Commentary
Measurement of surface ozone in South Africa with reference to impacts on human health

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At the bottom of the troposphere, the boundary layer (below the free troposphere) where we live and breathe, ground-level ozone (O_3) (also called surface O_3 because it forms just above the earth's surface) pollution has direct impacts on human health, agriculture and vegetation. Surface O_3 is a secondary atmospheric pollutant formed by reactions between oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) or carbon monoxide (CO) in the presence of sunlight. The sources of these O_3 precursors originate from a range of anthropogenic and natural processes (Oltmans et al., 2013). Stratospheric intrusions of O_3-rich air to the free troposphere that contribute to surface O_3 may also occur (Lin et al., 2012).

The distribution of O_3 throughout the troposphere is not homogenous since it extends in vertical (altitude) and horizontal (spatial) directions, as well as over different periods of time (temporal). In order to study O_3 phenomena on these different time and space scales requires that three characteristics of tropospheric O_3 are routinely measured viz.: (i) surface O_3 by ground-based monitoring stations; (ii) total column O_3 from satellites and (iii) the vertical profile of O_3 with balloon ozonesondes and aircraft monitoring.

Meteorological conditions play a significant role in chemical production and transport of surface O_3. The synoptic scale meteorology of southern Africa is largely characterised by semi-permanent anticyclonic high pressure systems (Tyson and Preston-Whyte, 2000). Stable atmospheric layers associated with anticyclonic circulation traps pollutants near the surface and transport these species over the region (Tyson and Preston-Whyte, 2000; Abiodun et al., 2014). The interaction between meteorological parameters (e.g. temperature, precipitation, clouds) and O_3 precursors determines the amount of surface O_3 produced (Balashov et al., 2014). In fact, temperature can be used as a simple proxy for meteorological influences as it was found that the correlation with temperature can account for most of the influence of meteorological variables on O_3 (Jacob et al., 1993).

Spatial and temporal surface O_3 variability have been studied in southern Africa (Zunckel et al., 2004; Martins et al., 2007; Josipovic et al., 2010; Lourens et al., 2011; Laakso et al., 2012). Two major field campaigns (SAFARI-92 and SAFARI 2000) were conducted to understand the effects of biomass burning emissions on O_3 over southern Africa, which provided important insights on the regional O_3 seasonal cycle (Diab et al. 1996). An analysis of surface O_3 measurements during 1999-2001, albeit limited to a few sites outside urban areas, showed that the highest O_3 concentrations occur over Botswana and the Mpumalanga Highveld where the springtime maximum concentrations range between 40 and 55 parts per billion by volume (ppb) but exceeded 90 ppb at times (Zunckel et al., 2004). Due to limited measured data for the southern African region, regional-scale photochemical modelling was conducted (Zunckel et al., 2006). Interestingly, the modelling study concluded that the formation of surface O_3 over the region is due to the combined contribution of precursors from both anthropogenic and biogenic origin.

Currently, measurements of surface O_3 in South Africa are conducted at a number of government- and industry-owned ambient air quality monitoring stations. The longest ongoing O_3 measurements are conducted at the South African Weather Service (SAWS) Cape Point Global Atmosphere Watch (GAW) station with measurements from 1983 up until present (Brunke and Scheel, 1998). This site is representative of background-maritime air with O_3 concentrations of 15 ppb in summer and 30 ppb in winter with an annual average of approximately 22 ppb. In addition to state- and industry-run stations, surface O_3 monitoring has been ongoing for almost five years at the Welgegund air quality research station (30 km north of Potchefstroom), which is considered a regional background site impacted by anthropogenic activities (Beukes et al., 2015). Long-term measurement data of O_3 spanning several years are beneficial as they account for the influence of inter-annual meteorological variability on the results.

Tropospheric O_3 profiles over South Africa indicate annual and decadal increases in O_3 levels in certain regions (Diab et al., 2003; Clain et al., 2009; Thompson et al., 2012). Oltmans et al. (2013) reported that the Cape Point station displayed a 15–20% O_3 increase from 1990 to 2000, followed by a period of zero-to-low growth. Most recently, O_3 sounding measurements at Irene from 1990-2007 showed a 30% increase per decade in O_3 concentration during the early winter period (Thompson et al., 2014). The cause for this winter time free troposphere increase was linked to long-range transport of emissions from South American megacities. The lifetime of O_3 in the troposphere is sufficiently long, i.e. in the order of days to months depending on the altitude (Jonson et al., 2010), to cause pollution on a global scale. However, the large increase in free tropospheric O_3 reported by Thompson et al. (2014) is not observed for surface O_3 in the South African Highveld (north-eastern South Africa) where it was reported that there was no change in surface O_3 on the Highveld for the period 1990–2007 (Balashov et al.,

2014). The Highveld is an industrialised region containing the majority of the coal-fired power plants in South Africa that emit large quantities of nitrogen oxides (NO + NO_2 = NO_x) that affects surface O_3 levels through their inter-related chemistry. Satellite images indicate the South African Highveld as a well-known NO_2 'hotspot'. This prompts the authors to ask, "Is tropospheric O_3 over southern Africa really increasing?" At present interannual variability and trends over southern Africa remain inconclusive, or at least complex and require further investigation.

Mean surface O_3 concentrations over southern Africa exhibit a pronounced seasonal and diurnal cycle. In general the seasonal maximum occurs in spring and the minimum occurs in autumn. At Welgegund the data show a late winter-spring (August to October) maximum for O_3. The observed late winter-spring O_3 maximum coincides with the biomass burning period in southern Africa, which occurs almost exclusively during winter and early spring, from July to October (Silva et al., 2003). Aghedo et al. (2007) reported that the largest contributor to surface O_3 pollution over Africa is biomass burning, while biogenic (isoprene) emissions makes a larger contribution to global O_3. The diurnal patterns of O_3 measurements are similar for all four seasons, increasing from a minimum at sunrise to maximum values in the early afternoon and then decreasing rapidly during sunset with O_3 continuing to decrease at night to a minimum again at sunrise. The increase during the day is due to photochemical formation of O_3. The decrease during the night and early morning is because of (i) the absence of sunlight that prevents the formation of O_3; (ii) O_3 removal due to titration of remaining O_3 by nitric oxide (NO) and (iii) O_3 loss due to dry deposition. Local O_3 titration (O_3 removal) was observed on several nights in October 2014 at the Welgegund station and is currently being investigated. Ambient O_3 is expected to be low at night (<30 ppb) but more surprising is the sharp drop in O_3 concentrations to (almost) 0 ppb recorded at the station. A major increase in NO_x concentration could be observed, peaking at the exact time when O_3 drops to almost zero.

The South African National Ambient Air Quality Standard (NAAQS) for O_3 is an 8-h running average of 61 parts per billion (ppb) not to be exceeded more than 11 times in a year. All stations in the South African Highveld and Vaal Triangle designated priority areas exceeded the NAAQS for O_3 in 2014, with the highest number of exceedances occurring in August-September-October. As mentioned above, this is the southern African burning season and points to biomass burning as the source of the O_3 precursors that may be responsible for the exceedances. Monitoring stations closely influenced by NO emissions demonstrate noticeable titration of O_3 by NO. The titration effect of O_3 by NO can assist in explaining why sometimes it is observed that the O_3 levels in a rural area are higher than those in urban and industrial areas. The monitoring station in the rural town Hendrina recorded 234 exceedances of the NAAQS in 2014, which may be attributed to a lack of NO emission sources in the area to titrate the O_3 formed.

The chemical interdependence between O_3, NO_x and VOCs is widely known, however this relationship is complex and non-linear. The production of O_3 requires NO_x and VOCs to exist in the correct ratios, and sunlight for the photochemical reaction to take place. When the VOC to NO_x ratio is high, O_3 formation is limited by the availability of NO_x (NO_x-limited), while when the VOC to NO_x ratio is low, O_3 production is limited by the availability of VOCs (VOC-limited). In general, increasing VOC concentrations mean more O_3, but increasing NO_x may lead to either more or less O_3 depending on the prevailing VOC-to-NO_x ratio (Seinfeld and Pandis, 2006). The industrialised Highveld is a good example where the large-scale variability of surface O_3 point to other factors (e.g. biogenic VOCs), which lead to some areas in the Highveld being NO_x-limited whilst others are VOC-limited.

The non-linear relationship between NO_x and O_3 is also illustrated by the "weekend effect". Since the early 1970s, researchers have reported the difference between weekday and weekend O_3 concentrations with higher O_3 concentrations occurring on weekends, particularly in urban areas. Traffic emissions should be higher during weekdays thereby providing more precursors (NO_x and VOCs) for O_3 formation. However contrary to this thinking, at weekends when emissions are reduced, the NO_x falls and the O_3 concentration rises. An explanation for the weekend effect is that due to the low level of NO_x emissions during the weekend, the reaction whereby NO removes O_3 by titration to form NO_2 is suppressed. Dumont (1996) also reported significantly higher O_3 levels in Belgian conurbations in the weekend compared to weekdays. However, the sum of O_3 and NO_2 (total oxidant), often called Ox, was similar no matter what day was taken. Total oxidant Ox is in fact a better measure of the real photochemical production of O_3 than O_3 itself, as O_x production and loss are independent of the rapid photochemical reactions that convert O_3 to NO_2 and vice versa in the urban and suburban atmosphere. By comparing day-of-week patterns in O_x to those in O_3, it was shown that titration by NO is the main source of a weekend effect in ozone. The weekend phenomenon has also been reported for Johannesburg (Padayachi et al., 2013).

The reduction of O_3 concentrations in South Africa requires control of either NO_x or VOC emissions, or both, depending on the limiting mechanism for O_3 production, since limiting solar radiation is not an option. An effective reduction policy for O_3 can only be achieved when the dependence of photochemical O_3 on the precursors of O_3 is determined definitively. The O_3-NO_x-VOC sensitivity needs to be investigated individually for different regions since there is no geographically uniform response to NO_x and VOCs (Hidy, 2000). In East Asia, for instance, all the megacities were found to be VOC-limited (NO_x-saturated) (Liu, 2008). Lourens et al. (2015) also found that O_3 formation in the Johannesburg-Pretoria megacity is VOC-limited. A VOC-only control strategy would be effective in these large urban areas but may be less beneficial downwind. In other areas with appreciable natural VOC concentrations leading to a NO_x-limited regime, measures to limit VOC emissions in these areas produced little or no effect on O_3 pollution. Therefore, a

combined VOC-NO_x strategy should be more effective than a VOC- or NO_x-only strategy in reducing O_3 over a large geographic area. The United States were partly misdirected in the first two decades of O_3 mitigation attempts, where models concluded O_3 production was VOC-limited, which led to a strong regulatory effort to target VOC emission reductions. However, there was mixed success in this control strategy. Later measurements and model calculations showed that O_3 production over most of the United States is primarily NO_x-limited, not VOC-limited. Early models underestimated emissions of VOCs from mobile sources (Pierson et al., 1990) and failed to account for biogenic VOCs (Chameides et al., 1988). In the long term it would be preferable to reduce both NO_x and VOC emissions appreciably to secure worthwhile reductions in O_3. In the short term it may be necessary to identify regions as NO_x- or VOC-limited in order to maximise the cost effectiveness of strategies.

Review of scientific evidence links ozone exposure to adverse health effects. Epidemiological studies have shown that atmospheric O_3 and fine particulate matter ($PM_{2.5}$) have the most significant influences on human health, including premature mortality. Most of the impacts of O_3 on human health relate to the respiratory system, which include reduced lung function, lung irritation and increased risk of mortality from long-term exposure (Jerrett et al., 2009). Atmospheric modelling studies have provided an estimate of the global burden of anthropogenic O_3 and $PM_{2.5}$ on premature human mortality. Mortality estimates vary with different models, but most recently, Lelieveld et al. (2013) estimated a global respiratory mortality of 773 000/year and found that the highest premature mortality rates are found in Southeast Asia and Western Pacific regions where more than a dozen of the most highly polluted megacities are located. This study did not include Africa.

An assessment of the health effects and economic valuation of O_3 pollution based on the impact pathway approach involves first, assessing population exposure associated with ambient concentrations, second, estimating the health impacts associated with population exposure, and third, valuation of the health impacts in monetary terms. A key challenge is the lack of specific data for South Africa. Firstly, reliable pollutant concentration data is needed for South Africa (especially for secondary pollutants such as O_3). Secondly, to quantify the health effects requires exposed population data, baseline incidence rates and concentration-response functions from epidemiological studies for the South African population, which is unfortunately not available. Thirdly, valuation of the health impacts in monetary terms requires costs for morbidity (illnesses) e.g. costs of hospitalisation, costs of treatment in the South African context and costs for mortality.

Recent evidence suggests that the health related impacts of O_3 could be significant (Jerrett et al., 2009). However, health risk quantification in South Africa generally does not consider O_3 as a key pollutant of concern. Since there is more evidence for particulate matter (PM) and concentration-response factors are more widely available, several studies use only PM as the indicator of ambient air pollution. However, selecting only one ambient air pollutant may underestimate the magnitude of the health effects. Adding the health effect estimates of another air pollutant uncorrelated with particulate matter (for example, O_3) can minimise the extent of this underestimation.

The issue of formation, effects and abatement of O_3 is complex due to its non-linear relationship with precursor species and its zone of impact extending to local and regional scales, which calls for spatially differentiated abatement strategies. Quantification of the health risks attributed to air pollution (including O_3) will determine the level of effort needed. Monetisation of health impacts might be viewed as contentious. However, in South Africa where economic growth, job creation and poverty alleviation are pressing issues, environmental priorities have to be compared in similar terms as economic priorities that are often deemed more valuable. In addition, the transboundary nature of O_3 requires international effort in developing effective policies to cope with the problem. For these reasons O_3 will continue to be a subject of intense research and collaboration.

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