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Contents

Letter from the editors

News

Feature: Ozone in southern Africa

Reviews

Articles

Letter from the editors
New Developments in the Clean Air Journal

The Clean Air Journal has a reputation for publishing high-quality research that is topical to the southern African region; this includes highlighting key issues to the southern African air quality community.

Special feature

In this issue we have a special "Features" section highlighting ozone in southern Africa. Due to the large (spatial and speciated) range of emission sources of ozone precursors, as well as our abundant sunshine, we know that the potential for high levels of ground-based ozone is high in the region. While South Africa does have standards that aim to mitigate the impact of ozone on human health, very little is known about the potential impact on agriculture in the region. If findings from international studies are applicable here, the impact may be very high! This Features section highlights new international research on the large impact of ozone on agriculture, as well as commentaries from South African scientists researching different aspects of ozone, its chemistry and its impacts in the region.

Publication Ethics and Malpractice Statement

In this issue we are officially launching the Clean Air Journal's Publication Ethics and Malpractice Statement (see page 5). This statement highlights the journal's commitment to adhering to the highest standards with regards to publication ethics by outlining the duties, responsibilities and obligations of the editors, the authors and the reviewers of the Clean Air Journal. The full statement is printed on page 5 in this issue, and is also be available on the Clean Air Journal website - www.cleanairjournal.org.za.

Google Scholar

The editors have also been working hard to make the research published in the Clean Air Journal more easily accessible to the research community. We have created a page on Google Scholar for the Clean Air Journal, and we have been linking articles published in previous issues of the Clean Air Journal to the Google Scholar journal page. We ask all researchers to add their publications in earlier issues of the Clean Air Journal to Google Scholar on their personal profiles so we can grow the online presence of Clean Air Journal articles in Google Scholar.

DOI numbers

In addition, starting in this issue, all articles will be assigned a DOI number to ensure that all Clean Air Journal articles will be easy to trace and locate online.

"Online Early" versions

Finally, the Clean Air Journal will be launching "Online Early" versions of articles in July 2015. Once an article is accepted into the journal, it will be published online with the designation "Online Early" in order to not delay the publishing of research findings.

Thank you

In closing, we would like to thank the community for their continued support of the Clean Air Journal as authors and reviewers; it is through your time and contributions that the Clean Air Journal has built and continues to grow its strong reputation for publishing high-quality research articles.

News
Ernst-Güenter Brunke

Ernst Brunke's journey with the Cape Point station began modestly in the late 1970's when he transferred from the Geological survey, where he was working at the time as a geologist in the Northern Cape. He was approached by the late Dr Eric Halliday, who is regarded as the founder of air pollution monitoring in SA, to come and work with him on a carbon monoxide measuring program at Cape Point. These measurements started in collaboration with the *Max Planck Institute* in Germany, and I'm sure Dr Halliday was also very much interested in Ernst's proficiency of the German language and protocols!

In those early days, the Cape Point program was housed in the two historical lighthouse keeper's cottages and this is where the measurements were conducted. During this time, Ernst's administrative offices were based in the Faure National Accelerator Center as part of the NRF. Over the years, the measurement program expanded (being part of the CSIR until 1997) and various instruments were added, including some crafty home-made meteorological inventions. Ernst was assisted for many years by Mr Ronnie Allan, who he fondly remembers as having to take at least three thermometers with him each time he had to take temperature readings, since Ronnie had a knack of destroying delicate instrumentation! In spite of the limited infrastructure of those early years, Ernst's problem solving abilities were legendary and he was always willing and ready to accommodate. Hans Linde recalls fondly that on one occasion, he and a delegation from NACA went for a station visit – only to be greeted with an impromptu slide show, displayed on the side of the fridge, and coffee made from the station's stock of distilled water!

During the past 35 years, the Cape Point program grew in stature and Ernst's name became synonymous with the success and fame that the facility enjoys today. Ernst's stature grew among the international scientific community when he started to present the Cape Point programme's data at numerous conferences and workshops. In 1995, two milestones were reached – largely due to his perseverance: (1) the Cape Point program was incorporated into the World Meteorological Organisation's Global Atmosphere Watch (GAW) network of global stations, at the time, the first and only such one in Africa, and (2) the inception of the new custom-build trace gas research laboratory – one of the most scenic and functional facilities of its kind within the GAW network. Shortly hereafter, in 1997, the facility also found its current home within the South African Weather Service's Climate Research division.

Since moving into the new laboratory in 1995, the GAW program has expanded and numerous international collaborative partners have joined (currently about 17 partners, from 12 institutions), but none was as influential and beneficial as the twinning partnership that Cape Point had with its German counterpart, the Fraunhofer Institute (IFU), under the auspices of the late Dr Eckhart Scheel. This international collaboration with the IFU extended far beyond just a partnership – Ernst and Dr Scheel developed a great professional and personal relationship that lasted over two decades, and which resulted in numerous internationally peer-reviewed publications and conference proceedings. An additional milestone for Ernst and the GAW program was his election to sit on the WMO GAW's Scientific Advisory Group on Greenhouse Gases, a position he has held until his retirement in 2015.

The station has had many challenges over the years, but Ernst's positive attitude of always seeing the glass as half full, has rubbed off on his colleagues as well. A popular activity for him over years was to regard the challenging task of having to cart the industrial gas cylinders up the 80m of 45o incline to the station, as "a free gym session" and always trying to motivate his colleagues in this manner. Needless to say – nobody bought into this viewpoint! Ernst's 110% dedication to his duties was further accentuated by the fact that he never left the station unattended over prolonged periods of time – even during December holidays, when he sacrificed his leave to attend to routine matters. Proof of this was the several months of accumulated leave he has accrued over time. Furthermore, he was more than willing to spend extra time at the Cape Point laboratory, quite often taking his camping equipment and tinned tuna meals along, to stay over a night or two in the laboratory when intensive repairs or calibrations were undertaken. Even now, on the start of his retirement, he has already indicated his willingness to assist the station's personnel when needed. I'm sure we haven't seen or heard the last of Ernst Brunke's melodious humming among the instrumentation racks of Cape Point!

Ernst is a long standing member of the NACA Western Cape Branch, probably from about the time that he joined the Cape Point programme. He was always willing and eager to do presentations, assist with advice, and to share his in-depth scientific knowledge with all. From the NACA family, we wish Ernst well with his retirement and call upon him to put all his energy and passion he had at work into himself and his family, and to enjoy life away from the office.

Casper Labuschagne
South African Weather Service Cape Point GAW

News
Laboratory for Atmospheric Studies launched

The University of Pretoria (UP), with support from Eskom and Sasol, recently launched the Laboratory for Atmospheric Studies (LAS). The laboratory is based at the University of Pretoria and will be a national centre of excellence that provides infrastructure and world-class education for studies and research in the atmospheric sciences.

The launch was attended by a numbe¬¬r of prominent academic and industrial experts from different universities in the country, including Eskom and Sasol, the South African Weather Service (SAWS), and the National Association for Clean Air (NACA), among others.

This laboratory was developed as a result of the Eskom-Sasol research collaboration in pursuit of developing scarce skills in scientific studies. This partnership will also promote data and information sharing among the companies.

At various levels the parties have collaborated on numerous research initiatives intended to address environmental issues of common interest, including ash and brine research, impacts of atmospheric emissions on ecosystems, monitoring and reporting on mercury, ambient air quality, and wet and dry deposition rates of sulphur and nitrogen compounds.

Prof Hannes Rautenbach from the Meteorology Unit at UP, said the laboratory is the first to bring experts from different fields such as meteorology and chemistry together to broaden the scope of atmospheric studies.

He said UP is ideally situated to host a focused entity for conducting research in atmospheric circulation, atmospheric processes and air quality.

“With Eskom and Sasol as partners, it is expected that the resources produced by the Laboratory for Atmospheric Studies will be utilised by both organisations and also meet the urgent regional need for skills,” he added.

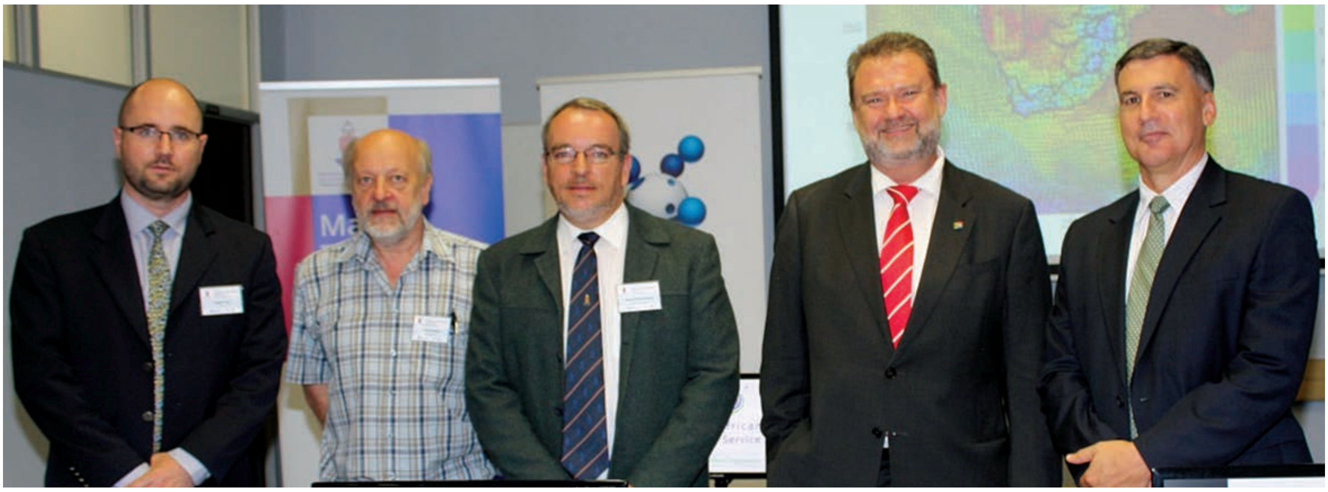
Prof Stephanie Burton, Vice-Principal for Research and Training at UP, said that collaboration with other universities, government and private sector organisations is important to the University. According to her, UP is recognised for its external, industrial partnerships.

“It is quite interesting to see the University engaging in creative activities such as this national research facility for air quality that we are launching today.”

Prof Burton said the facility will be relevant, particularly in the 21st Century, because of an ever-growing awareness of the fragile nature of the environment and our planet. She said these global issues can be addressed by means of global and collaborative responses.

“It is large consortia of research teams forming networks across the world that are able to address the problems we are faced with, especially in the field of atmospheric studies. It is very important and exciting for us that the University can play a role in a global initiative and make a difference nationally,” said Prof Burton.

The LAS is located in the University’s Geography Building. It has state-of-the-art computing facilities and can accommodate up to 20 students. It is open for use by people from all over the world thereby contributing to the ever-evolving field of atmospheric studies.



Attending the launch of LAS were (from left to right) Dr Gregor Feig (President: National Association for Clean Air); Prof Egmont Rohwer (Head: Department of Chemistry, UP); Prof Hannes Rautenbach (Meteorology Unit, UP); Dr Steve Lennon (Group Executive: Sustainability, Eskom); and Mr Rudi Heydenrich (Senior Vice-President: Research and Technology, Sasol).

News

Adoption of a Publication Ethics and Malpractice Statement

The Clean Air Journal has adopted a formal Publication Ethics and Malpractice Statement. The purpose of this statement is to outline the duties, responsibilities and obligations of the Clean Air Journal authors, reviewers and editors. By adopting this statement, the Editors and Editorial Board of the Clean Air Journal strive to highlight their commitment to adhere to the highest standards of publication ethics.

The below statement appears on the Clean Air Journal website - cleanairjournal.org.za.

Rebecca M Garland

The Clean Air Journal Publication Ethics and Malpractice Statement

The Clean Air Journal ethics statement has been developed based upon the "Code of Conduct and Best Practice Guideline for Journal Editors", the "Ethical Guidelines for Peer Reviewers", "Responsible Research Publication: International Standards for Authors", and "Responsible Research Publication: International Standards for Editors" developed by the Committee on Publication Ethics (COPE).

The Clean Air Journal editors should be informed of any actions by reviewers or authors that are not in-line with this statement. If there is suspected misconduct by an editor, the complaint should first be made to the co-editors. If the complaint is not satisfactorily resolved, then the complaint should be passed to the editorial board of the Clean Air Journal. In cases of suspected misconduct, the Editors and Editorial Board will use the best practices of COPE to assist them to resolve the complaint.

Duties, responsibilities and obligations of Authors

The author/s must acknowledge that the manuscript contains their own original research. Plagiarism and fraudulent data will not be tolerated in the journal.

It is the duty of the author to present a concise and accurate description of the research performed, together with an objective discussion of its significance, which will include the citation of relevant publications.

A manuscript must contain adequate detail and appropriate references that would allow their peers to replicate their work. The author/s should include only those people who made a significant contribution to the research. It is the responsibility of the corresponding author to ensure that all authors are in agreement of the content of the submitted manuscript as well as the publication of the paper.

The author/s must document that research that involved human or animal subjects was performed ethically.

Duties, responsibilities and obligations of Editors

The editors are responsible for what is accepted or rejected for publication in the journal, and should process manuscripts promptly.

The editor/s should give unbiased consideration to all submitted manuscripts, and have no conflict of interest with regards to the manuscripts that they accept or reject. For manuscripts submitted by the editors themselves to the journal, the editor who is the author will not have any input and will not participate in the editorial and review process.

The editor/s will clearly define the expectations of reviewers and authors, and will transparently and consistently apply standards.

The editor/s will promote the integrity of the published journal by issuing corrections and retractions when needed, pursuing suspected or alleged research and publication misconduct, and will endeavour to ensure that research published in the journal that involved human or animal subjects was carried out in an ethical manner.

Plagiarism and fraudulent data will not be tolerated in the journal.

The editor/s will treat all submitted manuscripts as confidential.

Duties, responsibilities and obligations of Reviewers

Reviewers should be prompt in accepting or declining an invitation to review, and will aim to complete review within time frame provided by the editor/s.

Reviewers will treat reviewed manuscripts as confidential.

Reviewers will declare any conflict of interests to the editor/s before accepting or rejecting an invitation to review.

Reviewers will be objective and constructive in their reviews and will provide sufficient details and references (where applicable) to support their comments and recommendations in the review.

Reviewers will acknowledge that peer review is a reciprocal endeavour and undertake to carry out their fair share of reviewing and in a timely manner.

Reviewers will only agree to review a manuscript where they have sufficient subject expertise to carry out a proper assessment.

References

CODE OF CONDUCT AND BEST PRACTICE GUIDELINES FOR JOURNAL EDITORS: http://publicationethics.org/files/Code%20of%20Conduct.pdf

COPE Ethical Guidelines for Peer Reviewers: http://publicationethics.org/files/Peer%20review%20guidelines.pdf

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Feature
Ozone in southern Africa

Ozone is one of the most important pollutants in South Africa. During 2014, all of the monitoring sites in the Vaal Triangle and Highveld priority areas were out of compliance with the National Ambient Air Quality Standards for ozone in terms of the number of reported exceedances. In South Africa, the focus of concern relating to ambient ozone has largely been in relation to human health, however, it has long been known that high levels of ambient ozone have a large detrimental effect on agricultural productivity. Recently, a number of articles have been published regarding the impact of ozone on agriculture and two of these are highlighted below.

Research Brief

Reduction of India's crop yield due to ozone

A recent study by Ghude et al (2014), published in *Geophysical Research Letters*, utilized the WRF-Chem model to estimate the ozone concentrations to the district scale at a resolution of 0.5° over India. They used the MOZART-4 chemistry scheme linked to the Goddard Chemistry aerosol Radiation and Transport aerosol scheme to simulate the ozone production. The emission inventories applied included the INTEX-B inventory for CO, SO_2, non-methane hydrocarbons, PM_{10}, $PM_{2.5}$, BC and organic carbon. Fire emissions were obtained from the FINNv1 inventory from the National Centre for Atmospheric Research (NCAR) and biogenic emissions from the MEGAN (Model of Emissions of Gases and Aerosols from Nature) model. Due to the high variability in the NO_x emission inventories for the region, the O_3 concentrations were simulated utilizing 6 differing NO_x inventories as an ensemble average. The NO_x inventories utilized included INTEX-B, EDGARv4.1, REAS, MACCity, SAFAR-India and Top-Down NO_x.

From the simulated ozone concentrations from each of the crop production seasons that were assessed, the ozone induced crop loss was calculated utilizing the AOT40 exposure metric for wheat, soybean, cotton and rice. The estimated losses in crop production as a result of the impact of ozone amounted to 5.3% (±3.1%) for cotton, 2.7% (±1.9%) for soybean, 2.1% (±0.9%) of rice and 5.0% (±1.2%) for wheat. The economic value of the loss is expected to amount to 1.29 (±0.47) billion US$ per year. The loss of wheat and rice alone is estimated to be enough to feed 94 million poor people in India. The authors ended the paper by stating that there is little known about the combined impacts of air pollution and climate change on agricultural production and suggested further research.

Research Brief

Threat to future global food security from climate change and ozone air pollution

A recent paper published by Tai et al. (2014) in *Nature Climate Change* examined the impact of both ozone pollution and climate change on agricultural production and food security at a global level. In this study, the authors utilized the Community Earth System Model (CESM) to simulate present day (2000) and future (2050) hourly temperature and ozone concentrations under two representative concentration pathways (RCP) as in the IPCC AR5 report. For this study, the two RCPs were:

- RPC4.5 - this is an intermediate pathway where pollution control measures are implemented world-wide and there is a global reduction in surface ozone, and
- RCP8.5 - which is an energy intensive pathway with increases in surface ozone occurring world-wide except for the USA and Japan.

The simulated results were used to develop metrics for temperature and ozone impact on the production of wheat, rice, maize and soybean. The metrics used for the temperature impact include, Growing Degree Days (GDD) and Killing Degree Days (KDD) which represent the number of days with a temperature conducive for crop growth and the number of days with a temperature high enough to result in the death of crops. The metrics used to assess the impact of ozone included AOT40, SUM06, W126 and M7 or M12, which are metrics that are used to describe the physiological impact of ozone on crop growth.

In terms of the temperature, strong and spatially varying responses to GDD and KDD were observed for all of the crops. Since ozone concentration is highly correlated with the temperature and it is possible that damage to crops at high temperatures is a result of ozone rather than temperature, a correction was applied for the ozone-temperature co-variation. It was found that on average ozone accounted for 24% of the KDD effect of wheat, 44% for rice, 9.8% of maize and 46% of soybean.

Under the RCP8.5 scenario, greater surface ozone concentrations led to substantial crop losses reducing total global crop production by 3.6%, however, in the RCP4.5 scenario reductions in surface ozone concentrations resulted in substantial gains to crop productivity in many regions, with an overall increase in food production of 3.1% compared to the 2001 scenario.

In comparison to the impacts of ozone, the two scenarios show a similar temperature impact on agricultural production of an 11% decrease. It is shown that the control of ozone, as in the RCP4.5 scenario, has the potential to offset some of the damage to agricultural production caused by increased temperatures (total crop losses reduced from 11% to 9%), while under the higher ozone scenario, agricultural crop loss is compounded to a combined 15% loss.

These changes in crop production are expected to have an important impact on the rates of undernourishment around the world. The authors suggest that due to the public health co-benefits of ozone control, the regulation of ozone may prove to be a practical strategy to help secure food production. The authors highlight the need for greater collaboration between farmers, air quality managers and agricultural policymakers to achieve the coordinated goals of improved public health and food security.

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Commentary

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

Tracey L. Laban, Johan P. Beukes, Pieter G. van Zyl
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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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Commentary
Modelling of ozone over South Africa: Needs and challenges

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With a large range of precursor emission sources, both anthropogenic and natural, surface ozone levels in South Africa have a potential to be high enough to impact human health and plant life. It is also noted that with the increase in anthropogenic emissions due to development on a national scale, these surface ozone levels are likely to increase, making air quality management a necessary priority in securing improved human health.

Numerous monitoring campaigns, as well as continuous measurements via monitoring networks, indicate that elevated surface ozone levels exist within and outside of urban conurbations. However, analyses of measurement data indicate that in some areas, the levels of ozone are not increasing (Balashov et al., 2014). The spatially complex interactions of precursor gases, and thus ozone formation, owe much to the distribution of regional emission sources. The Highveld region, for example, is dominated by coal-fired power generation and the petrochemical industry, but also occurrences of biomass burning. Cities are heavily influenced by emissions from domestic fuel burning and traffic. In terms of ozone and its long spatial range transport and formation, both the rural (also rural-industrial) and urban regions interact, creating exceedances of the national standard in areas far removed from the precursor emission source regions. This not only makes it difficult to describe the spatial and temporal distribution of surface ozone, such that meaningful impact assessments can be made, but also to manage the potential precursor emission sources as ozone formation becomes a regional issue. The current suite of measurements that have occurred and are continuing to occur around the country provide merely a glimpse into ozone and its chemistry over South Africa. Furthermore, even with better measurements, an understanding of the dominant processes that drive ozone formation (and in general the oxidative capacity of the regional atmosphere) is still elusive, at least in its ability to be spatially and temporally comprehensive. While it is still acknowledged that further measurements will indeed aid in adding pieces to the puzzle, a more involved investigation through informed and appropriate numerical modelling must be considered.

Air quality modelling, in the context of investigating ozone formation, will seek to describe regional atmospheric chemistry. These models are utilized as tools with which specific questions may be answered. Broadly speaking, in terms of ozone, these questions centre around:

1 - "How much ozone is being formed?" The answer to this question can feed directly into impact assessments, either for human health or ecosystems.

2 - "What precursor emission sources contribute to ozone formation?" The answer to this question firstly enables better management of ambient air quality through focused emissions interventions, and then also more generally allows an understanding of a region's chemistry (i.e., is the region NO_x or VOC limited?) such that larger, strategic emissions mitigation strategies may be developed.

An air quality model must be able to adequately simulate pollutant transport and transformation to answer these questions. What is required then is a scientifically up-to-date model, and inputs that are realistic and appropriate for the model's needs. Inputs often associated with air quality models are listed below:

- Meteorological data (for air quality (AQ) models not coupled to meteorological models): This data drives transport of pollutants within the model and provides moisture, temperature and pressure estimates for chemical processing.

- Emissions inventory: Since the air quality model simulates transport and transformation of emitted pollutants, the emissions inventory forms the most important input to the model. In modelling ozone, and thus atmospheric chemistry, all precursor emissions need to be accounted for at a fine temporal and speciated scale (for VOC and PM). These range from industrial to biogenic sources. The temporal detail ensures that diurnal and seasonal cycles, particularly important for biogenic and domestic fuel burning sources, are captured and the response from ozone formation is simulated. Additionally, since ozone formation depends on various chemical reactions involving NO_x and the many VOC compounds (each with their own reaction rates), it is necessary to disaggregate total VOC emission estimates into the constituents being considered by the chemical processing modules in the model.

- Photolysis rates (for AQ models not coupled to a radiative transfer simulation): Photolysis rates are assigned to individual photochemical reactions according to how much solar radiation is available, and is dependent on solar angle, column ozone, column clouds and column moisture in general. Initial rates may be determined externally to the air quality model by use of data regarding the optical state of the atmosphere (moisture, aerosol and ozone), a radiative transfer model, and a database to cross reference the impact of radiation on standard, photochemical reaction rates. These may be further modified within the air quality model based on simulated aerosol optical depth.

- Initial and boundary conditions: This data allows the model to contextualize a simulation within an appropriate representation of reality. The initial conditions serve only to initialize the model by providing ambient concentrations at the beginning of a model run, and are thus only important for a short time. The boundary conditions are, however, much more important as they indicate to the model at each time-step the amount of pollutants entering the model domain from the lateral (east/south/west/north) and upper (highest model level) boundary. This then will depend on the size of the model domain chosen; and is a necessity of limited-area models (as opposed to global models). The domain boundary is best located in areas that exhibit near uniform (or at least easily determined) pollutant concentrations, such as those that primarily experience air quality at background pollutant levels. Thus, background station monitoring data can be used. If the domain boundaries fall within areas of significant emissions or pollutant transport, then these will have to be represented at each boundary. This is a complex task, effectively having to model further pollutant emissions and transport outside of the model domain. This often necessitates an additional simulation, but on a larger and coarser grid that feeds into the finer grid. However it should be noted that even the larger grid would need boundary input. It is thus advisable to create the domain large enough to include all significant emission sources, as well as those that significantly impact the simulation area of concern. One approach to simplifying lateral boundary estimation (if one cannot increase domain size any further) is to use global chemistry transport model (e.g. MOZART and GEOS-CHEM) outputs to specify boundary conditions. If a national domain is selected, monitoring data from the Cape Point GAW station can be used as initial as well as boundary conditions, together with any measurements along the north and east boundaries, (e.g. stations at Kruger National Park).

In addition to the preparation of input data, numerous model options need to be selected, which can include time-step considerations, topography handling, type of chemical processors and mechanisms (generally simplification by grouping discrete species and reactions) for description. The choice of chemical mechanism to be used is an important one and performance trade-offs (since a more accurate chemical mechanism might contain more explicit species and thus be more computationally expensive), specific non-standard reaction inclusions (e.g. inclusion of mercury chemistry) and ability to provide emission input for the mechanism need to be considered.

Once a model is run it is necessary to assess performance through comparison with measurements. The continuous ozone monitoring occurring nationally is essential to this required evaluation, and consistent quality control is vital. It should also be noted that while ozone measurements within cities or close to large precursor emission sources are useful, those in rural regions are also important. Model performance for an ozone simulation is generally assessed on the ability of the model to predict the magnitude and timing of peak ozone events. Thus both ozone as well as precursor measurements are needed to assess the build-up of precursors during an episode and the resultant ozone formation. A particularly useful measurement to compare to model outputs would be that of VOC species, such as ethane (or ethene) or formaldehyde, on a continuous (or at least for a year) basis. This can provide direct insight into the model's chemistry simulation and emissions characterization used therein.

From the above, one may appraise the capacity in South Africa to develop model platforms for the simulation of ozone by considering each of the aspects required to run an air quality model. Capacity to generate meteorological data through numerical simulation is present within South Africa through the South African Weather Service (SAWS) and the various regional climate modelling groups. In fact, private consultants may even offer this service for a fee. Air quality monitoring (for use in performance assessment and boundary conditions) activity in South Africa is also relatively high; with academic and professional organisations conducting much research into methodologies and application. However, on this aspect there is still room for growth as the appetite for measurements of more than just the criteria pollutants increases due to greater complexity in air quality issues being tackled.

Currently, the most limiting factor in producing simulations of ozone in South Africa is the lack of accurate, credible and peer-reviewed emissions data of a high temporal and spatial resolution. Ideally, such information should also be vetted by national or provincial government (together with stakeholders) so that agreement is reached before modelling can be done as results can then be deemed "official" and then considered legally applicable. As it stands, there is no official national emissions inventory for any of the source classes of precursor emissions. The current piece-meal approach, focused on single sources or source categories, to constructing an emissions inventory cannot be used for simulating ozone, as the non-linear response introduced by chemical transformations only intensifies any impact from biases/incompleteness in an inventory. Only when all relevant sources of precursor gas emissions are captured in acceptable detail (i.e. spatial, temporal and species) can more accurate predictions of ozone be sought.

Even so, it should be noted that the air quality models used may be termed "research models" since the science behind many of the processes included are constantly changing as the research community resolve atmospheric chemical dynamics in more detail. There will thus also need to be a bridge to close the gap between policy and decision makers with the research community. A primary driver is an increase in computational resources, allowing these models to reduce the performance trade-offs often used. That is not to say that valuable conclusions cannot be attained from the current set of models, but rather an open scientific process needs to be followed in building and working with these models, such that expectations are maintained and results are correctly interpreted. In the local context, much of the research required will still fall upon emissions estimation before we can even begin to question the accuracy of air quality models due to their own inherent abilities.

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Commentary

Impacts of ozone on agricultural crops in southern Africa

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The potential for ozone (O_3) damage to agricultural crops, trees and native plants is well documented in literature. O_3 has been shown to cause a wide variety of effects to important agricultural crops including visible leaf injury, growth and yield reductions, as well as deteriorating nutritional quality in certain crops. O_3-induced damage is especially an issue of concern if it threatens food supply and the economies of countries that are based strongly on agricultural production. With the availability of global chemistry transport models, global and regional estimates of crop losses can be obtained (Van Dingenen, 2009; Avnery et al., 2011; Wang and Mauzerall, 2004). Present day global relative yield losses due to O_3 damage are estimated to range between 7% and 12% for wheat, 6% and 16% for soybean, 3% and 4% for rice and 3% and 5% for maize (Van Dingenen, 2009). In India it was calculated that O_3 damage to wheat and rice resulted in a nationally aggregated yield loss of 9.2%, that is sufficient to feed 94 million people living below the poverty line in that country (Ghude et al., 2014).

Agricultural crops contribute significantly to the economy in southern African countries. Staple crops in South Africa that meet the food needs for local consumption are maize and wheat, whilst economically important crops include sunflowers and sugarcane. These crops must be assessed for O_3-induced effects. The potential for elevated concentrations of O_3 is particularly high in many regions of South Africa because of the combination of intense and extended solar radiation, and the relatively high emission of precursor species, such as nitrogen oxides and volatile organic compounds, from human and natural sources. Rural and agricultural areas in southern Africa, subject to regional air pollution events could have even higher O_3 concentrations than industrialised areas (sources of O_3 precursors) if polluted air masses are transported to these areas.

An assessment of surface O_3 measurements over southern Africa indicated that maximum O_3 concentrations are between 40 and 60 ppb, but can reach more than 90 ppb during the springtime (Zunckel et al., 2004). Furthermore, modelled O_3 as part of the Cross Border Impact Assessment Project, indicated large areas on the sub-continent where surface O_3 concentrations exceed 40 ppb for up to 10 h per day (Zunckel et al., 2006). The implications are that at these levels of exposure southern African vegetation may be at risk to damage by O_3. Josipovic et al. (2010) did an assessment of critical level exceedance for O_3, utilising passive samplers and found O_3 levels below the critical levels. However, the methodology applied did not consider cumulative O_3 exposure over time, which really determines the long-term effects on crops. The seasonal pattern of O_3 in southern Africa reveals the highest concentrations during spring and winter, with lower concentrations during summer (Laakso et al., 2013). The diurnal cycle of O_3 is characterised by an increase from a minimum near sunrise to maximum values in the early afternoon, and decreasing to the early morning minimum (Zunckel et al., 2004). Therefore plant uptake of O_3 should be highest during midday and early afternoon when high rates of leaf gas-exchange coincide with rising O_3 concentrations.

O_3 enters the plant mainly through its open stomata (leaf pores) when plants take up carbon dioxide (CO_2) for photosynthesis. O_3 is a highly reactive molecule; inside the plant it produces several reactive oxygen species such as superoxides, peroxides and hydroxyl radicals. Among other negative effects, the oxidative action of O_3 destroys key enzymes and proteins, including the photosynthetic enzyme Rubisco, which will result in a much reduced photosynthetic efficiency. O_3 also causes damage to the stomatal apparatus resulting in the inability of the plant to control the opening and closing of the stomata. Reduced Rubisco and impaired stomatal function will cause less CO_2 being taken up by the plant leading to a reduced photosynthetic efficiency, and will ultimately lead to reduced growth rates and yield. At short periods of high concentrations of O_3, visible injury symptoms associated with O_3 damage include small flecks or stipples on leaf tissues. Visible injuries usually appears early in the growing season and continues to develop during the season. Continuous exposure over long periods to relatively low concentrations of O_3 may induce some of the same visible symptoms, including chlorosis (loss of chlorophyll), necrosis (premature death of cells and living tissue) and accelerated senescence (ageing) in leaves (De Temmerman et al., 2002). Injuries not visible to the naked eye result from pollutant impacts on plant physiological or biochemical processes. Some of these changes increase the resistance of the leaf to subsequent O_3 exposure whilst others decrease photosynthetic function.

O_3 damage to crops can be evaluated based on the AOT40, an index used in Europe that serves as the standard for protection of vegetation against O_3 pollution. AOT40 is defined as the accumulated O_3 exposure above a threshold concentration of 40 ppb during daylight hours of the growing season (UNECE, 2010). The AOT40 exposure index is cumulative, i.e. it integrates

$$AOT40\ (ppb\ h) = \sum_{i=1}^{n} ([\mathrm{O}_3]_i - 40), \qquad \text{for } \mathrm{O}_3 \geq 40 \text{ ppb}$$

exposure over time in order to detect long-term effects. Experimental data has shown that the impacts of O_3 on plants are often better related to accumulated exposure above a threshold concentration rather than the mean concentration over the growing season. The European AOT40 critical level is 3000 ppb h for agricultural crops (over a growing season of 3 months) and 5000 ppb h for forests. However the AOT40 approach has limitations since it does not directly reflect the O_3 absorbed by plant surfaces, with damage being calculated solely on the basis of ambient O_3 concentrations. O_3 flux, which is the rate at which O_3 is absorbed by plant surfaces, is a better measure of biological response. The use of an impact assessment method approach based on the actual flux of O_3 through the plant stomata is recommended, but requires additional information such as O_3 flux data and dose-response relationships of different plant species.

Experiments to determine dose-response functions for plants have used controlled-environment greenhouses, field chambers and free-air systems (U.S. EPA, 2006). Research studies have derived relationships between "O_3 dose" or "O_3 exposure" and the yield of the major crop species through controlled O_3 fumigation experiments under near-field conditions using open-top chambers. An open-top chamber research facility exists at North-West University where O_3 assessments have been performed on maize, snap beans, garden peas and canola plants, and have demonstrated adverse physiological and growth effects due to elevated O_3 levels. Most recently, a sugarcane trial is underway on two local cultivars to determine the effects of elevated CO_2 concentrations, elevated O_3 concentrations, and also the combined effects of elevated CO_2 with elevated O_3 in the absence of drought stress. To our knowledge, there is no quantitative data on O_3 exposure-plant response (E-R functions) for sugarcane currently available.

Compared to the control plants (exposed to charcoal-filtered air), sugarcane plants exposed to concentrations of 80 ppb O_3 for 9 hours a day (photoperiod) showed chlorotic and necrotic lesions on their leaves, leaf senescence, as well as stunted growth. Evidence from visual changes also suggests that sugarcane crops are more sensitive to the elevated O_3 early in the growth season, while later showing signs of recovery to sustained O_3 stress. In this trial, seedlings of sugarcane were used in the open-top chambers and O_3 fumigation only commenced after a few weeks, once the plants had reached some level of maturity. Plant response to O_3 may vary with physiological age and young plants are considered more sensitive to O_3 exposure in the early stages of development (Reiling and Davison, 1994 and references therein). Developmental stage plays a major role in determining plant sensitivity to O_3.

It is important to note that O_3 stress does not act independently, but is one of many stresses that will affect growth and productivity of crops. O_3 can also cause altered sensitivity to biotic (e.g. pest and pathogen attack) and abiotic stresses (e.g. drought, floods). In some regions of southern Africa, drought stress is more common than O_3 stress and the combination of O_3 stress and drought will often produce plant responses that are due primarily to the effect of drought (van Tienhoven, 2005). The more frequent occurrence of drought stress make plants in the southern African region more tolerant to O_3 stress compared to plants in Europe. Drought stress reduces the stomatal opening, and hence reduces O_3 uptake by the plant. There are also interactions between O_3 stress and other atmospheric gases that can modify the impact of O_3. For example, rising levels of atmospheric CO_2 are thought to ameliorate the influence of increasing ground-level O_3 concentrations i.e. plant stress caused by O_3 is offset by CO_2. O_3 stress on its own leads to foliar injury, suppressed growth and yield in plants, whereas elevated CO_2 generally enhances growth and yield; the combination of elevated O_3 and CO_2 can affect plant response differently compared to each stress occurring separately (Heagle et al., 1999). Also, the presence of other pollutants such as sulphur dioxide may act synergistically with O_3, increasing growth reductions (WHO, 2000).

(a)

Sugarcane leaves exhibiting visible injury from O_3 exposure: tiny, brown spots (stipples) and yellow patches early on – yellowing is a sign of chlorosis.

(b)

Sugarcane leaves exhibiting visible injury from O_3 exposure: reddish-brown lesions later on – a sign of necrosis.

There are two types of O_3 exposure, i.e. acute exposure where concentrations are high and range from 120 – 500 ppb for hours (as is the case at polluted sites), or chronic exposure where there is an elevated background concentration with daily peak concentrations of 40 – 120 ppb over several days in the growing season (Long and Naidu, 2002). But what is more damaging to plants, short-term exposure to very high O_3 concentrations or long-term exposure to moderate O_3 concentrations? In South Africa, chronic exposure in the range that can affect plants interspersed with short duration pollution episodes of peak concentrations often occurs. It has been stated that intermediate concentrations of O_3 may have the largest impact on crop yields (Krupa et al., 1995). On the other hand, Köllner and Krause (2000) pointed out that O_3 peaks are more important for yield losses than constant elevated O_3 exposure. Opinions therefore differ as to the extent of yield reductions resulting from periodic exposure to high concentrations (well above any supposed threshold) or chronic exposure to concentrations near the threshold. Nevertheless, more studies link chronic exposure to consequences of reduced growth and yield, adding that the severity varies for different crop species and also for different cultivars within a crop species.

Southern African impact studies to date have adopted the European AOT40 for assessing O_3 damage to crops (Avnery et al., 2011; van Tienhoven et al., 2006). However, despite the AOT40 for the southern African environment exceeding the European AOT40 level for crop damages (3000 ppb h), no vegetation damages have been reported. Van Tienhoven et al. (2005) explained that the reasons for this could be either that there is a lack of knowledge to distinguish between actual O_3-induced effects and effects from other stresses, or that the local vegetation may have had hundreds of years to adapt to elevated O_3 levels, as some Mediterranean species. The adaption aspect was also discussed by Scholes and Scholes (1998), who argued that local indigenous species, especially on the savannah, may be less sensitive to O_3 exposure compared to planted alien species such as pine and eucalyptus. The applicability of the AOT40 to tolerant southern African crops should be revisited. Note that while a value of 40 ppb (AOT40) has been employed in impact assessment research in Europe, a higher value of 60 ppb (AOT60) has been used in the U.S. The open-top chamber trials at North-West University have historically used 80 ppb O_3 treatments on maize, snap beans and canola, and found adverse physiological and biochemical effects on these species. Therefore these effects might be better related to the use of a higher threshold concentration than 40 ppb. However, the suitability of a higher threshold for South African species must still be established.

Most of the actions taken to control ground-level O_3 pollution are aimed at reducing human exposure to this pollutant. Given the concentration thresholds for effects, these measures may therefore be expected to have the greatest beneficial impact in terms of health, with somewhat less of an impact in relation to plants. The South African National Ambient Air Quality Standard for O_3 (8-h running average of 61 ppb) is based on World Health Organisation (WHO) guidelines that are primarily concerned with the protection of human health. Air quality guidelines based on the United Nations Economic Commission for Europe (UNECE) critical levels (UNECE, 1998) provide the best available scientific basis for the protection of natural ecosystems against O_3. However, country-specific research on exposure-response relationships is needed to provide sufficient data on the critical levels for South African vegetation (WHO, 2000). Information on critical levels is a means to update the existing air quality standards for ground-level O_3 which take into account not just the adverse effect on human health, but also on vegetative health, in order to protect the ecosystem as a whole.

O_3 impact studies focusing on local crop variants should be advanced using either the concentration-based AOT40 approach (good identification tool for crop damage, but not accounting for interacting stresses) or the flux-based approach (good yield loss assessment tool, but large data requirements). For the AOT40 approach, continuous ambient O_3 measurements are needed. For the flux-based approach, measurements of local environmental variables such as humidity and soil moisture (lower during droughts), temperature, radiation, vapour pressure deficit and wind speed are important parameters influencing O_3 uptake. Both these approaches will require exposure-response functions (concentration-response or dose-response) for local cultivars. The application of European crop exposure-response functions add to uncertainties in agricultural impact assessments. Therefore, local exposure-response relationships under ambient conditions, and in a changing climate, should be derived through routes such as open-top chamber experiments.

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Review
Daniel S. Wilks' book *Statistical Methods in the Atmospheric Sciences* (3rd Edition)

This book is an introduction to the *application* of statistical methods to atmospheric data. Every edition of *Statistical Methods in the Atmospheric Sciences* has been quite relevant to contemporary analysis of observed and modelled atmospheric data, but the book assumes that the reader has completed some introductory course, or has a working knowledge, in statistics. On the other hand, although I highly recommend this book to all atmospheric scientists, more complete and advanced texts than what this book offers may be what are required by professional statisticians.

During the course of my work on statistical weather and climate modelling, I have made extensive use of the book. In particular, I have referred to the book for the application of post-processing methods for weather and seasonal forecast downscaling, statistical downscaling of climate change projections, parametric and non-parametric tests, Monte Carlo techniques, multiplicity and field significance, probability distributions, return period calculation, forecast verification, hypothesis testing, linear regression, principal component analysis/regression and canonical correlation analysis. These topics cover only about a 1/4 of the content of a three-part book on statistics and probabilities, univariate as well as multivariate statistics. The book also covers topics such as Bayesian techniques, non-linear regression, ensemble forecasting, a chapter devoted to time series analysis, the multivariate normal distribution, discrimination and classification, and cluster analysis.

The book includes excellent practical examples and example data sets, numerous illustrations, exercises (and their solutions as an appendix), probability tables, comprehensive equations, and many pages of references. Overall, this is an excellent text book that can benefit both lecturers/supervisors and their students (likely to be best used from Honours level and up) in the atmospheric sciences in South Africa.

The book is available on Kalahari.com in both hardcover (R1212-00) and as an eBook (R1059-00). The 2nd and 1st editions are also still available. Although this book is expensive, I consider this book of such importance to my work (for both research and teaching) that I bought my own copy of the 3rd Edition the same day I heard it was released on Amazon, and am already saving for a possible 4th Edition that will in all likelihood not only expand on the material of the current issue but may also introduce additional relevant statistical methods in contemporary atmospheric science.

Reviewed by Willem A. Landman

Review
'The State of Green Technologies in South Africa' November 2014 Report

Green technologies encompass an evolving group of products, services and systems that aim to sustain green production and consumption processes. Renewable energy technologies, green buildings, and pollution prevention and abatement technologies are examples of green technologies. Commissioned by the Department of Science and Technology and carried out by the Academy of Science of South Africa (ASSAf), a consensus panel was convened to prepare this report on the state of green technologies in South Africa. The panel's tasks were to document the green technologies presently being used in South Africa; to identify gaps and opportunities where green technologies could be applied; and to recommend ways to promote the growth of green technologies.

In a 236-page report comprising 10 chapters, the panel provides comprehensive answers to these three overarching objectives. The panel found that while South Africa's policy environment is favourable for the adoption of green technologies, in general, South Africa's uptake of green technologies is below average when compared to other countries. Compared to the other sectors in the country, only in the energy sector has there been some uptake of green technologies. In the energy sector, co-benefits of green technology implementation would be air pollution reduction, for example, through point-source air pollution control, uptake of clean cookstove technology, and introduction of electric vehicles. Adoption of alternate renewable energy options such as solar and wind would also contribute to a reduction in ambient air pollution, and ultimately help to improve air quality-related adverse health outcomes.

Several barriers that inhibit innovation and prohibit effective implementation and uptake of green technologies are discussed in the report. These include, amongst others, institutional challenges, government bureaucracy, lack of political will, skills shortages, financial barriers, and human behaviour. In light of these barriers, challenges and opportunities garnered from local and international experience, the final chapter provides nine recommendations aimed at promoting implementation and development of green technologies in South Africa. Cognisant of the roles of business, government and society, the recommendations support the idea that green growth is necessary to grow South Africa's economy. Well written for a general audience, the report is an inclusive document of value to policy-makers, practitioners and researchers alike.

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Reviewed by Caradee Wright and Linda Godfrey

Spatial and temporal assessment of organic and black carbon at four sites in the interior of South Africa

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Abstract

Limited data currently exist for atmospheric organic carbon (OC) and black carbon (BC) in South Africa (SA). In this paper OC and BC measured in SA were explored in terms of spatial and temporal patterns, mass fractions of the total aerosol mass, as well as possible sources. PM_{10} and $PM_{2.5}$ samples were collected at five sites in SA operated within the Deposition of Biogeochemical Important Trace Species-IGAC DEBITS in Africa (DEBITS-IDAF) network. OC were higher than BC concentrations at all sites in both size fractions, while most OC and BC occurred in the $PM_{2.5}$ fraction. OC/BC ratios reflected the location of the different sites, as well as possible sources impacting these sites. The OC and BC mass fraction percentages of the total aerosol mass varied up to 24% and 12%, respectively. A relatively well defined seasonal pattern was observed, with higher OC and BC measured from May to October, which coincides with the dry season in the interior of SA. An inverse seasonal pattern was observed for the fractional mass contributions of OC and BC to the total aerosol mass, which indicates substantially higher aerosol load during this time of the year. The relationship between OC and BC concentrations with the distance that air mass back trajectories passed by biomass burning fires and large point sources proved that biomass burning fires contribute significantly to regional OC and BC during the burning season, while large point sources did not contribute that significantly to regional OC and BC. The results from a highly industrialised and populated site also indicated that household combustion for space heating contributed at least to local OC and BC concentrations.

Keywords

Black carbon (BC), Organic carbon (OC), Spatial, Temporal, DEBITS, IDAF

Introduction

Atmospheric aerosols have impacts on climate change and general air quality, which are determined by their physical (size, mass, structure, concentration and optical density) and chemical properties (Seinfeld and Pandis 2006). Typical chemical species present in atmospheric aerosols include wind-blown dust particles (e.g. pollen, bacteria, smoke, ash, sea salt), black carbon (BC), organic carbon (OC), sulphates (SO_4^{2-}) nitrates (NO_3^-), ammonium (NH_4^+) and trace metal species. Aerosols are generally classified according to their size, e.g. PM_{10} (aerodynamic diameter ≤ 10 μm), $PM_{2.5}$ (aerodynamic diameter ≤ 2.5 μm), PM_1 (aerodynamic diameter ≤ 1 μm) and $PM_{0.1}$ (aerodynamic diameter ≤ 0.1 μm) particulates (Slanina and Zhang 2004; Pöschl 2005). The baseline of uncertainty in aerosol radiative forcing is large and depends on the aforementioned aerosol characteristics, which can vary significantly on a regional and global scale (Slanina and Zhang 2004; IPCC 2013). General detrimental effects of atmospheric aerosol pollution on human health include increased cardiopulmonary and respiratory diseases (Gauderman et al. 2004), while $PM_{0.1}$ can even diffuse through the membranes of the respiratory track into the blood stream (Oberdőrster et al. 2004; Pöschl 2005). Environmental impacts of atmospheric aerosol pollution include acid deposition and eutrophication (Lazaridis et al. 2002; Pöschl 2005).

Atmospheric BC is emitted as a primary species, while OC can consist of primary and secondary aerosols (Putaud et al. 2004; Pöschl 2005). Major sources of BC and OC include incomplete combustion of fossil fuels, biomass burning and traffic emissions (Bond and Sun, 2005; IPCC 2013). OC is also emitted from biogenic sources and can be formed through the oxidation of volatile organic compounds (VOCs) (Pöschl 2005). BC absorbs terrestrial long-wave radiation that has a warming effect on the atmosphere, while OC, depending on their chemical properties, could absorb or reflect incoming solar radiation (IPCC 2013).

In general it is accepted that OC has a net cooling effect (IPCC 2013). After CO$_2$, BC is considered to be the second most important contributor to global warming (Bond and Sun 2005; IPCC 2013). The impacts of BC are especially significant on local and regional scales, since BC has a relatively short atmospheric lifetime (days to weeks) (IPCC 2013). Greenhouse gases (GHG) spend much longer periods in the atmosphere, i.e. between 10 to 100 years (de Richter and Caillol 2011).

Although Africa is regarded as the largest source region of anthropogenic atmospheric OC and BC (Liousse et al. 1996; Kanakidou et al. 2005), it is one of the least studied continents. Within Africa, southern Africa is an important source region. Biomass burning fires (anthropogenic and natural) are endemic across this region especially during the dry season when almost no precipitation occurs (Formenti et al. 2003; Tummon et al. 2010; Laakso et al. 2012).

Biomass burning fire plumes from southern Africa are known to impact Australia and South America (Swap et al. 2004). In addition, South Africa is the economic and industrial hub of southern Africa with large anthropogenic point sources (e.g. Lourens et al. 2011). However, the relative importance of OC and BC contributions from these anthropogenic sources in Africa are still largely unknown, although some papers have been published that considered sources in west African capitals (Doumbia et al. 2012; Val et al. 2013). Venter et al. (2012) used BC data that were collected at Marikana in the North West province (South Africa) to verify that the origin of CO and PM$_{10}$ was related to BC, while Collett et al. (2010) only presented a single diurnal plot for BC measured at Elandsfontein in the Mpumalanga Highveld. Hyvärinen et al. (2013) used BC data collected at Welgegund in the North West province to illustrate the use of a newly developed method to correct BC values measured with a multi-angle absorption photometer (MAAP), but did not go into further detail of the BC data.

Within the framework of the Deposition of Biogeochemical Important Trace Species (DEBITS)-International Global Atmospheric Chemistry (IGAC) DEBITS in Africa (IDAF) project (Galy-Lacaux et al. 2003; Martins et al. 2007), atmospheric gaseous and aerosol measurements have been performed continuously since 1994 at 7 sites in central and western Africa, as well as 3 sites in South Africa. Regarding carbonaceous aerosol, Martins (2009) determined BC and OC concentrations at two of the South African IDAF sites. However, these measurements were restricted to three two-week winter campaigns and one two-week summer campaign. This data have also not yet been published in the peer reviewed scientific domain.

In order to address the current knowledge gap, i.e. very limited OC and BC data for South Africa the main objectives of this paper are to present spatial and temporal assessments of OC and BC concentrations at the South African IDAF sites, determine the mass fractions of OC and BC of the overall aerosol mass, as well as to determine possible sources.

Experimental

Sampling sites

Aerosol samples were collected at five sampling sites in South Africa operated within the IDAF network, i.e. Louis Trichardt (LT), Skukuza (SK), Vaal Triangle (VT), Amersfoort (AF) and Botsalano (BS). The locations of these sites within a regional context are presented in Fig. 1. The South African IDAF sites are located in the north eastern part of the interior of South Africa. Mphepya et al. (2006) and Martins et al. (2007) have previously introduced LT and SK, but not the other sites. In order to contextualise all the sites a short description of each site is given in Table 1. LT, SK and BT are considered to be background sites.

In contrast, AF lies southeast of the internationally well-known NO$_2$ hotspot that is clearly visible from satellite observations over the Mpumalanga Highveld of South Africa (Lourens et al. 2012), while VT lies within a highly industrialised and populated area that has been proclaimed a national air pollution hotspot in terms of the South African National Environmental Management Act: Air Quality (Government Gazette Republic of South Africa 2005). Although not specified in Table 1, all the South African IDAF sites are likely to be impacted by local, as well as regional biomass burning fire emissions.

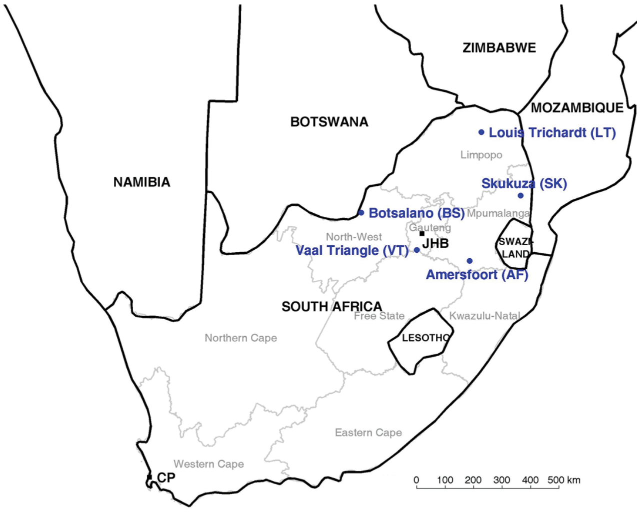


***Figure 1**: The location (blue dots) of the South African IDAF sampling sites where OC and BC measurements were conducted are indicated on a southern African map. Provincial borders with the provincial names within South Africa, as well as Johannesburg (JHB) and Cape Town (CP) are also included for reference*

***Table 1**: Geographic coordinates and short descriptions of South African IDAF sampling sites where OC and BC measurements were conducted*

Site	Location	Description
Amersfoort (AF)	27˚04'13"S 29˚52'02"E, 1628 m amsl	Semi-arid, within grassland biome, impacted by anthropogenic activities on the Mpumalanga Highveld
Louis Trichardt (LT)	22˚59'10"S 30˚01'21"E, 1300 m amsl	Semi-arid, within savannah biome, rural site predominantly used for agricultural purposes
Skukuza (SK)	24˚59'35"S 31˚35'02"E, 267 m amsl	Semi-arid, within savannah biome, regional background site in a protected area (Kruger National Park)
Vaal Triangle (VT)	26°43’29”S 27°53’05”E, 1320 m amsl	Semi-arid, within grassland biome, situated in the highly industrialized Vaal Triangle area, impacted by emissions from various industries, traffic and household combustion
Botsalano (BS)	25 32'28"S, 25 45'16"E	Semi-arid, within savannah biome, regional background site in a protected area (Botsalano Game Reserve)

Regional meteorology

Recently Laakso et al. (2012) and references therein gave an overview of the meteorology over the South African Highveld, as well as the interaction between meteorological patterns and pollutant levels. Therefore only a synopsis is presented here. Atmospheric circulation over the South African Highveld is dominated by an anti-cyclonic recirculation pattern throughout the year (Tyson and Preston-Whyte 2000), due to the dominance of a continental high pressure cell over the interior. This recirculation contributes significantly to the build-up of pollutants. This is especially significant during the cold dry winter (June – August) and early spring months (September – middle October) when strong inversion layers trap pollutants at several different heights inhibiting vertical mixing. This frequently causes an increase in atmospheric pollutant concentrations near the surface. In addition, the interior of South Africa is also characterised by a distinct wet and dry season. Almost all the precipitation occurs during the wet season from middle October to April, while nearly no precipitation takes place during the dry season from May to middle October. The lack of precipitation during the dry season leads to a decrease in wet deposition of pollutants and indirectly to the increase in pollutant levels due to the more frequent occurrence of large scale biomass burning fires. During the cooler autumn and cold winter months (May to August) household combustion for space heating is also a common occurrence in especially semi-formal and informal settlements (Venter et al. 2012).

Sampling

One 24-hour PM$_{2.5}$ and one PM$_{10}$ aerosol sample was collected on quartz filters (with a deposit area of 12.56 cm^2) once a month from March 2009 to April 2011 at each site. A total of 258 samples were collected, i.e. 52 samples for each site, except for BS for which only 50 samples were collected. Since both size fractions were sampled each month at each site, one half of the samples were PM$_{2.5}$ and the other half PM$_{10}$. The quartz filters were prebaked at 900°C for 4 hours and cooled down in a desiccator, prior to sample collection. MiniVol samplers developed by the United States Environmental Protection Agency (US-EPA) and the Lane Regional Air Pollution Authority were used during sampling (Baldauf et al. 2001). These samplers have a pump that is controlled by a programmable timer, which allows for the collection of samples at a constant flow rate over a pre-determined time period. In this study, samples were collected at a flow rate of 5 L/min, which was verified by using a handheld flow meter that was supplied with the MiniVol samplers. Filters were handled with tweezers while wearing surgical gloves, as a precautionary measure to prevent possible contamination of the filters. All thermally pre-treated filters were also visually inspected to ensure that there were no weak spots or flaws. After inspection, acceptable filters were weighed and packed in airtight Petri dish holders until they were used for sampling. After sampling, the filters were again placed in Petri dish holders, sealed off, bagged and stored in a portable refrigerator for transport to the laboratory. At the laboratory the sealed filters were stored in a conventional refrigerator. 24 hours prior to analysis, samples were removed from the refrigerator and weighed just prior to analysis.

OC and BC Analysis

Several methods can be used to analyse OC and BC collected on filters (Chow et al. 2001). It was decided to apply the IMPROVE thermal/optical (TOR) protocol (Chow et al. 1993; Chow et al. 2004; Environmental analysis facility 2008; Guillaume et al. 2008) by using a Desert Research Institute (DRI) thermal optical carbon analyser. In this method, filters are submitted to volatilization at temperatures of 120, 250, 450 and 550°C in a pure Helium (He) atmosphere and thereafter to combustion at temperatures of 550, 700 and 800°C in a mixture of He (98%) and oxygen (O$_2$) (2%) atmosphere. The carbon compounds that are released are then converted to CO$_2$ in an oxidation furnace with a manganese dioxide (MnO$_2$) catalyst at 932°C. Then, the flow passes into a digester where the CO$_2$ is reduced to methane (CH$_4$) on a nickel-catalysed reaction surface. The amount of CH$_4$ formed is detected by a flame ionization detector (FID), which is converted to carbon mass using a calibration coefficient. The carbon mass peaks detected correspond to the different temperatures at which the seven separate carbon fractions, which include four OC and three BC fractions, were released. These fractions were depicted as different peaks on the thermogram, of which the surface areas were proportional to the amount of CH$_4$ detected. The reflectance from the deposited sample is monitored throughout the afore-mentioned analysis. This reflectance usually decreases during the volatilization process due to the pyrolysis of OC. When oxygen is added, the reflectance is increased as the BC is burnt and removed. OC is defined as the fraction which evolves prior to re-attainment of the original reflectance (the non-absorbing light particles) and BC is defined as the fraction which evolved after the original reflectance has been attained (the light absorbing particles). The DRI instrument can detect OC and BC as low as 0.1 µg/cm^2.

Back trajectory analysis

Back trajectories of air masses were calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT 2014) model (version 4.8), developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler and Hess 2004). This model was run with meteorological data of the GDAS archive of the National Centre for Environmental Prediction (NCEP) of the United States National Weather Service and archived by the ARL (Air Resources Laboratory 2014a), which has a 40 or 80 km grid resolution, depending on the actual year considered (Nasa 2015). The HYSPLIT model computes air trajectories, as well as more complicated dispersion and deposition simulations. This model uses the Lagrangian- and the Eulerian approach. The Lagrangian approach uses a moving frame as the air particles move from their original location. The Eulerian approach uses a fixed three-dimensional grid as frame. The Lagrangian framework follows the transport of the air particles, while the Eulerian approach calculates the pollutant concentrations on a fixed grid. The Hysplit model is mainly used for tracking and forecasting the release of different pollutants (e.g. radioactive material, volcanic ash, wildfire smoke) from stationary or mobile emission sources (Air Resources Laboratory 2014b).

All back trajectories were calculated for 24 hours, arriving on the hour at a height of 100 m above ground level at each of the sites presented in Table 1. Although a number of uncertainties have to be taken into account when working with the HYSPLIT data (Air Resources Laboratory 2014c), the most relevant here was the spatial complexity of the area. Therefore, an arrival height of 100 m was chosen, since the orography in HYSPLIT is not very well defined, which could results in increased error margins on individual trajectory calculations if lower arrival heights were used. For back trajectories calculated in this manner, maximum error margins of 15 to 30% of the trajectory distance travelled have been reported (Stohl 1998; Riddle et al. 2006; Vakkari et al. 2011).

Correlation between back trajectory analysis and sources

In this study back trajectory analysis of air masses was employed to relate BC and OC concentrations measured at a specific sampling site with the closest distance between the trajectory calculated for a specific 24-hour sampling period and biomass burning fire events occurring during that time, as well as large point sources. Although a number of products can be used to obtain biomass combustion fire locations, the fire locations used in this paper were obtained from the remote sensing observations of fires from the MODIS collection 5 burned area product (Roy et al. 2008; MODIS 2014). Since MODIS burned area observations are obtained from a satellite passing over an area once a day, the 24-hour back trajectories were calculated to arrive at the middle of each 24-hour sampling period. Fig. 2 presents an illustration of the method applied for a specific sampling site to determine the shortest distance between a 24-hour back trajectory and burned areas identified within the period correlating closest to the sampling period. The distances between burned areas (indicated by the red areas) and a specific back trajectory were calculated for each of the hourly locations of the 24-hour back trajectory (indicated by the blue dots in Fig. 2). In the example presented here (Fig. 2), the symbol A indicates the shortest distance between hourly locations of this specific trajectory and burned areas. Similar calculations were made to determine the shortest distance that the afore-mentioned back trajectories had passed large point sources. In the graphical example presented here (Fig. 2), symbol B indicates the shortest distance between hourly locations of this specific trajectory and large point sources (i.e. petrochemical operations, coal-fired power stations and pyrometallurgical smelters) in the north-east of South Africa. Similar calculations were performed for each OC and BC sampling period, where after OC and BC levels were plotted against the shortest distances between back trajectory paths and fire events/large point sources for all days at all sites. Weakness of the afore-mentioned method were that downwind fires, very close to the monitoring site, could in some instances be the closest fire(s) and that dilution due to distance travelled by the trajectories were not considered.

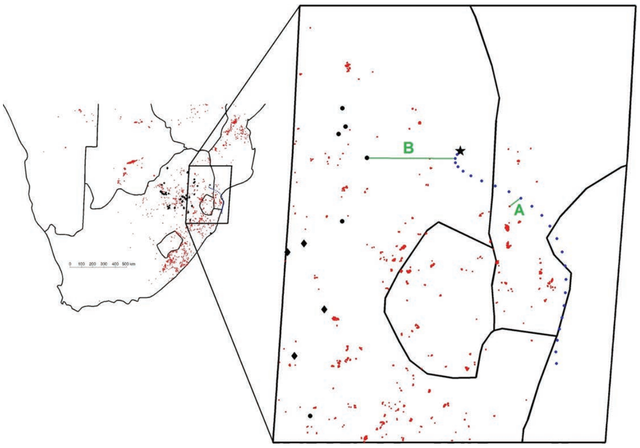


***Figure 2**: Example to illustrate the method applied to determine the shortest distance between 24-hour back trajectories and burned areas, as well as large point sources. The red areas indicate burned areas identified by the MODIS collection 5 burned area product on a specific overpass, the black markers large point sources (circles indicating pyro-metallurgical smelters and diamonds representing coal-fired power stations), while the blue dots represent the hourly locations of the example 24-hour back trajectory calculated for Skukuza (indicated by the black star). Symbol A indicates shortest distance between the trajectory and a burned area, while symbol B indicates the shortest distance that the back trajectory had passed a large point source.*

Results and discussion

Spatial assessment

In Fig. 3a and Fig. 3b box and whisker plots of the concentrations of OC and BC measured, in the $PM_{2.5}$ (a) and PM_{10} (b) size fractions at each of the sites for the entire sampling period, is presented, with OC/BC ratios also indicated.

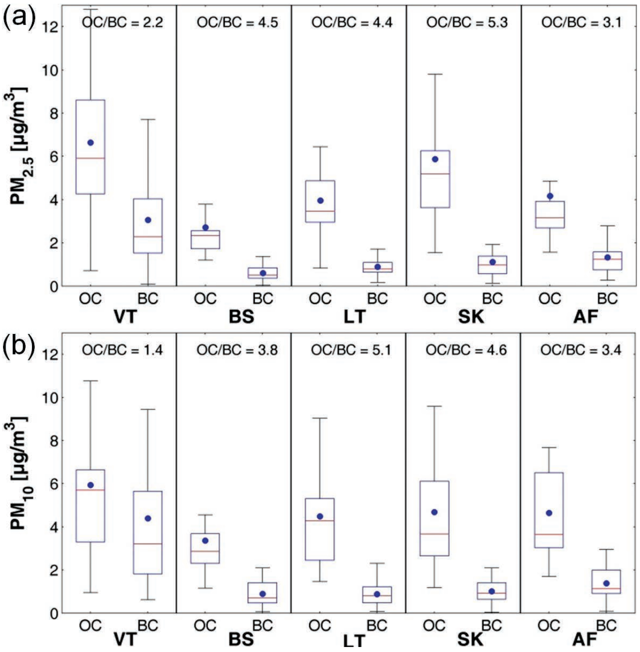


***Figure 3**: Statistical distribution of $PM_{2.5}$ (a) and PM_{10} (b) OC and BC measured at the various South African IDAF sites. The line in each box indicates the median, the dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ± 2.7 σ(99.3% coverage if the data has a normal distribution). The average OC/BC ratio for every site is also shown*

From Fig. 3 it is evident that OC concentrations were higher than BC levels at all the South African IDAF sites in the $PM_{2.5}$ (3a) and PM_{10} (3b) fractions. In general OC and BC concentrations in both size fractions were the highest at VT, with especially the BC levels being much higher compared to the other sampling sites. Therefore the OC/BC ratios of VT, i.e. 2.2 ($PM_{2.5}$) and 1.4 (PM_{10}), were also significantly lower than for the other sites. AF had the second lowest OC/BC ratio, i.e. 3.1 ($PM_{2.5}$) and 3.4 (PM_{10}), whereas the OC/BC ratios varied between 3.8 and 5.3 for the remaining sites. The reason for the higher OC and BC levels and the lower OC/BC ratio for VT can be ascribed to its location that is much different compared to the other sites. The VT is situated in an area where most of the South African petrochemical and related chemical industries are located, together with other large point sources that include two coal-fired power stations and numerous metallurgical smelters (Beukes et al. 2013). This area is also densely populated with large semi-formal and informal settlements. Venter et al. (2012) recently reported that the dominant source of PM_{10} measured at a site in a highly industrialised region in South Africa, with numerous semi- and informal settlements in close proximity, was household combustion. This indicates that household combustion for space heating and cooking in these settlements in the VT area could also be a significant source of OC and BC. Higher traffic volumes in this densely populated area will also contribute to OC and BC concentrations. Less dilution of BC and lower secondary formed OC due to the close proximity to the sources also contribute to the different observation at the VT site.

The OC concentrations at LT, SK and AF were in the same range in the PM_{10} fraction, while slightly higher OC levels were measured at SK in the $PM_{2.5}$ fraction compared to LT and AF. The lowest OC concentrations were measured at BS. The BC concentrations at BS, LT, SK and AF were in the same order in the PM_{10} and $PM_{2.5}$ fractions throughout the sampling period, although BC levels were slightly higher at the anthropogenically impacted AF (Table 1). LT, SK and BS are regarded as background sampling sites (Table 1).

It is also evident from Fig. 3 that most of the OC and BC species measured were in the $PM_{2.5}$ fraction, since OC and BC concentrations in the $PM_{2.5}$ fraction did not differ significantly compared to OC and BC concentrations in the PM_{10} fraction that also included $PM_{2.5}$ particulates. This indicates that the major sources of OC and BC are anthropogenic activities e.g. incomplete combustion of fossil fuels and household combustion, as well as biomass combustion fires that can be natural and anthropogenic in South Africa (Vakkari et al. 2014). An anomaly in the data was that the OC levels measured at VT were higher in the $PM_{2.5}$ fraction than in the PM_{10} fraction, which cannot be possible. This can be attributed to an artefact in the sampling method utilised. As described in the experimental section, PM_{10} and $PM_{2.5}$ samples were collected for the same sampling period with two separate MiniVol samplers with flows being checked prior and after sampling. Although no deviations were observed from the set point flow, it is possible that the sampling flow rate of 5 L/min was not maintained constantly in a single, or a small number of measurements, resulting in differences in sampling volumes. However, this anomaly was not present for any of the other sites. Additionally, the anomaly observed for the VT site does not detract from the conclusion made for all the sampling sites that the both OC and BC occurred mostly in the smaller size fraction, i.e. $PM_{2.5}$.

As previously mentioned, the OC/BC ratios of VT were significantly different compared to the other sites. However, it can also be stated that the OC/BC ratio of AF, i.e. 3.1 ($PM_{2.5}$) and 3.4 (PM_{10}), is in-between that of the directly anthropogenic impacted VT and the background sites, i.e. BS, LT and SK. According to Junker and Liousse (2008) biomass burning fire and biofuel emissions usually have higher OC/BC ratios than fossil fuel sources. The calculated OC/BC ratios therefore indicate that VT is mostly influenced by fossil fuel sources, while BS, LT and SK are more significantly influenced by biomass burning fire emissions. Mphepya et al. (2006) and others (e.g. Formenti et al. 2003) have previously indicated that SK is significantly influenced by biomass burning fire emissions during the dry season. The in-between OC/BC ratios at AF indicate impacts from biomass burning fire and fossil fuel combustion emissions. The OC/BC ratios therefore reflect the location and possible sources impacting the different IDAF sites, as indicated in Table 1.

The OC/BC ratios at the South African IDAF sites compare well with those measured in other studies. Cachier et al. (2005) reported OC and BC measurements at five sites in France, i.e. Martigues, Marseilles, Réaltor, Plan d'Aups and Dupail. OC/BC ratios determined at Martigues and Marseilles, which are considered to be impacted by anthropogenic activities, were 2.16 and 2.07, respectively, while Réaltor that is slightly removed from Martigues and Marseilles had an OC/BC ratio of 2.88. The OC/BC ratios for the two background sites, Plan d'Aups and Dupail, were 4.5 and 4.9, respectively. Chazette and Liousse (2001) determined an OC/BC ratio of 2.87 for Thessaloniki, which is the second biggest industrial city in Greece. Considering OC/BC ratio source characteristics proposed by Junker and Liousse (2008), it indicates that hard coal seems to be the dominant source type at VT, while typical OC/BC ratios associated with wood fuel, charcoal and motor gasoline correlated with OC/BC ratios determined at the other four South African IDAF sites. During SAFARI 2000, OC and BC samples were collected over the Atlantic Ocean just off the shore of Namibia and Angola from biomass burning fire plumes. The smoke of these biomass burning fires was widely distributed, and between one and two days old. In these samples the OC/BC ratios varied between 5.9 and 10.0 (Formenti et al. 2003). The higher OC/BC ratios reported by Formenti et al. (2003) can most likely be attributed to aging of the plumes and the absence of significant anthropogenic fossil fuel source contributions, which is also the case at the background South African IDAF sites, i.e. LT, SK and BS. Apart from the biomass burning fire emissions mentioned previously, these background sites are also influenced by re-circulating anthropogenic emissions from the South African Highveld.

As far as the authors could assess, the mass fractions of OC and BC as a function of the total aerosol mass, have not yet been investigated for South Africa. Therefore, in Fig. 4 box and whisker plots of the OC and BC mass fraction percentage of the total aerosol measured, in the $PM_{2.5}$ (4a) and PM_{10} (4b) size fractions, at each of the sites for the entire sampling period, are presented.

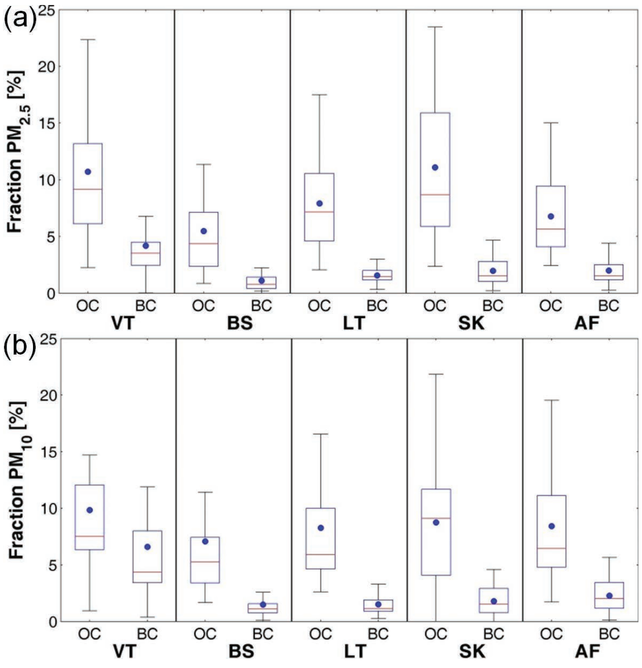


***Figure 4**: OC and BC as a mass fraction percentage of the total aerosol mass in $PM_{2.5}$ (a) and PM_{10} (b). The line in each box indicates the median, the dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ± 2.7σ (99.3% coverage if the data has a normal distribution)*

As expected, the OC mass fraction is higher than that of BC at all the sites for $PM_{2.5}$ and PM_{10}. The OC mass fraction percentage was up to 24%, while the BC mass fraction percentage was up to 12 % for all the sites in both size fractions. Putaud et al. (2004) reported $PM_{2.5}$ OC mass fractions to be 20-30% (rural sites) and 22-38% (near-city and kerbside sites), whereas PM_{10} OC mass fractions were 12-30% (rural sites) and 20-25% (near-city and kerbside sites) at 24 western European sites in winter. The BC contributions for $PM_{2.5}$ were reported to be 5-11% (rural sites) and 5-23% (near-city and kerbside sites), while the BC contributions for PM_{10} were 2-8% (rural sites) and 4-15% (near-city and kerbside sites). Yin et al. (2005) reported the OC mass fraction in Ireland for $PM_{2.5}$ as 30-40% (non-urban sites) and 10-30% (urban sites), while the PM_{10} OC mass fractions were 15-45% (non-urban sites) and 4-20% (urban sites). The $PM_{2.5}$ BC mass fractions were 25-30% (non-urban sites) and 8-10% (urban sites), while PM_{10} BC mass fractions were 12-22% (non-urban sites) and 3-5% (urban sites). From the afore-mentioned references it seems that the OC and BC measured at the South African IDAF sites were in the same order of magnitude, or lower than the mass fractions measured in western Europe. However, the study of Putaud et al. (2004) was biased towards winter, while all seasons are represented in the South African IDAF results. Additionally, fractional contribution to the overall aerosol load of sulphate has substantially decreased in first world countries where deSOx technology has been applied (Zhang et al. 2007). However, in South Africa sulphate is still the dominant aerosol species (Martins et al. 2007; Tiitta et al. 2014) since substantial deSOx technology have not yet been applied.

The OC mass fraction at SK and the BC mass fraction at VT were the highest in the $PM_{2.5}$ and PM_{10} size fractions. The high OC mass fraction at SK can be attributed to natural and anthropogenic sources. Mphepya et al. (2006) previously indicated the substantial impact of biomass burning fire emissions at SK. SK, LT and BS lies within the savannah biome (Mucina and Rutherford 2006), which emits more natural biogenic volatile organic compounds (BVOCs) than the Dry Highveld Grassland Bioregion wherein VT and AF lie (Mucina & Rutherford 2006). The atmospheric lifetime of BVOCs are mostly in the order of minutes to hours (Atkinson and Arey 2003), indicating that BVOCs can be transformed to less volatile species that could be collected as aerosols at sampling sites in close proximity of sources of BVOCs. In contrast, anthropogenic VOCs, which in general occur at higher concentrations than BVOCs in South Africa, have much longer atmospheric lifetimes (Jaars et al. 2014 and references therein), implying that the less volatile species are more likely to be formed further away from the source(s). SK also lies on the dominant path of air mass movement from the anthropogenic industrial hub of South Africa, which implies that primary emitted anthropogenic VOC species have enough time to oxidise to form less volatile secondary species that are measured in the OC fraction at SK. The BC high mass fraction at VT is due to this site being within a well-known anthropogenic source region as previously indicated and the nature of the sources occurring in this area.

Temporal assessment

As previously discussed, most of the OC and BC occurred in the $PM_{2.5}$ fraction, since there was not a significant difference between OC and BC concentrations in the $PM_{2.5}$ and PM_{10} fractions (Fig. 3). Therefore only the $PM_{2.5}$ measurements are presented and discussed further in this paper. A statistically meaningful seasonal temporal assessment for OC and BC concentrations could not be performed for each individual sampling site, since only one 24-hour $PM_{2.5}$ sample was obtained for each month at each site – one day cannot be construed as being representative of an entire month. However, since all 5 the South African IDAF sites are within a region with similar meteorological conditions and seasonal patterns, the results obtained at all the sites for the 2 years and 1 month measurement period were combined and statistically evaluated. Such a monthly temporal presentation of data gives a regional, rather than a site specific temporal impression. Box and whisker plot was not deemed appropriate to present the temporal statistical distribution, since there were too few data points per month, i.e. between 10 and 15. In Fig. 5 scatter plots indicating averages and standard deviations of the monthly OC (5a) and BC (5b) concentrations measured in the $PM_{2.5}$ fractions for all the sites over the entire sampling period, are presented (indicated in blue). Additionally, the VT data was also excluded from the dataset used to present the temporal pattern, which is indicated in another colour (red) in Fig. 5. This was done, since it was previously pointed out that the OC/BC ratio of the VT was substantially different compared to the other sites (Fig. 3), due to the close proximity and the nature of large point sources near the VT site.

From the data (Fig. 5), a relatively distinct seasonal pattern is observed, with higher OC and BC concentrations generally occurring during the period from May to September with the only exception being the lower OC levels observed for July. This seasonal trend was true, irrespective if VT was included or excluded from the dataset (indicated with different colours in Fig. 5). The period with generally higher OC and BC levels (May to September in Fig. 5) coincide with the onset of the dry season that is typically from May to early October in the interior of South Africa. During the wet season (middle October to April) aerosols are more frequently removed from the atmosphere through wet deposition. Furthermore, the peak frequency of biomass combustion fires occurs during the dry period in southern Africa. Fire burning frequency is especially high during late winter and early spring, i.e. August and September in southern Africa. The period with generally higher OC and BC levels also coincide with the time of the year that persistent low-level inversion layers trap pollutants close to the surface (Laakso et al. 2012), which leads to an increase in atmospheric concentrations of pollutant species. The colder months (May to August) are additionally characterised by increased household combustion for space heating (Venter et al. 2012), which could lead to higher atmospheric OC and BC concentrations. The possible contributions of sources of OC and BC associated with the meteorological conditions, as well as the occurrence of biomass burning fire events will be explored later in the paper.

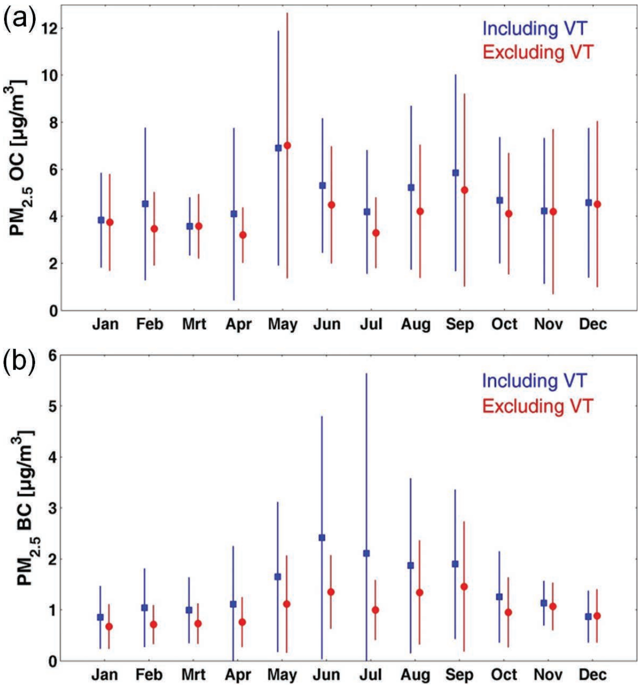


Figure 5: *Temporal variations of the average and standard deviation of OC (a) and BC (b) concentrations in the $PM_{2.5}$ fraction at all the sampling sites (blue) and at all the sampling sites excluding VT (red) for the entire sampling period, i.e. March 2009 to April 2011*

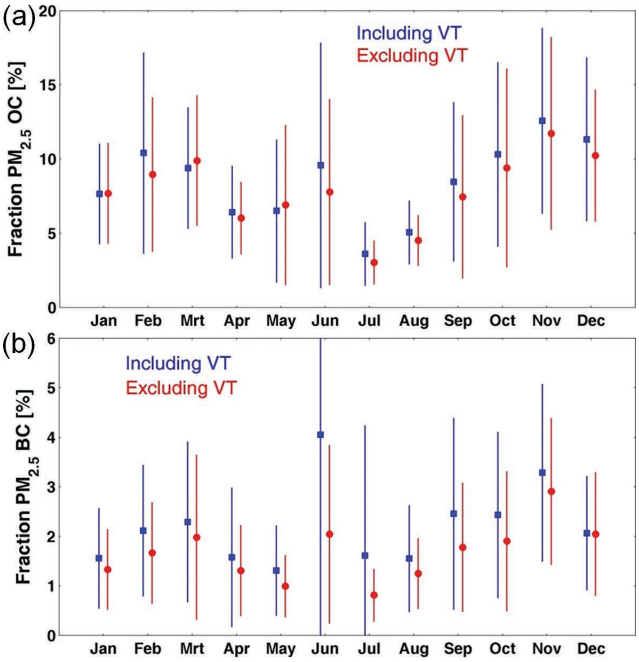


Figure 6: *Temporal variations of the average and standard deviation OC (a) and BC (b) mass fraction percentage in the $PM_{2.5}$ fraction at all the sampling sites (blue) and at all the sampling sites excluding VT (red) for the entire sampling period, i.e. March 2009 to April 2011*

In Fig. 6 temporal variations of the average and standard deviation OC (6a) and BC (6b) mass fractions of $PM_{2.5}$ for all the sites (including and excluding VT) over the entire sampling period are presented. With the exception of the OC and BC mass fractions of June, it is evident that the OC and BC seasonal mass fraction distribution (Fig. 6) is an inverse of the seasonal

OC and BC concentrations presented in Fig. 5. This indicates that although OC and BC concentrations are in general higher in the dry and cold period between May to August (Fig. 5), the atmospheric aerosol load during this period is also substantially higher, resulting in a lower fractional representation of OC and BC (Fig. 6). Unfortunately complete mass closure with all possible atmospheric aerosol species included could not be conducted during this study. Therefore it cannot be stated with certainty what other aerosol species are present in higher concentrations during May to August. However, it is likely that wind-blown dust concentrations will be higher during this time of the year, since less rainfall will result in higher wind-blown dust levels (Mphepya et al. 2004). Possible higher fractional sulphate content of aerosols in the dry season (Tiitta et al. 2014) could also contribute to the lower OC and BC mass fractions. Sulphate seems to be the dominant species in South African aerosols (Martins et al. 2007; Tiitta et al. 2014).

Possible sources of OC and BC

Although it seems obvious that biomass combustion fires contribute significantly to OC and BC concentrations, this was explored further. In Fig. 7 the frequency of biomass combustion fires (obtained from MODIS burned area measurements) from March 2009 to April 2011 (correlating to the sampling period in this study) are presented for southern Africa in the region between 15 – 35˚S and 10 – 41˚E. The numbers of fires within a 1000 km radius from the centre of the 5 IDAF sites are also indicated. From this data (Fig. 7) it is evident that the fires mainly occurred between June and October, which correlates with the seasonal pattern observed for OC and BC (Fig. 5). Furthermore, the highest frequency of fires occurred in August and September. The highest number of fire events recorded for southern Africa (15 – 35˚S and 10 – 41˚E) in a single month was approximately 1.2 million in September 2010. Roughly 550 000 of these biomass burning fire events took place within the 1000 km radius from the centre of the 5 IDAF sites.

As previously described, the distances calculated between back trajectories that arrived in the middle of each sampling period and biomass burning fire events recorded for the previous 24 hours were compared to OC and BC concentrations measured.

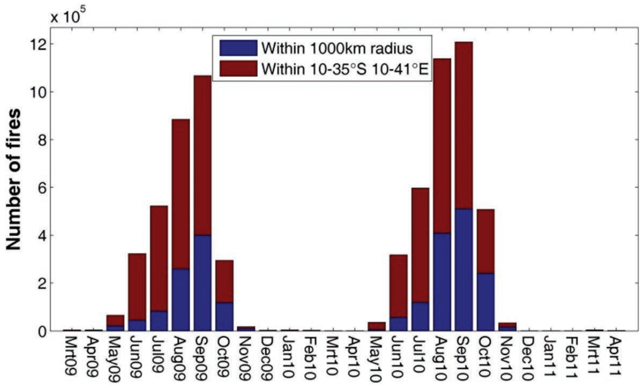
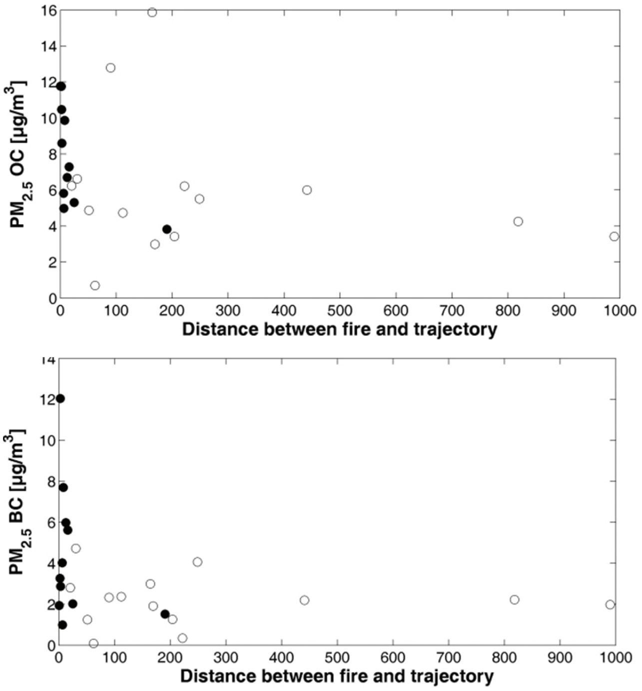
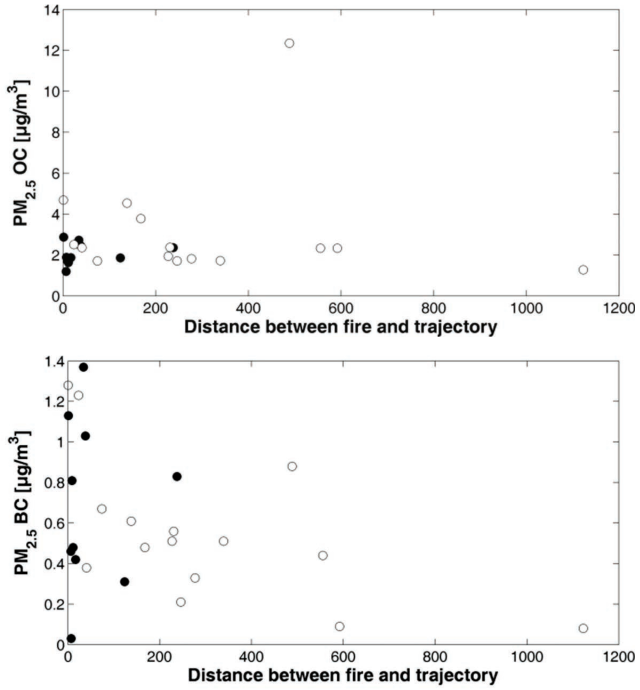


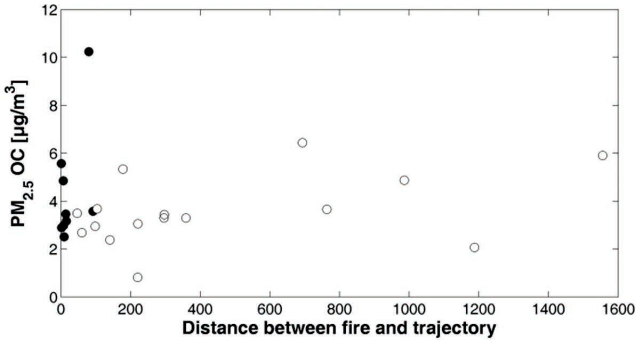
Figure 7*: The frequency of biomass burning fires (obtained from MODIS burned area measurements) from March 2009 to April 2011 in southern Africa (15 – 35˚S and 10 – 41˚E), as well as the number of fires within a 1000 km radius from the centre of the 5 IDAF sites*

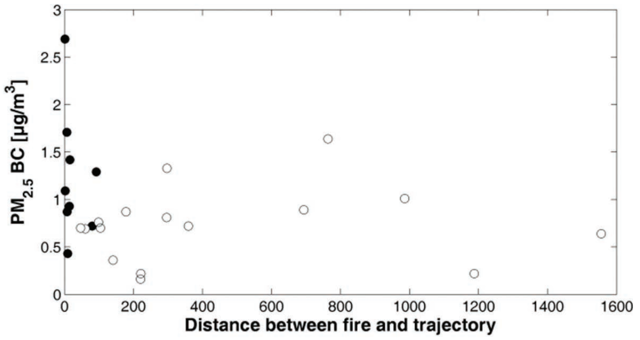


(a) VT

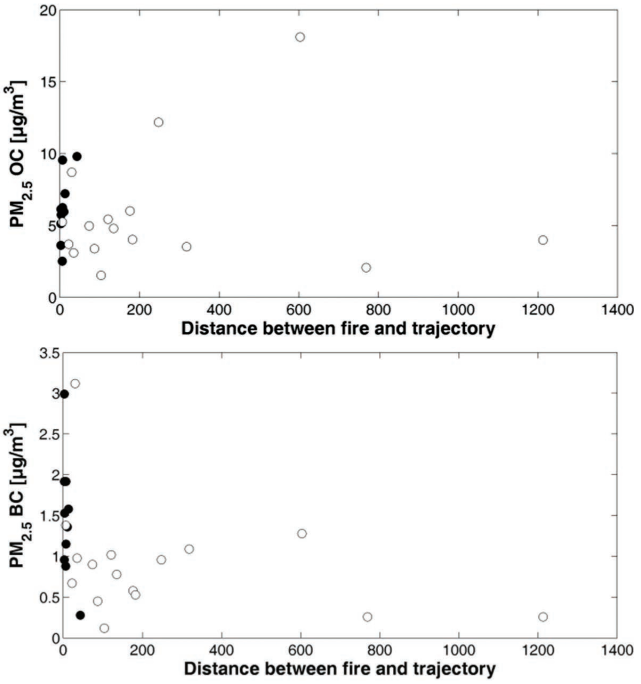


(b) BS

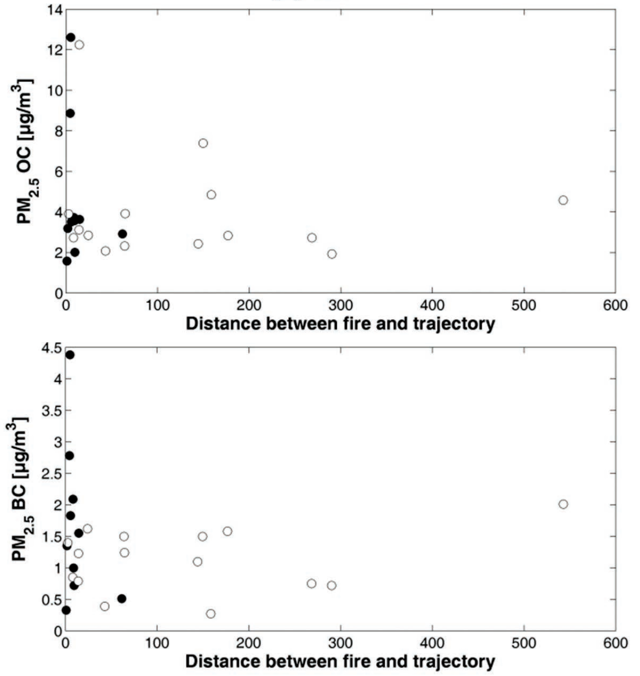




(c) LT



(d) SK



(e) AF

***Figure 8**: PM$_{2.5}$ OC and BC concentrations plotted against the shortest distances between the back trajectories and the fire events at VT (a), BS (b), LT (c), SK (d) and AF (e). The black dots represent the months during which most fires occurred (June to October), while the open circles represent months with fewer fire events (November to May)*

In Fig. 8 OC and BC concentrations measured for PM$_{2.5}$ are plotted against the shortest distances between the 24-hour back trajectories and fire events for each sample at VT (8a), BS (8b), LT (8c), SK (8d) and AF (8e). The black dots indicated OC and BC concentrations measured during months that most fires occurred, i.e. June to October, while the open circles represent months with no or very few fire events (according to Fig. 7).

From Fig. 8 it seems that higher OC and BC concentrations were measured when trajectories passed closer to fires during the months when most fires occurred (June to October). In contrast, during the months with fewer fires (November to May), OC and BC concentrations did not seem to be influenced by the distances between the trajectories and fires. This indicates that fires are a major source of OC and BC during the months with high fire frequencies, while OC and BC measured during the other months were mainly emitted from other sources in this region. It has to be mentioned that the observed relationship, i.e. higher OC and BC contribution from biomass combustion fires during months with more fires, are somewhat obscured due to all the averaging periods in the data, i.e. 24-hour sampling, calculation of a single trajectory in the middle of the sampling period and 24-hour clustering of fire events by MODIS burned area measurements. However, a good indication of the influence of biomass burning fires during the months with high fire frequencies is obtained.

In an effort to further explore the regional contribution of biomass combustion fires to OC and BC, the data presented in Fig. 8 for individual sites were combined Fig. 9 for OC (Fig. 9a) and BC (Fig. 9b). These two figures therefore give a regional, rather than a site specific perspective of OC and BC concentrations as a function of distance to the closest fire for each calculated back trajectory. Since the VT sampling site was within an industrialised and residential region that could lead to bias in the data presentation, OC and BC measured at this sampling site were excluded from Fig. 9. Additionally the data points where the shortest distance to the fire for a specific back trajectory was >45 km were not included in this analysis (Fig. 9). Although not well defined, there seems to be a general trend between the OC and BC concentrations and the distance that a back trajectory had passed over a biomass burning fire, as indicated in Fig. 9. As previously mentioned, the reason for the scattered nature of the data in Fig. 9 can be attributed to multiple averaging periods that had to be applied, i.e. 24-hour sampling, calculation of a single trajectory in the middle of the sampling period and 24-hour grouping of fire events by MODIS burned area measurements. Notwithstanding these data limitations, it is evident that OC and BC are higher if a biomass combustion fire event(s) had impacted on a back trajectory air mass during the months with higher frequency in fire events. Therefore, fires seem to contribute significantly to both OC and

BC concentrations during the period when biomass burning fires frequently occur, i.e. June to October.

Similar to the data presented in Fig. 8, $PM_{2.5}$ OC and BC concentrations were plotted against the shortest distance that a back trajectory had passed over large anthropogenic point sources (e.g. pyrometallurgical smelters and coal-fired power stations) in the north-eastern region of South Africa, for each sampling site during every 24-hour sampling period. Thereafter, the individual datasets of SK, LT and BS were combined to give a regional, rather than a site specific perspective. The AF data was excluded since it had a large point source in close proximity to it, while VT was also excluded since it was within a source region with many large sources nearby. Data points where the distance between back trajectories and large point sources were >45 km were also not included in the analysis. The combined SK, LT and BS dataset is presented as a second data series in Fig. 9. From this data it is evident that $PM_{2.5}$ OC and BC concentrations were not influenced by the distances that back trajectories had passed over large point sources. This indicates that the contribution of these large point sources is not as significant compared to the biomass combustion fires on OC and BC concentrations. The observation that large point sources do not contribute significantly to regional BC concentrations is feasible, since emissions regulations in South Africa have historically regulated particulate emissions (which included BC) much more stringently than gaseous emissions.

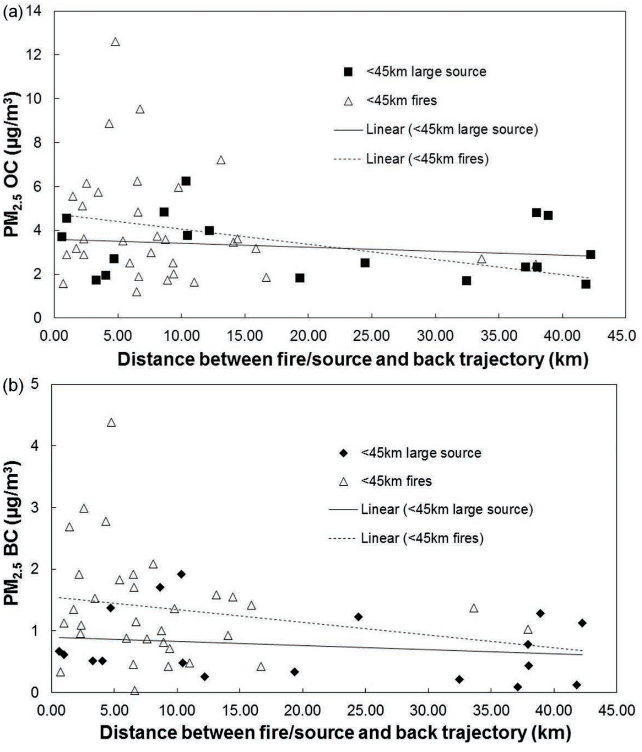


***Figure 9**: $PM_{2.5}$ OC (a) and BC (b) concentrations of June to October (months with higher fire frequency, according to Fig. 7) at all the sampling sites as a function of shortest distance between back trajectories and fires, excluding VT data and data where the shortest distances are >45 km. Additionally, $PM_{2.5}$ OC (a) and BC (b) concentrations of SK, LT and BS as a function of shortest distance between back trajectories and large point source, excluding data where the shortest distances are >45 km, are presented for the entire sampling period*

Another possible source of OC and BC that has already been mentioned, but not yet evaluated is household combustion. Venter et al. (2012) previously suggested that household combustion in informal and semi-formal settlements in South Africa could be a significant source of BC, at least on a local scale. Household combustion generally serves two basic needs, i.e. cooking or space heating. In an effort to determine the influence of household combustion for space heating on OC and BC concentrations, the $PM_{2.5}$ OC and BC concentrations of VT were plotted against the minimum temperature measured during the actual sampling periods (Fig. 10). The VT site was specifically chosen to perform this analysis, since many informal and semi-formal settlements are present in the immediate area surrounding the measurement site.

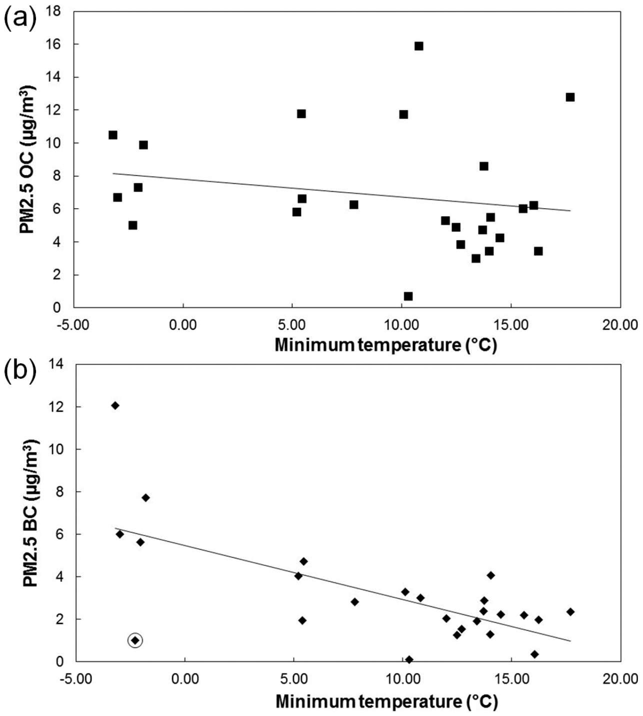


***Figure 10**: $PM_{2.5}$ OC (a) and BC (b) concentrations of VT plotted as a function of actual minimum temperature during the periods when the samples were collected*

As is evident from Fig. 10, both $PM_{2.5}$ OC and BC concentrations seems to be inversely related to the average monthly minimum temperature. This implies that lower temperatures resulted in an increase in household combustion for space heating, which seem to result in higher OC and BC emissions. However, a weaker correlation was observed for $PM_{2.5}$ OC and minimum temperature compared to the correlation found for $PM_{2.5}$ BC and minimum temperature. This can be comprehended, since measured OC consist of primary emitted and secondary formed particles, while BC is exclusively emitted as primary particles. Therefore a better correlation between minimum temperatures and the occurrence of household combustion for space heating for BC is expected. The coefficient of determination (R^2) value for the correlation between $PM_{2.5}$ BC and minimum temperature was found to be significant, i.e. 0.45. This correlation is even more significant, i.e. 0.63, if the single circled value in Fig. 10b is excluded from the dataset.

Conclusions

The OC and BC dataset presented in this paper is one of the largest presented to date in the peer reviewed public domain for South Africa. Therefore this publication makes a contribution to a research field that is very important, e.g. BC second most important climate forcing species, but neglected. However, the dataset and methods presented here have certain limitations. Probably the most significant limitations are due to the size of the dataset and the sampling frequency. For most of the sites only one 24-hour sample per month was collected for two years and one month. This relatively small dataset makes it difficult to statistically evaluate temporal and spatial aspects, as well source contributions. Therefore the results presented should be considered as indicative and not absolute. Additionally, it also indicates the need for more comprehensive studies of this nature to be conducted. Notwithstanding the afore-mentioned limitation the following indicative deductions could be made.

OC were higher than BC concentrations at all the South African IDAF sites in the PM_{10} and $PM_{2.5}$ fractions. Most OC and BC occurred in the smaller size fraction, i.e. $PM_{2.5}$. OC and BC concentrations, as well as OC/BC ratios reflected the location of the different IDAF sites, as well as the type of sources impacting the different sites. VT, which is situated in an industrial and urban location, had the highest OC and BC concentrations with the lowest OC/BC ratio. Of the sites investigated, it was also most-likely more significantly impacted by fossil fuel combustion. AF, which is influenced by an industrial source region, had the second lowest OC/BC ratio, while the background sites (BS, LT and SK) had the highest OC/BC ratios. The background sites were also likely to be impacted by non-fossil fuel sources such as biomass burning fires. The OC and BC mass fraction percentages varied up to 24% and 12 %, respectively, for all the sites in both size fractions.

A relatively well defined seasonal pattern was observed, with higher OC and BC concentrations measured from May to October, which coincided with the dry season and highest frequency of biomass burning events in the interior of South Africa. Seasonal OC and BC mass fractions for all the sites over the entire sampling period were found to be the inverse of the seasonal OC and BC concentrations. This indicates that although OC and BC concentrations are in general higher in the dry and cold period, the atmospheric aerosol load during this period is also substantially higher, which can most-likely be attributed to wind-blown dust.

Positive correlations between OC and BC concentrations with the distance that back trajectories passed over biomass combustion fires were observed, while no such correlations were observed for the distance that back trajectories had passed over large point sources. This seems to substantiate that biomass combustion fires contribute significantly to both OC and BC concentrations on a regional scale, while this is not the case for large point sources. Correlation of OC and BC concentrations with the minimum temperatures during the sampling periods at the VT site proved that household combustion for space heating in semi- and informal settlements contributed to OC and BC levels, at least on a local scale.

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The Richards Bay Clean Air Association: A Case Study for Success in Participatory Air Quality Management

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Abstract

Increasing population growth and rapid urbanisation in South Africa's major centres have resulted in a race for geographical space. The proximity of residential areas to industries is decreasing, and with this, the concern for air quality impacts on people's health. More stringent regulations and the roll-out of atmospheric emission licenses have attempted to curb this concern, at least from a legislative perspective, by limiting the levels of exposure to potentially harmful pollutants. However, implementation, accountability and active community involvement remain a problem in many areas across the country. Nevertheless, success stories in which public and private entities work together for better air quality management, do exist and offer an opportunity for learning. Established 17 years ago in response to a concern for the health of people living and working in Richards Bay, the Richards Bay Clean Air Association (RBCAA) brings together industry, government and the community with the common goals of improving air quality in the region and encouraging polluters to take responsibility for their actions. The tried and tested formula, and long term success of the RBCAA is a demonstration of the fact that integrated air quality management is not limited to the local authority and is better accomplished as a collective. This paper outlines the strengths and common obstacles faced by the RBCAA, with the goal of showcasing a template for success in unlocking clean air opportunities for all.

Keywords

air quality, industry, government, community, association

Introduction

On 17 October 2013, the International Agency for Research on Cancer (IARC)[1] declared that air pollution in its entirety is a potential carcinogen along with known dangers such as asbestos, tobacco and ultraviolet radiation. Accounting for over 220,000 lung cancer deaths worldwide in 2010, the agency now considers air pollution to be a serious environmental carcinogen.

In South Africa, the air quality is generally considered to be good. However, there are a number of "hotspots" around the country where severe air quality problems are experienced (DEA 2005). High ambient sulphur dioxide (SO_2) and fine particulate (PM_{10}) concentrations are common in these areas and primarily result of fossil fuel burning in the residential, industrial and power generation sectors (Scorgie 2012).

In 2007 an estimated 3.7% of national cardiopulmonary disease related deaths and 5.1% of trachea, bronchus and lung cancers in adults older than 30 years were attributed to ambient air pollution (CSIR 2012).

As a result of the rising population and rapid urbanisation in South Africa's major centres, the decreasing proximity of residential areas to industries, mine dumps, major traffic routes and other pollution sources is increasing and with this, the concern for people's health. Furthermore, economic development remains a priority and with this, come developments that affect air quality (National Development Plan 2011).

From a legal perspective, effective air pollution control was historically hindered by the absence of enabling legislation and cooperative governance (Scorgie, 2012). The promulgation of the National Environmental Management: Air Quality Act (Act 39 of 2004) represented a major step forward in the evolution of air quality management within South Africa. Many local governments have struggled with the implementation of the Act in light of poor budget allocations and skills shortages, leaving the authorities under-resourced, overwhelmed and unable to cope with the growing demands associated with air quality management.

Richards Bay, the case study area for this paper, is no exception.

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[1] *IARC - International Association for Cancer Research - is a cancer agency of the World Health Organization, which is based in Lyon, France.*

As a result of concerns regarding the levels of air pollution in the Richards Bay area, the Richards Bay Clean Air Association (RBCAA), a Section 21 company (not for gain) was established in 1997, prior to the promulgation of the Air Quality Act. Yet the Association remains both relevant and desired.

Opportunities exist for associations such as the RBCAA to augment the implementation of regulatory structures through participatory air quality management.

Using the RBCAA as a case study, this paper aims to determine how the Association is able to achieve participatory air quality management.

To answer this, we investigated the benefit of the RBCAA to industry, the community and local government and identify the strengths and common obstacles faced by the Association.

We also examined how different role players (civil society, industry, government and experts) work together for one common purpose, namely to tackle air quality problems within a given air shed and thereby unlocking clean air opportunities for all.

Methodology

Information collected for the purposes of this study comprised of the authors' experience[2], a literature review and non-random purposive[3] formal and informal stakeholder interviews (Patton 1990).

Eight key areas defining the RBCAA were identified for scrutiny. These included:

- Complaints handling and public participation.
- Data collection and reporting.
- Management structures – checks and balances.
- Accountability for pollution sources.
- Research and data usage.
- Air quality expertise within the association.
- Peer review of projects that have a potential air quality impact.
- Opportunities and challenges for collaboration.

Case study area

Richards Bay is located within the City of uMhlathuze, on the East coast of KwaZulu-Natal. The Port of Richards Bay is Africa's largest port with substantial bulk handling capacity and is home to the largest single coal handling facility in the world. The area incorporates various forms of commercial, light and heavy industrial activities, including two aluminium smelters, a kraft process paper mill, a phosphoric acid fertilizer plant, a ferrochrome plant, a mineral refining plant, sand mining activities and an expanding industrial development zone (IDZ). These industries have been the focus of most air quality concerns in the region (Umoya-Nilu 2014), although sugar cane burning, pesticide usage and dust associated with agricultural processes are also common.

The Association's history in brief

A petition against an emissions incident in 1994 at the Indian Ocean fertilizers (now Foskor) that forced the evacuation of the central business district, became the turning point that galvanized public pressure to resolve air pollution issues in Richards Bay (Savides 2011; Camminga 2014).

The RBCAA was established in the wake of this incident, spearheaded by ordinary concerned local residents.

The organisation gained traction over the three year period subsequent to the incident, and was able to formally register as a Section 21 company in 1997. Ever since, the RBCAA has existed with voluntary membership comprising the founder members as part of the initial public members, the public sector (represented through civil organisations), industry, and government.

Operating as a non-profit company, the association system is financed by its members using the 'polluter pays' principle. According to its Memorandum of Incorporation, RBCAA aims to "engage in research, primarily data capturing, monitoring and prediction of air quality in the City of uMhlathuze area, KwaZulu-Natal, South Africa, or such other areas as determined by the company's directors, against national and international air quality standards."

In order to achieve this, the RBCAA draws on four key components to measure, evaluate and report on the air quality in Richards Bay: (i) complaints, (ii) ambient air quality monitoring, (iii) ; emissions inventories and (iv) dispersion simulations.

According to the RBCAA Memorandum of Incorporation, key objectives of the RBCAA include (but, are not limited to):

- Ensuring that the information provided to and derived from the Association is demonstrably of the highest quality that may reasonably be achieved.
- Ensuring that the information so derived is available to all interested and affected parties and that the results will be interpreted in such a way that they are readily understood by all parties.
- Serving as a formal platform for communication between

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[2] *Golder Associates Africa was appointed to manage the operation of the RBCAA monitoring network in May 2013.*
Richards Bay Minerals is a member of the RBCAA Management Committee (MANCO)

[3] *According to Neuman (1997), a researcher may use non-random purposive sampling for interviews in 3 cases: to select unique cases that are specifically informative; to select members of a difficult-to-reach population; and where the researcher wants to identify particular types of cases for in-depth investigation. All these satisfied our criteria.*

industry and public in relation to air quality.

- Providing industry and government authorities with support in terms of air quality data, statistics and information.
- Highlighting potential risks and impacts related to new developments within the area and assist to maintain a balance between economic growth and a safe social environment.
- Encouraging and supporting improvement initiatives related to industry compliance in relation to air quality.
- Facilitating air emission complaints by all stakeholders and corrective action and responses to such by industry and organisations.
- Recording ambient air monitoring results to assist members in complying with their respective Atmospheric Emission License requirements.
- Modelling and graphically reporting emission dispersion to assist industry to assess impacts and to inform the general public (RBCAA, 1994).

Investigating the success of the RBCAA

Eight key areas defining the RBCAA were identified. These are discussed in terms of the strengths and common obstacles faced by the Association with the goal of showcasing the RBCAA as template for success.

Complaints handling and public participation

According to RBCAA's 2013 Annual Report, complaints are predominantly received in response to odour, clinical symptoms, abnormal visible emissions and smoke. The RBCAA has a formal complaints procedure, allowing any concerned party to lodge an air quality complaint via telephone, text message, email, its website, or verbally. Once received, the complaints are distributed to the member industries within 24 hours for resolution and source identification. Member industries in the affected area are then expected to respond within 24 hours to these complaints.

The complaints are followed up, ensuring that the incident is resolved amicably, and crucially, informing the concerned party of the source and the resolution.

As a result:

- Complainants have a sense of closure and empowerment in knowing that their experience/discomfort did not go unnoticed, and the relevant parties have been held responsible.
- Complainants understand what they have been exposed to, dispelling or justifying fears associated with symptoms such as nausea, headaches and difficulty breathing.
- Pollution sources are labouring to improve matters in the interest of not only legislative requirements, but also public perception.

The complaints are documented in a complaints log and categorised by emissions source, complaints type, and location of the complainant at the time of the incident. The complaints log is published in a monthly report adapted for the local newspaper and is freely available on the RBCAA website to the public for scrutiny.

This complaints procedure is reviewed annually to ensure that the system is effective, practical and easily implemented with a clear definition of the roles and responsibilities of all parties involved.

The RBCAA has received and apportioned over 3000 complaints in the past fourteen years (2000 – 2013) (Figure 1). This number could potentially be more were it not for the low level of access to internet and newspapers which remains a challenge, especially in the informal settlements of the City of uMhlathuze. According to the 2011 census, nearly 65% of households in South Africa do not have access to the internet (StatsSA, 2012), a statistic that should be carefully considered when establishing means of communication.

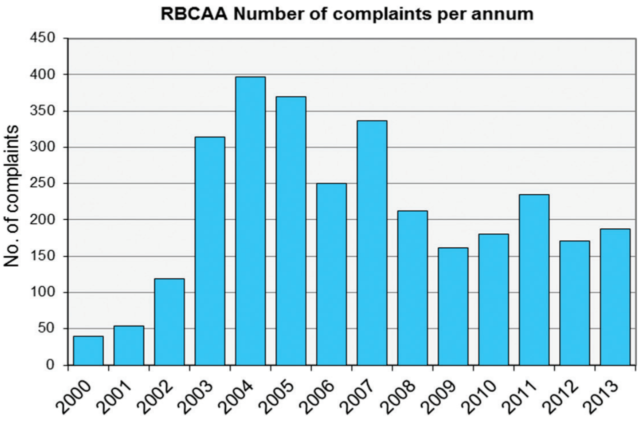

***Figure 1**: Number of complaints received by the RBCAA from 2000 to 2013.*

Data collection and reporting

Since 1997, the association has grown and established a real time monitoring network able to characterise the local ambient air quality by monitoring ground level pollutant concentrations. The monitoring network, operated, maintained and managed by an external service provider, comprises 11 continuous monitoring stations, recording meteorological data, SO$_2$, PM$_{10}$ and Total Reduced Sulphide (TRS) concentrations (Figure 2).

The monitoring and data collection network is robust and well maintained, with a system in place that satisfies the South Africa National Accreditation System (SANAS) requirements. (GAA, 2014). Furthermore, the appointment of an external service provider allows the RBCAA to remain objective and independent from the results.

Data collected from the RBCAA stations, together with emissions inventory data supplied by industry, is used in the HAWK real-time air dispersion model to predict pollution concentrations between the monitoring points. While the HAWK model is not a prescribed regulatory model[4], it allows for near real-time dispersion simulations, with the added benefit of utilising actual recorded meteorological data. It is for this reason that the HAWK model is also used to undertake case studies to determine the source of measured exceedances when a single source cannot be identified or apportioned.

The RBCAA also makes use of the regulatory prescribed CALPUFF air dispersion model on an annual basis to support and provide a comparison for the HAWK results.

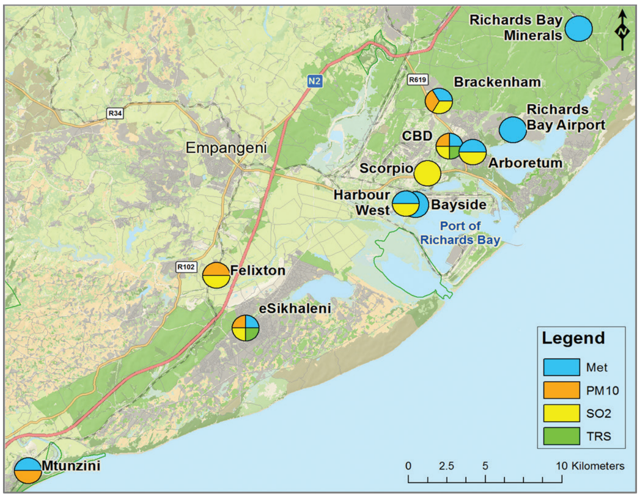

***Figure 2**: Location of the RBCAA monitoring stations.*

The maintenance and operation of the monitoring network accompanied by the cost of service providers and license agreements, makes running an association such as this a costly affair. Furthermore, financial constraints associated with the "polluter pays" mean that as electricity prices increase and industries reduce emissions, the RBCAA must develop sustainable strategies that will ensure the continuation of the association and its network. Common challenges associated with the operation of the network include:

- Power failures.
- Network connection failures.
- Temperamental instruments.

If left unresolved, such incidents can result in data capture falling below the 90% data recover rate required by SANAS for the data to be considered reliable. The RBCAA is able to overcome such obstacles by having a dedicated, responsible person, readily available to ensure that all the instruments are in good working condition. While this ensures an operational network, the costs associated with dedicated, skilled external service providers can be a challenge and needs to be taken into account before attempting to run such a system.

Management structures - checks and balances

There is a certain level of accountability that is required of a Section 21 company[5]. At the outset, due to the complexity of the compilation of the Memorandum of Incorporation, the services of a legal practitioner are recommended to assist in the preparation of the documentation.

A Section 21 company must also meet the following criteria:

- There must be at least 7 members and at least 2 directors.
- Be established for a lawful objective.
- Have as its main objective the promotion of religion, the arts, science, education, charity, social activity or a communal or group interest.
- Only use its income and property to promote the main objective.
- Not distribute its money or property to the members or staff unless they are being paid for work they have done.
- Keep financial and accounting records.
- Hold an annual general meeting (AGM).
- Appoint official, registered auditors.
- Have a registered physical address – not just a post box.

In addition to meeting the above criteria, the RBCAA holds a number of monthly meetings of the Management Committee (MANCO), quarterly meetings of the Board of Directors and AGMs. Progress with regards to the monitoring network, status of air quality, the association's budget and efficient management of the RBCAA are discussed during these meetings.

Aside from the costs associated with meeting the legal and financial criteria, maintaining the attendance and participation at the meetings can be a challenge and requires continuous attention and follow-up. Similarly, regular changes in industry representatives can affect continuity of the meetings as new representatives require time to familiarise themselves with the proceedings.

Accountability for pollution sources

According to Sandy Camminga, one of the founding members and current MANCO chair, "transparency from industry with regards to air emissions and especially significant process changes has greatly improved from the initial years of the association". This can be attributed to the trust based collaboration within the association. In fact, for industry members, the RBCAA has been a useful partner in ensuring that air quality abatement is prioritized and given the financial muscle it requires.

Industries are requested to investigate and promptly respond to complaints from the public with precise reason of the status of the industry at a specific time when a complaint was made. Complaints that are not related to the member industries are passed on to the City of uMhlathuze and the uThungulu District

[4] *According to South Africa Government Notice (GNR) No. 533 (11 July 2014)*

[5] *Section 21 companies are governed by the Companies Act 61 of 1973 as amended 2005*

Municipality air quality management units for resolution and report back to a particular entity where the source is determined. While some challenges associated with poor reporting are still present (Camminga 2014), these are rare and the commitment shown by industry representatives in solving air quality issues is a testament to the success of the Association in achieving its objectives.

Research and data use

Students, researchers, experts, consultancy firms, industry and government have made use of the RBCAA's long term data record in support of improving air quality management through research and modelling.

Due to the proximity of the industries to the monitoring stations and each other, industries are able to make use of the continuous, online datasets without each having to install, operate and maintain their own ambient monitoring network. It also allows industry to maintain an independence from the data. This greatly reduces costs for individual industries regarding the running of own air quality stations. Also the shared data ensures that it is easier and more practicable to apportion pollution sources for incidents resolution.

In collaboration with governmental institutions and industries, the RBCAA also undertake research projects. Examples include: A study on airborne spores in the Richards Bay area where a temporary pollen monitoring network was established in the area between 2001 and 2004 to monitor seasonal trends and to ascertain the origin and source of actual potential or health hazards from vegetation (Camminga 2014).The study found distinctive trends recorded at four sites over the three year monitoring period (Renaut and Bamford 2004), including:

- Elevated amounts of grass pollen, posing a moderate to high allergenic risk during August and September.
- A smaller increase in grass pollen numbers may pose an allergenic risk to sensitized individuals during mid to late summer: January to March.
- High quantities of fungal spores recorded annually during February and April, with the highest number of spores recorded during March.
- Fungal spore numbers regularly exceeded the high allergenic risk levels during the late autumn peak.

Through the special projects committee, the RBCAA is currently in the process of initiating a monitoring program for Hydrogen Fluoride (GAA 2014).

Air quality expertise within the association

The RBCAA has a wealth of air quality experience and expertise available at its disposal to assist in achieving its objectives by virtue of voluntary membership. Members include: BHP Billiton, Collateral Trading, Foskor, Grindrod, Island View Storage, Lafarge, Mondi Richards Bay, Mpact, Richards Bay Coal Terminal, Richards Bay Minerals, TATA Steel, Tongaat Hulett, Transnet Ports Terminal, Transnet National Ports Authority, Tronox, the Zululand Fire Protection Association and founder member Sandy Camminga.

Together, as captured in monthly minutes, experts in the Management Committee as well as Directors from member industries encourage new ideas and offer opportunities for collaboration and problem solving ensuring that there is always continuous improvement.

Peer review of projects that have a potential air quality impact

In addition to monitoring and evaluation, the RBCAA adds value to local air quality management by undertaking peer reviews on projects that have a potential to impact negatively on the environment and particularly the local air shed. This is mainly achieved through Environmental Impact Assessment (EIA) reviews by the EIA committee.

The RBCAA EIA committee reviews EIAs specifically related to air quality. These include EIAs for member industries as well as non-member industries. To avoid conflict of interest and maintain objectivity, a member industry/company proposing a development is excluded from reviewing their own EIA.

In 2011, Savides reported in the Zululand Observer newspaper, that: "*the RBCAA is always there when EIA's are in progress, adding its valuable scientific data to the pool of knowledge capital, fearlessly challenging potentially harmful outcomes, and advising on mitigation measures so that industry can expand without compromising the man in the street*".

Opportunities and challenges for collaboration

The RBCAA meteorological and measured pollutant concentration data is fed directly into the South African Air Quality Information System (SAAQIS), run by the South African Weather Service. In so doing, the information is made freely available to the government, industry and public nationally.

While the Provincial government and City of uMhlathuze played an important role in assisting in the initial establishment of the RBCAA, mandates preclude them from actively participating as a member of the RBCAA. However, observatory opportunities do exist which would allow the local Municipality to draw on the experience and expertise of the RBCAA.

The uThungulu District Municipality Air Quality Management Plan (UDM-AQMP) currently in development, presents an ideal opportunity for collaboration. The RBCAA has already provided valuable input towards the development of the AQMP and continues to do so through the due process (Umoya-Nilu 2014). The success of the Association and years of experience will make the RBCAA a highly beneficial partner in the successful implementation of the local UDM- AQMP.

In addition, as part of their mandate, the uMhlathuze Municipality is currently in the process of installing a monitoring network within Richards Bay area. This initiative presents a further opportunity for collaboration, data sharing and ultimately expansion the existing network coverage.

The RBCAA responded to a need for air quality monitoring at a time when there were no such systems in place in the region. Thus, rather than replicating the new governmental mandate for monitoring, the RBCAA is able to compliment and support this initiative, bringing with it a long term data record, established relationships, technical expertise and the trust of the local community.

Conclusions

It is clear that industry, civil society and local government have an important role to play in good air quality and environmental management.

In the words of Jim Phelps, formerly of the Zululand Environmental Alliance (ZEAL), in (Savides 2011): "*the RBCAA has done its best to work with polluting industries while raising serious concerns about air pollution in Richards Bay for the sake of the community and environmental health*".

The tried and tested formula and long term success of the RBCAA strengthens the fact that integrated air quality management is not limited to the local authority and is better accomplished as a collective.

Three key threads run through the RBCAA; (i) good management structures, (ii) participation and (iii) member commitment, without which the association would not have endured.

In addition, the peer and EIA review mechanism is an important aspect to ensuring quality service delivery and proper environmental control.

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A Geostationary Air Quality Monitoring Platform for Africa

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Abstract

African populations and economies are growing rapidly, but there are few surface observations to monitor the effects on air quality. Trend analysis of the 19-year record of space-based observations from remote sensors onboard low Earth orbit (LEO) satellites shows that anthropogenic pollution is on the rise. Conversely, biomass burning, the largest contributor to surface ozone, is declining. UV-visible instruments on LEO satellites with daily resolution have provided invaluable constraints on sources, evolution, and transport of air pollution in Africa. Sensors in geostationary orbit (GEO) with hourly resolution and a smaller ground pixel than current and past fleets of LEO satellites would further our understanding of air quality in Africa and address the dearth of surface monitoring sites on the continent. Africa has successfully launched Earth observation platforms to retrieve satellite imagery and should expand its remote sensing capabilities by joining the northern hemisphere constellation of GEO Earth observation satellites.

Keywords

Africa, air quality, low Earth orbit, geostationary, satellite, remote sensing

Introduction

Africa is experiencing rapid population growth, in particular West, East, and Central African countries, where fertility rates exceed 6 births per woman (Guengant and May, 2013). Economic projections for Africa are less certain. African countries are currently experiencing large positive economic growth. Nigeria could be the 13th largest world economy by 2050, but sustained economic growth there and in other African countries is contingent on strengthened political institutions, economic diversification, and increased access to reliable and affordable energy (PwC, 2013). Should Africa follow the development trajectory of Southeast Asia and India, degradation of air quality is guaranteed.

Indoor and ambient air pollution rank amongst the highest global burden of disease risks (Lim et al., 2012), largely from exposure to fine particulate matter with an aerodynamic diameter less than 2.5 μm, or $PM_{2.5}$ (Pope and Dockery, 2006). Surface ozone (O_3) affects human health to a lesser extent, but is phytotoxic to crops, threatening food security and agricultural revenue (Avnery et al., 2011). In Africa surface observations of atmospheric composition are sparse, environmental legislation is limited to a few countries, and only South Africa has well-defined standards and a widespread monitoring network (Kgabi, 2012). Still, successful environmental policy in South Africa is hindered by non-compliance (Groundwork, 2014), data gaps, and variable data quality (Hersey et al., 2015).

Sensors onboard satellites provide observations of pollutants and precursors in parts of the world that lack the resources, political will, or human capital to measure ambient air pollution. Even in North America and Europe satellite measurements are used to infer surface concentrations where monitoring is sparse (Lamsal et al., 2008; van Donkelaar et al., 2012). Here we provide a brief review of satellite observations of atmospheric composition used to better understand air quality in Africa. We consider measurements from UV-visible instruments onboard European Space Agency (ESA) and National Aeronautics Space Agency (NASA) low Earth orbit (LEO) satellites. We further discuss the value of a geostationary (GEO) air quality Earth observation platform over Africa.

Low Earth Orbit Earth Observing Platforms

General Features

The space-based global air quality monitoring network of LEO, sun-synchronous satellites began with the ESA Global Ozone Monitoring Experiment (GOME) in 1995. GOME was fully operational until 2003, had a spatial resolution of 40 km × 320 km (latitude × longitude), and required 3 days to achieve global coverage (ESA, 1995). Higher spatial resolution and daily global coverage is achieved with current sensors such as the Ozone Monitoring Instrument (OMI) that is 13 km × 24 km at nadir (Levelt et al., 2006). The next-generation ESA TROPOspheric Monitoring Instrument (TROPOMI), scheduled for launch in

2016, has 7 km × 7 km ground pixels at nadir (Veefkind et al., 2012).

Observations obtained with sensors on satellites are species concentrations within a column of air, retrieved using solar backscattered radiation in the UV-visible spectral range. Observed tropospheric gases include O_3, nitrogen dioxide (NO_2), sulfur dioxide (SO_2), formaldehyde (HCHO), and glyoxal (CHOCHO). Total column aerosol extinction optical depth (AOD) is derived with top of the atmosphere reflectance measurements obtained under cloud-free conditions (Torres et al., 2007). Other satellite products include absorbing AOD (AAOD), UVB daily erythemal dose, cloud fraction, and cloud top pressure.

Application to Africa

Top-down Emission Estimates

Figure 1 shows annual and seasonal mean concentrations of HCHO and CHOCHO (total column), NO_2 (tropospheric column), and SO_2 (planetary boundary layer (PBL) center of mass) for 2006-2007 from OMI at 13h30 local time, the OMI Equator crossing time (Appendix). Enhancements of NO_2, SO_2, and HCHO and CHOCHO provide constraints on emissions of NO_x (=NO + NO_2), SO_2, and reactive non-methane volatile organic compounds (NMVOCs), respectively, for improved air quality modeling. At increasingly fine resolution transport degrades (smears) the local relationship between the observed quantity (e.g. total column HCHO) and inferred emissions (e.g. isoprene from vegetation) (Turner et al., 2012), but smearing can be addressed with advanced inversion techniques, such as an adjoint (Kopacz et al., 2010).

Tropical vegetation in Africa is coincident with large seasonal enhancements in HCHO, a high-yield oxidation product of the biogenic VOC isoprene, a precursor of O_3 and particulate matter (Stavrakou et al., 2009a). Isoprene emissions in Africa have been inferred using OMI HCHO after careful screening for biomass burning and anthropogenic influence (Marais et al., 2012). Satellite-derived isoprene emissions are consistent with limited flux measurements, while the state-of-the-science biogenic emission inventory, MEGAN, can be an order of magnitude too high in the tropics (Marais et al., 2014a).

A HCHO hotspot over Nigeria, in particular in December-February (Figure 1) is from oxidation of reactive anthropogenic NMVOCs

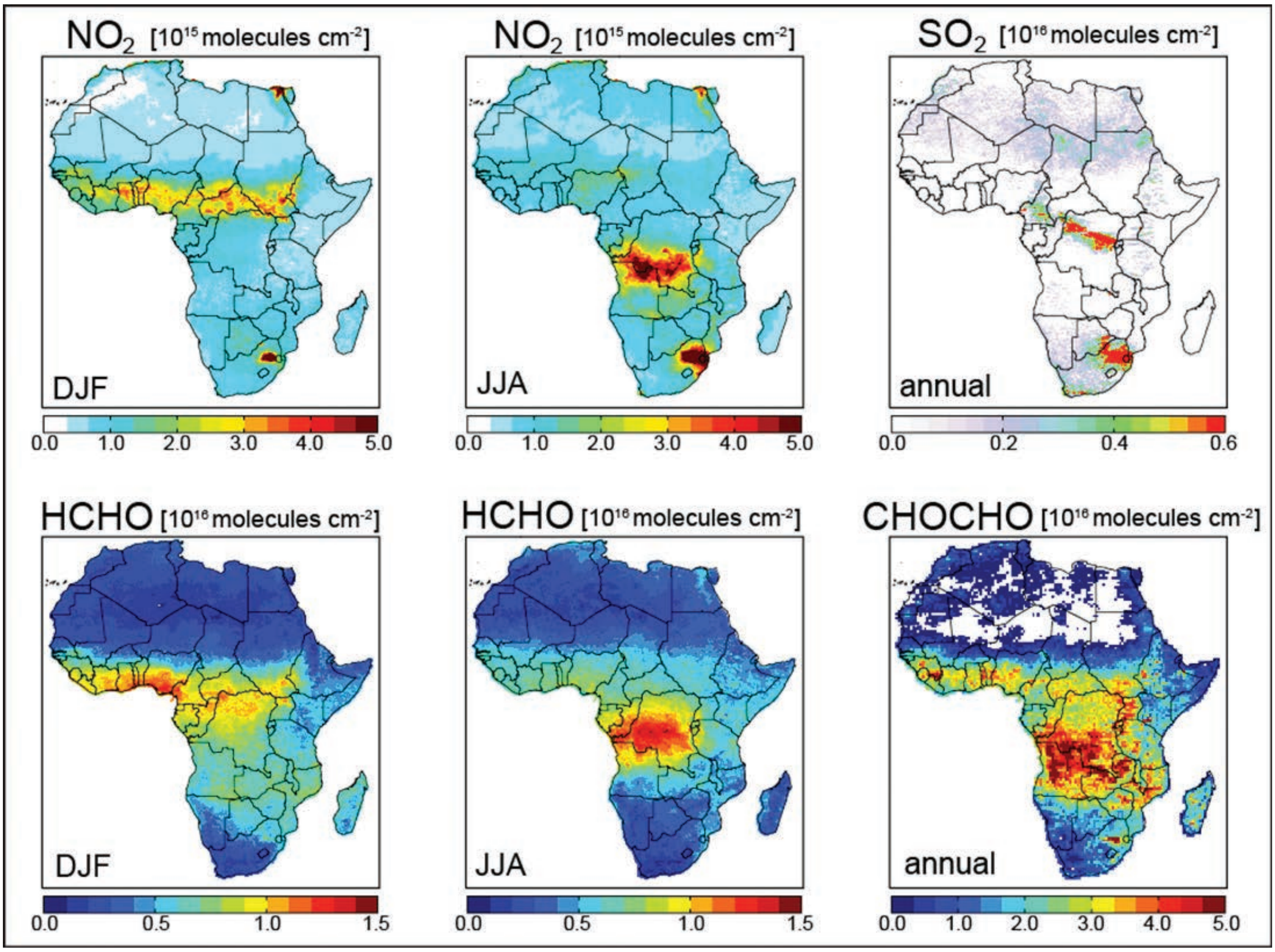

***Figure 1**: Mean concentrations of tropospheric nitrogen dioxide (NO_2), PBL-weighted sulfur dioxide (SO_2), and total column formaldehyde (HCHO) and glyoxal (CHOCHO) from OMI for 2006-2007.*

produced by inefficient sources of combustion and natural gas flaring and leakage. Marais et al. (2014b) found, with OMI HCHO, the chemical transport model (CTM) GEOS-Chem, and limited aircraft observations, that Nigerian 2006 anthropogenic NMVOC emissions were higher per capita than in China for the same year.

Satellite-derived NO_x emissions along the Highveld in South Africa, obtained with OMI tropospheric NO_2, show incorrect grid allocation of power plant and other industrial sources in the widely used EDGAR emission inventory. EDGAR likely overestimates mobile sources of NO_x in the Johannesburg-Pretoria metropolitan area (Stavrakou et al., 2014), but LEO satellites miss NO_x produced by vehicles during morning and evening rush hours (Lourens et al., 2014). The spatial extent of NO_x from soil bacteria along the Sahel, a global soil NO_x hotspot, was first seen with GOME NO_2 (Jaeglé et al., 2004). A recent study used OMI NO_2 and the GEOS-Chem CTM to estimate the magnitude of this NO_x source (Vinken et al., 2014).

Satellite observations of SO_2 are noisy, so that inference of emissions in Africa using standard retrieval techniques is limited to sizable point sources that include active volcanoes along the East African Rift Valley (Theys et al., 2013) and power plants in the Highveld region (Fioletov et al., 2013).

Dry season biomass burning makes the largest contribution to surface O_3 in Africa (Aghedo et al., 2007). The magnitude of the contribution, obtained by Aghedo et al. (2007) as the difference between a simulation with and without biomass burning, is sensitive to model emissions. Satellite-derived emissions of NMVOCs and NO_x highlight large regional biases in bottom-up pyrogenic inventories (Jaeglé et al., 2005; Stavrakou et al., 2009b). Models also represent African savanna fires, the dominant seasonal NO_x source in much of Africa, with fixed NO_x emission factors (NO_x produced as a function of biomass burned). Satellite NO_2 data show substantial temporal variability (Mebust and Cohen, 2013).

Air Quality and Emission Trends

Global surface concentrations of $PM_{2.5}$ have been derived with satellite AOD and the modeled relationship between the two (van Donkelaar et al., 2006). $PM_{2.5}$ is high in North and West Africa, predominantly from Saharan dust. The anthropogenic contribution in Africa is low, but rapid development will add to air quality concerns.

Observations from multiple sensors have been stitched together to generate a 19-year satellite record (1996-2014) of atmospheric composition. Positive, significant trends in HCHO in the megacities Cairo (Egypt), Lagos (Nigeria), and Kinshasa (DRC) suggest increasing emissions of NMVOCs (De Smedt et al., 2010). Similarly, increases in tropospheric NO_2 in Cairo, Lagos, and Algiers (Algeria) imply growth in NO_x sources (Schneider and van der A, 2012; Hilboll et al., 2013). Other African cities will likely join this list, as the world's fastest growing cities are in Africa (UN, 2014).

Using a 15-year record of satellite AOD Boys et al. (2014) identified a robust increase in $PM_{2.5}$ in southern Africa where there is also a positive trend in biomass area burned (Andela and van der Werf, 2014). $PM_{2.5}$ appears to be declining in Nigeria, but data coverage is limited due to cloudy conditions during the West African monsoon (Boys et al., 2014).

An African Geostationary Observation Platform

LEO sensors have been invaluable for investigating seasonal and multiannual variability in Africa (Section 2), but knowledge of diurnal evolution of atmospheric composition in Africa is limited.

Figure 2 shows the spatial extent of the planned (pre-2020 launch) constellation of Earth observing geostationary (GEO) sensors TEMPO (Chance et al., 2013), Sentinel-4 (Ahlers et al., 2011), and GEMS (Kim, 2012). Coverage is largely limited to the northern hemisphere. The Sentinel-4 viewing domain will vary seasonally, extending over much of North Africa in boreal winter. GEO satellites are positioned ~36 000 km above the Earth's equator and the planned instruments will observe the same point every hour at higher resolution than the deployed LEO satellites. The ground footprint of TEMPO, for example, is 2 km × 5 km at the center of the North American domain (Chance et al., 2013).

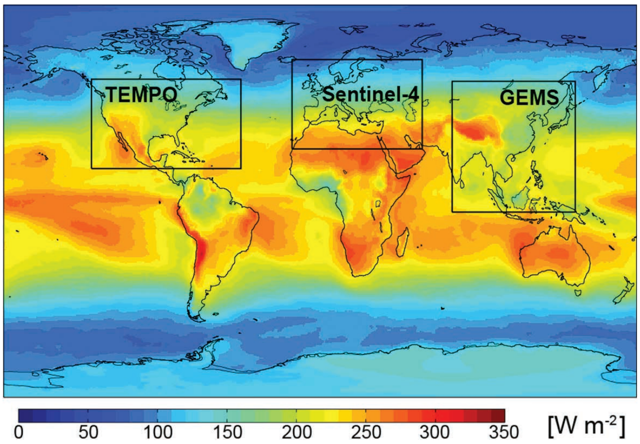

Figure 2*: MERRA 2006-2007 all-sky incident solar radiation overlaid with sampling domains of planned GEO Earth observation platforms.*

Planned GEO sensors sacrifice spatial coverage (Figure 2) for fine spatial and temporal (hourly) resolution. Higher sampling frequencies and spatial resolution increase signal-to-noise and the number of clear-sky observations. Finer spatial resolution of a GEO instrument would resolve sub-urban features, heterogeneous vegetation cover, and the many political boundaries in Africa. Hourly measurements provide information about diurnal evolution of emissions, chemistry, and pollution transport dynamics. Information gained from a GEO satellite will better constrain air quality models that are being developed at increasingly fine resolution.

Current LEO sensors have limited sensitivity to surface O_3 (Zhang et al., 2010) that will be addressed with TEMPO by extending the spectrum to include the visible Chappuis O_3 band (Chance et al., 2013).

The underlying map in Figure 2 is annual mean incident solar radiation flux (Appendix), used here as a proxy for sampling frequency of a remote UV-visible instrument. GEO satellites located above the Equator are ideally positioned to view Africa. Africa also has year-round sun, with some reduction in coverage over West Africa due to persistent clouds during the monsoon season. Large portions of the planned GEO sensors will go dark in boreal winter.

Already South Korea has launched the GEO GOCI satellite to monitor ocean color in the Korean Sea at 500 m spatial resolution (Choi et al., 2012). GEO satellites can be expensive and high mission costs of the US GEO-CAPE instrument (~$2 billion) have delayed that project (Fishman et al., 2012). The cost to launch TEMPO is reduced by including the instrument as a hosted payload on a commercial satellite (http://science.nasa.gov/missions/tempo/), and contracting simultaneous build and design of TEMPO and GEMS (Brown, 2013).

Africa has successfully deployed Earth observing multispectral imaging satellites either as independent countries or through the African Union (Ngcofe and Gottschalk, 2013). Data from these satellites are invaluable for disaster risk management, food security, and urban planning, but African nations need to invest in an instrument that monitors air quality across a continent already experiencing rapid growth. Skills scarcity on the continent can be addressed by training scientists at overseas institutions that specialize in retrieval and interpretation of remote sensing data. Instrument design and build can be outsourced to a private company, as is the case with TEMPO and GEMS (Chance et al., 2013).

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Appendix

Data used in this work are version 2 gridded monthly mean OMI tropospheric NO_2 (http://www.temis.nl/airpollution/no2.html); updated OMI HCHO and OMI CHOCHO products described in González Abad et al. (2015) and Miller et al. (2014), respectively; and NASA version 3 level 3 OMI PBL SO_2 (http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omso2e_v003.shtml). Net solar radiation flux is the NASA reanalysis MERRA product, version 2.3, obtained with the Giovanni visualization tool (http://disc.sci.gsfc.nasa.gov/giovanni).

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The MERRA 2006-2007 data used in this paper were obtained with the Giovanni online data system, developed and maintained by the NASA GES DISC. The authors would like to thank Christopher Chan Miller for providing the OMI glyoxal data and Gonzalo González Abad for providing the OMI formaldehyde columns.

Measurement of atmospheric black carbon in the Vaal Triangle and Highveld Priority Areas

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Abstract

Atmospheric black carbon is an important atmospheric pollutant; it has impacts on human health and a strong climate impact. Black carbon particles are functionally defined by their optical properties (viz. characteristics in light absorption). As a result, black carbon particles are derived from a wide range of sources, but are largely the result of incomplete combustion processes. In order to quantify the atmospheric load of black carbon particles, multi angle absorption photometer (MAAP) instruments have been installed in 8 of the ambient air quality monitoring stations in the Vaal Triangle and Highveld Priority areas. Three of the instruments have been in operation since 2012 and the other 5 were installed in August 2013. This paper presents an analysis of the initial black carbon monitoring data. The impacts of seasonality and meteorological conditions as well as the relationship of the black carbon concentration to PM_{10} and $PM_{2.5}$ concentrations are discussed.

Keywords

Vaal Triangle Priority Area, Highveld priority area, black carbon

Introduction

Black carbon (BC) is a component of the atmospheric aerosol that is highly absorbent of visible light and is resistant to chemical transformation (Petzold et al. 2013). Black carbon is formally defined through its optical properties as "ideally light absorbing substances comprised of carbon", this definition does not take into account the formation processes. Black carbon is predominantly formed through the incomplete combustion of organic materials; however pyrolysis and dehydrogenation of wood and sugars under anaerobic conditions may also result in its formation (Petzold et al. 2013). The fact that BC is largely formed through combustion processes makes it a useful indicator for combustion sources of particulate matter.

Black carbon makes up an important component of the particulate matter less than 2.5μm in aerodynamic diameter ($PM_{2.5}$) fraction and therefore is implicated in the health impacts of $PM_{2.5}$. It has been suggested that the BC concentration is a better indicator of the risk to human health from PM than the PM_{10} or $PM_{2.5}$ mass concentration (Janssen et al. 2012). Further evidence suggests that $PM_{2.5}$ mixtures with a large BC component have a more adverse health effect than other mixtures (Anenberg et al. 2011).

The absorption of solar radiation by BC significantly enhances the heating of the atmosphere. The influence of BC can cause changes in cloud cover and surface albedo, therefore affecting the Earth's radiative budget both directly and indirectly. These aerosol particles not only influence atmospheric temperature but cause considerable changes in atmospheric chemistry. Black carbon particles have a relatively short lifespan within the atmosphere and for this reason tend to have more localised effects, impacting the regions closest to the source (Bauer et al. 2010).

Since atmospheric BC has such strong human health and climatic impacts, and is an indicator of combustion sources of particulate matter, it was deemed necessary to monitor the concentrations of BC at locations in the Vaal Triangle and Highveld Priority areas. This study examines a 12 month period (September 2013 to August 2014) for the measurement of BC in the Vaal Triangle and Highveld Priority Areas with the aim of characterising the ambient BC concentrations in terms of the seasonal, diurnal and air flow patterns.

Methods

During 2012, Multi Angle Absorption Photometer (MAAP; Thermo Scientific) instruments Model 5012 for the measurement of atmospheric BC were installed in the Witbank, Secunda and Zamdela monitoring stations. During August 2013, further instruments were installed at the monitoring stations in Diepkloof, Sharpeville, Sebokeng, Three Rivers and Kliprivier in the Vaal Triangle Network. The specific instrumentation used for this study is presented in Table 1. The instruments report to the South African Air Quality Information System (SAAQIS)

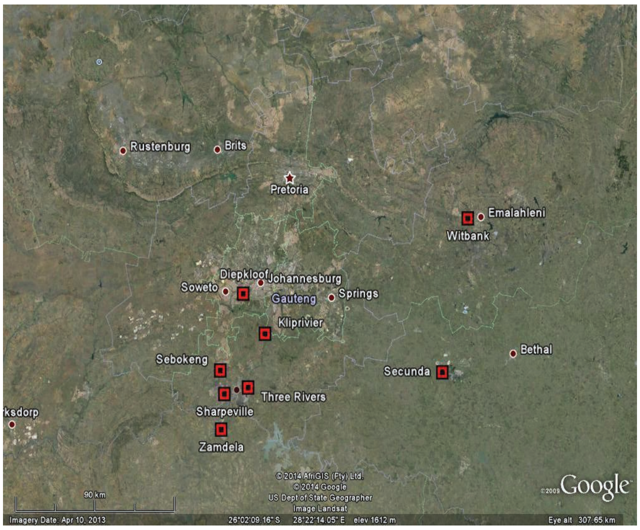

Figure 1: *Google Earth image showing locations of the monitoring stations*

(www.saaqis.org.za) at a 5 minute temporal resolution. In addition to the measurement of BC, all stations in the Vaal Triangle and Highveld Priority Area networks are instrumented for the measurement of PM_{10}, $PM_{2.5}$, SO_2, NO_x, CO, O_3, Benzene, Toluene and Xylene (BTX), and the meteorological parameters wind speed, wind direction, rainfall, temperature, pressure, humidity and solar radiation. All the data from the Vaal Triangle and Highveld networks are available from the SAAQIS, and has been validated to remove calibration periods, instrument drifts and spikes, all validation processes are detailed in the monthly network reports for the Vaal Triangle and Highveld Priority Area networks. These reports are available online on the SAAQIS website.

For this study, BC, PM_{10}, $PM_{2.5}$ mass concentration data and meteorological data for the period 1 September 2013-31 August 2014 was downloaded from the SAAQIS at an hourly temporal resolution for the Diepkloof, Sharpeville, Sebokeng, Zamdela, Three Rivers, Kliprivier Witbank and Secunda stations (Figure 1). The site and instrument specifications are presented in Table 1. The data was analysed using Excel and the "openair" package of R (Uria-Tellaetxe and Carslaw 2014).

It has been reported that there is an artefact in the MAAP instrument at high BC concentration (Hyvärinen et al. 2013). The correction suggested by Hyvärinen et al. (2013) was not applied for this study as not all of the parameters required for implementing the correction were logged, and the manufacturers did not recommend the implementation of the correction when inquiry was made. At high concentrations the instrument may under-report the BC concentration.

Results

The results for this study are divided according to the seasonal and diurnal effects; the impact of the wind direction and speed, and the relationship between the mass concentrations of BC and the other PM classes measured at the sites.

Table 1*: Site and instrument specifications*

Site	**BC instrument**	**PM instrument**	**Site characteristics**
Diepkloof	Thermo Model 5012 MAAP	Thermo FH62C14	Location in school in middle to low income residential with impacts from traffic light industry and domestic combustion
Sebokeng	Thermo Model 5012 MAAP	Thermo FH62C14	Location in community centre in low income residential with impact from metallurgical industry, and domestic combustion
Sharpeville	Thermo Model 5012 MAAP	Thermo FH62C14	Location in school in low income residential area with impact from metallurgical industry, and domestic combustion
Sharpeville	Thermo Model 5012 MAAP	Thermo FH62C14	Location in school in low income residential area with impact from chemical and petrochemical industry, and domestic combustion
Three Rivers	Thermo Model 5012 MAAP	Thermo FH62C14	Location in school in middle income residential area with impact from a coal power plant
Kliprivier	Thermo Model 5012 MAAP	Thermo FH62C14	Location in Police station in low income residential area with impact from traffic and domestic combustion
Witbank	Thermo Model 5012 MAAP	GRIMM EDM180	Location in school in low income residential area with impact from metallurgical industry, coal power generation and domestic combustion
Secunda	Thermo Model 5012 MAAP	GRIMM EDM180	Location in sports centre in low income residential area with impact from chemical and petrochemical industry, and domestic combustion

Average Concentrations

The average concentration of atmospheric BC is between 2.5 and 4.5 µg/m³ for all stations, however hourly values of up to 20 µg/m³ occurred at all sites except Three Rivers (Figure 2).

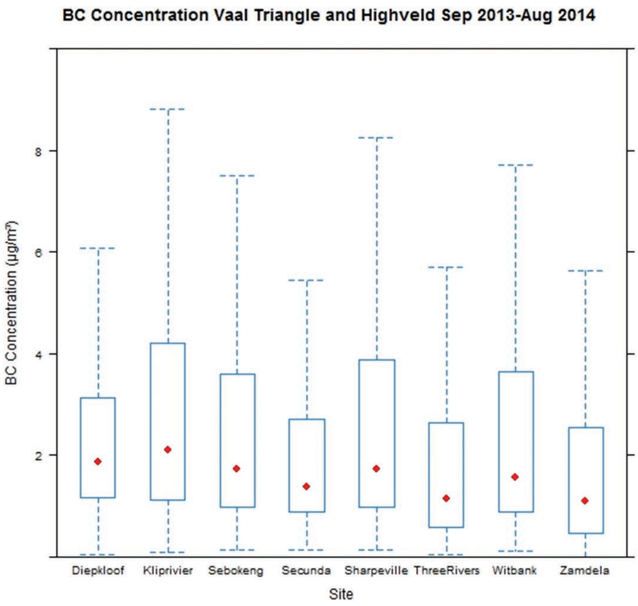

***Figure 2**: Average hourly BC concentration (μg/m^3) for all the sites for the period September 2013-August 2014*

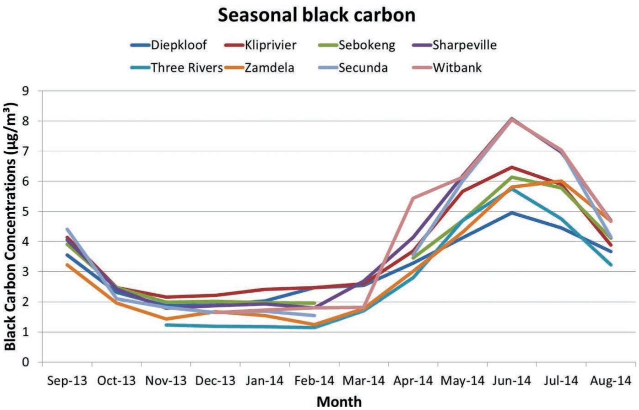

***Figure 3**: Monthly average concentration of BC for the eight sites for the monitoring period*

Seasonal and diurnal effects

A strong seasonal trend in the ambient concentration of atmospheric BC was observed (Figure 3). The concentration of BC increased significantly with the onset of winter. Increases in the ambient concentrations were observed during the months of April, May and June 2014, with reductions occurring from August. During the warmer months (October – March), the monthly average concentration remained fairly constant and similar between the stations. During the cooler months (April – September), stronger differences are observed between the sites, with higher concentrations being observed in the Witbank, Secunda and Sharpeville stations.

The "openair" calendar plot function for the Zamdela station during 2013 (Figure 4) illustrates that the BC mass concentration peaks during the cooler period (May – July as well as September) and remains fairly low during the warmer months. During the June and July period the daily average concentrations of BC vary with days of relatively low concentration following periods of high concentration, many of these periods of low BC concentration are associated with the passing of a cold front over the interior of the country, particularly on the 2 June 2013, 8 June 2013, 3 July 2013 and 28 July 2013. During September 2013 there is an increase in the BC concentrations; this is potentially due to long range transport of biomass burning emissions.

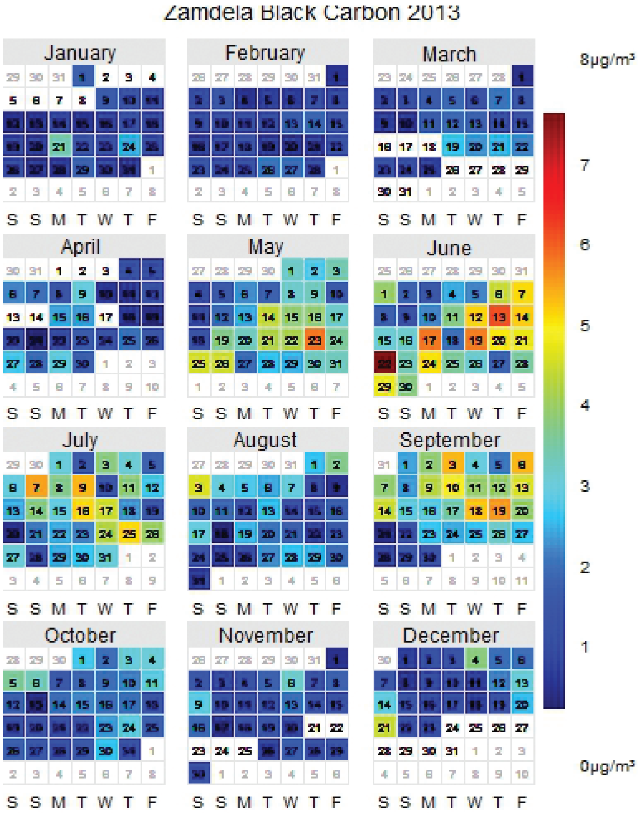

***Figure 4**: Calendar plot of the daily BC concentrations recorded at Zamdela for 2013*

The hourly profile of the ambient BC concentrations (for the entire time period) recorded at all the stations show a strong bimodal distribution (Figure 5) with peaks occurring in the mornings (5-8 am) and in the evenings (6-8 pm). The concentrations remain elevated during the night and then reduce during the day time. This pattern of increased concentrations is fairly typical of domestic burning emissions. This can be seen in more detail in Figure 6 which is a time variation plot of BC in Zamdela for the entire time period. The diurnal pattern of high BC concentration remains consistent across the days of the week, but the peak concentrations are reduced over the weekends and the morning peaks are spread out over a longer period on Saturday and Sunday, presumably due to people starting their activities later in the morning.

Impact of air flow

The "Polar Plot" function from "openair" plots the concentration of BC (in colour) in relation to the wind speed and wind direction (Figure 7). All the stations considered in this study show that local sources are important and high concentrations occur when there is a fairly low wind speed. Five of the stations in the

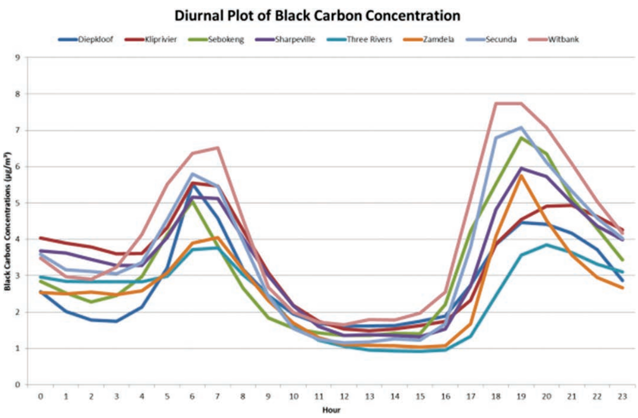

***Figure 5**: Diurnal characteristics of the ambient BC concentration*

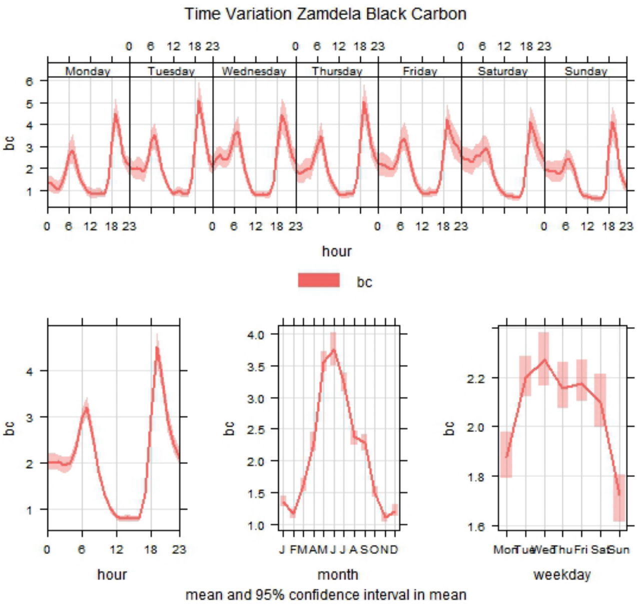

***Figure 6:** Time Variation Plot Zamdela BC. In this plot the top panel shows the diurnal pattern for each day of the week, while the lower panel shows the diurnal pattern for the year, the monthly average and the day of week concentrations. The mean for each time period is indicated by the red line with the 95% confidence interval in the mean shown in the shaded area.*

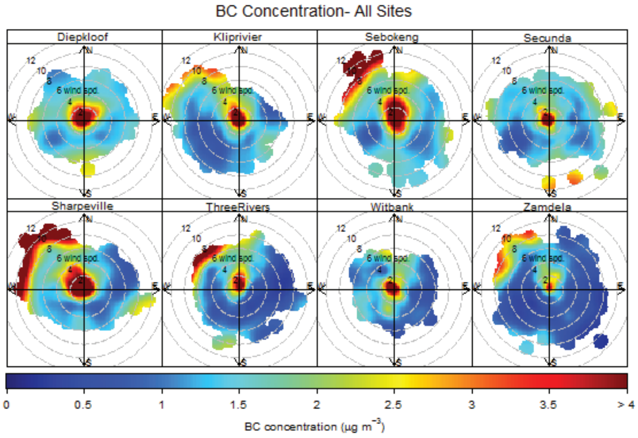

***Figure 7**: Polar plot of site specific BC concentration and meteorological conditions*

Vaal Triangle (Kliprivier, Sebokeng, Three Rivers, Sharpeville and Zamdela) also show high concentrations of BC associated with strong winds from the north-westerly directions sources to the north west of these stations may include the gold fields of Randfontein/ Carletonville and the Bojanala platinum belt, further analysis is required to identify potential sources. Zamdela shows very low BC concentrations associated with winds from the south and easterly sectors where there is very little industrial activity.

Relationship between BC, PM_{10} and $PM_{2.5}$

There is a strong relationship between the 1-hr mass concentrations of BC, and the concentrations of PM_{10} and $PM_{2.5}$ as shown in Figure 8. The mass concentrations of $PM_{2.5}$ and PM_{10} are plotted against each other while the BC concentration is represented by the colour of the point. It can be seen that as the concentrations of PM_{10} and $PM_{2.5}$ increase so do the concentrations of BC, however the BC concentration tracks more closely with the $PM_{2.5}$ values.

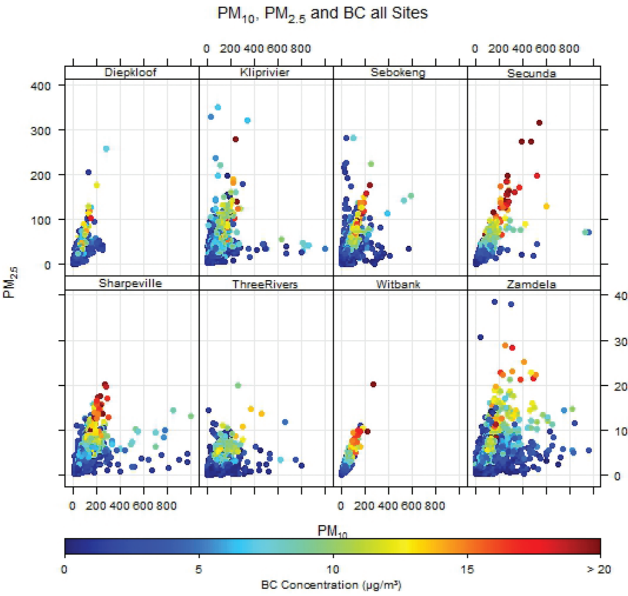

***Figure 8**: Scatter Plot 1-hr averaged mass concentrations of PM_{10}, $PM_{2.5}$ and BC*

Using the full time period of measurements (July 2012-June 2014) at Zamdela the monthly linear relationship between BC concentration and the $PM_{2.5}$ concentration was plotted using the linear relation function from "openair" (Figure 9). The "linear relation" function looks at the relation between two pollutants over differing time periods (in this case monthly) the error bars represent the 95% confidence interval while the red trend line represents the long term trend in the relationship. The ratio between BC and $PM_{2.5}$ changes seasonally with increases in the BC component during the winter months. The value of the plotted linear relationship is the ratio of BC:$PM_{2.5}$. While in general there is fairly good correlation between the concentrations of $PM_{2.5}$ and BC, the BC makes up a small portion of the total $PM_{2.5}$ concentration, typically less than 10%.

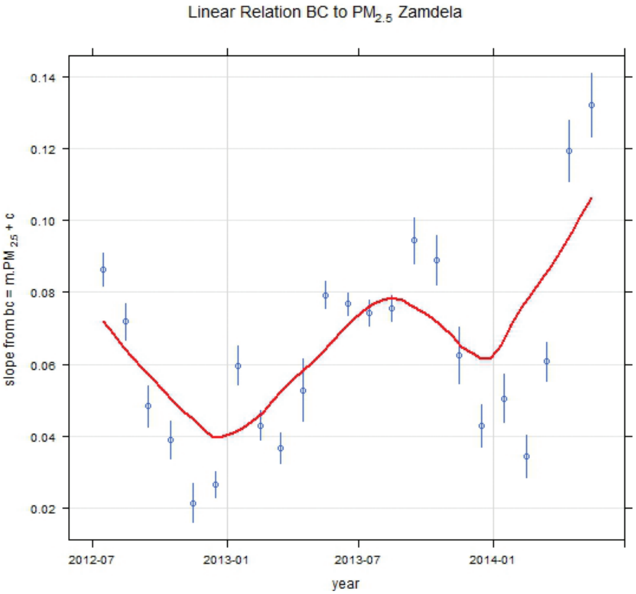

***Figure 9**: Time series of the monthly linear relation between black carbon and $PM_{2.5}$ at Zamdela for the period July 2012 to May 2014 blue points and error bars represent the monthly linear relationship between the parameters while the red line represents the trend in the monthly linear relationship observed*

Discussion

The ambient concentrations of BC are monitored at 8 ambient air quality monitoring stations in the Vaal Triangle and Highveld Priority Areas. The concentrations of BC show a distinct seasonal pattern, with higher concentrations occurring in the cooler months. This is similar to what has been reported previously in the North West Province (Venter et al. 2012). This observed seasonal trend is likely linked to greater emissions of BC from domestic burning and biomass burning sources, and the presence of highly stable atmospheric conditions, which reduce mixing. The diurnal profile shows a strong bimodal distribution with peaks in the early morning and evening. Such concentration profiles are indicative of either domestic combustion and/or traffic sources. Since the maximum BC concentrations occur between 5:00 and 7:00 in the morning and between 18:00 and 20:00 in the evening the predominant source may be domestic combustion as the maximum traffic flows are expected to occur later in the morning and finish earlier in the evening. This is confirmed when looking at the weekday diurnal profiles as the morning peak in BC concentration is spread over a greater time period as people tend to start their daily activities later on Sundays.

The analysis of the BC concentration in relation to the air flow indicates that for most of the stations local sources are important, however, the stations in the Vaal Triangle show high BC concentrations associated with strong winds from the north-west. In a previous study of ozone concentrations in the Vaal Triangle, high ozone concentrations were associated with biomass burning events and the approach of a cold front, drawing in air masses from the north west (Feig et al. 2014).

Black carbon accounts for approximately 6%-12% of the mass concentration of $PM_{2.5}$. The proportion of BC in the $PM_{2.5}$ fraction is impacted by season with a higher BC contribution occurring in the winter months, presumably due to the greater emissions from domestic and biomass burning sources.

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Human health risk assessment of airborne metals to a potentially exposed community: a screening exercise

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Abstract

Exposure to high concentrations of inhalable particulate matter (PM) is a known human health risk, depending on the chemical composition of the PM inhaled. Mogale City (Gauteng) is known for having several sources of airborne PM, however, less is known about the metals in the airborne PM. The aim of this study was to determine the metals in measured PM at Kagiso, Mogale City. An independent PM_{10} monitor was installed at the municipality's existing monitoring site. This monitor continuously monitored PM_{10} between 23 August and 9 October 2013 and simultaneously sampled particles below 20 µm in diameter onto a glass fibre filter. This filter was replaced once towards the middle of the monitoring period. These two filters were chemically analysed to determine their metal content (30 metals) by the South African Bureau of Standards accredited laboratory at the Council for Scientific and Industrial Research by means of Inductively Coupled Plasma Spectroscopy (ICPS) based on the US EPA Method IO-3.1. To provide an estimate of possible health risk, the metal concentrations were used in a screening US-EPA human health risk assessment (HHRA). Since the analysed metals were reportedly below the detection limit, three hypothetical exposure scenarios (S) based on US-EPA recommendations were created for the HHRA. In S1, concentrations were considered to be the same as the detection limit for each metal; S2 assumed concentrations to be 50% of the detection limit; and S3 put concentrations at 10% of the detection limit. Potential risks (should pollution worsen) of developing respiratory and neurological effects were identified depending on the hypothetical scenarios. Continuous long-term monitoring and chemical characterisation are necessary to confirm these preliminary findings.

Keywords

Human Health Risk Assessment, South Africa, mining, metals, PM_{10}, air pollution

Introduction

Metals are natural components of the Earth's crust. Many of these metals are needed in the human body in small amounts, such as iron (Fe) which is contained in haemoglobin, copper (Cu) and manganese (Mn) which are in enzymes, and chromium (Cr), which is a co-factor in the regulation of sugar levels (CDC, 2011). However, depending on concentrations, these trace elements may have detrimental health effects. Heavy metals such as lead (Pb), cadmium (Cd) and mercury (Hg) are detrimental to human health as they may bio-accumulate in the body, while others are carcinogenic, such as arsenic, beryllium, cadmium and nickel (CDC, 2011). Metals emitted from mining activities accumulate in soil in surrounding areas and contaminated soil then poses a hazard to human health (Kumar et al., 2014), as the metals may be absorbed by vegetables grown in the contaminated soil, leach into underground water sources, or become airborne through wind-blown dust. Humans may therefore, be exposed to these metals via inhalation, ingestion and/or dermal contact. Mogale City Local Municipality (MCLM) in Gauteng Province (South Africa) has a long history of gold mining. As a result, it has a number of mine dumps, some of which have not been rehabilitated. Activities within the MCLM that may contribute to concentrations of particulate matter (PM) in air include mining of minerals, quarrying of stone, extraction of clay and sandpits, use of motor vehicles, various heavy and light industrial activities, as well as domestic fuel burning (AQMP, 2013).

Focus-group discussions with MCLM residents in 2013 revealed that residents' perceived dust (PM) emissions in the area was responsible for most of their illnesses, including respiratory illness and cancer, and that dust was soiling their properties and damaging their appliances (Phala et al., 2012; Wright et al., 2014). One of the study recommendations was that the metal content of the PM should be characterised and possible health impacts from PM inhalation quantified using Human Health Risk Assessment (HHRA).

HHRA links environmental exposure to potential human health effects. The potential for detrimental health effects is assessed based on the United States Environmental Protection Agency (US-EPA) Human Health Risk Assessment Framework (US-EPA, 2014) as it relates to the physical and/or chemical properties of air pollutants and their concentrations. The framework comprises the following steps: (1) Hazard identification to determine whether exposure to a particular substance may result in detrimental human health effects; (2) Exposure assessment to determine environmental concentrations through source and emissions characterization, monitoring, and / or environmental fate, transport, and deposition modelling, and to estimate the magnitude, duration, and frequency of human exposure; (3) Dose-response assessment to estimate the relationship between dose, or level of intake of a substance, and the incidence and severity of an effect (Several agencies such as the US-EPA (IRIS, 2015), the World Health Organization (WHO) (WHO, 1999) and the Centre for Disease Control (CDC) (ATSDR, 2015) have developed databases for benchmark values, which are used to describe the dose-response relationships determined for various chemicals); and (4) Risk characterisation which combines all the information obtained in the previous three steps to describe whether a risk to public health is predicted.

Therefore, the aim of this article was to describe the chemical composition of PM measured at Kagiso, MCLM and to apply the HHRA in a screening exercise to estimate possible human health risks with the purpose of identifying metals for further investigation.

Methods

Study area

Kagiso, the community surrounding the monitoring station, formed the study area (Figure 1). The population density in Kagiso varies from 700 to 20 500 people per km^2 (AQMP, 2013). Nearly 30% of the population of 362 422 were considered vulnerable because they were either below 15 years or above 65 years of age (StatsSA, 2011). The majority (54.8%) of households had access to piped water inside the dwelling; also to electricity (85.9%) and weekly refuse removal (79.7%) (StatsSA, 2011).

Meteorological data from 2007 to 2012 indicated that the prevailing wind direction during spring (August and September), the period in which the current study was conducted, was from a north-westerly to northerly direction (AQMP, 2013). Meteorological data further indicated that the wind in the MCLM is calm for about 40% of the time and when the wind is blowing it is mostly at a speed of < 3 ms^{-1} (AQMP, 2013). There are mine dumps within four to five kilometres to the north and the north-west, as well as the south of the monitoring site, and two industrial areas (Factoria and Chamdor) resides to the north and north-west, respectively.

Monitoring and chemical analyses

The West Rand District Municipality operates an air quality monitoring station in MCLM and monitors air pollution including PM_{10}, however, chemical composition of PM_{10} is not routinely analysed. This site was chosen as the measurement location in this study for security reasons and to access electricity. A TOPAS Sira MC 090158/00 PM_{10} monitor was installed from 23 August 2013 to 9 October 2013. This instrument continuously monitored PM_{10} concentration. It also simultaneously sampled PM_{20} onto a glass fibre filter, recorded the volume of air pumped through as well as the mass deposited on the filter. The filter was changed once during this period to have two filters for analyses. The filters and a blank were chemically analysed for their metal content by the South African Bureau of Standards accredited laboratory at the CSIR, based on the US EPA Method IO-3.1 and using Inductively Coupled Plasma Spectroscopy (ICPS). The instrument also heated to 60 ˚C to drive off moisture and volatiles. The concentrations of each metal in air were subsequently calculated and used to determine potential exposure in a HHRA.

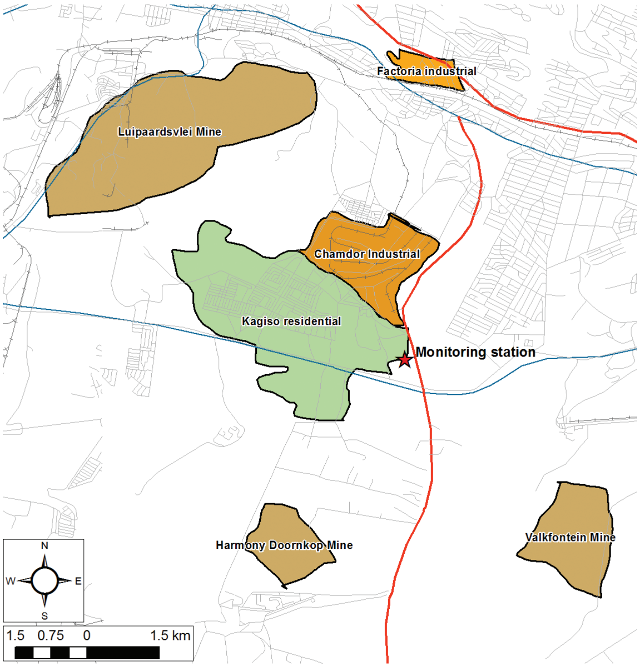

Figure 1: Location of Kagiso, other communities, mines and industrial areas in relation to the location of the measurement instrument used in this study located at the MCLM monitoring station.

Applying the HHRA framework

Three types of risk estimates were calculated in this quantitative HHRA: The (1) Hazard Quotient (HQ), which describes the potential for developing detrimental effects (other than cancer) from exposure to a hazardous substance; (2) Incremental (over and above the background prevalence) Cancer Risk, which is the probability of individuals developing cancer from exposure to a hazardous substance; and (3) Hazard Index (HI) was calculated to determine the total incremental cancer risk for the area (community).

For Hazard Identification, reliable databases, including those of the US-EPA, were reviewed to determine whether the elements identified during chemical analyses of the PM samples may be detrimental to human health. It was assumed in a worst-case scenario, that the Kagiso community, specifically, in the MCLM study area were continuously exposed (for example, mothers looking after small children at home) to the concentrations of PM_{10} and metals in air as determined by the monitoring and analyses of the short-term PM samples. Air was the medium and inhalation the route of exposure assessed. Where concentrations of metals were found to be below detection limits, hypothetical scenarios of exposure were created based on recommendations by the US-EPA (US-EPA, 2000), as follows: (a) Scenario 1 (S1): concentrations are the same as the detection limit for each metal; (b) Scenario 2 (S2): concentrations are 50% of the detection limit and; (c) Scenario 3 (S3): concentrations are 10% of the detection limit.

To obtain relevant benchmarks for the identified elements, the focus was on the most recently published standards or guidelines from reliable databases, including the US-EPA, WHO and CDC. A benchmark value is a value of exposure to pollutants that is believed to not be detrimental to even sensitive individuals in a population. In the case of air pollutants, the benchmark value is a "safe" concentration expressed as mass per volume.

A quantitative risk characterisation was performed, providing a numeric estimate of the potential for public health consequences from exposure to the metals concerned. This quantified potential was expressed as an HQ, which is unitless. The HQ is determined by the ratio between the expected exposure concentration of the metal and the benchmark value, which is an exposure that is assumed not to be associated with detrimental health effects. In the case of carcinogens, the incremental (over and above the background) cancer risk, which is a function of the 'Inhalation Concentration' and the 'Inhalation Unit Risk', was quantified. The Inhalation Unit Risk (risk per μg/m^3) is the unitless upper bound estimate of the probability of tumour formation per unit concentration of a chemical (Mitchell, 2004).

Results are given for the TOPAS measured PM_{10} concentrations and chemical composition followed by the results for each HHRA step and risk estimates for S1, S2 and S3.

Results and discussion

Particulate monitoring

PM_{10} concentrations measured by the TOPAS instrument exceeded the then South African 24-h ambient air quality standard of 120 μg/m^3 three times during the monitoring period of 23 August 2013 to 9 October 2013 (Figure 2). The current standard (since January 2015) of 75 μg/m^3 was exceeded 14 times during the same period. Sharp peaks were detected on 24 and 30 August 2013.

The South African Air Quality Information System (SAAQIS) website (www.saaqis.org.za) was consulted for results of monitored PM_{10} data from the municipality's monitoring station. Raw data were not available but a graph for the period 1 August to 30 September 2013 (Figure 3) showed incomplete data and although the 24-h standard of 120 μg/m^3 was not exceeded during the specified period, the current standard of 75 μg/m^3 was exceeded on at least six occasions. The highest peak of about 110 μg/m^3 was around the 30th of August, which coincided with the TOPAS peak, although lower in magnitude.

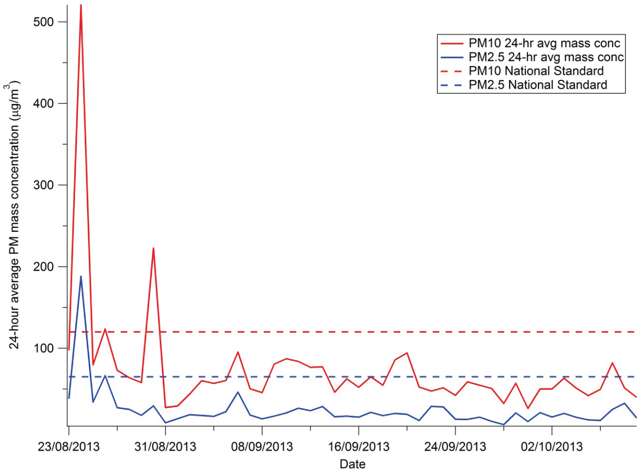

Figure 2: *PM_{10} concentrations monitored during the period 23 August 2013 to 9 October 2013.*

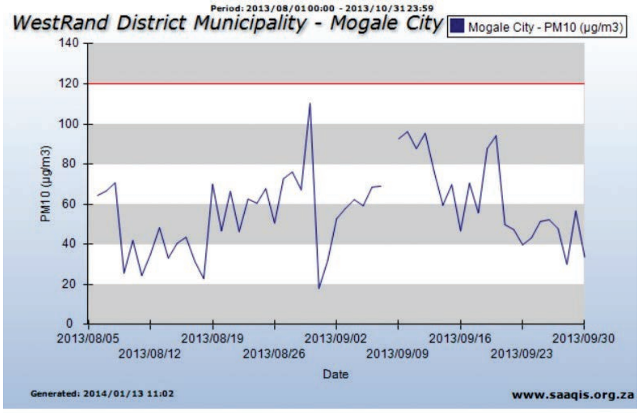

Figure 3: *PM_{10} concentrations monitored by the municipality monitoring station during the period 1 August to 30 September 2013 (graph generated in SAAQIS www.saaqis.org.za).*

Metal analyses

The two filters and a blank were chemically analysed for the presence of 30 metals, expressed in mg/kg. The results obtained were all below the detection limits for the individual metals (namely, calcium, magnesium, total phosphorous, potassium, nickel, silver, tin, titanium, bismuth, sodium, sulphur, aluminium, antimony, arsenic, boron, barium, beryllium, cadmium, cobalt, chromium, copper, iron, lead, lithium, manganese, selenium, silica, strontium, vanadium and zinc). The total weight of PM_{10} accumulated on the filter over each monitoring period was divided by the total volume of air sampled during that period to obtain a concentration (μg/m^3) per metal. Due to the fact that concentrations were below the detection limits, these concentrations were considered to be at the detection limit as a worst case scenario (S1). Two other scenarios were also assessed, namely concentrations at 50% of the detection limit (S2) and at 10% of the detection limit (S3).

Health risks assessed

Hazard identification

Non-cancer health effects caused by the metals analysed are mostly respiratory-related (metals included bismuth, boron, calcium, chromium, copper, iron, phosphorus, sulphur, titanium, tin, aluminium, antimony, beryllium, cadmium, cobalt, lithium, silica and vanadium, zinc and nickel), while some may cause neurological effects (lead, manganese and selenium) (CDC, 2011). Silver may cause argyria (bluish-grey skin), while arsenic, beryllium, cadmium and nickel have been identified as being carcinogenic (CDC, 2011).

Exposure assessment

The communities of concern were considered to be those around the monitoring station in the MCLM, with specific emphasis on Kagiso since it was the closest to the monitoring site. The concentrations for each scenario used in this HHRA are given in Table 1. In this worst-case scenario exercise, it was assumed that individuals were constantly (24 hours per day) exposed to the varying concentrations calculated for the different exposure scenarios. In terms of cancer risk assessment, it was assumed that the calculated concentrations were the concentrations that individuals were exposed to over a lifetime. It is not possible to completely avoid contact with these metals naturally found in the environment. The smaller the particles, the deeper they will penetrate into the lungs. The amount absorbed into the bloodstream will again depend on how well the particles dissolve. The more easily the particles dissolve, the more easily they may enter the blood stream. If the particles do not dissolve easily, they may remain in the lungs for longer periods of time. Some of the particles may leave the lungs through the normal clearing process while some may be swallowed.

Dose-response assessment

Numeric benchmark values obtained from reliable databases were used to describe the dose-response relationships. The preferred benchmark values used were those set on the basis of health effects in human beings and not those incorporating economic or social factors. Since people are normally exposed to metals in the air, predominantly in an occupational environment, and since the main route of exposure to metals is ingestion, a number of the elements did not have benchmark values for inhalation. Where no benchmark value could be found from reliable databases surveyed, the South African Occupational Exposure Limit (SA OEL) (SA Occupational Standards, 1995) was considered to indicate the level of toxicity of the element. These OELs are indicated in bold in Table 1. These were for aluminium, arsenic, antimony, barium, beryllium, bismuth, calcium, copper, iron, lithium, magnesium, silica, silver, selenium, sulphur, tin and zinc. In cases where there was no OEL for the element but only for a species of that element, that species is given in brackets in Table 1.

It must be noted that the application of occupational standards is not technically applicable in this case, because the samples were taken in ambient air and for a period longer than eight hours. In addition, occupational standards are set with healthy workers in mind, who are only exposed for eight hours a day and forty hours a week. Therefore, occupational standards are higher than ambient standards and they will not protect sensitive individuals (such as asthmatics and children) which ambient standards are supposed to do. However, it was decided to keep the pollutants for which only occupational standards were available as part of this assessment, because if the HQs of any of these pollutants with relatively high benchmark values were >1 it would indicate possible drivers of risk that can then be further investigated. Those metals for which no benchmark values could be found, namely sodium, potassium and strontium, were excluded from the HHRA.

Risk characterisation

Non-cancer risk estimates, expressed as HQs, were calculated for the metals and are presented in Table 2. HQ values > 1 indicate that the likelihood of detrimental non-cancer effects is enhanced while HQ values <1 indicate that the potential for detrimental health effects is minimal. The HQs of most (about 80%) of the metals analysed were below one, indicating that non-cancer detrimental health effects were unlikely. For six of the analysed metals (i.e. cadmium, cobalt, manganese, nickel, lead and vanadium), the HQs indicated a risk to human health in one or more of the exposure scenarios.

(a) Risk characterisation for S1

In S1, where the concentrations were assumed to be at the detection limit, the HQs indicated a risk of developing respiratory effects from cadmium, cobalt, nickel and vanadium and neurological effects from manganese and lead.

(b) Risk characterisation for S2

In S2, HQs indicated a health risk for respiratory effects due to exposure to cadmium, cobalt and nickel as well as neurological effects due to exposure to manganese and lead. The HQ for vanadium did not indicate a risk of respiratory effects in S2.

(c) Risk characterisation for S3

In S3, assuming that the exposure concentrations were 10% of the detection limit, only cadmium and cobalt posed a risk of respiratory effects as only the HQs for these two metals were above one.

(d) Cancer risk characterisation

The incremental cancer risks (Table 3) were estimated using the determined concentrations and the inhalation unit risk for each metal (from the US-EPA) known to be a confirmed human carcinogen. The HI is also presented in Table 3. The total incremental risk to develop cancer ranges from 1.73 in 1 000 in S3, to 17.7 in 1 000 in S1. Arsenic was found to be the main driver of the risk to cancer. The calculated incremental cancer risks are thus not only above 1 in a million, but also above 1 in 10 000. Evaluation of these risks against the US-EPA air office criteria which “strives to reduce risk for as many people as possible to 1 in a million, while assuming that the maximally-exposed individual is protected against risks greater than 1 in 10 000” indicates that these acceptable risks have been exceeded here.

Uncertainties and limitations

Several limitations and uncertainties should be considered when interpreting these findings. HHRA is a predictive process, therefore it only estimates what could occur. Due to the fact that concentrations were below the detection limits, these concentrations were considered to be at the detection limit as a worst case scenario at 50% of the detection limit and at 10% of the detection limit. While these scenarios are not representative of the status quo, should current air pollution interventions and management change, and PM levels increase, such scenarios may be experienced. Being prepared by having predicted, likely worst-case scenario health impacts supports the need for continuous improvement in air quality management and air pollution control in this area.

It is acknowledged that PM_{10} was monitored only during a short period and at one site only. Personal monitoring and time-activity data are the optimal method for exposure assessment, however, they were not possible in this small study. Although the instrument was calibrated, concentrations may not be representative for all the communities, particularly those furthest away from the monitoring site. However, this screening study aimed to understand the metals present in the dust. It did not aim to collect information on pollution sources. Although the monitoring data from the municipality at the same site may give additional data on PM_{10} exposure, the simultaneous capturing of the PM onto a filter for metal analysis was not possible from the instrumentation used by the municipality, and this was crucial for this exercise.

To address model uncertainty in this study, equations from the US-EPA were used, and applied benchmark values were based on national and international standards and guidelines which were set based on human health effects. In terms of selection of the pollutants of concern, the pollutants were pre-identified as those metals which the accredited laboratory could analyse for and which was present in the PM. Finally, in terms of the exposure pathway and route used, the risk assessment was based on inhalable PM and therefore the inhalation route was selected.

Conclusions

PM_{10} concentrations measured in this study exceeded the previous South African 24-h ambient air quality standard of 120 μg/m^3 three times during the monitoring period and the current standard (since January 2015) of 75 μg/m^3 14 times. Although the concentrations of metals determined in this study were below detection limits, and were not representative of all exposure periods and all seasons, or for all individuals in the local municipality, using US-EPA recommended scenarios, screening for possible carcinogenic and non-carcinogenic risks based on concentration and toxicity from metal exposure through inhalation was performed. Results provide an indication of which metals may drive human health risks in the area. Those pollutants identified as being potential risks should be investigated further.

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[i] *The size of the particles collected for chemical analysis was ≤ 20 μm.*

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***Table 1**: Concentrations of compounds of potential concern and their benchmark values.*

	Scenario 1		**Scenario 2**		**Scenario 3**	
Element	**Concentration (µg/m^3)**	**Benchmark Value (µg/m^3)**	**Concentration (µg/m^3)**	**Benchmark Value (µg/m^3)**	**Concentration (µg/m^3)**	**Benchmark Value (µg/m^3)**
Aluminium (respirable)	2.70	**5000**	1.36	**5000**	0.27	**5000**
Arsenic	2.70	**10**	1.36	**10**	0.27	**10**
Antimony (and compounds)	6.90	**500**	3.43	**500**	0.69	**500**
Barium compounds	6.90	**500**	3.43	**500**	0.69	**500**
Beryllium (and compounds)	1.4	**2**	0.68	**2**	0.14	**2**
Bismuth (undoped)	6.90	**10000**	3.43	**10000**	0.69	**10000**
Boron	10.20	300*	5.08	300*	1.02	300*
Cadmium	1.40	0.03*	0.68	0.03*	0.14	0.03*
Calcium oxide	68.40	**2000**	34.20	**2000**	6.84	**2000**
Cobalt	1.40	0.10*	0.68	0.10*	0.14	0.10*
Chromium III	1.40	5*	0.68	5*	0.14	5*
Copper	6.90	**1000**	3.43	**1000**	0.69	**1000**
Iron oxide (dust)	1.40	**5000**	0.68	**5000**	0.14	**5000**
Lead	2.70	0.5**	1.36	0.5**	0.27	0.5**
Lithium hydride	6.90	25	3.43	25	0.69	25
Magnesium	13.70	5000	6.83	5000	1.37	5000
Manganese (and compounds)	1.40	0.03*	0.68	0.03*	0.14	0.03*
Nickel	1.40	0.20*	0.68	0.20*	0.14	0.20*
Phosphorus (white)	13.70	20*	6.83	20*	1.37	20*
Silica	13.70	**100**	6.83	**100**	1.37	**100**
Silver	6.90	**100**	3.43	**100**	0.69	**100**
Selenium (and compounds)	1.40	**100**	0.68	**100**	0.14	**100**
Sulphur	13.70	**6000 000**	6.83	**6000 000**	1.37	**6000 000**
Tin	6.90	**200**	3.43	**200**	0.69	**200**
Titanium	6.90	10*	3.43	10*	0.69	10*
Vanadium	1.40	0.8*	0.68	0.8*	0.14	0.8*
Zinc	1.40	**500**	0.68	**500**	0.14	**500**

*Note. *MRL **SA National Standard SA-OEL figures in bold.*

***Table 2**: Non-cancer risk estimates of the elements analysed for the different exposure scenarios.*

	Scenario 1		Scenario 2		Scenario 3	
Element	**Concentration (μg/m^3)**	**Hazard Quotient (HQ)**	**Concentration (μg/m^3)**	**Hazard Quotient (HQ)**	**Concentration (μg/m^3)**	**Hazard Quotient (HQ)**
Aluminium	2.70	0.0005	1.36	0.0003	0.27	<0.0001
Antimony	6.90	0.01	3.43	0.007	0.69	0.001
Arsenic	2.70	0.27	1.36	0.14	0.27	0.03
Barium	6.90	0.01	3.43	0.007	0.69	0.001
Beryllium (and compounds)	1.40	0.68	0.68	0.34	0.14	0.07
Bismuth	6.90	0.0007	3.43	0.0003	0.69	<0.0001
Boron	10.20	0.03	5.08	0.02	1.02	0.003
Cadmium	1.40	45.48	0.68	22.70	0.14	4.55
Calcium	68.40	0.03	34.20	0.02	6.84	0.003
Cobalt	1.40	13.64	0.68	6.82	0.14	1.36
Copper	6.90	0.007	3.43	0.003	0.69	0.0007
Chromium III	1.40	0.27	0.68	0.14	0.14	0.03
Iron	1.40	0.0003	0.68	0.0001	0.14	<0.0001
Magnesium	13.70	0.003	6.83	0.001	1.37	0.0003
Manganese (and compounds)	1.40	4.55	0.68	2.27	0.14	0.45
Nickel	1.40	6.82	0.68	3.41	0.14	0.68
Phosphorus (white)	13.70	0.68	6.83	0.34	1.37	0.07
Selenium	1.40	0.01	0.68	0.007	0.14	0.001
Silica	13.70	0.14	6.83	0.07	1.37	0.01
Silver	6.90	0.07	3.43	0.03	0.69	0.007
Sulphur	13.70	0.002	6.83	0.001	1.37	0.0002
Tin	6.90	0.03	3.43	0.02	0.69	0.003
Titanium	6.90	0.69	3.43	0.34	0.69	0.07
Lead	2.70	5.46	1.36	2.73	0.27	0.55
Lithium	6.90	0.27	3.43	0.14	0.69	0.03
Vanadium	1.40	1.71	0.68	0.85	0.14	0.17
Zinc	1.40	0.003	0.68	0.001	0.14	0.0003

***Table3**: Incremental cancer risks estimates for the different exposure scenarios.*

	Scenario 1			Scenario 2			Scenario 3		
Element	**Concentration (μg/m^3)**	**Inhalation Unit Risk**	**Incremental cancer risk**	**Concentration (μg/m^3)**	**Inhalation Unit Risk**	**Incremental cancer risk**	**Concentration (μg/m^3)**	**Inhalation Unit Risk**	**Incremental cancer risk**
Arsenic	2.70	$4.3x10^{-3}$	11.6 in 1000	1.36	$4.3x10^{-3}$	5.8 in 1000	0.27	$4.3x10^{-3}$	1.1 in 1000
Beryllium	1.40	$2.4x10^{-3}$	3.3 in 1000	0.68	$2.4x10^{-3}$	1.6 in 1000	0.14	$2.4x10^{-3}$	0.3 in 1000
Cadmium	1.40	$1.8x10^{-3}$	2.5 in 1000	0.68	$1.8x10^{-3}$	1.2 in 1000	0.14	$1.8x10^{-3}$	0.3 in 1000
Nickel	1.40	$2.4x10^{-4}$	0.3 in 1000	0.68	$2.4x10^{-4}$	0.2 in 1000	0.14	$2.4x10^{-4}$	0.03 in 1000
Total HI			**17.7 in 1000**			**8.8 in 1000**			**1.73 in 1000**