may persist, mainly in the terminal bronchiolar units. As well as elucidating
1229 these effects in exposure studies, which naturally exclude the most sensitive or susceptible parts of
1230 the population, associations between ozone and mortality and morbidity have also been shown in
1231 epidemiological studies, covering the population at large.

1232 Early work on ozone health effects involved mainly exposure studies in chambers. On the basis of this
1233 work ozone was included in the first tranche of National Air Quality Standards in the US, with a
1234 standard of 80ppb as a 1 hour average, promulgated in 1971 as part of the US Clean Air Act. In
1235 Europe, the first edition of the WHO 'Air quality guidelines for Europe' in 1987 set a 1-hour guideline
1236 value of 75-100 ppb. This guideline was also based primarily on chamber studies. Since then much
1237 more evidence has accumulated regarding ozone effects, not least from epidemiology studies, and in
1238 the 2005 Global Update (WHO, 2005) the most recent WHO Guideline is now 50ppb expressed as the
1239 maximum 8-hour mean in a day. The same document also sets an interim target of 80 ppb as a daily
1240 maximum 8-hour mean, and a 'High Level' of 120 ppb daily maximum 8-hour mean where it notes
1241 that "significant health effects could occur" (interim) and that a "substantial proportion of vulnerable
1242 population affected" (high).

1243 Earlier WHO guidelines were based on these chamber studies on humans and animals, but the more
1244 recent 2005 Global Update from WHO mentioned above additionally used time series
1245 epidemiological studies (WHO, 2005). However, all guidelines up to and including 2005 referred to
1246 short-term exposures and health effects, but the 2005 report noted that at that time there was some
1247 evidence that long-term exposure to ozone may have chronic effects but the review concluded that
1248 the evidence was insufficient to recommend a guideline. The policy implications of these purely
1249 health-based guidelines are discussed in Section 5.

1250 As part of their 'Year of the Air' in 2013 the European Commission requested WHO to review the
1251 health effect evidence on the pollutants covered in EU air quality legislation, including ozone. The
1252 review was in two parts, firstly a review (REVIHAAP) of the health effect evidence itself, in the form
1253 of answers to policy-relevant questions prepared by the Commission, in consultation with the WHO.
1254 The final REVIHAP report is available at
1255 [http://www.euro.who.int/_data/assets/pdf_file/0004/193108/REVIHAAP-Final-technical-report-](http://www.euro.who.int/_data/assets/pdf_file/0004/193108/REVIHAAP-Final-technical-report-final-version.pdf)
1256 [final-version.pdf](http://www.euro.who.int/_data/assets/pdf_file/0004/193108/REVIHAAP-Final-technical-report-final-version.pdf) . The second part of the process involved a shorter project (HRAPIE) which
1257 recommended concentration-response functions for use in health impact assessments and other
1258 quantification, for example in integrated assessment modelling to underpin the EU policy process.
1259 The HRAPIE report is available at
1260 [http://www.euro.who.int/_data/assets/pdf_file/0006/238956/Health-risks-of-air-pollution-in-](http://www.euro.who.int/_data/assets/pdf_file/0006/238956/Health-risks-of-air-pollution-in-Europe-HRAPIE-project,-Recommendations-for-concentrationresponse-functions-for-costbenefit-analysis-of-particulate-matter,-ozone-and-nitrogen-dioxide.pdf)
1261 [Europe-HRAPIE-project,-Recommendations-for-concentrationresponse-functions-for-costbenefit-](http://www.euro.who.int/_data/assets/pdf_file/0006/238956/Health-risks-of-air-pollution-in-Europe-HRAPIE-project,-Recommendations-for-concentrationresponse-functions-for-costbenefit-analysis-of-particulate-matter,-ozone-and-nitrogen-dioxide.pdf)
1262 [analysis-of-particulate-matter,-ozone-and-nitrogen-dioxide.pdf](http://www.euro.who.int/_data/assets/pdf_file/0006/238956/Health-risks-of-air-pollution-in-Europe-HRAPIE-project,-Recommendations-for-concentrationresponse-functions-for-costbenefit-analysis-of-particulate-matter,-ozone-and-nitrogen-dioxide.pdf) .

1263 The REVIHAAP report addressed three questions relating to ozone where WHO and the European
1264 Commission felt a more recent assessment was warranted. The questions posed were

- 1265 (i) What new evidence on health effects has emerged since the review work done for
1266 the 2005 global update of the WHO air quality guidelines, particularly with regard
1267 to the strength of the evidence of the health impacts associated with short-term
1268 and long-term exposure to ozone?
- 1269 (ii) What new health evidence has been published in relation to the evidence or
1270 likelihood(sic) of a threshold below which impacts are not expected? and
- 1271 (iii) Based on currently available health evidence, what ozone metrics , health
1272 outcomes and concentration-response functions can be used for health impact
1273 assessment

1274 The answer to the first question noted that the earlier 2005 global update found evidence only for
1275 short-term effects on mortality and morbidity. However an important advance is that several cohort
1276 studies have now emerged showing associations between long-term exposures and mortality. Of
1277 particular importance are the studies using the large American Cancer Society cohort. A study
1278 (Krewski et al., 2009) using single pollutant models found an association between summertime
1279 average ozone and all-cause mortality as well as cardiopulmonary mortality, although the high
1280 correlation between PM_{2.5} and ozone in the summer months made it difficult to separate the effects
1281 of the two pollutants. A further study using the same cohort (Jerrett et al., 2009) found unstable risk
1282 estimates for ozone and all-cause, cardiopulmonary and cardiovascular mortality with only
1283 respiratory mortality being associated with ozone after adjustment for PM_{2.5}. For a more detailed
1284 discussion of these and other recent cohort studies (Smith et al., 2009; Zanobetti and Schwartz,
1285 2011; Lipsett et al., 2011) than space here permits, the reader is referred to the REVIHAAP report.

1286 In answering the second question regarding evidence for a threshold, the REVIHAAP report noted
1287 that epidemiological studies reporting an effect of long-term exposures to ozone on mortality do not,
1288 in general permit the firm identification of a threshold. However the report did draw some
1289 conclusions which are helpful to health impact studies.

1290 Earlier chamber exposure studies referred to above have been supplemented by more recent studies
1291 showing effects at lower levels. Studies since the 2005 global update have shown that healthy
1292 exercising human subjects showed impaired lung function at concentrations of 60ppb for 6.6 hours,
1293 relative to clean air controls (Kim et al., 2011). The report noted that the subjects were healthy adults
1294 and thus not representative of the general population, or of real-world combinations of susceptibility
1295 and exposure. The REVIHAAP report discusses a number of other studies which report adverse
1296 effects at concentrations lower than those in the above study and the reader is referred to that
1297 report for a more detailed discussion. The REVIHAAP report concluded that the evidence from
1298 epidemiological studies for a threshold for short-term exposures is inconsistent with some large
1299 multi-city studies which reported little evidence for a threshold down to near background ozone
1300 concentrations, whereas other short-term studies suggest a threshold between 10ppb and 45 ppb
1301 daily maximum 1-hour ozone. The report concluded that in summary the evidence for a threshold for
1302 short-term exposure is inconsistent but where a threshold is observed it is likely to lie below 45 ppb
1303 maximum 1 hour ozone.

1304 The third question, relating to quantification of the health impacts of ozone overlaps with the HRAPIE
1305 project, the second part of the WHO review for the European Commission. The REVIHAAP report
1306 concluded that a range of health outcomes could be used where baseline rates are known, including
1307 all-age, all-cause, cardiovascular and respiratory mortality, and for ages 65 and over respiratory and
1308 cardiovascular hospital admissions. The report concluded that the evidence supports the use of all-
1309 year coefficients for daily maximum 8-hour average ozone concentrations. Bearing in mind the
1310 discussions on a threshold REVIHAAP recommended that cut-off points be used at 35ppb for daily
1311 maximum 8-hour ozone 'for consistency with previous work using SOMO35...' (for definition of
1312 SOMO see §5 or e.g. (AQEG, 2009)). In an important further step, the report also recommended
1313 using a cut-off at 10ppb, i.e. SOMO10.

1314 This latter step is significant in that use of SOMO10 in assessing the effects of most future control
1315 strategies already in place or proposed in Europe (and probably elsewhere) are likely to lead to

1316 increases in health impacts from ozone exposures. The conclusions of the HRAPIE report essentially
1317 endorsed the findings of the REVIHAAP report, suggesting the use of SOMO10 and SOMO35, and an
1318 assessment of long-term exposure impacts as a sensitivity study.

1319 Interestingly, the Impact Assessment for the EU Clean Air package published on 18 December 2013
1320 (http://ec.europa.eu/environment/air/clean_air_policy.htm) only used SOMO35 to assess the health
1321 impact of proposed policies. This was justified on the grounds that below this level there are
1322 uncertainties in ozone modelling. However, it is convenient that using SOMO35 minimises the impact
1323 of increased ozone health impacts which are likely to result if SOMO10 is used. The policy process
1324 has yet to come to terms with the possibility that existing and planned control measures are likely to
1325 result in increased health impacts from ozone if a low threshold, or a long-term (annual or summer)
1326 average concentration is used in impact assessments. A recent modelling study (Heal et al., 2013b)
1327 which looked at the burden of health impacts from ozone in 12 regions in the UK incorporated the
1328 uncertainty over thresholds using a population weighted daily maximum 8-hour mean ozone metric
1329 with a cut-off at 35 ppb and also with no threshold. They also incorporated future temperature
1330 increases and changes in the tropospheric baseline of ozone, and showed that as expected the
1331 assumption of zero threshold gave much larger health impacts. Moreover they showed that under a
1332 no-threshold assumption health impacts (deaths brought forward and hospital admissions) in the
1333 'current legislation' scenario *increase* due both to the no-threshold assumption but also with the
1334 assumption of an increasing tropospheric ozone baseline. This interplay between the threshold
1335 assumption and the future trend in the tropospheric baseline has important implications for policy as
1336 discussed in section 5 below.

1337 A not dissimilar process in followed the US context as part of the periodic review process for NAAQS
1338 (National Ambient Air Quality Standards). In 2013 the US EPA produced its most recent and
1339 substantial integrated science assessment for ozone (<http://www.epa.gov/ncea/isa/>).

1340 Finally, an interesting new development bridging the gap between atmospheric chemistry and
1341 epidemiology is a time-series study of the associations between O_x (defined as $O_3 + NO_2$) and health
1342 outcomes (Williams et al., 2014). As well as having a sound basis in atmospheric chemistry given the
1343 rapid interchange between ozone and NO_2 , this also has a toxicological rationale since it is probable
1344 that both ozone and NO_2 cause harmful effects *via* oxidative stress (although it is recognised that NO_2
1345 could also act *via* other mechanisms). The study showed that the associations between O_x and
1346 mortality were stronger than for either of the two pollutants individually, but similar to the
1347 pollutants when used in a two-pollutant model. The preliminary conclusion is that in epidemiological
1348 studies of either ozone or NO_2 , some form of interaction should be incorporated, either as O_x or in a
1349 two-pollutant model. Single pollutant models for ozone or NO_2 should not be used.

1350

1351 **3.2 Ecosystems**

1352

1353 Ozone is phytotoxic. The primary ecosystem impact of ozone is *via* the stomatal uptake of ozone
1354 followed by reaction with the internal plant tissues generating highly reactive oxidants that interfere
1355 with physiological processes (see also §2.1.2) (Fowler et al., 2009; Matyssek et al., 2008; Matyssek et
1356 al., 2010). Ozone may also react with leaf cuticles and other external plant surfaces as well as the

1357 volatile compounds emitted by vegetation. Typical ozone effects on plants include reduced growth,
1358 less seed production, lower functional leaf area and earlier leaf senescence. Data compilation
1359 studies have shown that many species of plants are sensitive to ozone, including: agricultural crops
1360 such as wheat, tomato, soybean and rice and salad crops such as lettuce, spinach and onion (Mills et
1361 al., 2007a); grassland species such as clover species, buttercup and harebell (Hayes et al., 2007;Mills
1362 et al., 2007b); and tree species such as beech, birch and Holm oak (Karlsson et al., 2007). These
1363 effects impact on the important ecosystem services provided by plants, including food security,
1364 carbon sequestration, timber production, and protection against soil erosion, avalanches and
1365 flooding.

1366

1367 Ozone has been recognised as a pollutant causing damage to vegetation since the 1960s and a
1368 research programme to quantify crop loss in North America was established during the 1970s
1369 (Karnosky et al., 2007;Adams et al., 1982). These early studies showed that reductions in exposure
1370 to ozone of 40% would reduce the annual costs of ozone damage by \$3 billion (at 1980 prices). These
1371 early studies used metrics for ozone exposure which were simply the product of ozone mixing ratio
1372 and time above a threshold value (40ppb) and had units of ppb hours (AOT 40, see also section 5).
1373 Since then, analysis of data from over 700 studies of field-based ozone exposure of crops has
1374 indicated that many of our most globally important food crops such as wheat, soybean, maize and
1375 rice are sensitive or moderately sensitive to ozone (Mills et al., 2007a) with estimated global crop
1376 production losses owing to ozone totalling 79-121 million metric tons, worth \$11-18 billion annually
1377 (USD2000) (Avnery et al., 2011a). Global modelling results show that China, India and the United
1378 States are currently by far the most affected countries, bearing more than half of all global losses and
1379 threatened areas from ozone crop exposure (Teixeira et al., 2011;Sinha et al., 2015). In the US,
1380 recent work by Yue and Unger has shown that O₃ damage decreases GPP (Gross Primary
1381 Productivity) by 4–8% on average in the eastern US and leads to significant decreases of 11–17% in
1382 east coast hot spots (Yue and Unger, 2014). Research in China has looked at the ozone exposure for
1383 rice regions, finding that regions along the Yangtze and south China regions had the highest risks in
1384 2000, and these risks will double or triple by 2020 (Tang et al., 2014). In India, The total economic
1385 cost losses for ozone on crop yields in the Indian states of Punjab and Haryana amounted to USD6.5
1386 billion in the fiscal year 2012–2013 and USD3.7 billion in the fiscal year 2013–2014 (Sinha et al.,
1387 2015). It has been recently estimated that the nationally aggregated yield loss owing to ozone in
1388 India is sufficient to feed about 94 million people living below the poverty line (Ghude et al., 2014). In
1389 Europe, wheat yield losses were estimated at 14% due to ozone in the year 2000 in EU27 (plus
1390 Switzerland and Norway), equivalent to 3.2 billion Euros falling to 9% and 2 billion Euro in 2020 with
1391 implementation of current legislation (Mills and Harmens, 2011). It has been argued that plant
1392 breeding that incorporates O₃ sensitivity into selection strategies will be increasingly necessary to
1393 achieve sustainable production with changing atmospheric composition (Wilkinson et al.,
1394 2012;Booker et al., 2009). Future moves to biofuel crops could enhance the formation of ozone with
1395 concomitant negative health impacts (Hardacre et al., 2013;Ashworth et al., 2013).

1396

1397 Critical levels for effects of ozone on vegetation have been set and revised at a series of LRTAP
1398 Convention workshops from 1988 to date. Initial critical levels were based on mean concentrations,
1399 followed by AOT40-based values reflecting appreciation of the cumulative nature of effects and most
1400 recently critical levels have been derived based on stomatal fluxes. The latter take into account the

1401 modifying effects of climate (temperature, vapour pressure deficit, light), soil moisture, ozone and
1402 plant growth stage (phenology) on the amount of ozone absorbed by leaves (discussed in Section
1403 2.1.2a). Calculated using the DO₃SE model developed by Emberson et al. (Emberson et al., 2000),
1404 the stomatal ozone flux method thus allows the dynamics of stomatal opening and therefore ozone
1405 uptake to be modelled throughout the growing season. For example, using the DO₃SE model
1406 parameterised for a specific species, the substantially higher stomatal uptake of 80 ppb of ozone
1407 under warm humid conditions with adequate soil moisture than at higher temperatures with lower
1408 humidity and drier soils would be captured. The flux methodology also incorporates the natural
1409 ozone detoxification capacity of plants by accumulating the Phytotoxic Ozone Dose of ozone above
1410 an ozone threshold flux of $Y \text{ nmol m}^{-2} \text{ s}^{-1}$ (POD_v, units nmol m^{-2} projected leaf area). The value for “Y”
1411 varies between species, with the highest values being for crops such as wheat and potato and the
1412 lowest for some tree species such as beech and birch. The LRTAP Convention’s Modelling and
1413 Mapping Manual now contains flux-based critical levels for ozone effects on food security (wheat,
1414 potato, tomato yield), carbon sequestration and timber production (Norway spruce, beech and birch)
1415 and biodiversity in conservation-grade grasslands (Mills et al., 2011b;Mills, 2014).

1416

1417 The use of the flux-based methodology is supported by recent analyses indicating that field evidence
1418 of ozone effects in Europe fits more closely with areas of greatest risk when flux-based rather than
1419 AOT40-based maps are produced. Furthermore, Fares et al. (Fares et al., 2013a) showed a strong
1420 correlation between measured and modelled fluxes in a mixed pine and oak Mediterranean forest
1421 and epidemiological studies conducted in Switzerland provided supporting evidence for both critical
1422 levels for deciduous trees and the DO₃SE parameterisation.

1423

1424 Reduced carbon assimilation owing to ozone by forests globally has been estimated by Sitch et al
1425 (Sitch et al., 2007) to represent a substantial contribution to the indirect radiative forcing of climate
1426 by ozone (see Figure 29). Through these effects on the productivity of ecosystems and the potential
1427 effects on biodiversity, ozone has become the most important pollutant threat to terrestrial
1428 ecosystems globally and is likely to remain so through most of the current century. Witting et al
1429 (2009) have shown that the carbon sink strength of northern hemisphere forests is likely reduced by
1430 current ozone and will be further reduced in future if ozone rises therefore implying that a key
1431 carbon sink currently offsetting a significant portion of global fossil fuel CO₂ emissions could be
1432 diminished or lost in the future (Wittig et al., 2009).

1433

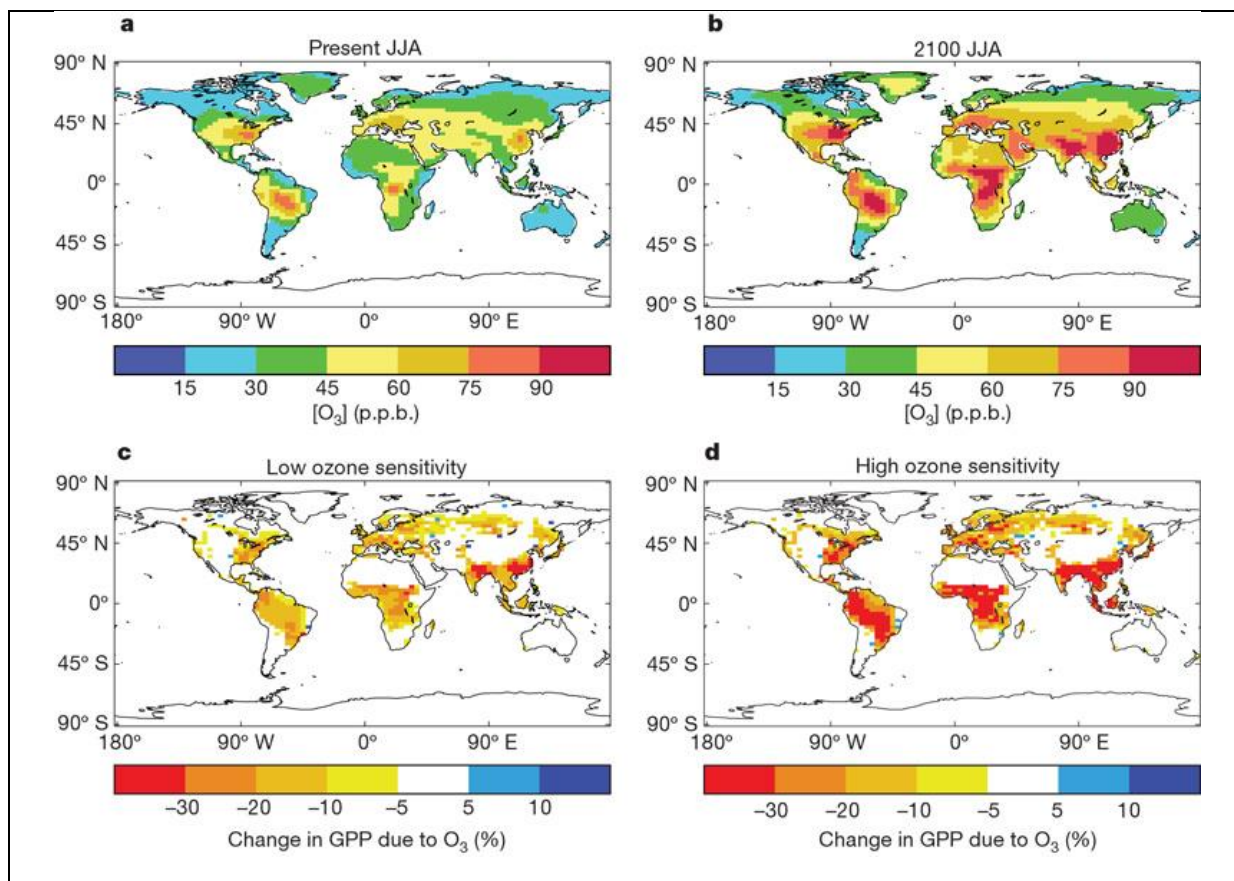


Figure 29 - a,b - Modelled diurnal (24-h) mean surface [O₃] in pbb averaged over June, July and August (JJA) for the present day (**a**) and the year 2100 under the highly polluted SRES A2 emissions scenario (**b**). **c, d**, Simulated percentage change in gross primary productivity (GPP) between 1901 and 2100 due to O₃ effects at fixed pre-industrial atmospheric [CO₂] for 'low' (**c**) and 'high' (**d**) ozone plant sensitivity (Sitch et al., 2007).

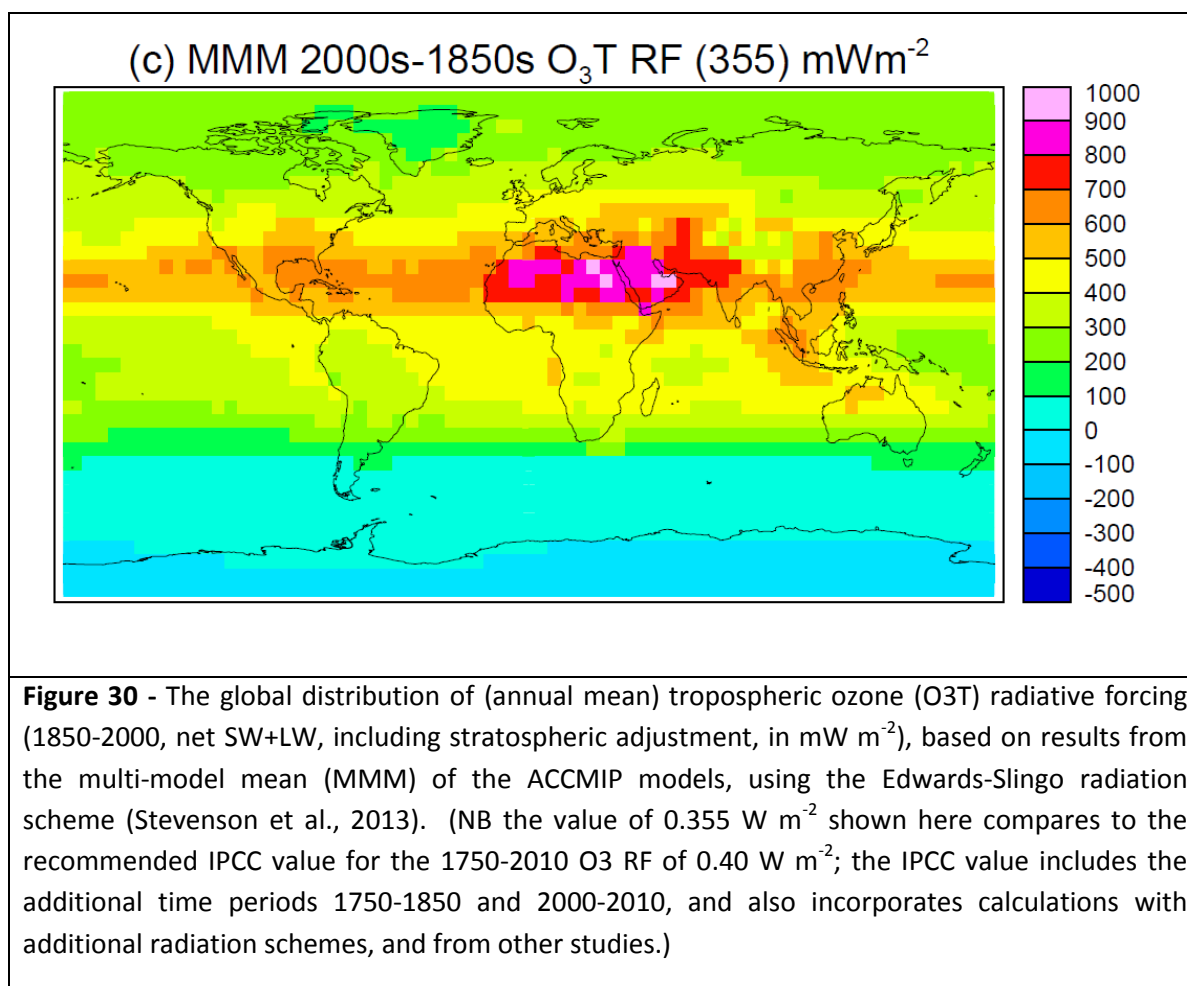
1434

1435 In a recent review, Fuhrer looked at the ozone risk for crops and pastures in respect of future climate
 1436 and concluded that the facets of exposure, leaf uptake and the plant's defence capacity are likely to
 1437 change with a combination of changing anthropogenic ozone precursor emissions and climatic
 1438 conditions. For example, in areas where the frequency of hot/dry periods is projected to increase
 1439 ozone episodes may become more frequent and cumulative exposures will grow, but leaf uptake of
 1440 ozone will decline. In contrast, in more remote rural areas with rapid warming and less drying, ozone
 1441 risks are likely to grow because of increasing hemispheric transport of pollution leading to peak
 1442 ozone levels at times when plant sensitivity is high (Fuhrer, 2009). Tai et al (Tai et al., 2014) have
 1443 shown that warming reduces global crop production by >10% by 2050. In the range of the scenarios
 1444 used ozone changes either exacerbate or offset a substantial part of the climate impacts. The
 1445 authors note that given the competing sensitivities to heat or ozone that it is possible to measure the
 1446 relative benefits for climate adaptation versus air pollution regulation for food security (see also
 1447 (Avnery et al., 2011b)). It is of further concern that new evidence suggests that ozone can reduce the
 1448 sensitivity of plants to drought by interfering with stomatal control mechanisms (Wilkinson and
 1449 Davies, 2010;Wagg et al., 2012), thereby exacerbating effects of extreme weather events.
 1450

1451
1452

3.3 Impact of Ozone on Climate

1453 Tropospheric ozone interacts with both solar (short-wave, SW) and terrestrial (long-wave, LW)
1454 radiation – consequently changes in its distribution can generate radiative forcings (RF) and lead to
1455 changes in climate. In their Fifth Assessment Report of climate change, IPCC found that changes in
1456 tropospheric ozone between 1750 and 2010 had generated a global mean radiative forcing of +0.40
1457 (90% confidence range: 0.20 to 0.60) $W m^{-2}$ (Myhre et al., 2013). This was largely based on the
1458 ACCMIP assessment which considered changes in ozone (1850-2000) simulated by 17 different global
1459 models, and calculations from three different radiation schemes (Stevenson et al., 2013). The
1460 ACCMIP results were augmented by simulations back to 1750 and up to 2010 by the OsloCTM2
1461 model (Skeie et al., 2011), and were broadly consistent with earlier assessments from the literature.



1462

1463 An important feature of the O₃ RF is that, in comparison to the RFs from the well-mixed greenhouse
1464 gases, it is more spatially variable (see Figure 30). The largest changes in ozone since 1750 have
1465 occurred over the industrial regions that are the main sources of ozone's precursors (NO_x, CO, and
1466 VOCs) (see also section 2.3). The industrial emission focus is tempered somewhat by ozone's other
1467 key precursor, CH₄, which is relatively well-mixed due to its decadal lifetime, and also by ozone's
1468 lifetime of a few weeks, which allows transport to reduce zonal heterogeneities. In addition, to the
1469 variations in ozone changes, the spatial distribution of the O₃ RF also depends on other factors. The

1470 LW RF is largest where the temperature difference between the surface and the tropopause reaches
1471 a maximum: that is over land in the tropics and sub-tropics. The SW RF is largest over more reflective
1472 surfaces e.g., snow/ice and desert. The presence of clouds reduces the LW RF, and also modulates
1473 the SW RF. This combination of contributing factors leads to the net (LW+SW) O₃ RF peaking over the
1474 southern margins of the northern mid-latitudes and sub-tropics over land, and in particular over N.
1475 Africa and the Middle East (Figure 30).

1476 Shindell et al (Shindell et al., 2009;Shindell et al., 2005) and Stevenson et al (2013) have attributed
1477 the O₃ RF to O₃ precursor emissions (CH₄, NO_x, CO and VOCs). Results from these studies are
1478 reported in the ‘emissions-based’ RF summary diagram of the IPCC-AR5-WGI Summary for
1479 Policymakers (IPCC, 2013). Stevenson et al (2013) found that increases in anthropogenic emissions of
1480 CH₄, NO_x, CO and NMVOCs are respectively responsible for 44±12% (±1 standard deviation range,
1481 based on results from 6 different global models), 31±9%, 15±3% and 9±2% of the 1850s-2000s ozone
1482 RF. All these O₃ precursors also affect the abundance of atmospheric OH, and hence the lifetime of
1483 longer-lived greenhouse gases such as CH₄. Consequently, emissions of ozone precursors generate
1484 further impacts on climate in addition to those related to changes in ozone; often these additional
1485 climate impacts occur over different timescales, and the net integrated impact on climate of
1486 emissions of a particular ozone precursor are complex to diagnose e.g. (Fuglestvedt et al., 2010). A
1487 further complication is that net impact on atmospheric composition, and hence climate, depends
1488 upon the location of ozone precursor emissions, both in the horizontal e.g., (Fry et al., 2012) and
1489 vertical e.g. (Stevenson and Derwent, 2009).

1490 A major source of uncertainty in the O₃ RF is the pre-industrial distribution of ozone (see Section 2.2).
1491 The few measurements that do exist are mainly thought to be unreliable, but the two more rigorous
1492 datasets, from Montsouris in Paris and Pic du Midi, a mountain top site in central France (Marengo et
1493 al., 1994), suggest that current generation models significantly overestimate late 19th century ozone
1494 levels (Cooper et al., 2014). Cooper et al. (2014) highlight that global models significantly
1495 underestimate recent trends in surface ozone, suggesting that they overestimate past ozone levels.
1496 Consequently, there are suggestions that the ozone RF may be substantially underestimated (also
1497 see, e.g., (Mickley et al., 2001)). It is unclear how these apparent discrepancies in surface ozone
1498 translate into uncertainties in O₃ RF, which is more strongly related to changes in the upper
1499 troposphere. The error estimate quoted by IPCC makes only a cursory attempt to include this source
1500 of uncertainty. Other sources of uncertainty are estimated from the model spread in the 1850-2000
1501 change in ozone, and differences between radiation schemes. Nevertheless, the uncertainties
1502 associated with O₃ RF are far smaller than those due to, e.g., aerosol, because the key source of
1503 uncertainty is the O₃ change rather than our understanding of the fundamental processes involved.
1504 For example, the radiative forcing from aerosols has a larger uncertainty because we are less sure of
1505 the changes in aerosol since the pre-industrial, both in terms of their magnitude and geographical
1506 distribution, but also because the aerosol forcing originates from changes in multiple different
1507 aerosol types, including mixtures of different aerosol species, with highly uncertain optical properties
1508 (Fuzzi et al., 2015).

1509 The spatial structure of the climate response to a particular radiative forcing is not directly related to
1510 the spatial distribution of the RF, but the climate response is typically spread out over the same
1511 latitudes e.g. (Shindell et al., 2010).

1512 The efficacy, or relative effectiveness of an O₃ RF relative to a CO₂ RF in generating a global mean
1513 surface temperature change, has been estimated by Hansen et al. (Hansen et al., 2005) and Stuber et
1514 al. (Stuber et al., 2005). For stratospherically adjusted RFs, Stuber et al (2005) found that the
1515 tropospheric O₃ efficacy has values in the range 0.7-1.7, with O₃ changes in the lower troposphere
1516 showing higher efficacies than the upper troposphere, and O₃ changes in the extra-tropical N.
1517 Hemisphere showing higher efficacies than globally uniform changes. The spatial dependence of the
1518 efficacy appears to relate to the interactions with climate feedback mechanisms e.g., (Shindell,
1519 2014).

1520 It is quite arbitrary (and often fraught) to consider RFs owing to ozone changes in the troposphere
1521 and stratosphere separately, not least because the tropopause is often difficult to locate (e.g.,
1522 (Prather et al., 2011)), and because coherent ozone changes often straddle the tropopause e.g.
1523 (Gauss et al., 2006;Shindell et al., 2013). Changes in tropopause height and morphology associated
1524 with climate change (e.g., (Wilcox et al., 2012)) suggest that there may be very important chemistry-
1525 climate feedbacks related to ozone, such as those related to changes in the Brewer-Dobson
1526 Circulation (e.g. (Hegglin and Shepherd, 2009;Nowack et al., 2015)).

1527

1528 4 Recent Advances

1529

1530 The topics in this section have been selected to represent areas of active research highlighting recent
1531 advances associated with key sources or with particular chemical environments. The diversity of
1532 topics reflect the improved understanding of the richer and more diverse range of interactions
1533 between atmospheric ozone, other parts of the Earth system and human activity.

1534 4.1 Megacities

1535

1536 As of 2007 more than half of the world's population now lives in urban areas, and many of them in
1537 megacities (Zhu et al., 2012). This statistic is often cited, but what defines an 'urban' area or a
1538 'megacity'? While these definitions evolve and differ often depending on the context, here we will
1539 consider a common definition of a megacity that is a city or urban agglomeration of greater than 10
1540 million people (Molina and Molina, 2004). As per Parrish et al. (2011), megacities are dense centres
1541 of population, economic activity, and pollutant emissions, but also areas where effective pollution
1542 control strategies could realize maximum benefit (Parrish et al., 2011). Ground-level ozone is a
1543 serious air quality issue in many of the world's megacities. Monitoring and measurement campaigns
1544 have documented ozone levels exceeding air quality standards in many megacities. For example,
1545 based on the UNECE and WHO guidelines for protection of human health, daily 8-hr ozone should
1546 not exceed 60 ppb on more than 25 days per calendar year. In Delhi, India this threshold was
1547 exceeded approximately 45 days per year on average during the 7 year period (1997-2004), a
1548 significant concern for human health in the megacity (Ghude et al., 2008), especially since ozone
1549 concentrations there are still on the rise (Chelani, 2012). While some cities have extensive
1550 monitoring of ozone (and ozone precursors, more often NO_x than NO_x and NMVOCs), others have
1551 limited to no measurements. Consider South America. Buenos Aires, Argentina for example, has very
1552 few ozone measurements, so that the overall situation with regard to ozone pollution cannot be
1553 thoroughly assessed for the city (Zhu et al., 2012). Sao Paulo, Brazil on the other hand has a more
1554 extensive monitoring network and increasing ozone concentrations have been observed over the last
1555 decade, despite decreases in other pollutants such as NO_x and CO, as well as regular violations of the
1556 national ozone air quality standard (Sanchez-Ccoyllo et al., 2006;Zhu et al., 2012). A variety of
1557 reported ozone concentrations from megacities are shown in Table 2.

1558 Sources of ozone precursors in megacities include, but are not limited to, traffic-related emissions,
1559 combustion of fossil fuels, solvent use, domestic biofuel usage and industrial activities such as power
1560 generation. The relative contribution of sources and specific activities leading to the local ozone
1561 precursor compound mix varies depending on location, including between cities. For example, in Sao
1562 Paulo, Brazil light-duty vehicles are run on ethanol or gasoline/ethanol mix fuels and ethanol from
1563 sugar cane accounts for 65% of all fuel consumed (de Fatima et al., 2012); light-duty vehicles in North
1564 America predominantly run on gasoline which in some cases contains a small fraction of ethanol; in
1565 China gasoline-powered vehicles dominate the vehicle fleet, but there is also significant use of
1566 liquefied petroleum gas (LPG) for some types of vehicles in the fleet (Liu et al., 2008). Overall, the
1567 emissions from vehicles/traffic dominate as a major (if not the main) source of ozone precursors in
1568 many megacities, especially because growing vehicle fleets generally accompany megacity
1569 development (Parrish and Zhu, 2009). For example, Shanghai, the largest city in China with a

1570 population of roughly 23 million, has undergone rapid development; between 1996 and 2008
1571 industrial gross output increased by ≈ 4 times and the number of cars increased from 0.47 to 2.61
1572 million (Tie et al., 2013). Other megacities in which vehicles are cited as the top or among the top
1573 sources of ozone precursors are Cairo, Delhi, Istanbul, Los Angeles, New York, Mexico City, Sao Paulo,
1574 and the Ruhr-Rhein metropolitan region (Chelani, 2012;de Fatima et al., 2012;Parrish et al.,
1575 2011;Khoder, 2009;Im and Kanakidou, 2012;Melkonyan and Kuttler, 2012;Bon et al., 2011). In cities
1576 like Lagos in Nigeria it is a combination of traffic and open biomass burning driving large ozone
1577 exceedances from emission of NMVOCs (Marais et al., 2014).

1578 Extreme events in terms of air quality have also been documented in a number of megacities. These
1579 result from a combination of elevated emissions and meteorological conditions (e.g., stagnant, hot,
1580 sunny) that lead to extremely high concentrations of ozone, typically for a short duration. During the
1581 summer of 2010 in Moscow, blocking anticyclonic meteorological conditions with record-breaking
1582 high temperatures led to larger than normal evaporative emissions from fuels, paints, etc, as well as
1583 emissions from a large number of forest and turf fires, in addition to the 'normal' megacity emissions
1584 (Zvyagintsev et al., 2011;Elansky et al., 2011). These conditions which persisted from July through
1585 mid-August resulted in maximum hourly mean concentrations of ozone that peaked at 134.2 ppbv
1586 (Elansky et al., 2011). An oft cited example of extreme ozone was during the European heat wave
1587 during summer 2003, which adversely affect the residents of a number of European megacities. For
1588 about 2 weeks at the beginning of August a high pressure system was centred on Western Europe,
1589 resulting in record-setting temperatures exceeding 40° C, and accompanied by a persistent
1590 photochemical episode. In France, the highest hourly ozone value reached 208.5 ppbV and
1591 concentrations regularly exceeded the EU threshold of 90 ppbV (Lee et al., 2006;Vautard et al.,
1592 2005;Stedman, 2004;Tressol et al., 2008).

1593 Because of their high population density, the adverse health effects of elevated ozone levels affect a
1594 disproportionately large fraction of the population. A recent study investigated the health impacts of
1595 air pollutants in Tehran, Iran where the annual 8 hr average ozone concentration in 2010 was 34
1596 ppbV, with a maximum 8 h concentration of 93.5 ppbV during the summer period. The health impact
1597 owing to ozone was estimated to cause an excess total mortality of 819 out of 47,284 people in a
1598 year, relative to 2,194 cases for PM₁₀ (Naddafi et al., 2012). For comparison (from a study using the
1599 same method), they cited the excess total mortality for PM₁₀ was 677 out of 1,308,000 people for
1600 Milan, Italy, located in the megacity region of the Po Valley (Naddafi et al., 2012). Cifuentes, et al.
1601 (Cifuentes et al., 2001) assessed the health benefits associated with reductions of PM and O₃ from
1602 climate change mitigation strategies (2000-2020) in 4 megacities – Santiago, Sao Paulo, Mexico City,
1603 and New York. Without going into detail, substantial premature deaths could be avoided from such
1604 policies; in all cases the adverse health effects avoided from ozone were significantly less than those
1605 from PM (Cifuentes et al., 2001). Generally, small but substantial associations between ozone and
1606 total mortality are found in epidemiological studies (Bates, 2005).

1607 The emissions from megacities also have an effect on the surrounding region. In many cases the
1608 urban areas have been identified to be VOC-limited, where high NO_x concentrations in the cities
1609 suppress ozone concentrations (Im and Kanakidou, 2012;Tie et al., 2013). For example, a modeling
1610 study conducted in the context of the MILAGRO measurement campaign in Mexico City identified
1611 that reductions in VOC emissions led to decreases in maximum ozone concentrations while NO_x
1612 emission reductions led to increased maximum ozone concentrations, demonstrating that the urban

1613 core of the Mexico City metropolitan area was VOC-limited, a conclusion supported by the *in-situ*
1614 measurements. The surrounding mountain/rural areas were identified as mostly NO_x-limited,
1615 although the range of these areas was meteorologically dependent (Song et al., 2010). This
1616 suppression of ozone by high NO_x has been identified as generally more characteristic of
1617 extratropical megacities in the northern hemisphere, relative to tropical cities, because of differences
1618 in transport patterns. Tropical cities are more influenced by rapid convective transport, while the
1619 extratropical cities (despite the Mexico City example) allow for a greater build-up of local pollution
1620 (Butler and Lawrence, 2009). Local/regional transport of these air masses into the surrounding areas
1621 can lead to greater concentrations outside of the megacities. For example, in Tokyo, modelling
1622 studies showed that sea breezes developed during the daytime transported emissions from the
1623 urban centre to the north, which caused enhanced ozone in downwind areas 50-100 km away
1624 (Kondo et al., 2010). Furthermore, regional enhancements of ozone during summer were found in
1625 the area (200 km x 200 km) surrounding the Tokyo metro area (Kondo et al., 2010). A modelling
1626 study looking at the impacts of Istanbul (and Athens) on air quality in the East Mediterranean also
1627 found much lower concentrations of ozone within the (mega)cities owing to significant NO_x
1628 emissions depressing O₃. The rural sites in the surrounding area had much higher ozone
1629 concentrations, 11-24 ppbv (9-14 ppbv) greater in summer (winter) than in the urban areas,
1630 emphasizing the importance of the megacity emissions on regional air quality (Im and Kanakidou,
1631 2012). Further sources of emissions in areas surrounding the megacity regions also play a role in
1632 ozone formation. For example, the photochemistry in plumes transported out of London or the Ruhr-
1633 Rheine region will be influenced significantly by further emissions sources, while this is much less the
1634 case for e.g., Cairo which has far fewer emissions sources in the surrounding area (Hodnebrog et al.,
1635 2011). Biogenic emissions will also influence ozone formation downwind of cities. For the Shanghai
1636 region, results from a model study suggested that ozone formation was enhanced in the city plumes
1637 in the downwind region because of the strongly VOC-limited conditions in the plume which resulted
1638 in continuous ozone production during transport. Reasons for this were oxidation of OVOCs and CO
1639 in the plume, and biogenic isoprene emissions (Tie et al., 2013). Finally, an estimate of the footprint
1640 of southeastern megacities in South America found contributions in excess of 30% to downwind
1641 levels of surface ozone under certain conditions (Zhu et al., 2012).

1642 Considering ozone concentrations as a relative contribution to the global scale, megacities contribute
1643 a small amount to global ozone (Stock et al., 2013). In a model 'annihilation' experiment where the
1644 emissions from grid cells containing megacities were removed, emissions from megacities
1645 contributed only 0.84% to the global average tropospheric ozone column density, proportionally
1646 smaller than the 6% of global anthropogenic ozone precursor emissions from megacities (Butler et
1647 al., 2012). This however does not represent human health exposure to ozone in megacities and is
1648 also a global average.

1649 Previous work has shown that individual megacities are not well represented by global emission
1650 inventories compared to the detailed city-scale inventories (Butler et al., 2012), which can be an
1651 issue when trying to model ozone on a larger scale. Additional complexity is added by the non-
1652 linearity of the atmospheric chemistry involved in ozone production processes. Hodnebrog et al.
1653 investigated the importance of resolution for the representation of large scale tropospheric ozone
1654 from megacity emissions and found that higher resolution was much more important for local air
1655 pollution studies than for larger climate studies, as might be expected, due to the integration of
1656 relatively small changes over a large volume (changes in the resolution of meteorology were not

1657 considered) (Hodnebrog et al., 2011). A key point was whether or not the model resolution could
 1658 capture the NO_x saturated regime within the plume common to many megacities (Hodnebrog et al.,
 1659 2011). That said, recent work by Siour, et al. has shown that for chemistry transport models, using a
 1660 ‘zooming’ technique (introducing higher resolution ‘zooms’ to certain areas within a coarser overall
 1661 resolution) allows for better representation of scale interactions, including better representation of
 1662 megacity areas, such as the BeNeLux region (Siour et al., 2013). With the growing interest in the
 1663 study of urbanization, more research and improved methods are still needed to develop a better
 1664 understanding of pollutants such as ozone in megacities and their effects on all scales.

1665 **Table 2** - Reported mean O₃ for megacities.

Location	Mean O ₃ (ppbv)*	Statistic/year	Ref
Beijing, China	31	6 site average, 2001-2006, JJAS	(Tang et al., 2009)
Bangkok, Thailand	17	Annual average, 1-hr, 1995-2008	(Zhu et al., 2012)
Cairo, Egypt	46	Dec 2004-Nov 2005	(Khoder, 2009)
Delhi, India	24	1997-2004, annual avg	(Ghude et al., 2008)
London, UK	19 (38 µg m ⁻³)	Annual average hourly data; suburban site (Eltham) 2009	http://uk-air.defra.gov.uk
Los Angeles, CA, USA	122	2005-2007, national 8-hr ozone design values (daily 8-hr max from running avgs)	(Cox et al., 2009) (accessed 8.8.13)
Mexico City, Mexico	93	City plume, avg from flight measurements, MIRAGE-MEX campaign	(Tie et al., 2009)
Tehran, Iran	34 (68.84 µg m ⁻³)	2010, annual 8-hr avg	(Naddafi et al., 2012)

1666 *concentrations originally reported in µg m⁻³ were converted to ppbv using the simple conversion of
 1667 1 ppb = 2.0 µg m⁻³, assuming 1 atm pressure and 25° C.

1668

1669 4.2 Biomass burning

1670

1671 Wildfires/Biomass burning are the second largest source of carbon dioxide emissions, after fossil fuel
 1672 combustion with ca. 1-2 GtC/year (IPCC, 2013). Tropical biomass burning dominates total emissions
 1673 with boreal fires (50-70°N) accounting for around 9% of all fire carbon emissions. Burning is thus a
 1674 major component of the carbon cycle having a direct global impact on climate (van der Werf et al.,
 1675 2010). Further, there is also an indirect impact because biomass burning is a significant source of
 1676 ozone precursors (e.g. CO, NO_x, VOCs) and aerosol particles. Indeed, Jaffe and Widge (Jaffe and
 1677 Widge, 2012) estimated that global wildfires produce approximately 170 Tg of ozone per year, which
 1678 is 3.5% of all tropospheric ozone production. However, as they pointed out, many areas of
 1679 uncertainty remain in wildfire-related ozone production. These uncertainties centre around the
 1680 interplay of fire emissions, chemical reactions within the plumes, aerosols effects on chemistry and
 1681 radiation and atmospheric dynamics (local and downwind meteorological patterns). These factors,
 1682 along with a strong interannual variability of the fire activity itself, make the assessment of global

1683 impact a challenge. The impact of boreal forest fires is less documented and quantified than tropical
1684 biomass burning.

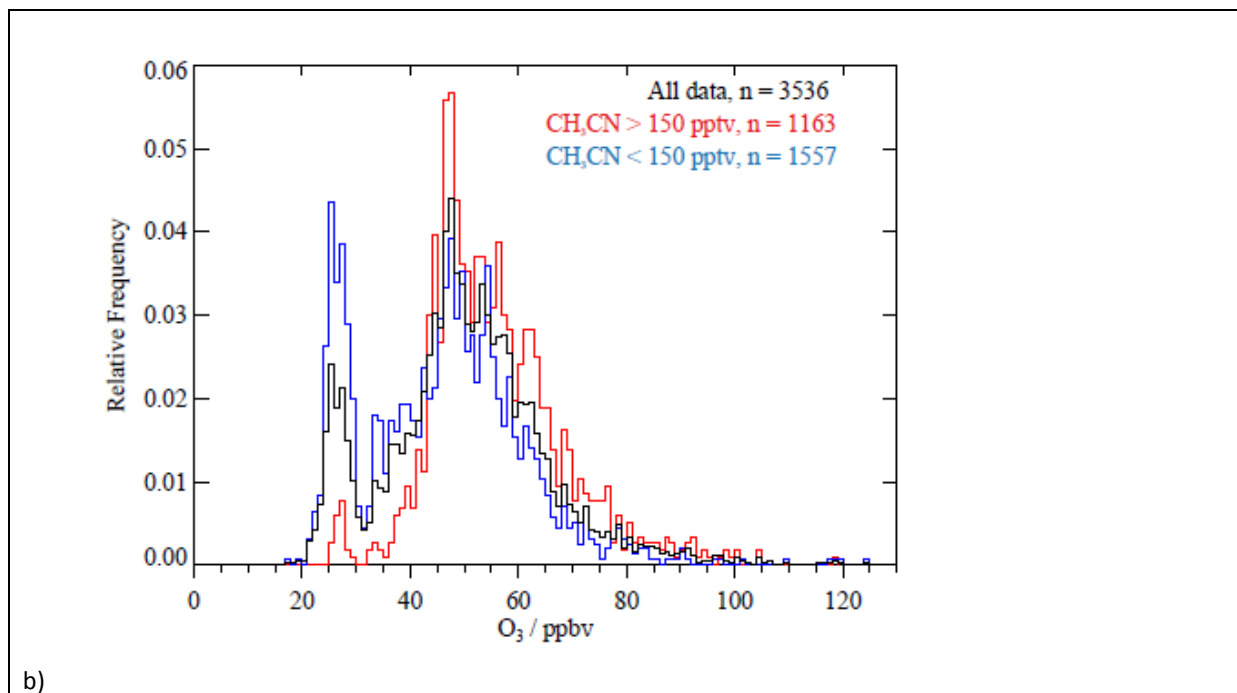
1685
1686 Recently, the atmospheric chemistry challenge of biomass burning in Boreal regions provided the
1687 motivation for the Quantifying the impact of BOREal forest fires on Tropospheric oxidants over the
1688 Atlantic using Aircraft and Satellites (BORTAS) campaign, held in July-August 2010 and 2011 over
1689 Eastern Canada and Western Atlantic. The objective of BORTAS was to better understand the
1690 chemical evolution of plumes emitted from the burning of biomass, with a particular emphasis on the
1691 net production of tropospheric ozone and downwind impacts on air quality ((Palmer et al., 2013) and
1692 references therein) (see Figure 31). Parrington et al (Parrington et al., 2013) have shown that ozone
1693 formation increases with plume age. They used NMHC ratios (extensively described for this BORTAS
1694 campaign in (Lewis et al., 2013)) to estimate photochemical ages of the observed biomass burning
1695 plumes between 0 and 10 days. Parrington et al., (Parrington et al., 2013) found that Ozone
1696 Production Efficiency (OPE) increased with plume ages as calculated by NMHC ratios. They show
1697 $\Delta O_3/\Delta CO$ enhancement ratios increasing from 0.020 ± 0.008 ppbv/ppbv in plumes with photochemical
1698 ages less than 2 days to 0.55 ± 0.29 ppbv/ppbv in plumes with photochemical ages greater than 5
1699 days. According to this study, it seems that the aerosol loading is one of the main drivers of such OPE,
1700 as aged plumes were typically associated with low aerosol loading and relatively high OPE. In one of
1701 the BORTAS flights that made multiple interceptions of a plume with high aerosol loading, Parrington
1702 et al. (2013) report that the photolysis rate of NO_2 was reduced by a factor of approximately 2 within
1703 this plume, suggesting that increased optical depth of the plume can reduce the photolysis rate of
1704 NO_2 to form ozone.

1705
1706 Still in the frame of BORTAS and WMO-GAW programme, results exploring NMVOC ozone precursors
1707 from measurements of biomass-burning (Lewis et al., 2013) have suggested that biomass burning
1708 can be the largest fractional contributor to observed benzene, toluene, ethene and propene levels in
1709 many global locations. The extrapolated widespread biomass burning contribution to atmospheric
1710 benzene, a heavily regulated air pollutant, suggesting a pragmatic approach when setting air quality
1711 targets as tailpipe and solvent emissions decline in developed countries.

1712
1713 Jaffe and Widger (2012) also indicated that boreal wildfires are likely to produce less NO_x on average
1714 than fires in other biomes. This observation makes sense with a more obvious impact of biomass
1715 burning on ozone production in the tropics than at mid-high northern latitudes. However, boreal
1716 wildfires may have diverse impacts on the global ozone distribution as they are also often linked to
1717 convection and pyro-convection allowing thus the injection of ozone precursors and particulate
1718 matter up to the upper troposphere-lower stratosphere where long-range transport processes can
1719 widely distribute the emissions. Subsequent photochemical processes leading to ozone production
1720 and their impact on larger scale may be different than in the tropics. Several groups are actively
1721 developing algorithms and models to derive appropriate injections heights for biomass burning
1722 emissions (e.g. (Kaiser et al., 2012; Freitas et al., 2007)). Depending on the fire radiative power (FRP)
1723 and size of the fire, Freitas et al. (Freitas et al., 2007) have shown that plumes from fires are likely
1724 able to reach 10 km altitude. Based on a statistical analysis of 5 years of satellite observation by MISR
1725 (Multi-angle Imaging Spectrometer) over North America, Val Martin et al. (Martin et al., 2010) have
1726 shown that the median altitude of plumes is found below 3 km altitude for boreal forest fires. A

1727 significant fraction (4-12%) of those plumes are injected above the boundary layer and are more
1728 spread-out vertically depending on the atmospheric stability conditions. In comparison, tropical
1729 biomass burning plumes are mostly limited to the first km of the atmosphere.

1730
1731 Numerous studies report high mixing ratios of biomass burning products, CO in particular, measured
1732 in the middle to upper troposphere and eventually up to the lower stratosphere, thousands of km
1733 from the fire sources (e.g. (Nedelec et al., 2005;Cammass et al., 2009;Fromm et al., 2010;Elguindi et
1734 al., 2010)). Biomass burning signatures from Canadian forest fires have also been observed in the
1735 lower troposphere at the Pico Observatory on the opposite of the North Atlantic (Val Martin et al.,
1736 2006). Implications for the ozone budget in Boreal regions are not as direct as in the Tropics.
1737 Photochemical impact remains uncertain. Clearly, long range transported biomass burning plumes
1738 can influence Europe (Cook et al., 2007;Real et al., 2007) though the impact is variable (Hudman et
1739 al., 2004). More recently, European fires in Portugal and Russia have been shown to contribute to air
1740 pollution (Tressol et al., 2008;Martins et al., 2012) and the frequency is expected to increase with
1741 climate change (Carvalho et al., 2011). Besides their impact on air quality over populated mid-
1742 latitudes, boreal fires are also of particular importance for the Arctic region. For example, the
1743 ARCTAS mission held in April 2008 and June-July 2008 was designed to observe spring time fires from
1744 Siberia, and summertime fires plumes from Canada and Siberia along with their impact on Arctic
1745 pollution (Jacob et al., 2010) (see also section 4.8).
1746



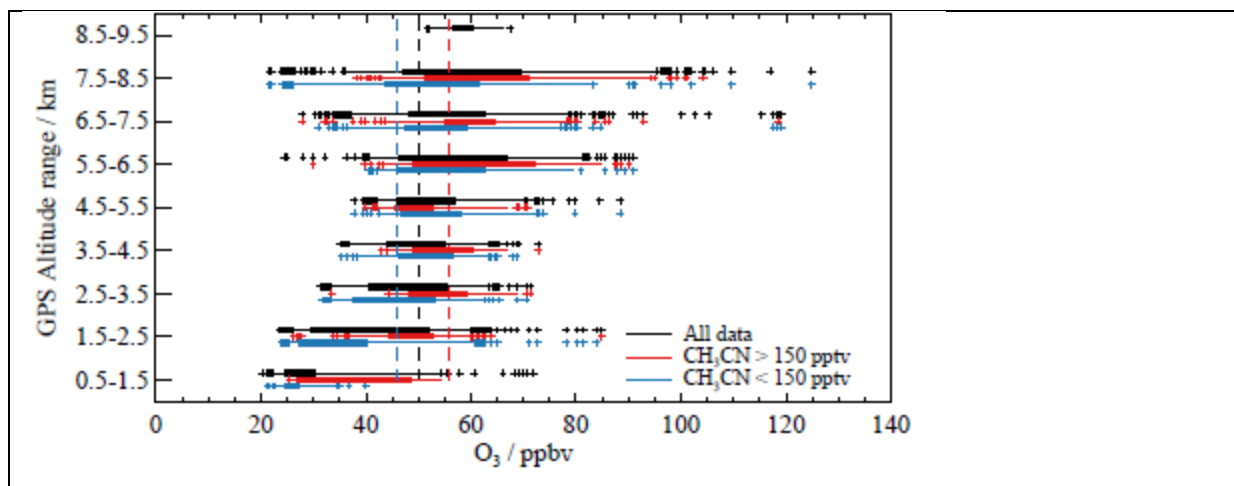


Figure 31 – a) Frequency distribution for ozone over the BORTAS (Palmer et al., 2013) flights, the black line are the measured mixing ratios, where the red line shows the distribution of measurements identified as biomass burning plumes using a threshold of CH_3CN mixing ratios greater than 150 pptv, and the blue line shows measurements made in air masses with CH_3CN mixing ratios less than 150 pptv. ; b) the same data plotted as a box and whisker (solid boxes show the range of the 25th to 75th percentiles and whiskers show the range of the 5th to 95th percentiles with outliers shown as plus symbols) (GPS) altitude profile (Parrington et al., 2013).

1747

1748 Biomass burning in the tropics has long been recognized as the major source of tropospheric ozone
 1749 locally and regionally (Fishman et al., 1990;Thompson et al., 1996;Sauvage et al., 2006;Jonquieres et
 1750 al., 1998;Thompson et al., 2003c). Tropospheric seasonal cycles of ozone are in phase with the local
 1751 biomass burning season (coinciding with the dry season) of each region. It is worth noting one
 1752 exception over Equatorial Africa (Gulf of Guinea and adjacent continent) which is impacted by two
 1753 biomass burning regions, one from each hemisphere. For example, over Lagos, Nigeria, ozone
 1754 enhanced layers are observed in December-February when burning occurs regionally and also in July-
 1755 August when biomass burning occurs over southern Equatorial Africa (Sauvage et al., 2005;Sauvage
 1756 et al., 2007b). Such processes have been further investigated in the frame of AMMA (Reeves et al.,
 1757 2010;Thouret et al., 2009;Mari et al., 2008). Similarly, over Brazzaville, the seasonal cycle of ozone
 1758 peaks in July-August but a secondary maximum appears in January-February due to transport of
 1759 ozone and precursors from fires occurring in the northern hemisphere (Sauvage et al., 2005;Sauvage
 1760 et al., 2007b). Thus, the so-called zonal wave-one as described by Thompson et al., 1999 and Sauvage
 1761 et al., 2006, which describe the ozone maximum over the South Atlantic and adjacent continents
 1762 clearly designates biomass burning as the main contributor of the ozone burden in the tropical lower
 1763 to middle troposphere at least. Biomass burning in the tropics may have a global impact too. The
 1764 extreme El-Nino event in 1997 and the consequent long lasting fires in Indonesia (Siegert et al., 2001)
 1765 have contributed to the increase of CO and other trace gases (e.g. CO_2) observed globally from late
 1766 1997 through 1998.

1767

1768 4.3 Role of biogenics in the formation of ozone

1769

1770 There is much debate as to the influence of biogenic VOCs in urban (Calfapietra et al., 2013), regional
 1771 and global ozone budgets. Variation in natural plant emissions of ozone precursors can influence

1772 ozone concentrations. Goldstein and Galbally suggested we cannot account for the loss of
 1773 approximately half the non-methane organic carbon entering the atmosphere (Goldstein and
 1774 Galbally, 2007) much of biogenic origin.
 1775

1776 Much of the focus on biogenic VOCs and ozone is on isoprene and the monoterpenes owing to their
 1777 apparent dominance of the global VOC budgets (see Figure 22). New insights from field
 1778 observations, models and quantum chemistry into isoprene chemistry and its impacts have been
 1779 recently reviewed by Whalley et al. (Whalley et al., 2014). Some of the new radical chemistry from
 1780 isoprene oxidation is detailed in section 4.10 and the emissions in section 2.3. This section deals with
 1781 the relationships between biogenics and formation of ozone.

1782 Work by Hewitt et al has suggested that the circadian rhythms of the isoprene emitters have an
 1783 effect on the ozone budgets (Hewitt et al., 2011) (see Figure 32), but there has been some debate as
 1784 to the nature of the circadian control (Keenan and Niinemets, 2012).

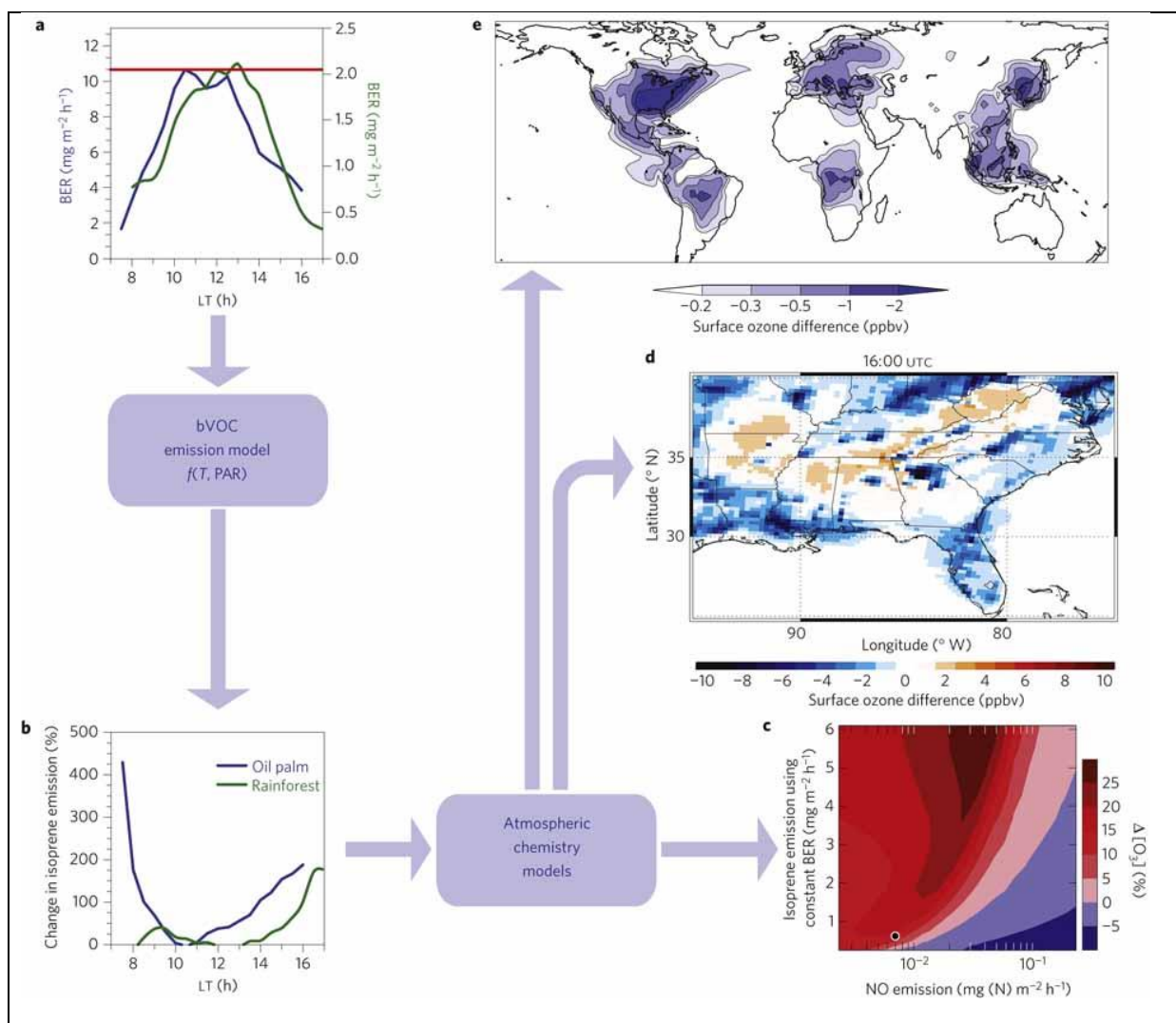


Figure 32 - The effect of a circadian rhythm based biogenic emission rate (BER) on ozone; **a**) The oil palm plantation (blue) and rainforest (green) BERs of isoprene compared with a constant BER (red). **b**), The differences in isoprene emission rates between constant (red line in **a**) and circadian-controlled BERs (oil palm: blue; rainforest: green); **c**), Changes in ground-level ozone resulting from changing isoprene and nitrogen oxide emission rates. **d**), Changes in regional-scale modelled ground-

level ozone for 11:00 LT using an 'oil palm' circadian-controlled BER compared with a constant BER. e, Changes in global-scale modelled ground-level ozone for July using the same scenario as d (Hewitt et al., 2011).

1785

1786 Model calculations have indicated that the biogenic isoprene emissions represent a major
1787 uncertainty in the achievement of AOT40 levels by a factor of at least two (EEA, 2009). The impact of
1788 North American (NA) isoprene on European ozone has been assessed and it has been shown that
1789 future increases in NA isoprene emissions could offset decreases in EU surface O₃ resulting from
1790 controls on NA anthropogenic emissions (Fiore et al., 2011). Archibald et al. have shown that there is
1791 a significant impact of mechanism uncertainties on the global impact of isoprene chemistry on ozone
1792 (Archibald et al., 2011). Recent estimates from Zare et al (Zare et al., 2014) found BVOC to be the
1793 most significant contributor to ozone formation over land areas in the NH enhancing the mixing ratio
1794 by about 11%. In the Pearl River Delta in China (Situ et al., 2013) ozone is sensitive to the BVOC
1795 levels particularly in urban areas. At a regional European scale, biogenic emissions increase O₃,
1796 locally, while reducing PM_{2.5} levels (Tagaris et al., 2014). At the city scale, modelling has shown that
1797 O₃ concentration can be increased by 37 ppb in Seoul, Korea owing to biogenic isoprene emission
1798 and transport of its key oxidation products into the metropolitan area (Lee et al., 2014).

1799 The role of isoprene nitrates has been highlighted as a key uncertainty in ozone and NO_x chemistry
1800 (Horowitz et al., 2007). In the tropics regional simulation of ozone is shown to be very sensitive to the
1801 removal and export of NO_x by isoprene nitrates (Paulot et al., 2012). For example, in South America
1802 and New Guinea, the high ratio of isoprene to-NO_x emissions makes isoprene nitrates chemistry the
1803 primary sink of NO_x. Paulot et al. (2012) suggest that the impact of isoprene photooxidation on
1804 tropical ozone is not limited to the regional scale but can have a long-range effect as a result of
1805 dynamic and photochemical processes such as efficient vertical mixing (through deep convection)
1806 and low boundary layer HO_x (as a result of high biogenics and low NO_x emissions). It is suggested
1807 that these physical and chemical conditions, promote the oxidation of isoprene outside of the
1808 boundary layer, where its contribution to ozone production is amplified (Paulot et al., 2012).
1809 Enhancing the isoprene oxidation mechanism for isoprene-nitrates in a global model and running it
1810 over the USA, Mao et al (Mao et al., 2013) have shown that the dependence of surface ozone on
1811 isoprene emission is positive throughout the U.S., even if NO_x emissions are reduced by a factor of 4,
1812 as well as the chemistry leading to the export of nitrates to the background atmosphere. Browne et
1813 al (Browne et al., 2014) have shown that the monoterpene nitrates have the potential to impact
1814 ozone levels over the remote continental boundary layer. The change in global O₃ burden due to an
1815 increase in BVOC emissions associated with temperature depends critically on the assumed
1816 treatment for the fraction of NO_x recycled from isoprene nitrates (Ito et al., 2009).

1817 A future uncertainty revolves around the impact of biofuels on ozone concentrations, via changes to
1818 vegetation (Ashworth et al., 2013) and BVOC emissions (Porter et al., 2012).

1819 There is significant debate about the role of a wide range of biogenics in ozone chemistry under
1820 future climate e.g. (Andersson and Engardt, 2010;Wiedinmyer et al., 2006) with up to a factor five
1821 difference between different models for Europe (Langner et al., 2012c). It has been recently shown
1822 that the choice of isoprene chemical schemes in climate models can be important (Squire et al.,
1823 2015). A limiting role of increased CO₂ on the potential of ozone precursor emissions from the
1824 vegetation has been recently noted at the global scale (Lathiere et al., 2010). Earlier studies showed

1825 that the vegetation response to climate change is important in driving BVOC emissions and
1826 subsequent formation of ozone (Sanderson et al., 2003).

1827 Several other studies have focused only on the regional impact of climate change (Langner et al.,
1828 2012a;Langner et al., 2012c;Andersson and Engardt, 2010;Manders et al., 2012;Hedegaard et al.,
1829 2008;Hedegaard et al., 2013b;Katragkou et al., 2011). They found a general increase of ozone
1830 concentrations owing to increasing biogenic emissions and favourable conditions for the build-up of
1831 ozone pollution as a result of increased temperature, more frequent summer blocking and heat
1832 waves and increased shortwave radiation. Whereas all these studies agreed on the main outcome of
1833 climate change on ozone in Europe, they also pointed out significant differences depending on the
1834 regional climate model used. The main factors influencing these differences are the projections of
1835 cloud cover and frequency of stagnation episodes that are highly variable across the ensembles of
1836 regional climate projections.

1837

1838 4.4 Halogens

1839

1840 Halogens (chlorine, bromine, iodine) influence the concentrations of ozone in the troposphere either
1841 directly, by reacting with O₃ itself e.g.



1843 or indirectly, by affecting its sources and sinks. Indirect influence results in production or destruction
1844 of O₃, depending on the conditions. Halogens, especially chlorine, react with VOCs to form peroxy
1845 radicals, which convert NO into NO₂, and change the OH/HO₂ ratio e.g. *via*



1847 followed by HOBr photolysis to give OH). Reactions between halogen species and nitrogen oxides
1848 also affect the NO/NO₂ ratio, and form stable compounds, which can act as nitrogen reservoirs and
1849 allow long-range transport of O₃ precursors. A detailed model analysis by Saiz-Lopez et al (Saiz-Lopez
1850 et al., 2012a) estimated that halogens are responsible for up to 10% yearly depletion of the total
1851 tropospheric O₃ column (and up to 20% in the tropical troposphere), especially in the middle and
1852 upper troposphere. The model calculations by Parrella et al. (Parrella et al., 2012) and Long et al.
1853 (Long et al., 2014) generally agree with these estimates. The Long et al. (2014) model analysis
1854 suggest that models may overestimate the role of bromine (and the extent of ozone destruction),
1855 because they tend to overestimate marine aerosol, especially in the Southern Hemisphere.

1856 Our understanding of the role of halogens in ozone chemistry ultimately depends on our
1857 understanding of the physio-chemical processes that release, transform and destroy halogen species
1858 into the atmosphere. There are significant uncertainties in our knowledge of the source processes
1859 and geographical distribution of halogens and severe limitations in the databases of chemical kinetics
1860 parameters (Abbatt et al., 2014). Part of the problem is related to the difficulty in measuring
1861 halogens species at the low concentrations found in the atmosphere (Finlayson-Pitts, 2010): this area
1862 of research has been very active in recent years and many of the most recent advancements in our
1863 knowledge are related to developments in the field of analytical chemistry, particularly mass
1864 spectrometry.

1865 Very detailed reviews have been published in recent years both on halogen chemistry in general
1866 Saiz-Lopez & von Glasow (Saiz-Lopez and von Glasow, 2012) and on specific aspects of halogen
1867 chemistry, such as bromine (Sander et al., 2003), iodine (Saiz-Lopez et al., 2012b;Carpenter, 2003)
1868 and Polar chemistry (Simpson et al., 2007). These reviews detail the broader picture of halogen
1869 chemistry and the focus hereafter will be on recent advances that directly affect tropospheric ozone.

1870

1871 Overall, observations of halogen species in the boundary layer show a consistent picture across the
1872 globe (see (Saiz-Lopez and von Glasow, 2012)), with comparable levels of reactive halogens in
1873 different unpolluted/semi-polluted regions, and more variable levels of reactive halogens in
1874 continental/coastal environments, reflecting the larger variability in their sources and sinks under
1875 polluted conditions.

1876 The major source of chlorine and bromine in the boundary layer is known to be sea-salt: current
1877 model parameterizations are able to reproduce measured BrO levels in the unpolluted MBL
1878 reasonably well (Keene et al., 2009;Sommariva and von Glasow, 2012;Saiz-Lopez et al., 2012a).
1879 However, models struggle to reproduce total bromine and particulate bromide concentrations and
1880 their diurnal cycles, suggesting that our understanding may be limited by the lack of speciation of
1881 bromine in current analytical techniques.

1882 Inorganic chlorine observations are better constrained, although concurrent measurements of Cl₂
1883 and HOCl, especially under semi-polluted conditions (Keene et al., 2009;Lawler et al., 2009;Lawler et
1884 al., 2011), are difficult to reconcile and BrCl, which the models predict as one of the major
1885 components of total Br, has not been detected in marine environments. It is unclear whether the
1886 models-measurements disagreements are due to instrumental issues or to some fundamental
1887 problem in our understanding of the chemistry, particularly in the aqueous phase (Long et al.,
1888 2014;Sommariva and von Glasow, 2012), but they make it difficult to accurately assess the effect of
1889 chlorine and bromine on ozone under unpolluted and semi-polluted conditions.

1890 In the past few years, several groups have reported observations of significant concentrations of
1891 ClNO₂ (from 80 ppt to over 2000 ppt) in a variety of environments and under different conditions
1892 (Osthoff et al., 2008;Kercher et al., 2009;Thornton et al., 2010;Mielke et al., 2011;Mielke et al.,
1893 2013;Phillips et al., 2012;Riedel et al., 2012;Riedel et al., 2013;Wagner et al., 2012). These studies
1894 indicate that nocturnal formation of ClNO₂, *via* reaction of N₂O₅ with aerosol chloride, followed by its
1895 photolysis at sunrise to form Cl + NO₂ is a strong and widespread source of reactive chlorine in the
1896 polluted troposphere. In addition, to kick starting VOC oxidation in the morning before the formation
1897 of OH, the ClNO₂ mechanism also acts as a NO_x reservoir, preventing NO₂ loss overnight as HNO₃ and
1898 hence making it available in the morning to form O₃. Although these two effects are not yet fully
1899 decoupled and understood (see discussion in (Young et al., 2014)), it is clear that this chemistry is
1900 potentially very important for ozone formation in polluted environments. Osthoff et al. (Osthoff et
1901 al., 2008), Thornton et al. (Thornton et al., 2010) estimated that up to 13 ppb additional ozone can
1902 be formed *via* this chemistry. It must be noted, however, that the actual impact on local ozone may
1903 be much less than that, because of the effect of transport and local circulation on ozone levels
1904 (Sarwar et al., 2012;Simon et al., 2010;Simon et al., 2009). Furthermore, model analysis suggests that
1905 recirculation of air masses from urban coastal areas over the ocean may lead to high Cl₂ levels during
1906 the night, thus increasing VOC oxidation and ozone formation at sunrise (Pechtl and von Glasow,
1907 2007), a mechanism which has particular relevance for coastal megacities.

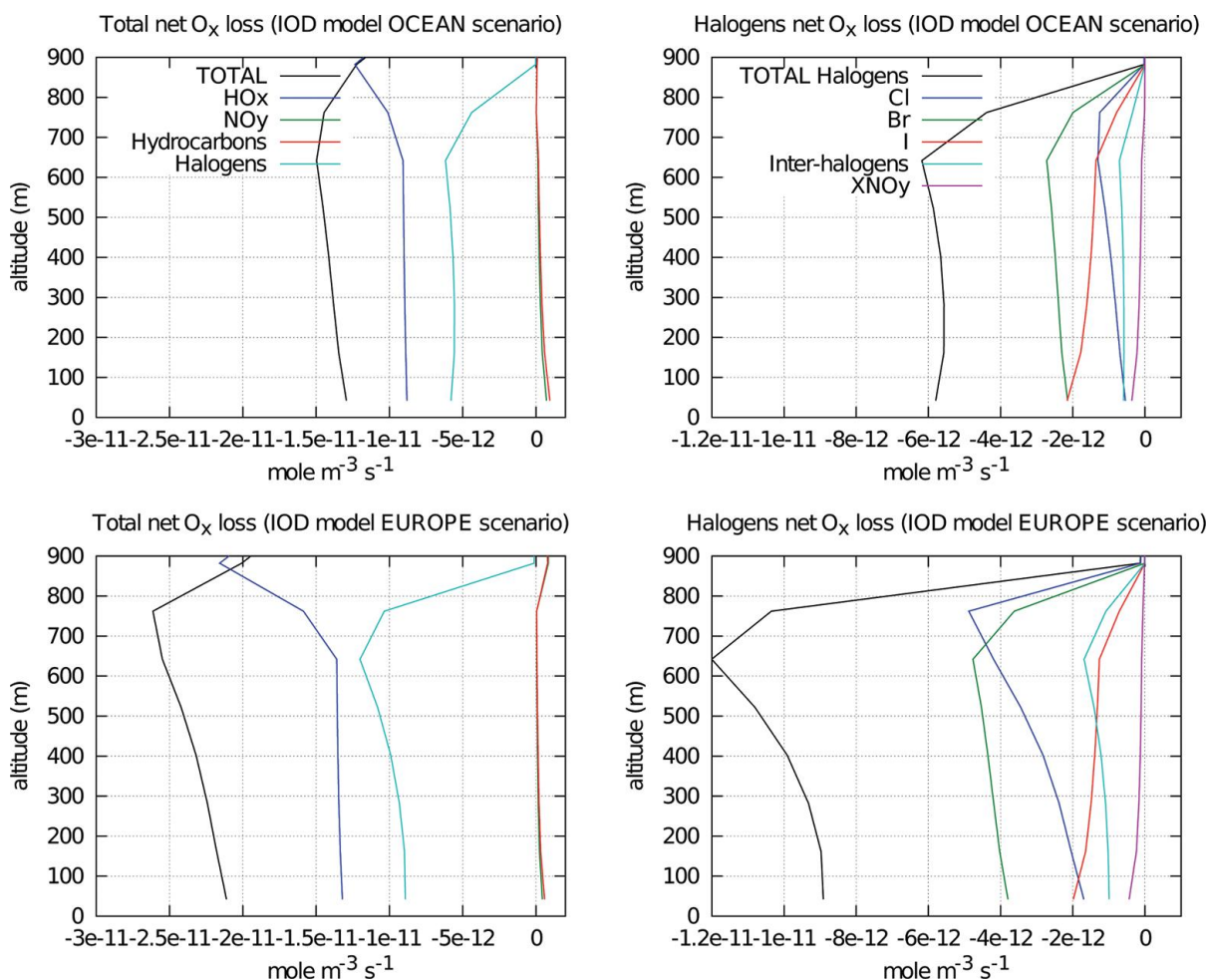
1908 There are several inconsistencies in the observations of reactive iodine, especially under conditions
1909 representative of the open ocean: for example, Carpenter et al. (Carpenter et al., 2010) highlighted
1910 the discrepancy between observations of IO made by different groups at the Cape Verde islands,
1911 while Mahajan et al. (Mahajan et al., 2010), found that IO concentrations in the eastern Pacific did
1912 not agree with the observations of Chlorophyll-a and Dissolved Organic Matter, and were much
1913 lower than the SCIAMACHY satellite observations. Additionally, the measured emission rates of
1914 iodinated VOCs are unable to explain the observed levels of IO and I₂ (Carpenter et al., 2013; Jones et
1915 al., 2010b; Grossmann et al., 2013; Lawler et al., 2014). Several mechanisms have been introduced to
1916 explain the observations and are still under active discussion (e.g., (Lawler et al., 2014; Carpenter et
1917 al., 2013; MacDonald et al., 2014)). Some of these discrepancies may be explained by assuming
1918 seasonal or yearly cycles of the iodine sources, but there are also several uncertainties in the iodine
1919 chemical mechanism (Sommariva et al., 2012; Saiz-Lopez et al., 2012b). The many uncertainties in
1920 iodine sources and chemistry make it difficult to assess accurately the role of iodine as ozone sink in
1921 unpolluted/semi-polluted conditions, especially over the open ocean. Although the sources and
1922 chemistry of iodine species are still being debated, it is well established that iodine species do not
1923 react with VOC and, when NO_x levels are high, they form stable iodine nitrates (INO_x) which can be
1924 taken up on aerosol, leading to net loss of NO_x (and hence O₃). In addition, recycling of INO₃ in the
1925 gas-phase



1927 may increase ozone depletion by up to 60% (Mahajan et al., 2009).

1928 The interaction between iodine and ozone also leads to the formation of ultra-fine particles under
1929 certain conditions (e.g. coastal regions with strong emissions of iodine from macro-algae,
1930 (McFiggans, 2005)), although this process, and its impact on local O₃ concentrations, is not yet
1931 completely understood. Recent work has shown increased O₃ deposition velocities during low tides,
1932 owing to direct deposition to macro-algae and/or to O₃ involvement in iodine-mediated particle
1933 formation (McFiggans et al., 2010).

1934



1935
1936

1937 **Figure 33** - Vertical profiles at midday of total and halogen induced net O_x loss in an unpolluted (OCEAN scenario) and semi-polluted (EUROPE scenario) marine boundary layer (Sommariva and von Glasow, 2012).

1940

1941 All recent observational and modelling studies of halogen chemistry generally agree that reactive
 1942 halogen species are present in the unpolluted/semi-polluted marine boundary layer at levels that
 1943 result in significant depletion of tropospheric ozone and loss of O_x . Read et al. (Read et al., 2008),
 1944 Sommariva & von Glasow (Sommariva and von Glasow, 2012) and Saiz-Lopez et al. (Saiz-Lopez and
 1945 von Glasow, 2012) calculated the contribution of halogens to ozone destruction using different
 1946 models. The results, varying from 3 to 14 ppb per day, indicate that halogens overall are the second
 1947 most important sink for O_x in unpolluted and semi-polluted conditions, accounting for up to a third
 1948 of total ozone loss in the tropical troposphere (Figure 33). Bromine is twice more important than
 1949 chlorine as ozone sink, and iodine is potentially more efficient than bromine although its
 1950 concentration shows a steeper vertical gradient, making it less important than bromine and chlorine
 1951 above 500-600 m (Sommariva & von Glasow, 2012). It must also be noted that the co-presence of
 1952 iodine and bromine makes the loss of ozone more efficient than if bromine alone were present, due
 1953 to the multiplying effect of inter-halogens reactions (e.g., $IO + BrO$, (Read et al., 2008)). In polluted
 1954 regions, due to the higher concentrations of NO_x , the oxidation of VOC by Cl and, to a lesser extent,
 1955 Br, results in net ozone production. For example, Finley & Saltzmann (Finley and Saltzman, 2008)

1956 calculated that the levels of dihalogens (up to 26 ppt of Cl₂ and up to 9 ppt of Br₂) observed in
1957 California could account for up to 10% of measured ozone.

1958 The role of halogens in the boundary layer is likely to be impacted, and possibly become even more
1959 relevant for O₃ photochemistry, by changes in the Earth System, which may alter the formation of
1960 marine aerosol, as well as increased emissions of acids and acid precursors, which affect the halogen
1961 activation processes (Long et al., 2014).

1962

1963 At Polar latitudes (> 60°), periodic ozone depletion events (ODE) have been observed since the mid-
1964 1980s and have been linked to bromine release from the snowpack (Simpson et al., 2007) with
1965 observed BrO levels ranging from 5 to 41 ppt (Roscoe et al., 2014; Saiz-Lopez and von Glasow, 2012).
1966 Recently, novel observations of BrO (Liao et al., 2011) have shown that “BrO clouds” tend to be
1967 distributed homogeneously over scales of a few km during ODE, while Salawitch et al. (Salawitch et
1968 al., 2010) found that BrO columns are correlated with the height of the tropopause, although some
1969 “hotspots” are related to free tropospheric or stratospheric intrusions.

1970 There is much less information regarding iodine and chlorine in Polar Regions. Chlorine presence has
1971 been inferred only by VOC ratios in the past; recently Pohler et al. (Pohler et al., 2010) and Liao et al.
1972 (Liao et al., 2014) have reported the first observations of ClO (up to 24 ppt) and Cl₂ (up to 100 ppt),
1973 respectively, in the Arctic. These findings suggest that Cl may enhance O₃ depletion in the Polar
1974 Regions, mostly *via* its close coupling with bromine chemistry (with the ClO + BrO reaction
1975 contributing up to 73% to ozone depletion). Iodine species (IO) have been detected in Antarctica at
1976 levels comparable to BrO (~20 ppt, (Saiz-Lopez et al., 2008)), which increase O₃ loss rate by up to 3
1977 times. Only one study reported IO in the Arctic at <3.4 ppt (Mahajan et al., 2010); whether this is due
1978 to differences between the two Polar regions (e.g., biological communities or sea ice characteristic) is
1979 at present unclear.

1980 Many questions remain on the mechanism of release of chlorine/bromine species from the
1981 snowpack (see (Abbatt et al., 2012) for a detailed review). An important issue is whether it can
1982 explain observed HOx and NOx levels (Saiz-Lopez et al., 2008; Bloss et al., 2010), as well as observed
1983 halogens levels. A modelling study by Thomas et al. (Thomas et al., 2011), Thomas et al. (Thomas et
1984 al., 2012) indicated that up to 10 ppt of tropospheric BrO can be explained by a mechanism involving
1985 nitrate formation in the interstitial snow; if this is the case, the resulting formation of NOx may
1986 compensate the depletion of O₃ due to reactive Br, possibly leading to net ozone formation.
1987 Additionally, since bromine release is connected with first-year sea ice (Saiz-Lopez and von Glasow,
1988 2012), changes in sea ice formation due to climatic change are likely to affect ozone photochemistry
1989 significantly.

1990

1991 The importance of localized sources of halogens, such as salt lakes, salt beds, saline soils and
1992 marshes, for O₃ photochemistry is at present unclear. Large concentrations of bromine and iodine
1993 (up to 200 ppt of BrO (Tas et al., 2005) and up to 10 ppt of IO, (Zingler and Platt, 2005)) have been
1994 reported over the Dead Sea (Israel) causing O₃ as low as 2 ppb; however, observations in other
1995 locations have shown much lower values (e.g., 6 ppt of BrO and 15 ppt of ClO over the Great Salt
1996 Lake, (Stutz et al., 2002)). The database of observations is very sparse and shows large variability
1997 between different locations, suggesting that the local characteristics (e.g, latitude, pH, geology,

1998 ecosystem and local meteorology) of the salt lakes are crucial in determining the strength of halogen
1999 emissions and therefore of the magnitude of the ODE they trigger (Smoydzin and von Glasow, 2009)
2000 Chlorine and bromine species have also been detected in volcanic plumes at ppm and ppb levels,
2001 respectively (Saiz-Lopez and von Glasow, 2012), leading to ozone depletion inside the plume which
2002 can persist for at least 3 days and possibly longer (see (von Glasow, 2010), for a detailed discussion).
2003 Similar chemistry may be expected from other types of volcanic activity, such as volcanic fields,
2004 vents, fumaroles, etc... and may affect ozone levels both in the boundary layer and in the free
2005 troposphere. The extent to which halogens from volcanic activity affect ozone photochemistry on a
2006 larger (regional/global) scale depends on several variables, including the type, frequency and extent
2007 of volcanic activity, the mixing with the background air and the synoptic circulation.

2008

2009 Besides the injection of halogen species by volcanic activity (see above), the main sources of
2010 halogens in the free troposphere are believed to be the oxidation of halocarbons, the uplift of
2011 aerosol and stratospheric intrusions (Saiz-Lopez and von Glasow, 2012), although direct observations
2012 are scarce. Pommier et al. (Pommier et al., 2012) found evidence of biomass burning from Siberian
2013 fires as a source of BrO (>5 ppt) in the Arctic free troposphere, although the release mechanism is
2014 unclear; Roscoe et al., (Roscoe et al., 2014) compared ground based and remote sensing
2015 measurements in Antarctica and concluded that they could only be reconciled by assuming large
2016 amounts of BrO at high altitudes, in broad agreement with the findings by Koo et al. (Koo et al.,
2017 2012).

2018 Jones et al. (Jones et al., 2010a) found a strong association between high altitude ODEs and
2019 atmospheric low pressure systems which drive the formation of large scale BrO clouds over
2020 Antarctica. Free troposphere-boundary layer dynamic may also be important outside the Polar
2021 Regions. For example, Long et al. (2014) suggested that the accumulation of insoluble bromine in
2022 the free troposphere (*via* sulphur oxidation by HOBr and/or HBr condensation on aerosol) may
2023 explain the observed Br enrichment of submicron aerosol after entrainment of these species back in
2024 the boundary layer. These recent findings suggest the presence of large concentrations of inorganic
2025 Br at high altitudes in the troposphere and model calculations show that they may account for 3-15%
2026 reduction in tropospheric O₃ (von Glasow and Crutzen, 2004). Lary (Lary, 2005) has examined the
2027 role of halogens in the free troposphere using chemical data assimilation technique and concluded
2028 that chlorine and bromine can affect significantly the levels of methane (10-50% of the total
2029 oxidation rate) and ozone in the upper troposphere, especially at Polar and tropical latitudes.

2030 Recently, IO has also been observed in the tropical and sub-tropical free troposphere at
2031 concentrations between 0.2 and 0.4 ppt (Dix et al., 2013;Puentedura et al., 2012). Assuming 0.5 ppt
2032 of BrO and 0.6 ppt of IO, Dix et al. (2012) estimated that iodine accounts for 11% and 26% of total
2033 ozone loss in the free troposphere and in the boundary layer-free troposphere transition region,
2034 respectively.

2035

2036 4.5 Tropospheric ozone and global perturbation of the nitrogen cycle

2037

2038 The drivers of enhanced tropospheric ozone are emissions of the precursors, NO_x and VOC, and
2039 viewed globally the hot spots for ozone production coincide with the areas of largest NO_x emissions
2040 (Stevenson et al., 2006), most notably in Europe, North America and Asia. Thus the effects of
2041 elevated tropospheric ozone are coupled to anthropogenic emissions of NO_x, an important
2042 anthropogenic contribution to the current global cycling of fixed nitrogen (Nr), to distinguish it from
2043 the atmospheric reservoir of unreactive N₂. Recent assessments of the global nitrogen cycle have
2044 quantified the major natural and anthropogenic fluxes of Nr (Sutton et al., 2011; Galloway et al.,
2045 2004). The scale of the human perturbation of the global nitrogen cycle is substantial, with
2046 approximately half of the 413 Tg-N annual fixation of atmospheric nitrogen into reactive oxidized NO_y
2047 and reduced, NH_x forms (Fowler et al., 2013b) contributed by anthropogenic activities (Lu et al.,
2048 2013). Within this total, most of the nitrogen fixed annually is by industrial production of ammonia in
2049 Haber-Bosch industrial plants and within soils and oceans by microbial processes. Only a small
2050 fraction of this Nr is emitted to the atmosphere (see Figure 34). The emissions most important for
2051 tropospheric ozone production are of NO_x from combustion, in vehicles and industry, which totals
2052 approximately 40 Tg-N annually, just 10% of total Nr production.

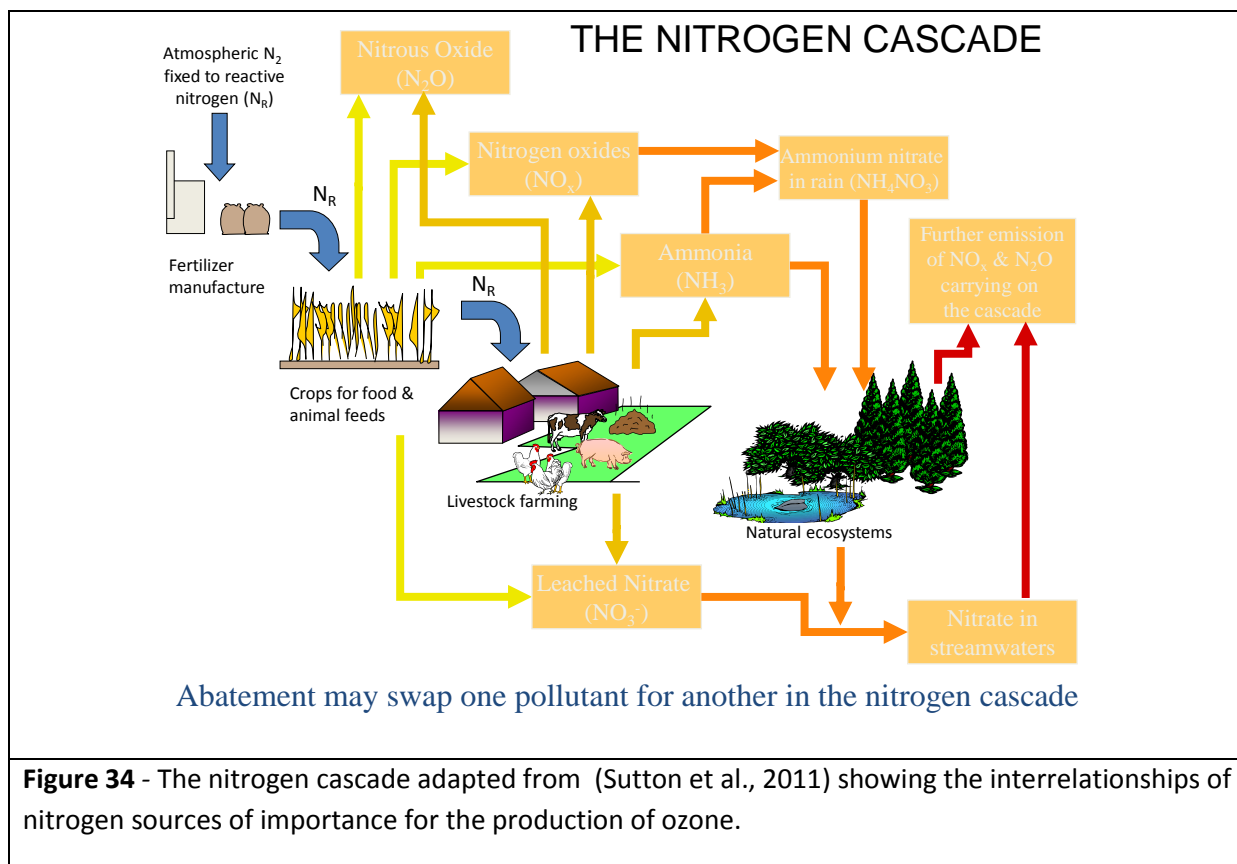
2053 While the focus of this review is tropospheric ozone, it is important to recognise the wider impacts of
2054 the human perturbation of the nitrogen cycle (Fowler et al., 2015). These include eutrophication of
2055 terrestrial and marine ecosystems, reductions in biodiversity of terrestrial ecosystems over Europe
2056 and North America, widespread effects on human health from the aerosols containing nitrogen
2057 compounds and radiative effects on global climate and reductions in stratospheric ozone from
2058 elevated N₂O emission, as detailed by Erisman et al (Erisman et al., 2013). The negative effects of
2059 contamination of the environment by nitrogen compounds has been extensively documented for
2060 Europe (Sutton et al., 2011) and North America (Suddick et al., 2013). However, evidence from Asia
2061 and especially China and India is increasing rapidly and the absolute values for deposition of Nr in
2062 these regions are among the largest globally and effects on ozone production and terrestrial
2063 eutrophication are widespread.

2064 Relatively little research on the effects of nitrogen emission has been reported in the tropics, but
2065 new evidence from work in SE Asia by Hewitt et al (Hewitt et al., 2009) suggests that these regions
2066 are very sensitive to emissions of NO_x which are projected to increase substantially over coming
2067 decades as natural rainforest ecosystems are replaced by agriculture e.g. plantations of oil palm.

2068 One of the distinctive features of the nitrogen cycle is the rapid transformation of nitrogen
2069 compounds within, and transfers between the atmosphere, vegetation, soils, fresh and marine
2070 waters. Thus emissions of oxidized nitrogen to the atmosphere are rapidly oxidized and deposited
2071 into terrestrial ecosystems, where it may be transformed into amino acids and subsequently
2072 decomposed to ammonium following decay and returned to the atmosphere as ammonia. In the
2073 processes within this short sequence, the NO_x in the atmosphere may have generated ozone,
2074 reduced the lives of humans breathing NH₄NO₃ containing aerosols and contributed to species loss in
2075 terrestrial ecosystems. The same emitted N atom may have contributed to a series of different
2076 effects within the Earth system before it is returned back to the atmospheric reservoir as N₂
2077 following denitrification in soils or within the ocean. This effect has been referred to as the nitrogen
2078 cascade (Galloway et al., 2003) and shows a very large range of effects of reactive nitrogen on
2079 climate, terrestrial and marine ecosystems and on human health. A full analysis of the global effect of

2080 nitrogen has yet to be completed, but assessments have been recently published for Europe (Sutton
2081 et al., 2011) and for North America (Suddick et al., 2013).

2082



2083

2084 One further aspect for consideration is the coupling between tropospheric ozone, carbon uptake in
2085 the terrestrial biosphere and nitrogen (Simpson et al., 2014). It has been recently shown that
2086 limitations of available nitrogen for sufficient plant growth reduce the negative impact of
2087 tropospheric ozone on carbon uptake in plants, leading to a smaller indirect change in radiative
2088 forcing than previously calculated (Kvalevåg and Myhre, 2013).

2089 4.6 Challenges in modelling ozone

2090

2091 Models are the integrator of the chemical and physical knowledge with respect to ozone in the
2092 atmosphere. They are much relied on for analysis of observational data, hindcasting, policy support
2093 and forecasting across a range of temporal and spatial scales. Models vary much in scale, resolution
2094 and with physical/chemical complexity.

2095 With respect to current global ozone, Young et al. (Young et al., 2013) compared modelled (ACCMIP
2096 models) and observed (ozone-sonde and satellite (OMI/MLS)) present-day spatial distributions and
2097 seasonality of global tropospheric ozone. The models captured the seasonality well at most locations.
2098 Based on the comparison to OMI/MLS data the models typically overestimated annual mean
2099 tropospheric column ozone at 0-50°N by \approx 0-30% and underestimate it at 0-50°S by \approx 0-25%. Similarly,

2100 re-analysis model data for ozone from MACC shows biases of -5% to +10% with respect to
2101 ozonesondes and aircraft data in the extratropics, but with larger negative biases in the tropics
2102 (Inness et al., 2013). These results indicate that models don't fully represent the processes
2103 controlling the present-day ozone distribution.

2104 Parrish et al. (Parrish et al., 2014) have shown that three of the ACCMIP models, driven by trends in
2105 emissions, underestimate observed trends in surface ozone over the period since ~1950, at NH mid-
2106 latitudes; similar results have been found earlier, e.g. (Schultz et al., 2007b). Cooper et al. (Cooper et
2107 al., 2014) extended this analysis to show that models also underestimate trends in other regions.
2108 These observations suggest that modelled ozone appears to be rather too insensitive to emissions
2109 perturbations (or possibly that historical emissions changes are not well described, see section 2.3).
2110 Emissions remain a key uncertainty for global models (Frost et al., 2012).

2111 Hess and Zbinden (Hess and Zbinden, 2013) and Hess et al. (Hess et al., 2014) find that the evolution
2112 of stratospheric ozone, and how this ozone is transported into the troposphere, is a major
2113 determinant of historical inter-annual variability of NH mid-latitude ozone throughout the
2114 troposphere, and may have significantly contributed to long-term trends. This work indicates that
2115 global models need a detailed representation of stratospheric and UT/LS processes in order to
2116 simulate ozone trends and variability correctly.

2117 Further challenges to models include, the representation of different aspects of ozone chemistry
2118 (e.g., isoprene: (Archibald et al., 2010;Dunker et al., 2014); halogens: (Yang et al., 2005;Saiz-Lopez et
2119 al., 2012a); chemical mechanism (Saylor and Stein, 2012)) and deposition (Val Martin et al., 2014).
2120 For models to represent many of these processes, adequate resolution is required (Colette et al.,
2121 2014).

2122 A couple of studies (Wu et al., 2007;Wild, 2007) have argued that much of the variance in ozone
2123 production across models can be explained by differences in NO_x emissions, inclusion of
2124 nonmethane volatile organic compounds (NMVOCs, mostly biogenic isoprene) and ozone influx from
2125 stratosphere-troposphere exchange. Model tagging offers insights into separating processes such as
2126 transport and chemistry (see e.g. (Garny et al., 2011)).

2127 The challenge for global modellers is prioritising and including all relevant processes in a model with
2128 sufficient resolution and while keeping it sufficiently computationally efficient so that it can be useful
2129 for a wide range of studies.

2130 A large range of models are used to address ground-level ozone at the regional scale (Kukkonen et
2131 al., 2012). Taking into account only emission control policies for the present or near future (2010 or
2132 2020), several multi-model exercises have been conducted in support to the Clean Air For Europe
2133 programme (CAFE). The CityDelta project (Cuvelier et al., 2007) aimed to predict the impact and
2134 uncertainty of emission reductions of several emission scenarios for 2010 in several European cities.
2135 The same exercise was carried out at the larger scale of the European continent (EuroDelta: (van
2136 Loon et al., 2007)). At the continental scale the efficiency of emission reductions was demonstrated
2137 but models provided a large spread of responses in city centres. The ability of an ensemble of six
2138 chemistry transport models to capture recent observed ozone trends was also discussed by Colette
2139 et al. (Colette et al., 2012). They found that models efficiently captured the increase in NO_x saturated
2140 areas, such as the Benelux region and the decrease in NO_x limited areas (many rural regions in

2141 Europe). The quantitative skill of the model was however difficult to retrieve owing to the lack of
 2142 significant trends throughout Europe over the period selected for the experiment. They also
 2143 emphasized that modelled trends were highly sensitive to the trends in precursors prescribed in the
 2144 inventory which exhibited some significant inconsistencies compared to observations of NO₂, in
 2145 particular.

2146 A regional model comparison of ozone is shown in Figure 35. The comparison found that no one
 2147 model was the 'best' model on all days, indicating that no single air quality model could currently be
 2148 relied upon to inform policymakers robustly in terms of NO_x- versus VOC-sensitivity. For this reason
 2149 coupled to basic statistical arguments, it was argued that it is important to maintain diversity in
 2150 model approaches (Derwent et al., 2014).

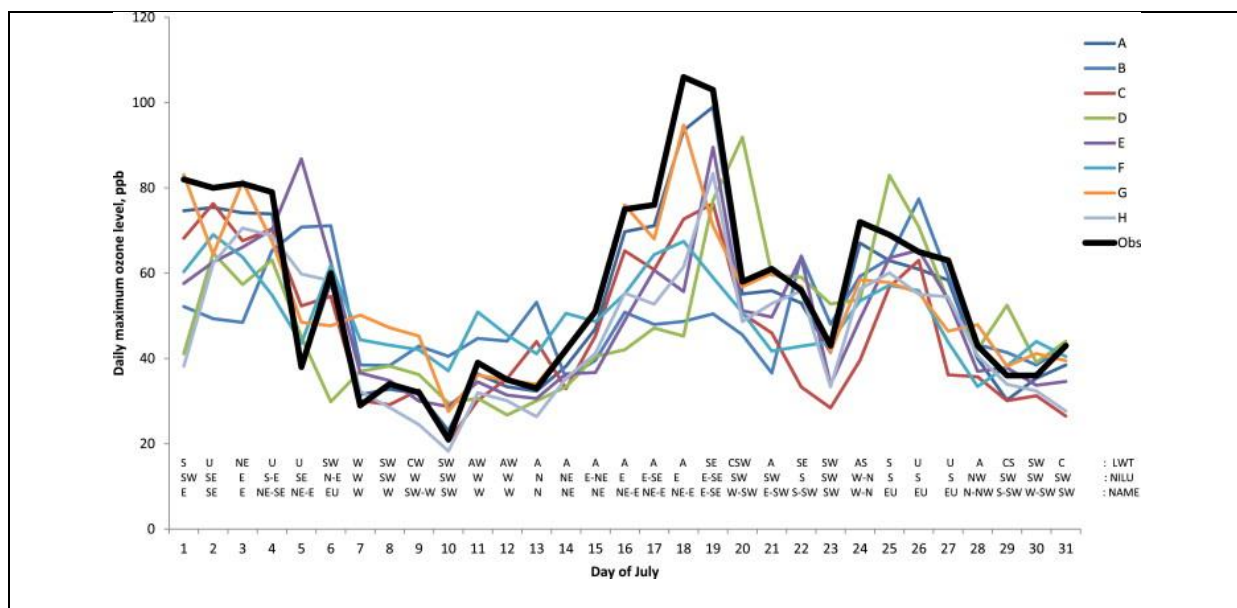


Figure 35 - Daily maximum hourly ozone concentrations for eight models A-H in a comparison exercise against observations for July 2006 at Harwell, Oxfordshire, UK. Also shown are the daily advection regimes as Lamb Weather types (LWT), NILU FLEXTRA trajectories (NILU) and NAME air history maps (NAME), see (Derwent et al., 2014)

2151

2152 With respect to regional models Kukkonen et al. (Kukkonen et al., 2012) have highlighted the most
 2153 prominent gaps of knowledge for chemical weather forecasting models; these include emission
 2154 inventories, the integration of numerical weather prediction and atmospheric chemical transport
 2155 models, boundary conditions and nesting of models, data assimilation of the various chemical species
 2156 (see e.g. (Gaubert et al., 2014)), improved understanding and parameterization of physical processes,
 2157 better evaluation of models against data and the construction of model ensembles.

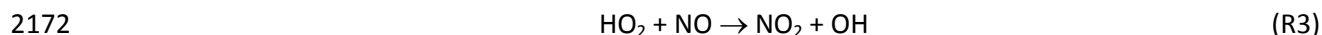
2158 It is clear that next generation models will push to greater resolution on the regional scale (Colette et
 2159 al., 2014).

2160

2161 **4.7 Lightning**

2162

2163 Globally, lightning flashes occur about 50 times per second, equal to 4.3 million times per day and
2164 roughly 1.5 billion times per year. Lightning flashes dissociate N₂ molecules, leading to NO production
2165 (Schumann and Huntrieser, 2007), a key source of NO_x in much of the troposphere, especially the
2166 tropical upper troposphere (Schumann and Huntrieser, 2007;Grew, 2008;Grew et al., 2012a;Levy
2167 et al., 1996). More than 80% of summertime upper tropospheric NO_x above the eastern United
2168 States is produced by lightning (Cooper et al., 2009) and can be significant contributor to surface
2169 ozone (Hudman et al., 2009). Lightning NO_x (NO₂) has been detected from space (Beirle et al.,
2170 2010;Choi et al., 2005). The lightning produced NO perturbs atmospheric composition in several
2171 ways relevant to climate, as NO is an important determinant of OH/HO₂ ratios *via* the reaction:



2173 Given sufficient UV radiation and a supply of HO₂, NO_x will efficiently generate O₃ (see section 2.1.1).
2174 Figure 36 shows modelled contribution of individual sectors in terms of NO_x emissions, including
2175 lightning, to the tropospheric ozone column (Grew et al., 2012a). Toumi et al (Toumi et al., 1996)
2176 highlighted that O₃ production from lightning NO_x (L_{NO_x}) may represent an important positive climate
2177 feedback, if a warmer world generates more lightning (Reeve and Toumi, 1999).

2178 However, in addition to leading to O₃ production (see section 2.1.1), equation (R3) enhances OH. This
2179 increases the methane removal *via* the reaction:



2181 shortening the CH₄ lifetime, and hence reducing its atmospheric concentration, exerting reducing
2182 radiative forcing (RF) (e.g. (Derwent et al., 2001;Wild, 2007;Wild et al., 2001)).

2183 Any perturbations to NO_x (including lightning) will potentially lead to climate feedbacks *via* the
2184 biosphere, through deposition of NO₃ and O₃, and impacts on the carbon cycle (e.g. enhanced or
2185 reduced uptake of CO₂ by vegetation; (Sitch et al., 2007;Felzer et al., 2007)). It is unclear if the net
2186 effect on CO₂ would result in a positive or negative RF.

2187 Most studies suggest more lightning (NO_x) in a warmer world (Schumann and Huntrieser,
2188 2007;Williams, 2005;Banerjee et al., 2014), but these are typically based on the Price and Rind (Price
2189 and Rind, 1992) parametrization that links L_{NO_x} emissions to cloud top height (raised to the power 4.9
2190 over land; to a lower power over ocean). Other parametrizations link L_{NO_x} emissions to cloud ice (see
2191 e.g. (Finney et al., 2014;Tost et al., 2007)), and as warming increases, ice declines, and so does LNO_x
2192 (Jacobson and Streets, 2009). In addition, some schemes relate L_{NO_x} to aerosols (Yuan et al.,
2193 2012;Venevsky, 2014), with potentially complex links between climate and L_{NO_x}. With global
2194 warming, tropical stability increases (Held and Soden, 2006;Chou et al., 2013) tending to reduce
2195 convection. However, the tropopause tends to rise, allowing convection to reach greater heights. In
2196 the Price and Rind (1992) scheme, the higher tropopause affect typically dominates, although there
2197 can be regional increases/decreases in some models (e.g., Stevenson et al., 2005).

2198 In summary, the literature suggests that L_{NO_x} increases lead to higher levels of O₃, OH, nitrate, and
2199 secondary aerosols in general, but less CH₄, and have unknown impacts on CO₂. It remains unclear if
2200 the net impact of increases in L_{NO_x} on climate is warming or cooling; it is also unclear if L_{NO_x}
2201 represents a positive or negative climate feedback.

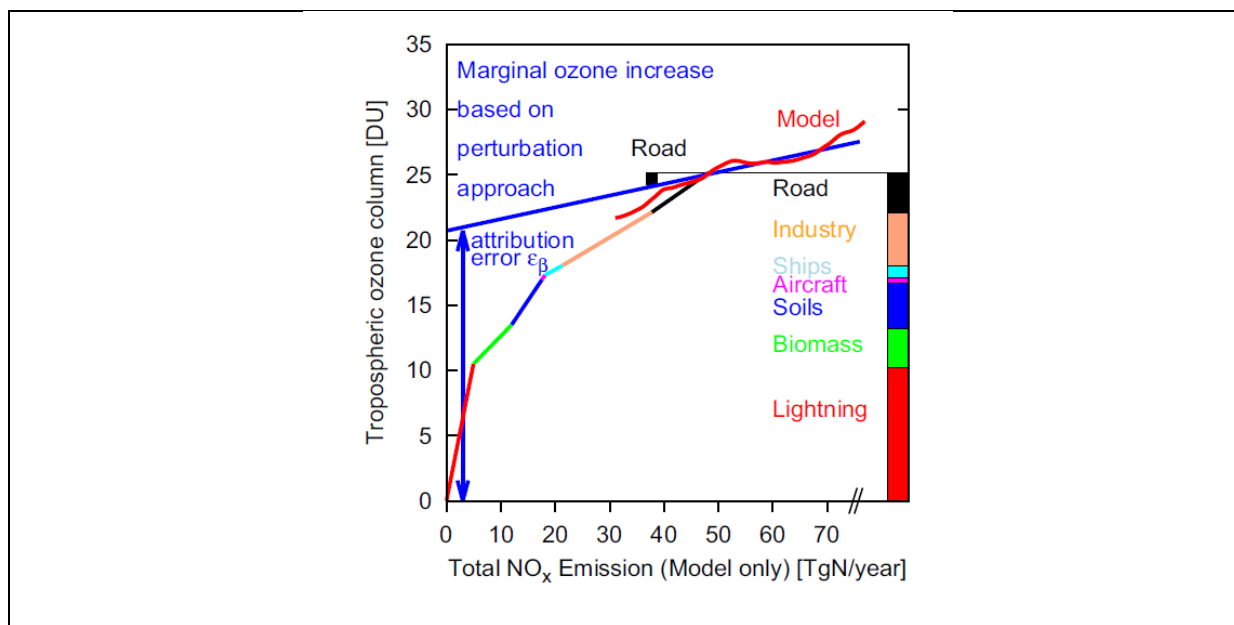


Figure 36 - Contribution of individual sectors in terms of NO_x emissions to the tropospheric ozone column (Grewe et al., 2012b).

2202 4.8 Arctic

2203 The Arctic is under-going rapid change as a result of global warming. This can, in part, be attributed
 2204 to production of ozone from tropical and mid-latitude emissions of ozone precursors, especially
 2205 methane. Climate change together with economic drivers, is also opening up the Arctic to new
 2206 sources of pollution, such as shipping or oil/gas extraction which may lead to significant local or
 2207 regional increases in surface ozone and associated impacts on Arctic air quality and deposition to
 2208 fragile ecosystems (Law and Stohl, 2007).

2209 Observed Arctic O₃ mixing ratios vary between 20 and 40 ppbv at the surface and increase with
 2210 altitude up to the tropopause (8-10 km) (Hirdman et al., 2010). Even though annual data on Arctic O₃
 2211 is rather limited, significant differences can be seen in the seasonal cycle at different locations, driven
 2212 by both remote and local processes (see Figure 37) (Hirdman et al., 2010). Certain sites, such as
 2213 Barrow (Alaska) or Alert (Canada), show evidence of halogen influenced depletion during the spring
 2214 months. As discussed in section 4.4, halogen chemistry over sea-ice or snow covered regions can lead
 2215 to very low or even near-zero O₃ concentrations near the surface in the Arctic spring (e.g. (Barrie et
 2216 al., 1988)). Other sites, such as Zeppelin, exhibit a spring maximum. Higher concentrations in the
 2217 spring appear to be due to O₃ formation from precursors related to the breakdown of Arctic Haze at
 2218 this time of year in the lower and middle troposphere (Emmons et al., 2003). Arctic Haze builds up
 2219 during the winter each year as a result of transport of mid-latitude pollution into the Polar dome (e.g.
 2220 (Barrie et al., 1981)) and contains elevated levels of O₃ precursors (CO, VOCs, NO_x) as well as PAN, an
 2221 important source of NO_x (e.g. (Hov et al., 1989)).

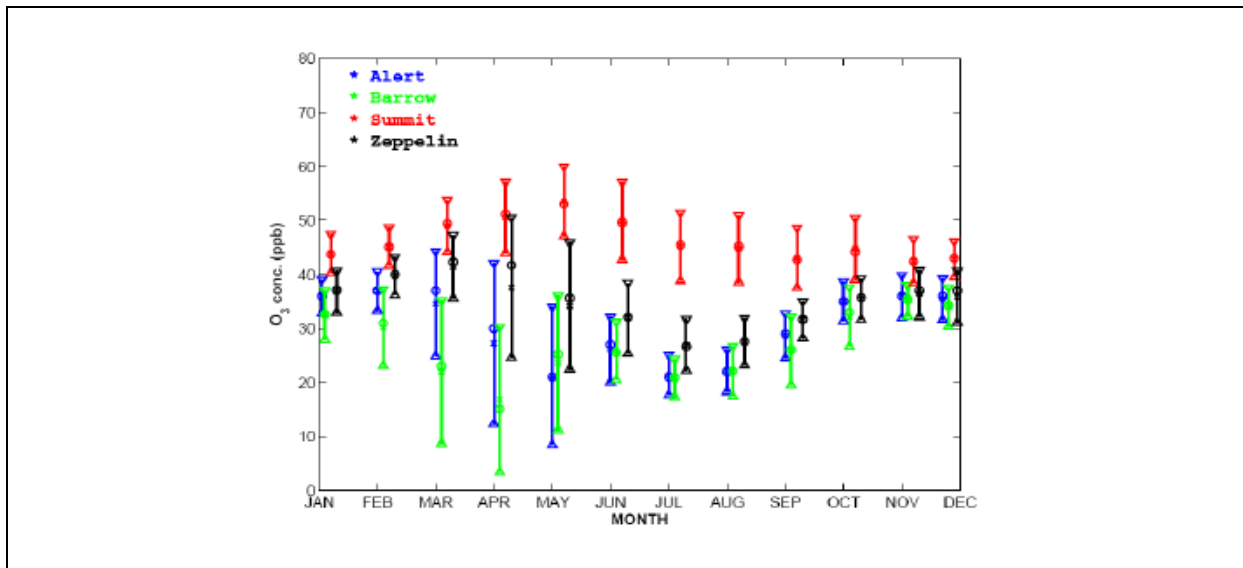


Figure 37 - Seasonal cycle of O₃ at various surface sites in the Arctic. From (Hirdman et al., 2010).

2222 Summit, which is at a higher elevation (3 km), on Greenland, has a late spring/ early summer
 2223 maximum, likely owing to transport of polluted air masses, primarily from North America, but which
 2224 could also include a contribution from snow NO_x emissions (e.g. (Grannas et al., 2007)) or from the
 2225 stratosphere. There are indications that O₃ concentrations continue to increase in the Arctic both at
 2226 the surface and at higher altitudes in the troposphere. Hess and Zbinden (Hess and Zbinden, 2013)
 2227 reported an increasing trend in the European Arctic middle troposphere (500 hPa) of 0.36+/-0.23
 2228 ppb/yr from ozonesonde measurements over the period 1996-2010, and Oltmans et al. (Oltmans et
 2229 al., 2006;Oltmans et al., 2013) reported a trend of 0.87+/-0.50 %/yr from surface measurements in
 2230 1992-2004 at Alert in the Canadian Arctic.

2231 Several studies have examined sources of pollution transported to the Arctic (Mauzerall et al., 1996).
 2232 In a multi-model assessment, Shindell et al. (Shindell et al., 2008) examined precursor emission
 2233 sensitivities to emissions from different mid-latitude source regions on the Arctic and found, for
 2234 example, European CO emissions to be important in the winter. However, surface Arctic O₃ in winter
 2235 was most sensitive to European NO_x owing to the domination of strong titration (O₃ removal) in air
 2236 masses. This was also confirmed by Hirdman et al (Hirdman et al., 2010)). Emissions from Asia and
 2237 Europe have been found to be important sources of Arctic O₃ in spring in the free troposphere
 2238 together with stratospheric injection although relative contributions vary between studies and years
 2239 (Wespes et al., 2012;Shindell et al., 2008). Based on analysis of ARCTAS data (Jacob et al., 2010),
 2240 Wespes et al. (2012) found that European anthropogenic emissions were important for lower
 2241 tropospheric summertime Arctic O₃ in contrast to a previous study (Shindell et al., 2008). Production
 2242 of O₃ from PAN decomposition in air masses transported from mid-latitudes has also been identified
 2243 as an important source of Arctic tropospheric ozone in the summer months (Walker et al., 2012).
 2244 Indeed, aircraft observations collected during POLARCAT-IPY show elevated PAN and CO
 2245 concentrations in air masses transported from Asian and North American anthropogenic emission
 2246 regions in summer 2008 ((Law et al., 2014) and references therein). Boreal forest fires are also an
 2247 important source of PAN and, due to their proximity to the Arctic, plumes can be transported to high
 2248 latitudes during the spring and summer months (Brock et al., 2011;Singh et al., 2010). Whilst little O₃

2249 production appears to occur close to boreal fires (Alvarado et al., 2010;Paris et al., 2010), several
2250 recent studies have shown O₃ production downwind from boreal fires in the Arctic during the
2251 summer months (Wespes et al., 2012;Parrington et al., 2012;Thomas et al., 2013). Nevertheless, O₃
2252 production is higher in air masses influenced by anthropogenic emissions.

2253 However, global and regional models still struggle to capture vertical distributions of trace gases,
2254 including ozone in the Arctic. CO concentrations are often underestimated even in multi-model
2255 simulations carried out as part of the POLARCAT model inter-comparison project (POLMIP) using the
2256 same emission datasets (Monks et al., 2014;Emmons et al., 2014). Discrepancies appear to be related
2257 to either differences in oxidative capacity (OH) or vertical transport of pollutants from mid-latitude
2258 source regions into the Arctic. Modelled concentrations of NO_y species such as PAN or HNO₃ also
2259 show large variability and significant discrepancies compared to measurements (Arnold et al., 2014)
2260 pointing to lack in our understanding about chemical processing in polluted air masses transported to
2261 the Arctic (Law et al., 2014).

2262 As a short-lived climate forcer, tropospheric O₃ contributes to Arctic warming. For example, Shindell
2263 et al. (Shindell et al., 2006) estimated that anthropogenic emission increases since 1900 could be
2264 responsible for 25% of surface temperature changes in the Arctic. Shindell (Shindell, 2007), based on
2265 the results from one model, estimated that about 50% of the Arctic radiative forcing owing to ozone
2266 may be coming from O₃ produced at mid-latitudes (impacting poleward heat transport) and about
2267 50% from ozone produced in the Arctic. New local sources of pollution may also impact Arctic O₃ in
2268 the future such as increased emissions from shipping (Granier et al., 2006) or oil and gas production.
2269 Dalsøren et al. (Dalsoren et al., 2013) examined impacts of future shipping on radiative forcing in the
2270 Arctic and found, particularly in the high-end scenario (from (Corbett et al., 2010)), that O₃ radiative
2271 forcing from shipping is important in the summer and transit season (May to October) when sea-ice
2272 is at a minimum.

2273 **4.9 Unconventional oil and natural gas production: “fracking” and air quality**

2274
2275 Fossil fuel energy production is rapidly transforming and expanding owing to unconventional oil and
2276 natural gas extraction techniques, with implications for regional-scale ozone production.
2277 Unconventional oil and natural gas is extracted from tight geological formations (such as sandstone,
2278 coal and shale) through the use of hydraulic fracturing (also known as fracking) and directional
2279 drilling (Field et al., 2014;Bickle, 2012). These techniques allow wells to be drilled vertically into a
2280 shale formation and then horizontally through the formation, after which a mixture of water, sand
2281 and chemicals is pumped into the well at high pressure, fracturing the rock and allowing oil and gas
2282 to escape.

2283
2284 In the USA, the most extensive extractors of unconventional gas/oil, the shale plays (a name for the
2285 deposits) are located in many large basins across the country, primarily in the Rocky Mountains,
2286 Great Plains and the Appalachian Mountains. In terms of natural gas, the most productive shale
2287 plays are the Marcellus Shale (West Virginia, Pennsylvania, New York) (Kargbo et al., 2010) and the
2288 Haynesville-Bossier Shale (Texas and Louisiana). The greatest unconventional oil production is from
2289 the Bakken (North Dakota, Montana), Eagle Ford (Texas) and the Niobrara (Wyoming and Colorado)
2290 shale formations (Administration, 2014b).

2291

2292 In 2012 the USA produced 8.9 million barrels of oil per day (this includes crude oil, shale oil, oil sands
2293 and natural gas liquids), the third largest producer in the world, behind Russia and Saudi Arabia.
2294 However, the USA is the world leader in producing oil and natural gas from hydraulic fracturing with
2295 1.6 million barrels per day extracted from tight oil formations in 2012. Projections suggest that
2296 hydraulic fracturing will produce 4.5 million barrels per day by 2035, accounting for most of the US
2297 increase in oil production (BP, 2013). The US is poised to become the largest producer of liquid fuels
2298 in the world, primarily due to tight oil growth (BP, 2014a).

2299
2300 In 2012 the USA was the world's largest producer of natural gas, producing 681 billion cubic meters
2301 (Bcm). US production of shale gas output is projected to rise from 255 Bcm/yr in 2012 (37% of total
2302 production) to 672 Bcm/yr in 2035 (BP, 2014b). Shale gas was just 2% of US natural gas production in
2303 2004 but by 2035 it will be 63%. However, these oil and natural gas projections are highly uncertain
2304 with the quantity of oil produced in 2040 differing by a factor of two under a scenario of high oil and
2305 gas resources vs a scenario of low oil and gas resources (Administration, 2014a).

2306
2307 With the increase in unconventional oil and natural gas has come an increase in fugitive emissions of
2308 hydrocarbons to the atmosphere in quantities great enough to influence local and regional-scale
2309 ozone production (Katzenstein et al., 2003;Kemball-Cook et al., 2010;Edwards et al., 2014). This
2310 impact was revealed in an unexpected way during early 2008 when hourly average ozone mixing
2311 ratios exceeded 140 ppbv during February in the rural Upper Green River Basin, of Wyoming (Schnell
2312 et al., 2009). In situ measurements revealed that the high wintertime ozone levels were due to a
2313 strong temperature inversion that trapped NO_x and hydrocarbon emissions from the natural gas
2314 industry. The trapping of the emissions was facilitated by high mountains on three sides of the basin.
2315 A key contributor to the ozone formation was deep snow cover which reinforced the temperature
2316 inversion, and also reflected UV radiation back through the inversion layer, essentially doubling the
2317 amount of available UV radiation necessary for ozone production. This phenomenon has also been
2318 observed in the Uintah Basin, Utah, impacted by both oil and natural gas extraction (Edwards et al.,
2319 2013;Edwards et al., 2014). Multiple years of data from these two regions demonstrate that without
2320 deep snow cover, the high ozone values do not occur (Oltmans et al., 2014). Recent work in the UK
2321 context (Sommariva et al., 2014) has shown the range and difference in UK shale VOC profiles.

2322
2323 The impact of emissions from the oil and natural gas industry on ozone outside of these rural,
2324 mountain-ringed basins is less certain. For example, field studies have been carried out across the
2325 Denver-Julesburg Basin in north-eastern Colorado to quantify emissions from the oil and natural gas
2326 industry but accurate estimates for some gases are complicated by emissions from nearby urban
2327 areas (Pétron et al., 2012). However, relationships between particular VOCs can be used to clearly
2328 distinguish oil and natural gas emissions from urban emissions. VOC measurements from a site on
2329 the northern edge of the Denver metropolitan area were analysed to demonstrate that more than
2330 50% of the VOC-OH reactivity was attributable to emissions from oil and natural gas operations,
2331 indicating that these emissions are a significant source of ozone precursors (Gilman et al., 2013).

2332
2333 Several recent studies using chemical transport models suggest that emissions from the oil and
2334 natural gas industry can produce local and regional scale ozone enhancements (Kemball-Cook et al.,
2335 2010;Rodriguez et al., 2009;Carter and Seinfeld, 2012;Olague, 2012). The reliability of these
2336 modelling studies is limited by the emissions inventories which are difficult to accurately produce

2337 owing to the heterogeneity of sources: type of gases emitted from a shale play; number of active
2338 well heads; integrity of infrastructure; emissions associated with well-completion vs. well operation;
2339 usage of venting or flaring (Field et al., 2014). The most recent U.S. EPA estimates indicate that NO_x
2340 emissions from US petroleum and related industries only amounted to 5% of total US anthropogenic
2341 NO_x emissions in 2013, but doubled between 2004 and 2013 (Agency, 2014). Likewise VOC emissions
2342 increased by a factor of four over the same period, accounting for 14% of total US anthropogenic
2343 VOC emissions in 2013. However, these U.S. EPA estimates are highly uncertain. The U.S. EPA
2344 recently stated that it had not anticipated the tremendous nationwide growth in this sector and that
2345 it has limited directly-measured air emissions data from several important oil and gas production
2346 processes. The report recommends that the EPA produce a comprehensive strategy for improving air
2347 emissions estimates for oil and natural gas production (Agency, 2013). Until the emission inventories
2348 can be improved great uncertainty will surround model estimates of the impact of the oil and natural
2349 gas industry on ozone pollution.

2350
2351 One final consideration of the potential for the oil and gas industry to affect tropospheric ozone is
2352 through its impact on global methane levels. Methane leaks from the oil natural gas industry may be
2353 a contributing factor to the renewed increase in global methane concentrations (Nisbet et al., 2014).
2354 For example, hydraulic fracturing in Utah may locally leak 6 to 12% of gas production to the air
2355 (Karion et al., 2013). Kang et al (Kang et al., 2014) have highlighted the issue of abandoned wells and
2356 their significance. Figure 38 shows data from a series of studies including satellite remote sensed
2357 data that all show significant methane leakage beyond official EPA estimates (Schneising et al.,
2358 2014;Kort et al., 2014). However, owing to the great uncertainty of many aspects of global methane
2359 emissions, especially from US unconventional oil and natural gas activities (see e.g. (Allen et al.,
2360 2013)), much more research is required to understand the impact of unconventional oil and natural
2361 gas activities on global methane concentrations (Brandt et al., 2014).

2362

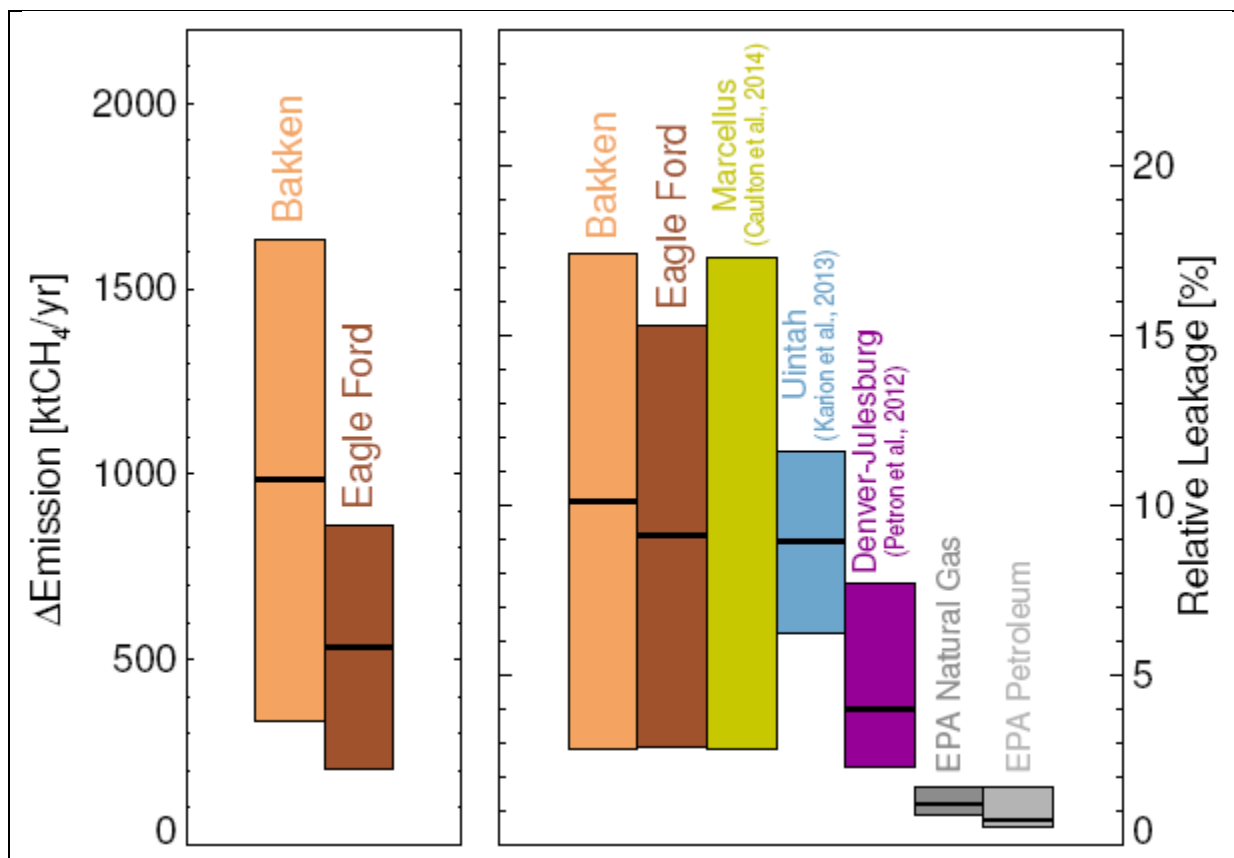


Figure 38 - Estimated methane emissions are shown for the targeted regions Bakken in light brown, and Eagle Ford in dark brown from satellite remote sensing measurements (Schneising et al., 2014). Shown are absolute emission increases (2009–2011 relative to 2006–2008) in the left panel, and the leakage rates relative to production in the right panel, with the 1σ uncertainty ranges. For comparison, leakage estimates from previous studies in Marcellus (2012) (Caulton et al., 2014), Uintah (2012) (Karion et al., 2013), Denver-Julesburg (2008) (Pétron et al., 2012) . EPA bottom-up inventory estimates for natural gas and petroleum systems (2011) are shown for comparison (EPA, 2014).

2363

2364 4.10 Radical Chemistry, Radical changes

2365

2366 Radicals are central to the chemistry of the atmosphere; from the destruction of O_3 in the
 2367 stratosphere, to the production and destruction of O_3 in the troposphere, radicals drive atmospheric
 2368 composition change (Monks, 2005). The inorganic HO_x radicals (OH, HO_2) are regarded by many in
 2369 the field of atmospheric chemistry as the most influential of all radicals, as such a great amount of
 2370 effort has gone into understanding their impacts and fate in the atmosphere (Heard and Pilling,
 2371 2003; Monks, 2005; Stone et al., 2012).

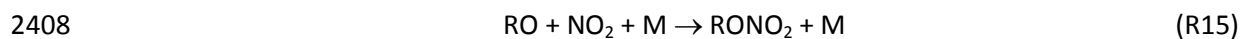
2372 Recent laboratory and modelling studies have shifted attention to improved understanding of the
 2373 fate and role of organic radicals. The organic radicals of importance to atmospheric chemistry can be
 2374 classified as organic peroxy radicals (RO_2) (section 2.1.1), organic oxy radicals (RO) and the so called
 2375 Criegee intermediates (CI), a class of bi-radical compounds believed to be formed mainly from the
 2376 reaction of O_3 with alkenes.

2377

2378 In the following section we briefly review the main aspects of the chemistry of organic radicals and
2379 highlight the latest discoveries in their chemistry. Significant use of the review of Orlando and Tyndall
2380 (Orlando and Tyndall, 2012) is made and for further details we refer the reader to their work.

2381 RO₂ are produced in the atmosphere by the OH (and NO₃) initiated oxidation of VOCs. Once formed
2382 RO₂ are lost *via* reactions with NO, HO₂ and other RO₂. Whilst reactions with halogens (X) and
2383 halogen oxides (XO) have been known about for several decades, their importance for inclusion in
2384 studies of tropospheric O₃ chemistry has traditionally been expected to be small (see section 4.4 for
2385 more details). The RO₂ + NO reaction is known to have two product channels. The first forming NO₂,
2386 hence propagating tropospheric O₃ formation; the second channel leads to the production of an
2387 organic nitrate (RONO₂) *via* a complex rearrangement, the exact mechanism of which is still uncertain
2388 (Dibble, 2008). We will not dwell on the chemistry of RONO₂ here, but suffice it to say these moieties
2389 allow O₃ precursors to be transported over great distances owing to their much longer atmospheric
2390 lifetime than NO₂. The kinetics of the RO₂ + NO reaction limit the RO₂ lifetime to only a few seconds
2391 when [NO] > 1 ppbv (see section 3.1 of Orlando and Tyndall 2012 for references). Broadly speaking
2392 the RO₂ + NO reaction can be classed as the most important of the RO₂ loss reactions to include for
2393 modelling O₃ production in the troposphere. The products of the reaction between RO₂ and HO₂
2394 depend strongly on the structure of the RO₂ (Orlando and Tyndall, 2012). Traditionally the reaction
2395 between RO₂ and HO₂ has been thought of as a radical sink, hence limiting the propagation of RO₂ +
2396 NO reactions and so reducing the potential O₃ production. The major product of this reaction for an
2397 alkyl RO₂ (R'RCHOO) is an organic hydroperoxide (ROOH), a compound that is predicted to be lost
2398 from the atmosphere *via* deposition or aqueous uptake faster than its photodissociation can reform
2399 precursor radicals. The kinetics of the self (RO₂ + RO₂) and cross reactions (RO₂ + R'O₂) of RO₂ (see
2400 section 3.5 of Orlando and Tyndall 2012 for references) limit the importance of these reactions to
2401 laboratory studies and parts of the atmosphere where concentrations of RO₂ are high (e.g. high BVOC
2402 emission regions).

2403 For RO₂ to have a big impact on the composition and chemistry of the atmosphere they must
2404 propagate radical production. RO are produced almost exclusively as products of the reactions of RO₂
2405 with NO. In general RO are very reactive and either undergo unimolecular decomposition (on the
2406 time scale of milliseconds) or react with O₂ producing HO₂ radicals (see section 2.1.1). Archibald et al.,
2407 (Archibald et al., 2007) used a box model to investigate the importance of the reaction:



2409 and concluded that for CH₃O, reaction 15 could be a significant source of CH₃ONO₂ under the high
2410 NO₂ conditions found in many megacities, but that the unimolecular decomposition and reaction of
2411 O₂ with RO limits the importance of reaction 15 to CH₃O only.

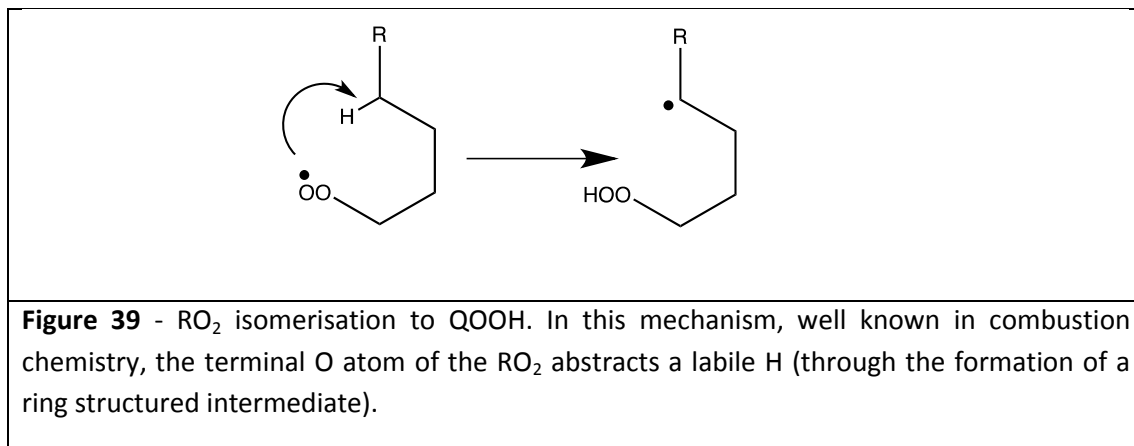
2412 Owing to very significant disagreement between model simulations and observations of HOx radicals
2413 in pristine environments (Whalley et al., 2011; Lelieveld et al., 2008), a number of recent studies have
2414 focused on trying to better understand the role of NOx free radical propagating chemistry for RO₂. In
2415 pristine environments the loss of RO₂ was traditionally thought to be dominated by the radical
2416 terminating reaction between RO₂ and HO₂. However, for acyl RO₂ (RC(O)OO) recent work has shown
2417 that the reaction of RO₂ with HO₂ has a major radical propagating product channel generating OH
2418 and RO₂ (see section 3.4 of Orlando and Tyndall 2012 for references). Based on this evidence
2419 Lelieveld et al., (2008) postulated that the reaction of RO₂ with X (where X reacted with a rate

2420 coefficient similar to that for RO₂ + NO) propagated radicals and was able to reconcile the model
2421 measurement disagreement for HO_x in the Amazon. However, Lelieveld et al. (2008) were unable to
2422 provide direct evidence for the structure of the unknown reaction partner, X. In much earlier
2423 modelling work, Frost et al., (Frost et al., 1999) speculated that near-IR absorption by RO₂ could lead
2424 to intramolecular conversion and yield HO_x radicals. Whilst a great deal of work has been performed
2425 identifying the absorbance features of RO₂ in the near IR (e.g. (Kline and Miller, 2014)), to date there
2426 has been almost no laboratory evidence of HO_x formation following absorption by RO₂ in the near-IR.
2427 However, Maccarone et al (Maccarone et al., 2013) have recently shown that arylperoxy radicals
2428 (RO₂ derived from aromatic hydrocarbons) are able to photo-dissociate in the visible spectrum to
2429 yield O(³P), and hence produce O₃ in the troposphere, without the need for NO_x. As highlighted by
2430 the work of Lelieveld et al. (2008) and Frost et al (1999), modelling experiments are increasingly
2431 being used to help direct laboratory studies in the search for radical propagating reactions. Archibald
2432 et al. (Archibald et al., 2009) investigated the possible reaction between RO₂ and OH using a simple
2433 box model of the marine boundary layer (MBL). In their study Archibald et al. (2009) suggested three
2434 different mechanisms for the RO₂ + OH reaction yielding three unique product sets, two propagating
2435 radicals and the third leading to the formation of alcohols. The reaction they modelled was, at the
2436 time, very speculative and as such no kinetic studies had been performed. As such Archibald et al.
2437 (2009) used the kinetics of RO₂ + X and RO₂ + XO reactions as analogy. Their model calculations
2438 concluded that the RO₂ + OH reaction would have little impact on HO_x under conditions encountered
2439 in the MBL. Recently Bossolasco et al., (Bossolasco et al., 2014) have measured the direct kinetics for
2440 the reaction between RO₂ and OH and have shown that it is extremely fast ($k \approx 2.8 \pm 1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$),
2441 potentially twice as fast as the upper limit used by Archibald et al. 2009. The importance of this
2442 reaction under conditions similar to those found by Lelieveld et al. (2008) is yet to be explored.

2443 Whilst unimolecular RO₂ isomerisations have been known about in combustion chemistry (where T >
2444 600 K) for several decades (e.g. (Hughes et al., 1992)), the importance of this process for the loss of
2445 RO₂ in the troposphere was thought insignificant - until recently. The RO₂ isomerisation proceeds *via*
2446 internal H atom abstraction from the terminal oxygen of the -OO group to produce what in
2447 combustion chemistry is referred to as a QOOH (see Figure 39). Using *ab initio* calculation, Peeters et
2448 al. (Peeters et al., 2009) and Da Silva et al. (Silva et al., 2009) independently suggested a mechanism
2449 for RO₂ isomerisations in the oxidation of isoprene that they postulated could help improve the
2450 model-measurement mismatch reported by Lelieveld et al. (2008) for HO_x in pristine conditions. The
2451 focus on isoprene peroxy radicals has led to a number of new discoveries in the lab as well as from a
2452 theoretical point of view. Thanks, largely to developments in mass spectrometry and other analytical
2453 techniques, new products (isoprene epoxydiols – IEPOX; hydroperoxyaldehydes - HPALDS) have been
2454 elucidated, and their mechanisms and impacts on reconciling the “HO_x problem” tested (Crouse et
2455 al., 2011;Paulot et al., 2009). In their work on updates to the chemical mechanism of isoprene
2456 oxidation, Archibald et al. (Archibald et al., 2010) reviewed several of the proposed mechanisms and
2457 concluded that whilst the isomerization reactions proposed by Peeters et al (2009) had the most
2458 promise in reconciling the model-measurement disagreement, the reported parameters could not be
2459 fully reconciled with atmospheric observations of other species and existing laboratory data without
2460 some degree of parameter refinement and optimization, which would probably include a reduction
2461 in the peroxy radical isomerisation rates and a consequent reduction in the OH enhancement.
2462 Indeed, Crouse et al. (Crouse et al., 2011) provided the first laboratory evidence for the RO₂
2463 isomerisations in the isoprene system but derived rate coefficients for the processes that where

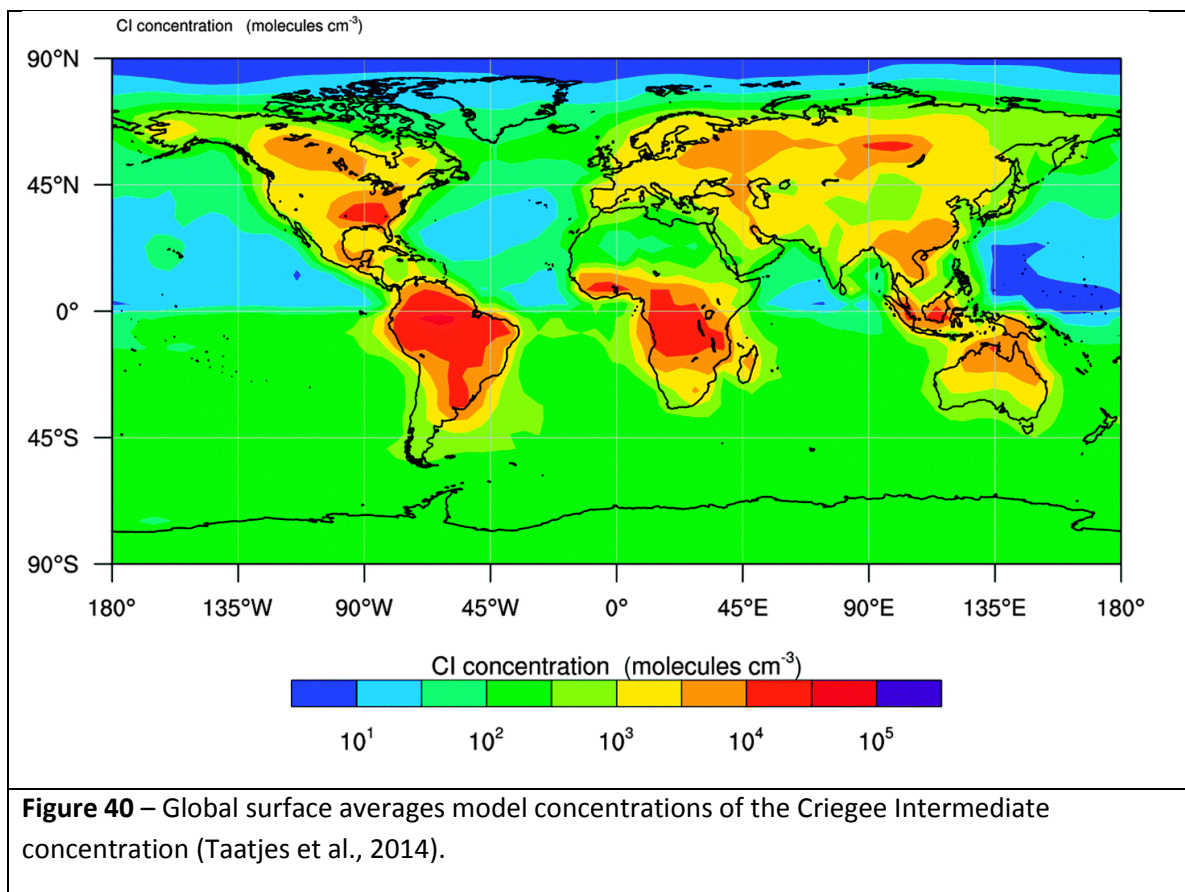
2464 much smaller than those calculated by Peeters et al. (2009). However, modelling studies using the
2465 kinetics derived from their study suggested that 10-20% of isoprene RO₂ would undergo
2466 unimolecular isomerisations (Crouse et al., 2011) and as such this is an important process to include.

2467



2468

2469 An astonishing amount has been learnt about the atmospheric chemistry of the Criegee
2470 Intermediates (CI) over the last few years. Pioneering work carried out at the synchrotron Advanced
2471 Light Source (Taatjes et al., 2008) provided the first detection and subsequent direct measurements
2472 of the kinetics of the CI (Welz et al., 2012). Traditionally CI have been thought to have been formed
2473 exclusively from the ozonolysis reaction of alkenes (as originally proposed by (Criegee, 1948)).
2474 However, the recent laboratory studies on small CI have utilized novel chemical routes, which avoid
2475 the reaction with O₃. For example, a large number of groups have used CH₂I₂ as a reagent for the
2476 formation of CH₂OO (*via* photolysis and reaction with O₂). It should be noted that CH₂I₂ one of the
2477 major iodine containing VOCs emitted in the marine boundary layer (Saiz-Lopez et al., 2011) and may
2478 be a direct source of CI in this environment. McCarthy et al. (McCarthy et al., 2013) have shown that
2479 CH₂OO can also be produced *via* passing a mixture of CH₄ and O₂ through an electric discharge
2480 (through what remains an as yet unknown mechanism). Based on this evidence McCarthy et al.
2481 (2013) have postulated that it is likely that CH₂OO can be formed in the upper and free troposphere,
2482 given the large mixing ratios of CH₄ and O₂ in the upper troposphere and the relatively high density of
2483 electrical discharge (in the form of lightning flashes). Given that many of the reactions between O₃
2484 and alkenes have small rate coefficients ($\sim 10^{-17} \text{ cm}^3 \text{ s}^{-1}$) it is important that these non-ozonolysis
2485 routes to CI production be quantified using model studies in order to better understand the burden
2486 of CI in the troposphere (see Figure 40).



2487

2488 Of fundamental importance to understanding the chemistry of CIs is knowledge of their physical
 2489 properties. McCarthy et al. (2013) have used a combination of methods to determine the geometry
 2490 of CH₂OO, in good agreement with the work of Su et al. (Su et al., 2014). As well as now having great
 2491 insight into the geometry of CH₂OO, a number of studies have shed light on the absorption spectrum
 2492 of CH₂OO in the UV/vis (e.g. (Beames et al., 2012;Sheps, 2013)) Beames et al., (2012) and Sheps
 2493 (2013) have shown that there is strong absorption by CH₂OO in the 320-400nm range. Whilst this
 2494 may have implications for additional loss of CH₂OO by photolysis, the large cross section in this
 2495 region has the benefit of making cavity ringdown spectroscopy laboratory studies of the kinetics of
 2496 CH₂OO (and other CIs) possible – opening up a number of avenues for greater understanding of these
 2497 ephemeral but crucial intermediates in the oxidation of VOCs in the atmosphere.

2498

2499 What seems to be emerging from the plethora of laboratory studies on the kinetics of CI reactions is
 2500 that they react very fast! For example, Su et al. (Su et al., 2014) have shown that the bimolecular
 2501 self-reaction of CH₂OO has a rate constant near the gas kinetic limit ($k = 4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$). Su et al.
 2502 (2014) determined that the reaction proceeds *via* a CH₂OO dimer – where the zwitterionic character
 2503 of the CH₂OO allows for barrierless addition of the terminal O atoms with the central C atom. This
 2504 dimer is predicted to dissociate to produce two CH₂O (formaldehyde) and O₂ in its excited electronic
 2505 state (O₂(¹Σ_g)). Such a fast self-reaction has implications for the analysis of previous laboratory
 2506 studies in this system. Similarly fast kinetics have been observed for CIs reacting with organic acids.
 2507 Using a combination of time resolved laboratory experiments, Welz et al. (2014) (Welz et al., 2014)

2508 have very recently shown that the reactions of the C1 and C2 Cls with HCOOH and CH₃COOH are
2509 several orders of magnitude faster than previously inferred from alkene ozonolysis reactions
2510 ($k \sim 1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$). Although products of the reaction were not detected, it is likely that highly
2511 condensable products will form, potentially contributing to SOA formation and growth. Although it is
2512 interesting to note that the Cl seem more reactive than RO₂ with a number of compounds, it is
2513 paramount to understand the dominant loss processes of the Cl in order to understand their
2514 abundance. Before many of these direct kinetic experiments were performed it was widely assumed
2515 that in the troposphere the reaction with H₂O would dominate over other loss reactions, in spite of
2516 slow (although uncertain) kinetics. Welz et al. (Welz et al., 2012) reported an upper limit for the
2517 CH₂OO + H₂O reaction rate coefficient ($k = 4 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$). Relative rate experiments have yielded a
2518 number of other estimates of the rate coefficient for this. Ouyang et al. (Ouyang et al., 2013), who
2519 studied the reaction of NO₂ with CH₂OO, estimated $k = 2.5 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$. In their study, Ouyang et al.
2520 were able to show that the reaction produces NO₃ – the most important oxidant at night. So far
2521 inclusion of this reaction into modelling studies has not been performed and estimates of the
2522 importance of this process for night-time chemistry are needed. Based on detection of HCHO, Stone
2523 et al. (Stone et al., 2014) were able to put an upper limit on the reaction of the Cl with H₂O of $k = 9 \times 10^{-17}$
2524 $\text{ cm}^3 \text{ s}^{-1}$, significantly smaller than the estimates for this reaction by Welz et al. (2012). They
2525 suggested that this much lower reactivity may mean that previous conclusions from modelling
2526 studies where H₂O was calculated as the dominant loss process may need to be revised. Combining
2527 the results of Welz et al. (2014) and Stone et al. (2014) we speculate that it is possible that in many
2528 environments where organic acids are present at the ppb level, reaction with these acids may be the
2529 dominant loss process for Cl. Interestingly, Taatjes et al. (Taatjes et al., 2013) have shown that the
2530 *anti*-CH₃CHOO Cl reacts with H₂O very fast ($k = 1.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$), suggesting that the lack of reaction
2531 between CH₂OO and H₂O may not be representative of all Cl.

2532

2533 5 Policy context

2534

2535 Within the policy context, much of the focus on ozone has been on ozone as an air pollutant (e.g.
2536 (OECD, 2012; EEA, 2007, 2009, 2011; Royal Society, 2008; Fowler et al., 2013a). As recently stated the
2537 aim of much policy with respect to ozone and air quality is “to achieve levels of air quality that do not
2538 result in unacceptable impacts on, and risks to, human health and the environment” (Fowler et al.,
2539 2013a) (see also section 3) within some measure of reasonable cost. This process requires an
2540 understanding of the messages from research and monitoring activities to develop new insights.
2541 Policy, to date, requires methods of assessing compliance to metrics that quantify impact. Owing to
2542 the transboundary nature of ozone, much focus has been on regional and hemispheric impact of
2543 metrics and mitigation.

2544 Throughout this section certain metrics will be detailed, the main two of which are AOT40, the
2545 seasonal accumulated exposure above 40 ppb (80 $\mu\text{g}/\text{m}^3$) during daylight hours, this is normally
2546 expressed as a cumulative exposure (ppb h or ppm h) and SOMO35 the sum of the amounts by which
2547 maximum daily 8-hour concentrations of ozone (in $\mu\text{g}/\text{m}^3$) exceed 70 $\mu\text{g}/\text{m}^3$ (35 ppb) on each day in a
2548 calendar year.

2549
2550

5.1 Policy Metrics for ozone

2551 Ozone is a powerful oxidant which can cause adverse effects on human health and vegetation. As a
2552 result, air quality standards for ozone have been established to mitigate these effects. Ozone can also
2553 damage some materials, particularly rubber and plastics, but no standards specifically address these
2554 effects. Ozone is a unique pollutant in that different areas of the ozone concentration frequency
2555 distribution are affected by different mechanisms and hence could require significantly different
2556 policy responses. The averaging times of different ozone metrics are also of crucial importance for
2557 policy (see e.g. (Pappin and Hakami, 2013;Lefohn et al., 2010)).

2558 Health-related standards have up to now been expressed as one hour or eight-hour averages, the
2559 latter arising originally from chamber studies of human exposures where the maximum effects were
2560 observed over exposures of around eight hours. Such short term peak ozone concentrations based
2561 on averaging times of the order of hours, such as those observed in ‘smog’ episodes, are formed
2562 from the well-known VOC/NO_x chemistry (see section 2.1.1). These reactions occur typically over
2563 timescales of hours to a few days, in conditions of low wind speed and strong sunlight, and hence the
2564 spatial scale of such episodes and the policy response area, is of the order of 100s to ~1,000
2565 kilometres. Controls on precursor emissions across Europe are therefore required to mitigate these
2566 peaks within European nations. Figure 41 shows a comparison of a number of national and
2567 international ozone air quality standards.

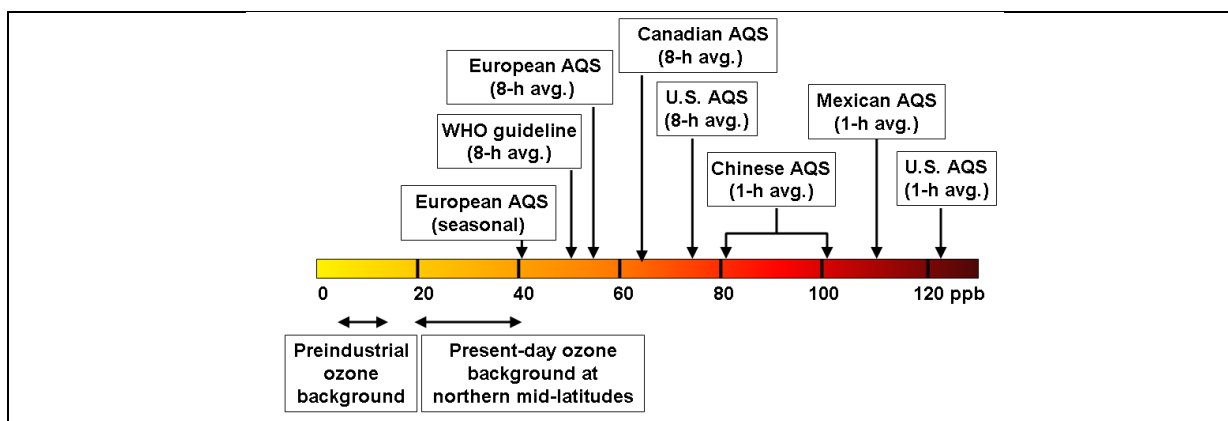


Figure 41 – Ozone Air Quality Standards (AQS) in ppb. Different national and international standards are noted as well as estimates for northern midlatitudes of the preindustrial background (i.e., O₃ abundances with all anthropogenic emissions of NO_x, CO, VOC, and CH₄ switched off, and before current climate and stratospheric O₃ change) and the present-day baseline abundances (i.e., the statistically defined lowest abundances of O₃ in air flowing into the continents, typical of clean-air, remote marine sites) from (Council, 2009a).

2568

2569 Effects on vegetation however are more closely related to longer term exposures and in the recent
2570 EU Ambient Air Quality Directive (Directive 2008/50/EC) for example, the Target Value (see below)
2571 for the protection of vegetation is expressed in terms of AOT40 as an accumulated value from May to
2572 July (defined in more detail later). This longer exposure period, with a threshold close to the
2573 tropospheric baseline ozone level means that emission controls would be required over a much
2574 wider area than those to mitigate the health-related one/eight hour average concentrations
2575 discussed above, and could also involve other, more long-lived precursors such as methane.

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There are several levels of ‘standard’ in use, with differing legal status. For example, the fundamental health effect evidence is used to inform the setting of WHO Air Quality Guidelines, below which the pollutant in question will not have adverse effects on public health. The Guidelines are set without regard to the technological, economic or social issues which might affect their achievability. In setting legally based standards however, some flexibility is often introduced to allow for difficulties of achieving the levels and/or to allow for year-to-year meteorological variability. For short-term standards this usually takes the form of allowing a number of exceedences of a given concentration over a year, and/or averaging over several years as in the case of the USA. Some health standards in place around the world are shown in Table 3.

Table 3 – Comparison of world health standards for ozone

Country/region	Ozone level (ppb)	Averaging time	Nature of level
WHO	50	Daily max. 8-hr mean	Guideline ¹
EU	60	8 hour running	Target value ²
	60	Average	Long Term Objective
USA	75	8 hour	National standard ³ primary and secondary
California	90	8 hour	State standard not to be exceeded
	70	1 hour	
UK	50	8 hour	Objective ⁴
Canada	63	8 hour	2015
	62	8 hour	2020
			Both ‘voluntary guidelines’
Mexico	80	8 hour	5 th maximum taken over 1 year

¹ WHO also quotes 120ppb daily max. 8 hr mean as having ‘significant health effects’ and gives 80ppb daily max. 8 hr mean as an interim target.

² EU value not to be exceeded on more than 25 days per calendar year averaged over 3 years.

³ USA value – the 3-year average of the fourth-highest daily maximum 8-hour average measured at each monitor in an area must not exceed 160µg/m³/0.075 ppm

⁴ UK Objective maximum 8-hour running mean in a day, not to be exceeded more than 10 times per year

	110	1 hour	
China	80	1 hour	Grade I
	100	1 hour	Grades II and III (Liu et al., 2013b)
India	50	8 hour	
	90	1 hour	

2588

2589 Although in some cases the ‘headline’ concentration value in different countries’ standards may be
2590 similar, the number of allowed exceedences of short term levels is crucially important in determining
2591 their relative stringency. These criteria are shown on the footnote to the Table 3. Moreover, the
2592 status of the standards is also very important. In the USA, the National Ambient Air Quality Standard
2593 (NAAQS) for ozone has the same mandatory legal status as those for the other criteria pollutants. In
2594 the EU however this is not the case as it was recognised that no single Member State could control
2595 the ozone levels measured within its territory because of the transboundary nature of ozone
2596 formation during ‘smog’ episodes (Royal Society, 2008). In the EU Directives therefore, the ozone
2597 standard is a Target Value as opposed to a mandatory Limit Value in the case of the other pollutants.
2598 A Limit Value is ‘to be attained within a given period and not to be exceeded once attained’. Target
2599 Values in contrast, are ‘to be attained *where possible* over a given period.’ The mandatory aspects of
2600 ozone control in the EU are contained within the National Emission Ceilings Directive which sets
2601 mandatory emission ceilings for individual Member States for NO_x and VOCs, which are designed,
2602 *inter alia*, to achieve reductions in ozone levels.

2603 There are also standards in place to protect against damage to vegetation. In the EU Directive there
2604 is a Target Value of 18,000 µg/m³ · hours for AOT40, defined as the sum of the difference between
2605 observed hourly concentrations greater than 80 µg/m³ (≈ 40 parts per billion) and 80 µg/m³ over a
2606 given period using only the one-hour values measured between 8.00 and 20.00 Central European
2607 Time (CET) each day. In the US the 8- hourly NAAQS in Table 3 is also designed to protect against
2608 damage to vegetation, so the spatial scale of policy responses to protect against vegetation damage
2609 in the EU and the USA are potentially quite different (see <http://www.epa.gov/ncea/isa/>). In the last
2610 decade, the LRTAP Convention (Convention on Long-range Transboundary Air Pollution) has
2611 introduced stomatal flux-based critical levels for vegetation that are species-specific and relevant for
2612 protecting against effects of ozone on food security, carbon sequestration and timber production,
2613 and biodiversity (see Section 3.2 and Mills et al. (Mills et al., 2011a) for further details).

2614 Two further recent developments have important implications for policy responses for mitigating
2615 ozone concentrations. First, the work of the CLRTAP (Convention on Long-range Transport of
2616 Atmospheric Pollutants) Task Force on Hemispheric Transport of Air Pollution has highlighted that
2617 intercontinental transport of ozone and its precursors can make significant contributions to the
2618 exceedance of air quality standards and can even cause exceedances in their own right (HTAP, 2010).
2619 This has already led to challenges to air quality standard enforcement in California (Hand, 2014). In
2620 the case of Europe this suggests that emission reduction strategies should take into account

2621 measures and policies in North America. Likewise, plans to reduce ozone in North America should
2622 take into account emissions in Asia.

2623
2624 The second development relates directly to potentially new metrics to protect human health from
2625 adverse effects of ozone and the existence or otherwise of a no-effect threshold. The recent review
2626 of the health effect literature by WHO (WHO, 2013) has concluded that there is now evidence
2627 showing associations between long term (summer mean) ozone concentrations and respiratory
2628 mortality, and weaker associations with cardiorespiratory mortality. WHO recognised the
2629 uncertainties in this area but nonetheless suggested that long-term average WHO Guidelines and a
2630 long-term (possibly a summer mean) Target Value should be considered by the European
2631 Commission.

2632 In parallel with these conclusions, the REVIHAAP report (WHO, 2013) also noted that evidence for a
2633 no-effect threshold for short-term impacts was inconclusive but recommended that SOMO10 as well
2634 as SOMO35 should be used in health impact assessments. These findings are significant for future
2635 policy on ozone. Long-term (summer) averages, as noted earlier, are partly determined by
2636 hemispheric or global emissions; to attain a threshold of 10 ppb hourly average in SOMO10 would
2637 also imply reductions of emissions on a global scale. If the evidence behind these emerging
2638 conclusions strengthens then the geographical scale of ozone reductions strategies will need to be
2639 extended beyond the regional level to hemispheric or global scales (Hsu et al., 2013).

2640

2641 [5.2 Ozone mitigation and baseline ozone](#)

2642

2643 Observational evidence suggests that baseline ozone concentrations as they effect Europe have been
2644 rising up until about 2000 (Wilson et al., 2012;Parrish et al., 2009;Simmonds et al., 2004;Jenkin,
2645 2008;Derwent et al., 2006), though currently they appear to be falling (Logan et al., 2012; Parrish et
2646 al., 2012). An increasing background contribution to European ozone levels could represent a
2647 substantial future challenge to the attainment of ozone limit values (Derwent et al., 2010). With an
2648 increasing background contribution there is a requirement to control more ozone of anthropogenic
2649 European origin to achieve the limit. Models have shown (Derwent et al., 2010;Szopa et al., 2006)
2650 that the benefit to European emission controls can be significantly counterbalanced by increasing
2651 background ozone. These results were confirmed in a long-term perspective (2050) by Colette et al.
2652 (2013) who emphasized that air quality legislation was indeed anticipated to bear its fruit in reducing
2653 ozone exposure in the future, even if under a business as usual scenario such as the RCP8.5, climate
2654 change and long range transport.

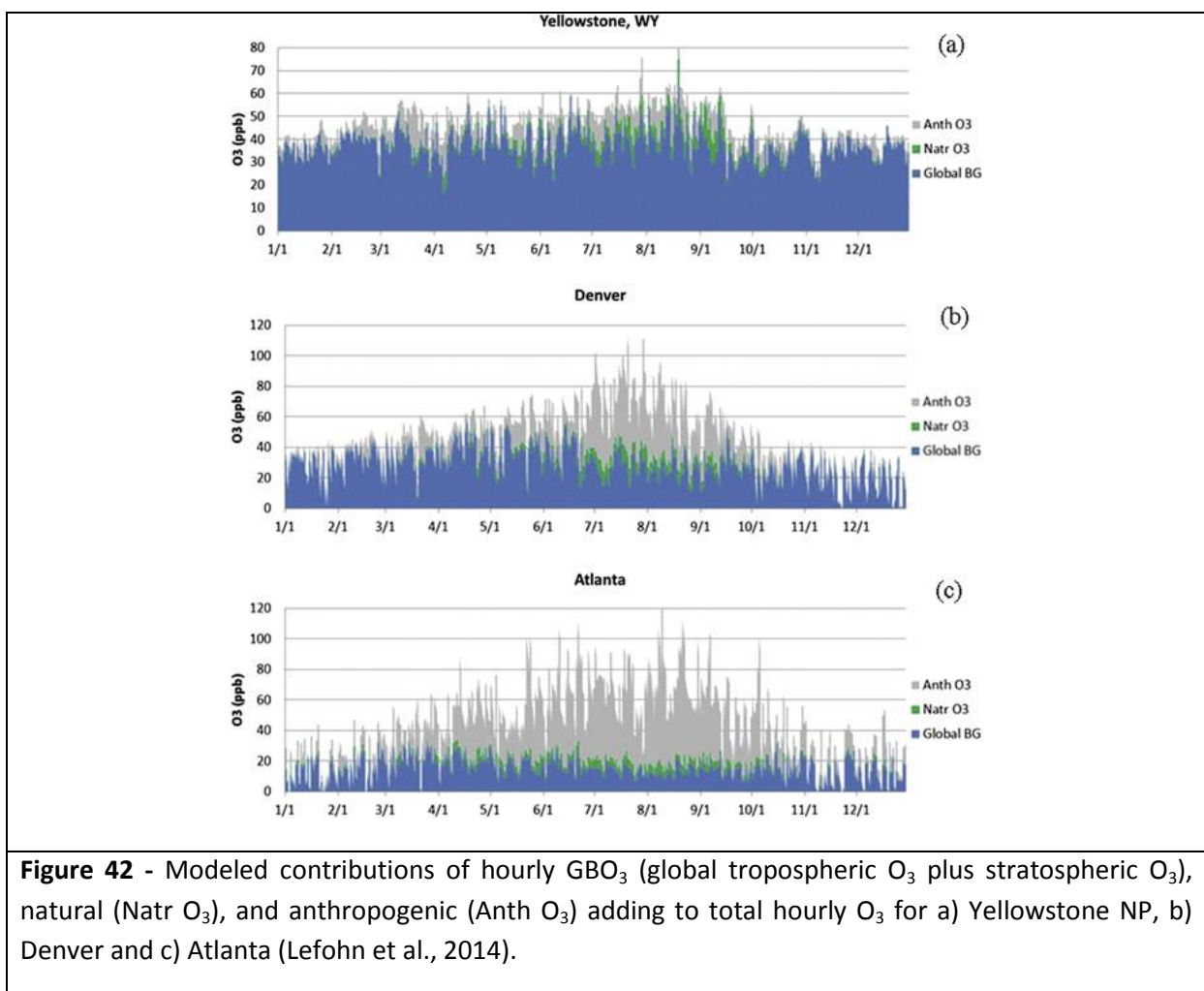
2655 Similarly, in the US context there has been much debate as to the contribution and quantification of
2656 background ozone and its effect on the attainment of standards (Lefohn et al., 2014;Fiore et al.,
2657 2014;Prather et al., 2003;Fiore et al., 2002). Lefohn et al (2014) have explored the concept of an
2658 emissions-influenced background in an attempt on a continental scale to partition the controllable
2659 ozone (see Figure 42). Fiore et al (Fiore et al., 2014) noted that the largest model differences in the
2660 calculation of North American Background ozone, in this case a model construct, were linked to
2661 differences in contributions from the stratosphere, wildfires, lightning and isoprene chemistry.

2662 Prather et al. noted in a model study that the background ozone might be a northern hemispheric
2663 problem given future emission scenarios (Prather et al., 2003).

2664 The recent results of the 2013 revision (Amann et al., 2013a) of the European Thematic Strategy on
2665 Air Pollution (TSAP) indicate that the reduction of 10% of the 25,000 anticipated deaths attributed to
2666 ozone ambioned by the 2005 TSAP for European emission reductions should be safely achieved in
2667 2025 with about 18,000 annual premature deaths under the scenario currently planned.

2668 Fowler et al, in their recent report on research findings in support of the EU air quality policy argued
2669 that “more attention needs to be given to treating ozone as a hemispheric transboundary issue”
2670 (Fowler et al., 2013a) (see section 5.3).

2671



2672

2673 5.3 Hemispheric transport of ozone and its precursors in the policy context

2674

2675 Substantial efforts have been undertaken to quantify the importance of long-range transport of
2676 ozone from distant source regions as part of UNECE HTAP (HTAP, 2010). More than 20 global models
2677 conducted idealised source-receptor experiments to quantify hemispheric transport of ozone and its

2678 precursors and the key findings are reported in Fiore et al (Fiore et al., 2009) and HTAP (HTAP, 2010).
2679 20% reductions in anthropogenic precursor emissions from North American, East Asian and South
2680 Asian sources reduce annual mean EU O₃ by about 0.4, 0.2 and 0.1 ppbV, respectively (HTAP, 2010).
2681 The influence of LRT has a seasonality, with the largest impact in spring (March-April: ~0.8 ppbV) and
2682 minimum impact in late summer (July-September: ~0.45 ppbV) (HTAP, 2010). This influence may
2683 appear small, but the equivalent O₃ response to a 20% emission change over Europe itself is 1.5-2.0
2684 ppbV in summertime, and is close to zero on a regional mean basis in winter when titration is
2685 important. It is worth noting that the HTAP emission reductions (20%) have been exceeded in reality
2686 over Europe for the 1990-2009 period (EEA, 2011). By scaling the 20% emission changes to the
2687 actual regional emission changes and accounting for the nonlinearity in ozone responses, (Wild et al.,
2688 2012) derived the ozone trend over Europe from 1960-2000 along with the contributions from the
2689 EU, external sources (i.e. LRT) and changing atmospheric CH₄. An increase of about 6.5 ppbV is
2690 calculated between 1960 and 1990, and a slight decrease from 1990-2000. More than half of the
2691 1960-1990 trend came from non-European sources (2.1 ppb) and CH₄ (1.6 ppb), with only 2.8 ppb
2692 from changes in EU emissions. Interestingly trans-Eurasian transport of air pollutants has been
2693 implicated in the enhancement of ozone in western China (Li et al., 2014b).

2694 A number of studies have focussed on the contribution of increasing precursor emissions over Asia to
2695 ozone over North America. Reidmiller et al. (Reidmiller et al., 2009) have used the HTAP simulations
2696 to demonstrate that precursor emissions from both East Asia and Europe influence the policy-
2697 relevant maximum 8-hour average (MDA8) ozone metric, but note that regional emission controls
2698 over North America are 2-10 times as effective at reducing this ozone metric as the equivalent
2699 controls in these foreign regions. However, Lin et al. (Lin et al., 2012a) demonstrate that Asian
2700 emissions may contribute as much as 8-15 ppb ozone to MDA8 in the south-western US in springtime
2701 on days when ozone exceeds 60 ppb, indicating the important role that long-range transport may
2702 play in ozone exceedences. More recent work by Lin et al. (Lin et al., 2014a) has shown that
2703 transport of the export-related Chinese pollution contributed 0.5-1.5% of ozone over the western
2704 United States in 2006. This Chinese pollution also resulted in one extra day or more of
2705 noncompliance with the US ozone standard in 2006 over the Los Angeles area and many regions in
2706 the eastern United States. Equivalent studies focussing on air quality metrics in Europe have yet to
2707 be performed, but are likely to show smaller impacts given the greater transport distances from
2708 regions showing substantial emission increases.

2709 Transport within Asia has been considered in a recent HTAP study showing that O₃ from East Asian
2710 sources affects the most densely populated parts of South Asia (Chakraborty et al., 2015).

2711 **5.4 Impacts of climate change**

2712

2713 Jacob and Winner (Jacob and Winner, 2009) and more recently von Schneidmesser et al (von
2714 Schneidmesser et al., 2015) have undertaken a comprehensive review of the impacts of climate
2715 change on air quality, including ozone. Despite regional differences, the dominating signal is one
2716 towards an increase of ozone levels induced by global warming (Stevenson et al., 2006), that led Wu
2717 et al (Wu et al., 2008) to coin the term “climate penalty”. The possible pathways for such a penalty
2718 include increasing continental temperatures, changing atmospheric humidity and changes in the
2719 prevalence of stable, anticyclonic conditions trapping pollutants in the boundary layer and possibly

2720 leading to higher surface ozone even without changes in anthropogenic precursor emissions. These
2721 meteorological factors may be supplemented by climate-driven changes in biogenic emissions of
2722 isoprene and in dry deposition of ozone. It is worth noting that in the lower free troposphere and in
2723 remote surface regions ozone is expected to decrease owing to increased water vapour in a warmer
2724 world (Jacob and Winner, 2009). There is some debate as to the magnitude of any climate penalty
2725 e.g. Tai et al. (Tai et al., 2013) indicates that in the presence of CO₂-isoprene interaction, the
2726 projected change in isoprene emission by 2050 will be largely offset or even reverse in sign, leading
2727 to much reduced sensitivity of ozone and SOA (by >50%) to climate and natural vegetation

2728 Bloomer et al. (Bloomer et al., 2009) estimated the magnitude of these effects from surface ozone
2729 observations over the US at about 2.2 ppb per degree C and Pfister et al have shown increasing
2730 summertime ozone levels (Pfister et al., 2014) under various climate scenarios. These effects have
2731 been quantified over Europe in several model studies (Colette et al., 2013;Meleux et al.,
2732 2007;Langner et al., 2012a;Langner et al., 2012c;Andersson and Engardt, 2010;Manders et al.,
2733 2012;Hedegaard et al., 2008;Hedegaard et al., 2013b;Katragkou et al., 2011). The general order of
2734 magnitude of the climate penalty over Europe is a few ppb by the middle of the century. Langer et al
2735 (Langner et al., 2012b) point out a larger increase at the 95th percentile of hourly ozone, suggesting
2736 that the effects of climate change may be particularly important during high ozone events. The
2737 effects of changes in isoprene emissions and dry deposition have been quantified separately by
2738 Andersson and Engardt (Andersson and Engardt, 2010) who find increases in mean ozone of up to 5
2739 ppb by 2050 in some parts of western Europe, with as much as 60% of this change attributed to
2740 decreased dry deposition, and with increased isoprene emissions contributing up to 1 ppb. As noted
2741 above large uncertainties remain regarding the impact of climate change on biogenic emissions, with
2742 up to a factor five difference in isoprene change reported in a multi-model ensemble (Langner et al.,
2743 2012c).

2744 There are few studies that proposed quantitative comparisons of the relative impact of climate
2745 change and air pollution mitigation strategies on surface ozone. Existing investigations all agree on a
2746 larger impact of air quality policies (Tagaris et al., 2007;Hedegaard et al., 2013a;Colette et al., 2013),
2747 endorsing to the efficiency of currently planned mitigation strategies, despite external penalties
2748 brought about by climate change and long range transport.

2749 It should be noted however that studies focusing on the impacts of climate change use long-term
2750 projections (typically 2050) which have substantive precursor mitigation. Given the magnitude of the
2751 response to precursors changes, the sensitivity to the choice of the scenario is worth noting (Fiore et
2752 al., 2012a). Pioneering studies relied on projections originally designed for climate projections (SRES
2753 (Nakicenovic et al., 2000) or RCPs (van Vuuren et al., 2011), but the ozone precursor information in
2754 such scenarios was solely provided to assess radiative forcing and their use for surface air quality
2755 projections constitutes a deviation from their original purpose. The various scenarios make differing
2756 assumptions for future air pollution emissions and therefore, describe a wide range of future
2757 emissions over large world regions. Any downscaling in regions that exhibit large spatial
2758 heterogeneities could be problematic leading to inaccurate results (Amann et al., 2013b). The use of
2759 emission projections relying on policy relevant emissions factors such as the Global Energy
2760 Assessment (Riahi et al., 2012), the ECLIPSE (Klimont et al., 2013a) or PEGASOS datasets are more
2761 reliable.

2762 While the implications of these effects for surface ozone and air quality policy are substantial, there
2763 is still considerable uncertainty in the magnitude of these indirect climate effects, and improved
2764 understanding of the processes controlling these atmosphere-land surface interactions is needed.

2765

2766 6 The future – Air Quality and Climate

2767

2768 Recently, pollutants that typically fall under the ‘air quality’ categorization have been receiving
2769 increasing attention for their role in climate change and their impact on radiative forcing. More
2770 specifically, significant focus has been on ozone, methane (as a GHG and an ozone precursor), and
2771 aerosol constituents (mostly the black carbon (BC) component). Significant potential exists for co-
2772 benefits with coordinated air quality and climate policies. A number of reviews have recently
2773 addressed various aspects of the linkages between air quality and climate, from the chemistry
2774 interactions to the policy implications (von Schneidemesser and Monks, 2013;Isaksen et al.,
2775 2009;Fiore et al., 2012b;Unger, 2012). For more details, see these reviews. Here, a brief overview of
2776 the topic will be given, with a focus on ozone and the latest developments.

2777 In addition to being an air pollutant with significant adverse health effects, ozone is also a
2778 greenhouse gas. A recent estimate of ozone’s radiative forcing effect (from pre-industrial times to
2779 the present day) is $+0.40 \text{ W m}^{-2}$ (Myhre et al., 2013), other estimates include $+0.44$ and $+0.23$ (Unger,
2780 2012;Fiore et al., 2012b). For comparison, the RFs attributed to methane and CO_2 are $+0.48 \text{ W m}^{-2}$
2781 and $+1.66 \text{ W m}^{-2}$, respectively (Myhre et al., 2013). The ozone precursors NO_x , NMVOCs, and CO,
2782 have little to no direct effect on climate, but influence climate and radiative forcing through their
2783 effects on ozone and methane, as well as atmospheric oxidant concentrations and indirect
2784 ecosystem effects [(von Schneidemesser and Monks, 2013) and references therein]. Reductions in
2785 NMVOCs and CO tend to be synergistic and result in overall decreases in RF, although the effects can
2786 be fairly minor, especially for NMVOCs (Collins et al., 2013). The effect of NO_x on climate/radiative
2787 forcing is much less straightforward. A variety of interactions, feedbacks, and ecosystem effects
2788 confound the picture for NO_x , resulting in significant uncertainty and often times competing effects
2789 on climate. A variety of modelling studies have evaluated the various direct and indirect effects
2790 (Collins et al., 2010;Collins et al., 2013;Shindell et al., 2009;Fry et al., 2012;Colette et al., 2011) and a
2791 summary can be found in von Schneidemesser and Monks (von Schneidemesser and Monks, 2013).
2792 More research is needed on this topic.

2793 Methane, an important greenhouse gas in its own right, is also an ozone precursor. With a lifetime of
2794 approximately a decade in the atmosphere, methane is well-mixed globally and therefore has a
2795 significant influence on background ozone levels. Methane is a distinct win-win possibility for air
2796 quality and climate in that reductions in methane emissions would decrease ozone, including
2797 baseline ozone, and thereby lessen adverse impacts on vegetation and human health, but also
2798 benefit climate by reducing 2 GHGs simultaneously (Fry et al., 2012;Shindell et al., 2012;Isaksen et
2799 al., 2014). A model study investigated the air quality (O_3) and climate benefits of methane reductions
2800 and found that O_3 reductions were relatively linear with respect to reductions in methane emissions.
2801 In addition, the CH_4 emission reductions did not depend strongly on location, as the climate and air
2802 quality benefits were realized globally, which would allow for the most cost effective emission
2803 controls to be implemented (Fiore et al., 2008).

2804 However, the interactions go both ways. Not only does ozone affect the climate, but changes owing
2805 to climate change will also influence ozone production. This effect is known as the ‘climate penalty’.
2806 A variety of effects resulting from a changing climate will potentially influence ozone concentrations,
2807 some increasing ozone, some decreasing ozone (Rasmussen et al., 2013). Many of these effects are

2808 associated with a significant amount of uncertainty. Climate change induced increases in methane
2809 emissions from wetlands, stratosphere-troposphere exchange of ozone, lightning NO_x, and regional
2810 stagnation all consistently lead to increased ozone when investigated, while increases in dry
2811 deposition and humidity consistently lead to decreases in ozone (Fiore et al., 2012b; Isaksen et al.,
2812 2009). Other climate change induced effects such as increased wildfires have a much more uncertain
2813 effect on ozone. For example, for a regional study in California, climate-related perturbations
2814 (temperature, biogenics and water vapour) led to combined peak 1 h ozone increases of up to 11 ppb
2815 (Millstein and Harley, 2009).

2816 In a model ensemble study by Colette et al. (Colette et al., 2012) future (2030) air quality in Europe
2817 owing to just air quality policy or air quality and climate policy was compared. The base case included
2818 all current and planned air quality measures up to 2030 and was compared to a 'sustainable' case
2819 with the air quality as well as climate measures (2° target and energy efficiency improvements).
2820 Depending on the scenario annual mean O₃ was found to slightly increase over NO_x saturated areas
2821 but the overall O₃ burden would decrease substantially, including exposure to detrimental levels of
2822 O₃ for health (Kinney, 2008). The air pollution measures were responsible for the main improvements
2823 in ozone, but an additional co-benefit of at least 40% (depending on the indicator) was attributed to
2824 the climate policy (Colette et al., 2012). A study by Crawford-Brown et al. (Crawford-Brown et al.,
2825 2012) focused on the co-benefits to O₃- and PM-related health effects resulting from implementation
2826 of climate policy in Mexico. A base case scenario was compared to a decarbonisation scenario where
2827 CO₂ emissions in Mexico would be reduced by 77% by 2050. The co-benefits to air quality were
2828 reductions in O₃ of 11-13% by 2050. The reduction in non-fatal diseases from O₃ and PM related
2829 health co-benefits was valued at \$0.6 billion per year (Crawford-Brown et al., 2012). Both of these
2830 studies show that there are significant benefits to pursuing coordinated policies for air quality and
2831 climate, and not only for the improvement of O₃ related air quality. Rypdal et al have commented on
2832 the challenges for putting tropospheric ozone in climate agreements (Rypdal et al., 2005).

2833

2834

2835

2836 **7 Conclusions**

2837

2838 Ozone remains central to atmospheric chemistry as the initiator, propagator and product of
2839 photochemistry. Its influence is felt on human health, ecosystems and climate. Ozone though
2840 ubiquitous remains an enigma. In many places in the Northern Hemisphere mid-latitudes ozone in
2841 some senses remains a paradox, the high summertime peak levels decreasing but the regional
2842 background levels rising (Fishman et al., 2014; Parrish et al., 2012). Globally this points to the need
2843 to treat ozone across the range of scales, a transboundary issue, but with an emphasis on the
2844 hemispheric scales (Fowler et al., 2013a; Simpson et al., 2014). Recent air pollution episodes in
2845 Europe have pointed to the continuing need to think about the how climate change policies interact
2846 with air quality policy and what can be learnt from current episodes (Monks, 2014). There remain a
2847 number of clear challenges for ozone such as explaining surface trends, incorporating new chemical
2848 understanding, ozone-climate coupling as well as a better assessment of impacts.

2849

2850 With respect to the future, studying the atmospheric chemistry of ozone relies on the continuing
2851 interplay of laboratory studies of fundamental parameters being integrated with our best theories
2852 using numerical models and evaluated against in situ observations. This “three-legged” stool
2853 approach is generic, but is a vital model to use to understand not only ozone but the wider chemistry
2854 in the atmosphere (Abbatt et al., 2014).

2855 One area implicit in this review, which hasn’t been discussed explicitly, has been the role of
2856 observations in understanding, quantifying and describing ozone across the scales. Observations of
2857 ozone and its precursors underpin and drive the development of our knowledge base (Laj et al.,
2858 2009). Bowman has argued that the global nature of pollution and climate change requires a new
2859 observing system for ozone (Bowman, 2013). A key feature of the system should be the ability to
2860 predict and attribute ozone to emissions. A combination of satellites, ground-based remote sensing
2861 and ground-based observations are needed with geostationary observations (Lahoz et al., 2011)
2862 being an observational anchor (see Figure 43).

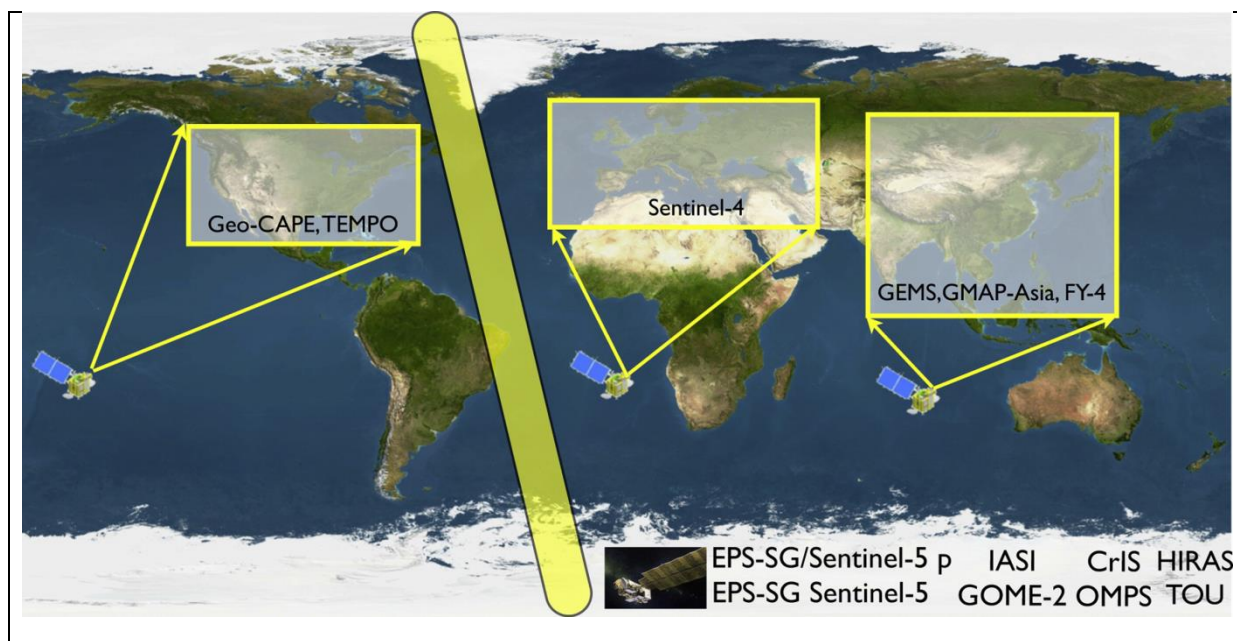


Figure 43 - Constellation of geostationary and low-earth orbiting satellites planned for the coming decade that will measure tropospheric ozone. Current instruments that measure tropospheric ozone, e.g., TES or OMI, but will not be continued in the future are not listed (From (Bowman, 2013)).

2863

2864 It is clear that space observations offer the global view and repeatability not easily available from
 2865 other observing systems. Measurement of ground-level ozone from space still remains a significant
 2866 challenge (Foret et al., 2014;Duncan et al., 2014). There is future potential for global observations of
 2867 tropospheric ozone from space either directly (Sellitto et al., 2013) or through a combination with
 2868 models (Zoogman et al., 2014;Martin, 2008). Duncan et al (Duncan et al., 2014) have recently
 2869 reviewed the application of satellite data to air quality application including common mistakes to
 2870 avoid.

2871 The growth of small sensors for a range of trace species including ozone has the potential to offer
 2872 insights on unheralded spatial and temporal timescales (Snyder et al., 2013;Mead et al.,
 2873 2013;Piedrahita et al., 2014). As illustrated in Figure 44, there are potential new avenues opened up
 2874 for air quality monitoring by the deployment of extensive networks of these sensors all the way
 2875 down to personal sensing (e.g. (Wheeler et al., 2011;Andersen et al., 2010)). The absolute
 2876 measurement of ozone remains a challenge with some of these sensors owing to interferences
 2877 (Mead et al., 2013). New developments suggest these configurations of sensor technologies can give
 2878 long-term atmospheric performance for the measurements of ozone (Williams et al., 2013;Bart et al.,
 2879 2014).

2880 There may yet be new links and biospheric feedbacks driven by ozone to be explored. For example,
 2881 the effect of elevated O₃ and whitefly herbivory significantly increased tomato volatiles, which
 2882 attracted *E. Formosa* wasps and reduced the whitefly feeding on tomatoes (Cui et al., 2014).

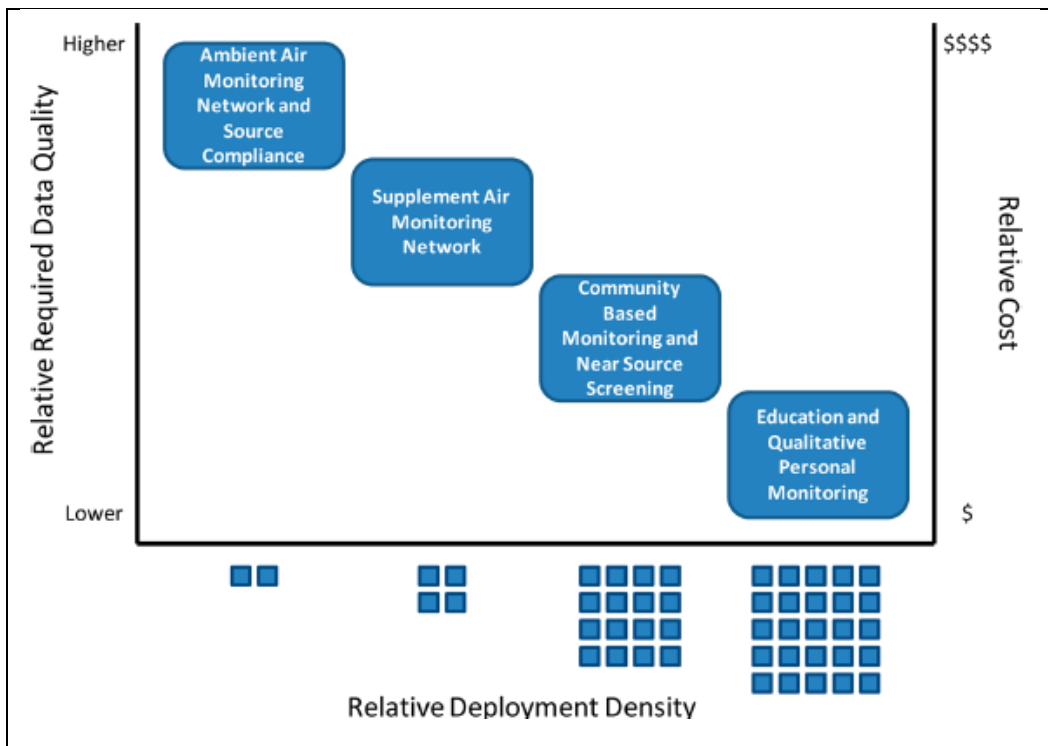


Figure 44 – Relative data, quality, cost and deployment density for small sensor networks for air quality (Snyder et al., 2013).

2883

2884 There are interesting attempts to make public outreach on the effects of ozone on plants and crops.
2885 Fishman et al, have described a establishment of an “Ozone Garden” (Fishman et al., 2014). The
2886 garden provides real-time measurements of O₃ concentrations as well as firsthand observations of
2887 the detrimental effects of this pollutant. Meteorological data, as well as the O₃ concentrations from
2888 the monitor, are recorded and publicly disseminated in near-real time *via* the internet.

2889 Looking forward it is clear that levels and patterns of global ozone will continue to change, impacting
2890 global warming, air quality, global food production and ecosystem function. There remains a need for
2891 continuing research to quantify impacts and interactions across all the scales. The issues around
2892 tropospheric ozone are not “solved” (Guerreiro et al., 2014) and new data continues to shed light on
2893 more aspects of ozone and its interactions in the global atmosphere.

2894

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2897

2898 **Acknowledgements**

2899

2900 This review was prepared as part of the European Commission project ACCENT Plus (grant agreement
2901 265119).

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2903

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