Opposite OH reactivity and ozone cycles in the Amazon rainforest and megacity Beijing: Subversion of biospheric oxidant control by anthropogenic emissions

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HIGHLIGHTS

- Atmospheric OH reactivity was measured in a rainforest and a megacity.
- Amazon reactivity peaked by day, was isoprene dominated, and anticorrelated to CO_2.
- Beijing reactivity peak in rush hour, was dominated by NO_2 and correlated with CO_2.
- With high daytime reactivity in the rainforest, ozone remains low and constant.
- Despite lower reactivity in megacity air, ozone increased strongly by day.

ARTICLE INFO

ABSTRACT

The Amazon rainforest in Brazil and the megacity of Beijing in China are two of the most strongly contrasting habitats on Earth. In both locations, volatile chemicals are emitted into the atmosphere affecting the local atmospheric chemistry, air quality and ecosystem health. In this study, the total reactivity in air available for reaction with the atmosphere's primary oxidant the OH radical, has been measured directly in both locations along with individual volatile organic compounds(VOC), nitrogen oxides(NOx), ozone(O_3) and carbon dioxide(CO_2). Peak daily OH-reactivity in the Amazon 72 s^{-1}, (min. 27 s^{-1}) was approximately three times higher than Beijing 26 s^{-1} (min. 15 s^{-1}). However, diel ozone variation in Amazonia was small ($\sim$5 ppb) whereas in Beijing $\sim$70 ppb harmful photochemical ozone was produced by early afternoon. Amazon OH-reactivity peaked by day, was strongly impacted by isoprene, and anticorrelated to CO_2, whereas in Beijing OH-reactivity was higher at night rising to a rush hour peak, was dominated by NO_2 and correlated with CO_2. These converse diel cycles between urban and natural ecosystems demonstrate how biosphere control of the atmospheric environment is subverted by anthropogenic emissions.

The Amazon rainforest is the world's largest contiguous ecosystem and species rich biome (Pimm et al., 2014; FAO, 2011). Being over 6 million km^2 it is around two thirds the area of the United States and it plays an important part in the Earth's hydrological, energy and carbon cycles (Davidson et al., 2012; Gloor et al., 2012).

The forest has developed to its present size over the past 55 million years (Maslin et al., 2005), and much of it today remains in a pristine state, without direct human influence. In contrast, the megacity Beijing has grown over several thousand years to a globally important metrope with an area of ca. 17,000 km^2 and an official population of over 21 million people.

The Amazon fulfills its energy requirements directly from the sun via photosynthesis, assimilating (gross) an estimated

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26.4 Pg yr^{-1} (based on 30.4 tC ha^{-1} yr^{-1} and 8.7 $\times$ 10^8 ha in 1998) (Malhi et al., 1998), more than half that of 40.8 Pg yr^{-1} by all tropical (Beer et al., 2010). A fraction of this carbon (typically up to 5%) is re-released by vegetation to the atmosphere as volatile organic compounds (VOC) (Kesselmeier et al., 2002). These species mix with NOx (NO + NO$_2$) emitted from microbial soil processes (Behrendt et al., 2014). In contrast Beijing derives its energy primarily from the combustion of fossil fuels such as coal, oil and gas, expending circa 206 million tonnes coal equivalent in 2007 (Zhang et al., 2014), which equates to ca. 123 tC ha^{-1} yr^{-1}. Combustion of fossil fuels in power plants, heavy industry and traffic also leads to the emission of both NOx and VOC (Parrish et al., 2009). After entering the atmosphere, NOx and VOC are oxidized, primarily by the OH radical and to a lesser extent by NO$_3$ and O$_3$. Depending on the ambient NOx and VOC mixing ratios O$_3$ can be generated (Haagen-Smit, 1952) which is harmful to human health and plants (Jerret et al., 2009; Skarby and Sellden, 1984).

In this study we have taken a new holistic approach and directly measured the OH reactivity of air in Amazonia and Beijing. OH reactivity is the instantaneous total ambient loss frequency of OH radicals (in unit of s^{-1}) derived from the combined reactivity of all individual species present. This fundamental property of the atmosphere has been accessible since the development of a direct measurement method for OH reactivity approximately 15 years ago (Calpini et al., 1999; Kovacs and Brune, 2001) and this optically based, laser induced fluorescence technique has been widely applied since (Ren et al., 2003; Sadanaga et al., 2004; Ingham et al., 2009). Recently a new chemical method for determining in-situ OH reactivity was reported, termed the comparative reactivity method (CRM) (Sinha et al., 2008). The latter method is based on the detection of a VOC with proton transfer reaction mass spectrometry (PTR-MS) at relatively high concentration. Consequently, the CRM method also has a growing number of practitioners (Nölscher et al., 2012; Dolgorouky et al., 2012). In order to compare OH reactivity behavior from a pristine biogenic source dominated region with a polluted, anthropogenic source dominated environments we have deployed the CRM PTR-MS OH reactivity system in the Tropical rainforest (September) and in Beijing (August). Data were taken at approximately the same time of year, height above ground (38 m in the Amazon and 20 m in Beijing) and using the same measurement technique and data processing method. We compare the absolute values, diel cycles and chemical composition of the overall OH reactivity. Finally we contrast the response in ambient O$_3$ to the daytime photooxidation of the reactive compounds in both environments.

1. Methods

1.1. Rainforest site

Measurements were conducted in September 2012 at the Amazon Tall Tower Observatory (ATTO) circa 135 km north-east of Manaus (02.14° S, 58.99° W, 120 m above sea level), in Central Amazonia. The area is surrounded by dense, non-flooded upland forest (terra firme). Air was drawn at 16 L/min through a heated, insulated, 3/8″ (0.953 cm) diameter PTFE Teflon inlet line mounted at 38.3 m (top of canopy). PTR-MS OH reactivity, PTR-MS VOC, Ozone and NO were sampled through the same inlet. Comprehensive details of the site are given elsewhere (Andreae et al., 2015).

1.2. Beijing site

Measurements were conducted in August 2013 from the roof laboratory of a 6 story Peking University Campus building (39.98° N, 116.31° E), approximately 20 m above street level. Air was drawn through an insulated 14.9 m Teflon inlet at 7 Lmin^{-1} and a substream was sampled at 200 cm^3 min^{-1} by PTR-MS and Gas Chromatograph-Mass Spectrometer (GC–MS). The campus is sited close to the 4th ring of the city of Beijing some 10 km from the center and within 500 m of a 5 lane highway.

1.3. OH reactivity

In this study we use the comparative reactivity method (CRM) which has been described in detail previously (Sinha et al., 2008). In this method, a reactive molecule (in this case pyrrole, C$_5$H$_4$N), which is not normally present in air, is passed through a glass reactor and its mixing ratio recorded (at ppb levels) with a suitable detector (here PTR-MS). Then, OH radicals are generated in the glass reactor by a constant light source to react with pyrrole, first mixed with clean zero air and then with ambient air containing many other OH reactive species. Comparing the amount of pyrrole exiting the reactor with zero air and with the ambient air allows the OH reactivity in ambient air to be determined. In a sense the air is "provoked" to yield the relevant information directly rather than by inference based on many single measurements (Williams, 2008). This method was applied to the OH reactivity measurements in Beijing and Amazonia. It has been shown that elevated NO mixing ratios can cause an interference in the OH reactivity measurement. While this was not a problem in the Amazon where NOx levels were low, in Beijing flows were set such that the ambient air was diluted with clean zero air and a correction was applied to all measurements greater than 2 ppb NO based on the response of the reactor to changing NO when measuring propene. The CRM method was able to measure OH reactivity down to 3 s^{-1} estimated by the minimum observable modulation above three times the standard deviation (σ) of the noise (measured in zero air). The measurement showed good agreement and linear response when compared to known amounts of reactivity provided in the form of isoprene, propane and propene via compressed gas standards (Air Liquide and Beijing Chengweixin Gases Ltd.). The overall uncertainty in the measurement was 16% including errors in detector (5%), rate coefficient (14%), gas standard (5%) and flow dilution (2%).

1.4. VOCs

VOCs were measured by PTR-MS (Ionicon, Austria) equipped with a quadrupole detector which has been described in detail elsewhere (Lindinger et al., 1998) In the rainforest, an additional PTR-MS was used to determine ambient mixing ratios of isoprene, its photochemical products including MACR + MVK and several other species (Yáñez-Serrano et al., 2015). In Beijing, the PTR-MS system was used to monitor OH reactivity and additional VOC characterization was provided by a GC–MS system. The VOC GC–MS (SHIMADZU) was coupled to a cryogen free cold trap system (Wuhan Tianhong Instrument Co., Ltd., China). It was calibrated with two pressurized standard gases: PAMS 56 NMHCs and TO-15 (Linde Electronics and Specialty Gases, China). Full details of the system are given elsewhere (Wang et al., 2014). The PTR-MS system for VOC in both locations was calibrated using a pressurized gas standard (Apel-Riemer Environmental, stated accuracy 5%) and overall measurement uncertainty was assessed as <25%.

1.5. Ozone, NOx, CO$_2$

The rainforest NO mixing ratio was measured using the chemiluminescence technique (NO Chemiluminescence analyzer, model CLD TR-780, Ecophysics, Switzerland), calibration was via a pressurized NO standard resulting in an overall uncertainty of <5%.

Ozone was measured by an UV-absorption technique using a Thermo Electron 49c analyzer (Thermo, Electron, USA), using Nafion dryers to minimize effects of changing water vapor concentrations. Calibration was achieved using ozone calibration unit model 146C (Thermo Environmental), giving an overall uncertainty of 0.5 ppb. Mixing ratios of CO_2 were measured by non-dispersive infrared absorption techniques (Licor-7000, LICOR, Lincoln, USA), calibrated using pressurized CO_2 standards in the range 400–500 ppm, with an overall uncertainty of <1% In Beijing ozone was also measured by UV absorption (Thermo Electron 49i) and calibrated with the model 146C ozone calibrator, giving an overall uncertainty of 0.5 ppb. NOx was measured by chemiluminesence (NO–NO$_2$–NOx analyzer, model 42i trace level, Thermo Electron, USA) and calibrated to a pressurized NO gas standard (Beijing Hua Yuan Chemical Gas Industry Company, China), gaving an overall uncertainty of 5%. CO_2 measurements were made by an advanced non-disperse infrared (NDIR) instrument (CO_2 analyzer model 410i, Thermo Electron, USA). Calibration of CO2 was performed weekly to a pressured CO2 standard gas, overall uncertainty <5%.

2. Results

Fig. 1 shows the diel (24 h) cycle of median OH reactivity for a) the Amazon rainforest site over 10 days (20th–29th September 2013) and b) the central Beijing site over 17 days (10th–27th August 2013). For the rainforest, OH reactivity shows a clear diel cycle with values increasing from circa 27 s^{-1} at 06:00 LT (local time)

up to a maximum of 72 s^{-1} between 12:00 and 15:00 LT which corresponds to the maximum light intensity and temperature. Following a short duration minimum in OH reactivity around 18:00, see Fig. 1a, OH reactivity decreases steadily through the night from 55 to 27 s^{-1} between 21:00 and 06:00 LT. The values reported here are comparable to the 2 h section of OH reactivity data measured late afternoon in the Suriname rainforest at 50 m, average 53 s^{-1} (Sinha et al., 2008) and to a larger dataset taken in the Borneo rainforest at 5 m, campaign average noontime maximum 29.1 s^{-1}, diel variation between 5 and 45 s^{-1}, with a maximum of 83.8 s^{-1} (Edwards et al., 2013). The diel profile of CO_2 in the rainforest is opposite to that of the OH reactivity, as photosynthetic uptake by day draws the mixing ratios down from 425 ppm to 385 ppm while respiration by night serves to return ambient mixing ratios to the aforementioned peak values shortly before dawn (06:00 LT).

In Beijing, the diel cycle in OH reactivity is converse to that measured in the rainforest with levels that are 2–3 times lower. A maximum in OH reactivity of circa 27 s^{-1} is attained between 06:00 and 09:00 LT. Thereafter OH reactivity decreases to below 15 s^{-1} by 14:00. After 22:00 LT the OH reactivity increases sharply and remains between 16 and 26 s^{-1} through the night. The maximum corresponds to both the daily peak in traffic and shallow early morning mixed layer. The minimum coincides with the development of a deeper mixed layer. The sharp increase in the evening occurs with the re-establishment of the nocturnal boundary layer. The values of OH reactivity in Beijing are comparable to those reported for New York (Ren et al., 2003), which varied from 15 to
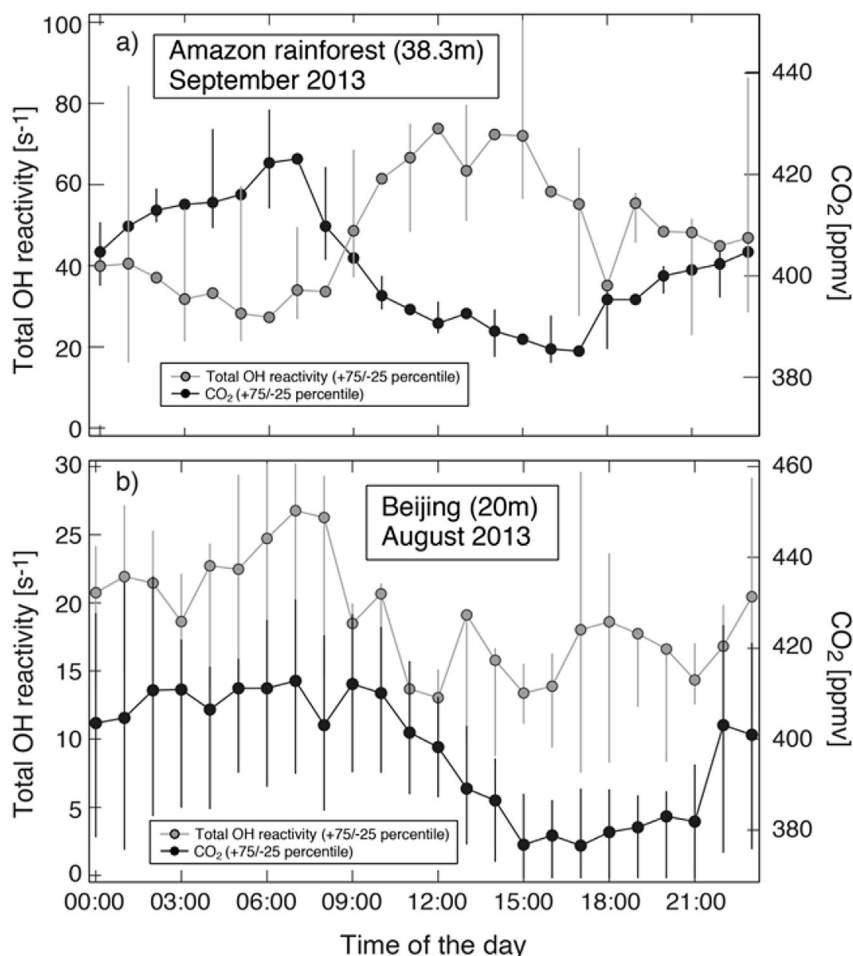

Fig. 1. a. Median diel cycle of OH reactivity and CO_2 for the Amazon. b Median diel cycle of OH reactivity and CO_2 for Beijing. Vertical bars represent the range of 25–75% of the data.

25 s^{-1} with an average of 19 ± 3 s^{-1}; but lower than data for Tokyo (Sadanaga et al., 2004), which ranged between 33 and 50 s^{-1} (15:00–17:00 only). The Beijing data are also closely comparable to those from Mexico City (Shirley et al., 2005), where OH reactivity of ca. 25 s^{-1} was measured for most of the day, except in the Mexican rush hour when 120 s^{-1} was reached. The strong influence of traffic emissions on megacity air composition including Beijing is well established (Parrish et al., 2009). It is worth noting that Beijing CO_2 shows a similar diel behavior to the Beijing OH reactivity, being highest at night. Thus the variance of CO_2 with time-of-day in Beijing matches closely that from the rainforest albeit with a smaller amplitude 380 ppm–410 ppm Beijing compared to 385–425 ppm rainforest. However, while CO_2 and OH reactivity correlate over the diel cycle in Beijing (r = 0.45), they anticorrelate in the rainforest (r = −0.86).

Fig. 2 a and b shows the contributions of selected species to the overall OH reactivity in a) the rainforest and b) Beijing. In the rainforest, isoprene (2- methyl butadiene) is expected to be a strong contributor to total OH reactivity due to its strong light and temperature dependent emissions (Guenther et al., 2006) and its high reaction rate coefficient with OH (1×10^{-10} molec cm^{-3} s^{-1}) (Atkinson et al., 2004). From Fig. 2a it can be seen that both total OH reactivity and the reactivity contribution of isoprene increased in the morning following first light 06:00 until 12:00 LT. Thereafter, isoprene reactivity decreased from 25 to 18 s^{-1} (between 12:00 and 05:00; corresponding to mixing ratios of 10.4–7.5 ppb). It is clear that although isoprene is an important contributor to the total OH reactivity, there exists significantly more reactivity

than is explained by isoprene alone. The oxidation products of isoprene (methyl vinyl ketone, methacrolein and isoprene peroxides measured at protonated mass 71) are also shown in Fig. 2. They contribute less than half the OH reactivity than isoprene. This has been noted previously in the field in rainforests (Edwards et al., 2013), boreal forests (Nölscher et al., 2012), and temperate forests (Di Carlo et al., 2004) though not in single molecule chamber studies (Fuchs et al., 2013; Nölscher et al., 2014). The missing reactivity has been attributed to both unmeasured primary biogenic emissions and the unmeasured photochemical products of isoprene and other emissions (Sinha et al., 2010; Nölscher et al., 2015).

In Beijing, the main contributing species to the total OH reactivity are different to those of the rainforest. High temperature combustion associated with heavy industry and traffic sources provides, via NO emission, a strong source of NO_2 which reacts rapidly with OH (1.2×10^{-11} molec cm^{-3} s^{-1}) (Atkinson et al., 2004). The diel profile of NO_2 is shown with total OH reactivity in Fig. 2b. It can be seen that NO_2 is more important than isoprene to the overall OH reactivity in this environment. Aromatic compounds also represent a significant source of reactivity in Beijing (Shao et al., 2009; Wang et al., 2012), and the summed reactivity contribution from included benzene, toluene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, ethyl benzene, m- and p-xylene, o-xylen, p-diethylbenzene, i-Propylbenzene, n-Propylbenzene, m-ethyltoluene, o-ethyltoluene, are also shown in Fig. 2 for comparison.

Fig. 3 shows the behavior of local tropospheric ozone that results from the specific amounts and composition of OH reactivity emitted in both locations. In the case of the rainforest, despite high measured OH reactivity and likely O_3 reactivity through the presence of isoprenoids, the O_3 diel cycle varied relatively little (9–19 ppb). There is slightly increasing ozone by day (06:00 until 15:00) and decreasing, more variable levels by night. In contrast, Beijing shows strong O_3 production during the day from less than 10 ppb at 06:00 to peak mean values of nearly 80 ppb from 13:00–16:00.

3. Discussion

Ozone is harmful to both plants and humans (Jerret et al., 2009; Skarby and Sellden, 1984). Here we have examined two environments, rich in life and sensitive to ozone damage, which have sharply contrasting impacts on their local ozone levels. Although the total OH reactivity in Beijing is less than that of the rainforest, daytime ozone production in the city environment was an order of magnitude higher. It should be noted that we here compare reactivity data using the same measurement and data work-up method, from approximately the same time of year (August–September) and from approximately the same height above ground (38 m and 20 m).

Key factors contributing to the contrasting ozone behavior are: the NOx component of the OH reactivity; the OH recycling ability of the main VOC emissions, the timing of the emissions to the atmosphere; and the surrounding surface area. NOx (NO + NO_2) catalyzes photochemical ozone formation (Haagen-Smit, 1952) through the reaction of RO_2 with NO to RO and NO_2, which yields ozone when NO_2 photolyzes back to NO (via $O + O_2 \rightarrow O_3$). The high NO levels in Beijing (median 0–9 ppb) relative to the rainforest (<1 ppb) are likely the most important factor in the net ozone production differences observed, since the threshold for ozone production (rather than loss) is around 50–100 ppt NOx. The VOC components of ambient OH reactivity can also impact ambient OH directly (and thereby oxidation capacity), depending on the degree to which each species consumes OH during oxidation. Isoprene, the main VOC component measured by PTR-MS in the rainforest by day (Williams et al., 2001)
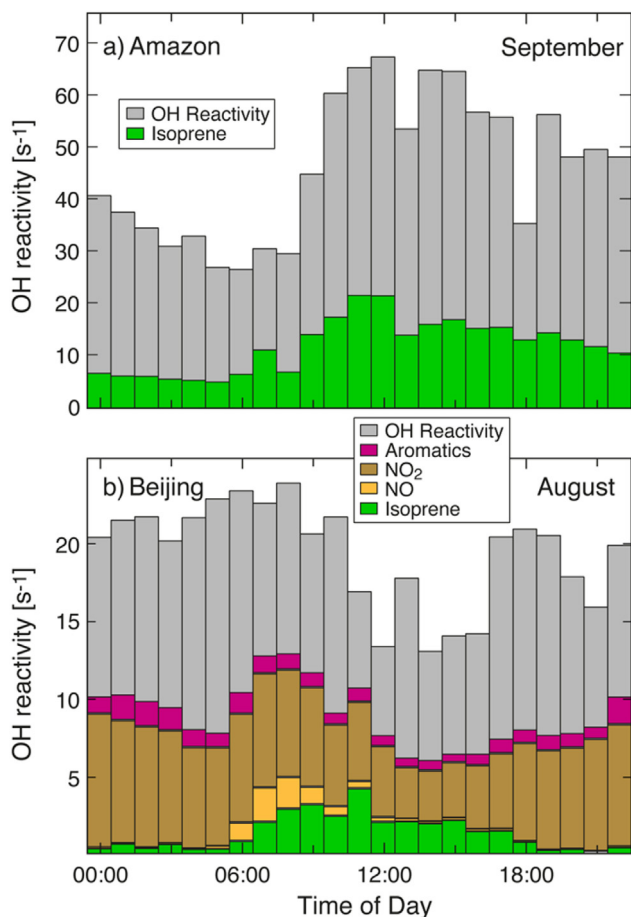

Fig. 2. The total OH reactivity compared to the contributions of isoprene and NOx for the Amazon (a) and Beijing (b).
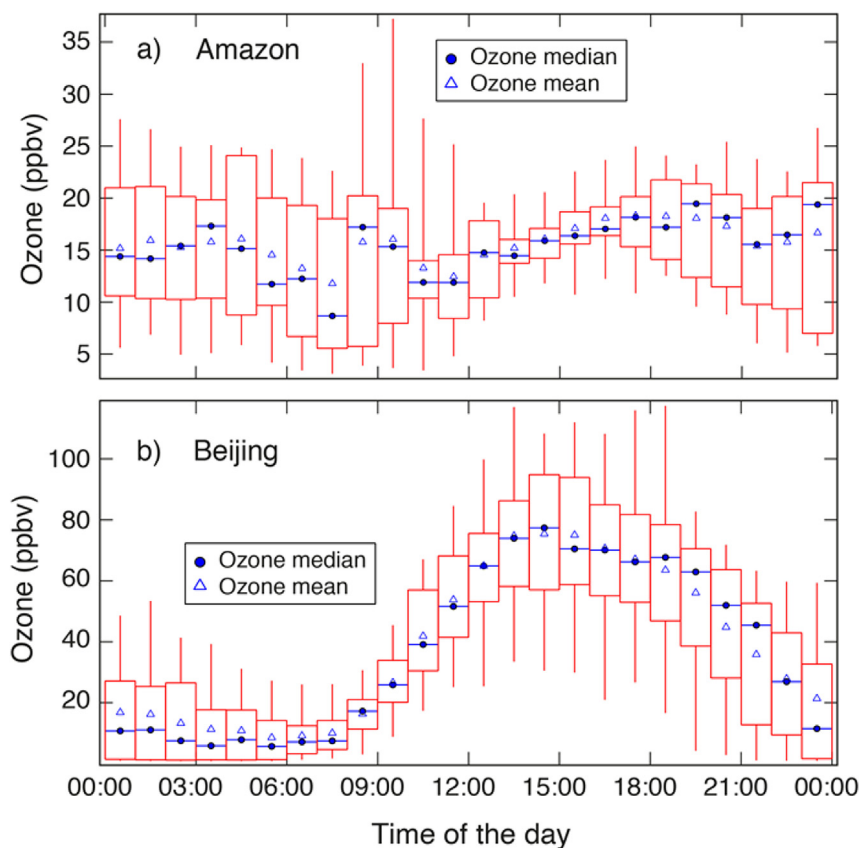
Fig. 3. Diel cycles of median ozone for the Amazon (a) and Beijing (b). Dots mark medians, triangles averages, the boxes the extent of 75–25% of the data and the whiskers 90–10%.

has been shown to recycle OH efficiently based on field measurements (Lelieveld et al., 2008), on theoretical studies (Peeters et al., 2009) and on chamber study results (Fuchs et al., 2013). In the case of Beijing, isoprene is not as important to the overall OH reactivity as NO_2 see Fig. 2. NO_2 does not recycle OH in the gas phase but instead forms nitric acid which is rapidly deposited. Aromatic VOC which are abundant in the urban environment (Shao et al., 2009; Wang et al., 2012) are not thought to recycle OH to the same extent as isoprene, although considerable uncertainty remains in the underlying mechanisms. Modeling sensitivity studies show that trimethyl benzene species are significantly more efficient at producing ozone than isoprene under typical continental conditions (Derwent et al., 1998). Recent measurements of OH in Beijing indicate there is a source of OH at night (Lu et al., 2014) although it has not been identified. It is interesting to note that in the case of isoprene the main first order products when NO_x is present (methacrolein and methyl vinyl ketone) are less reactive than isoprene itself so that with time the overall OH reactivity decreases as has been observed in chambers (Nölscher et al., 2014). In contrast aromatic species have more reactive first order products so that the OH reactivity provided by carbon in this form will increase with time.

Another factor in the differing extents of ozone production in the rainforest and Beijing is the timing of the NO_x and VOC emissions to the atmosphere. In the case of the city, fresh NO_x and VOC are co-emitted at daybreak by rush-hour traffic, optimizing the conditions for ozone production throughout the sunlit part of the day. In contrast, in the rainforest, NO emissions are relatively weak and constant through the day as the bacterial soil sources are primarily dependent on the relatively invariant temperature and soil moisture (Behrendt et al., 2014). While VOC emissions from rain-

forest soils are known to occur, the majority of the rainforest OH reactivity is found at canopy level by day, similar to isoprene and monoterpenes (Yáñez.Serrano et al., 2015; Nölscher et al., 2015). Thus the rainforest ecosystem emits NO at low levels continuously throughout the day while OH reactivity (decoupled from NO) peaks by day at the time of maximum vertical mixing, boundary layer depth, and when the atmosphere's main oxidant, the OH radical, is highest. In Beijing, significant nocturnal emission into the shallower nighttime boundary layer causes total OH reactivity to be highest by night, again priming ozone production for the following day. A final factor in the contrasting ozone behavior is the surface area for deposition available in both environments. Uptake of NO_2 and ozone are significantly higher to vegetation surfaces than to brick and concrete so that trees are being advocated for urban air quality improvement (Pugh et al., 2012). Strong dry deposition of oxygenated VOC to vegetation has also been reported (Karl et al., 2010).

The impact of human beings on planet Earth has increased rapidly over the past 60 years, and now more than 50% of the human population lives in cities (Williams and Crutzen, 2013). This study highlights how differently OH-reactive species from the natural vegetation and anthropogenic city sources impact the local atmosphere in terms of harmful tropospheric ozone. Despite Beijing having three times less maximum OH reactivity, it produces some ten times more harmful photochemical ozone each day. The apparent insensitivity of total OH reactivity as a pollution diagnostic suggests that it will be more instructive for future pollution control strategies to use separate NO_x- and VOC- reactivities (where VOC reactivity = Total OH reactivity−NO_x-reactivity) (Kirchner et al., 2001). Nonetheless, OH reactivity measurements in cities can be useful in future to assess the completeness of the emission

inventory (Williams and Brune, 2015). The locations represent two extreme cases: from a megacity containing freshly emitted pollutants and characterized by a VOC-sensitive ozone production chemistry, to a NOx-sensitive ozone production chemistry in the rainforest (Sillman, 1999). The average ratio of VOC reactivity/NOx reactivity is 47 in the case of the Amazon and 0.6 in Beijing. Following the example of the rainforest, city dwellers should therefore 1) reduce NOx significantly, 2) decouple NOx and VOC emissions, 3) time emissions to coincide with maximum turbulence and OH, 4) when VOC species are emitted, then OH efficient and low ozone producing species should be preferred, 5) increase deposition in cities by introducing trees (albeit with low VOC emissions). However, reducing NOx can lead to ozone increases, as the ozone produced per oxidized NOx (ozone production efficiency per NOx) increases as NOx decreases from urban to rural levels (Pusede and Cohen, 2012). The composition and timing of emissions are closely linked to current technology and daylight lifestyle preferences. Finally, introducing trees can also exacerbate photochemical ozone production by increasing VOC in a NOx rich environment (Owen et al., 2003), though the combined effect of leaf surfaces and BVOC emissions on ozone uptake and decomposition make the estimation of a net effect on ozone challenging (Calfapietra et al., 2013). The problem of reducing city pollutants is a complex issue with a long history. Nonetheless it is worth noting that the forest emits considerably more OH reactivity to the air while sustaining an oxidizing environment with relatively invariant low ozone, conducive to low leaf damage, effective VOC signaling between insects and plants, and safer DNA transport by pollen. The city uses the atmosphere merely as an immediate repository for waste products, at inopportune times and with species (NOx) that catalyze ozone formation. As a result atmospheric chemical processes rapidly produce ozone and other secondary pollutants which are harmful for human health and plants (Chan and Yao, 2009).

4. Conclusion

In this study we have measured OH reactivity in two starkly contrasting environments. The measurements were made using the same measurement system, at approximately the same time of year and height above ground. They show strongly contrasting behavior in amount of OH reactivity, the key contributing species, and the diel cycles. The method for measuring OH reactivity employed here (CRM-PTRMS). Many of the previous measurements cited here have used LIF techniques, some of which have been recently shown to suffer significant interferences (Mao et al., 2012). Thus characterization with an independent technique is valuable and the degree of correspondence reassuring. The data presented highlight how the chemistry of the natural atmospheric environment maintains a low constant ozone level despite being inherently more reactive to OH. Moreover, it is shown that the introduction of NOx, even with modest absolute OH reactivity relative to the rainforest, is sufficient to rapidly produce harmful tropospheric ozone.

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