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Discussions

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Ambient aromatic hydrocarbon measurements at Welgegund, South Africa

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Abstract

Aromatic hydrocarbons are associated with direct adverse human health effects and can have negative impacts on ecosystems due to their toxicity, as well as indirect negative effects through the formation of tropospheric ozone and secondary organic aerosol that affect human health, crop production and regional climate. Measurements were conducted at the Welgegund measurement station (South Africa) that is considered to be a regionally representative background site. However, the site is occasionally impacted by plumes from major anthropogenic source regions in the interior of South Africa, which include the western Bushveld Igneous Complex (e.g. platinum, base metal and ferrochrome smelters), the eastern Bushveld Igneous Complex (platinum and ferrochrome smelters), the Johannesburg–Pretoria metropolitan conurbation ($>$ 10 million people), the Vaal Triangle (e.g. petrochemical and pyrometallurgical industries), the Mpumalanga Highveld (e.g. coal-fired power plants and petrochemical industry) and also a region of anti-cyclonic recirculation of air mass over the interior of South Africa. The aromatic hydrocarbon measurements were conducted with an automated sampler on Tenax-TA and Carbopack-B adsorbent tubes with heated inlet for one year. Samples were collected twice a week for two hours during daytime and two hours during night-time. A thermal desorption unit, connected to a gas chromatograph and a mass selective detector was used for sample preparation and analysis. Results indicated that the monthly median total aromatic hydrocarbon concentrations ranged between 0.01 to 3.1 ppb. Benzene levels did not exceed local air quality standards. Toluene was the most abundant species, with an annual median concentration of 0.63 ppb. No statistically significant differences in the concentrations measured during daytime and night-time were found and no distinct seasonal patterns were observed. Air mass back trajectory analysis proved that the lack of seasonal cycles could be attributed to patterns determining the origin of the air masses sampled. Aromatic hydrocarbon concentrations were in general significantly higher in air masses that passed over anthropocentrically impacted regions. Interspecies correlations and ratios gave

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some indications of the possible sources for the different aromatic hydrocarbons in the source regions defined in the paper. The highest contribution of aromatic hydrocarbon concentrations to ozone formation potential was also observed in plumes passing over anthropocentrically impacted regions.

1 Introduction

Atmospheric measurements in developed countries are well established, while less emphasis is placed on environmental issues in developing countries, since resources are mostly utilised for economic growth. For this reason, Africa is one of the least studied regions with respect to air quality (Laakso et al., 2006). South Africa has the largest industrialised economy in Africa and is known for its diverse anthropogenic pollutant sources, which include agriculture, metallurgical and mining operations, coal-fired power generation, petrochemical operations, coal dumps and transportation (Lourens et al., 2011). Unique meteorological conditions are prevalent in South Africa, which include relatively high atmospheric temperatures and solar radiation that increases photochemical activity in the atmosphere, while dominant anti-cyclonic climatology and the presence of low-level inversion layers in winter cause trapping of pollutant species (Tyson et al., 1996).

Atmospheric volatile organic compounds (VOC) are emitted from both natural and anthropogenic sources (Bates et al., 2000; Brasseur et al., 1999; Hewitt, 1999). Anthropogenic VOC emissions result from petrochemical industries, combustion processes (e.g. fossil fuel, power plants), vehicular emissions, storage and transport of fuel, usage and production of solvents, hazardous waste facilities and landfills (Srivastava et al., 2005; Derwent et al., 2000; Kourtidis et al., 1999; Jose et al., 1998). Biomass burning (veld fires) can also be an important source of VOC, especially in southern Africa, where large-scale biomass combustion occurs every year in the dry season (e.g. Crutzen and Andreae, 1990; Crutzen et al., 1979). However, these emissions are

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difficult to evaluate, as they are highly dependent on fuel type, humidity and burn rate (Lobert et al., 1990).

A large fraction of anthropogenic VOC consist of aromatic hydrocarbons of which benzene, toluene, ethylbenzene and o, p, m-xylene (BTEX) are the most commonly measured species. Aromatic hydrocarbons participate in complex chemical reactions in the atmosphere to form secondary pollutants. Although reactions of aromatic hydrocarbons do not directly produce ozone (O_3), they play a role in O_3 formation when they are oxidised by the hydroxyl radical ($^\bullet$OH) in the troposphere, producing peroxyl radicals ($RO_2^\bullet$) and hydroperoxy radicals ($HO_2^\bullet$) that then oxidise nitric oxide (NO), which removes a sink for O_3 (Atkinson, 2000). Aromatic hydrocarbons can also react with nitrate radicals (NO_3) (Atkinson, 1994; Penkett et al., 1993) and halogen radicals (Finnlayson-Pitts et al., 1986). Various researchers have investigated gas-phase photo-oxidation of aromatic hydrocarbons (e.g. Birdsall et al., 2010; Arey et al., 2009; Coeur-Tourneur et al., 2006; Johnson et al., 2005; Johnson et al., 2004; Takekawa et al., 2003; Calvert et al., 2002 and references therein; Olariu et al., 2002; Volkamer et al., 2002).

VOCs are also associated with adverse human health effects (Mukund et al., 1996; Kostiainen, 1995; Sweet and Vermette, 1992; Edgerton et al., 1989; Duce et al., 1983) and can also be harmful to ecosystems (Atkinson, 2000; Dewulf and Van Langenhove, 1997; Kuran and Sojak, 1996; Derwent, 1995). Benzene, for instance, is known as a genotoxic carcinogen (Hellén et al., 2002; WHO, 2000) and is closely linked to the induction of leukaemia. Studies have also indicated that VOCs can have detrimental impacts on crop production that is important for global food security (Zunckel et al., 2006).

Limited research has been conducted to determine the emission rates of biogenic VOCs in southern Africa (Harley et al., 2003; Otter et al., 2002a, b; Swap et al., 2002a, b; Greenberg et al., 1999, 2002; Guenther et al., 1996). Even less data are available to characterise aromatic VOC levels in South Africa. Benzene is the only aromatic hydrocarbon that has a standard included in the National Ambient Air Quality Standards

(NAAQS) (Government Gazette, 2009). According to the knowledge of the authors, only Lourens et al. (2011) conducted a study on BTEX concentrations that was published in the peer-reviewed public domain. This study was limited to measurements in the industrialised Mpumalanga Highveld and Vaal Triangle for one year. Additionally, some post-graduate studies focusing on BTEX have been conducted (van der Walt, 2008; Burger, 2006; Chiloane, 2005), but these were not published in the peer-reviewed public domain. Various industries also perform VOC measurements in South Africa to comply with legislation, but these results are in most instances not peer-reviewed and not available in the public domain.

To at least partially address the above-mentioned knowledge gap, i.e. very limited data on atmospheric aromatic hydrocarbons in South Africa, measurements were conducted for one year at the Welgegund measurement station. This station was strategically positioned to enable measurements of air masses that have passed over the regional background, as well as all the major anthropogenic source regions in South Africa (Beukes et al., 2014).

2 Measurement location and methods

2.1 Site description

The Welgegund measurement station (www.welgegund.org) is situated approximately 100 km west from Johannesburg (Fig. 1) on the property of a commercial farmer. The station is considered to be a regionally representative background site with no direct impacts from pollution sources in close proximity. The entire western sector (from north to south-east) contains no major point sources and can therefore be considered as representative of relatively clean regional background. The site is, however, impacted by plumes from major anthropogenic source regions in the interior of South Africa, which include the western Bushveld Igneous Complex (WBIC), the eastern Bushveld Igneous Complex (EBIC), the Johannesburg–Pretoria metropolitan conurbation (> 10

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million people), the Vaal Triangle, the Mpumalanga Highveld and also a region of anticyclonic recirculation of air mass over the interior of South Africa. The impacts of regional biomass combustion occurring mainly in the dry winter and spring are also observed at Welgegund. A detailed description of the Welgegund measurement station and related source regions was recently presented by Beukes et al. (2014). In Fig. 1, the location of Welgegund is indicated (latitude 26°34′10″ S, longitude 26°56′21″ E, 1480 m a.s.l.) within a regional perspective that also indicates the large point sources and source regions.

2.2 Measurement methods

The measurement instruments were placed inside a Eurowagon 4500u (length 4.5 m, width 2.1 m, height 2.3 m) measurement container. A detailed description of the measurement instruments, operation procedures, data analysis, as well as calibration and maintenance procedures has been presented by Beukes et al. (2014), Tiitta et al. (2013), Petäjä et al. (2013), Hirsikko et al. (2012), Venter et al. (2012), Vakkari et al. (2011) and Laakso et al. (2008).

2.2.1 Aromatic hydrocarbon measurements

The VOC measurement campaign was conducted for one year (9 February 2011 to 4 February 2012) in order to observe seasonal variability. Samples were collected twice a week for two hours during daytime (11:00 to 13:00 local time, LT) and two hours during night-time (23:00 to 01:00 LT) on Tuesdays and Saturdays. VOC were sampled at a height of 2 m a.g.l., with a 1.75 m long inlet. The first 1.25 m of the inlet was made from stainless steel and the second 0.5 m was made of Teflon. The stainless steel part of the inlet was heated to 120 °C using heating cables and thermostats (Thermonic) to remove O_3 that could possibly lead to sample degradation (Hellén et al., 2012). The O_3 removal efficiency was checked with an O_3 monitor at regular intervals, which revealed

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that O_3 concentrations decreased from median values ≥ 30 ppb (Beukes et al., 2014) to < 2 ppb.

Prior to sampling, all adsorbent tubes were tested for leaks and preconditioned with helium for 30 min at 350 °C at a flow of 40 mL min^{-1}. After treatment, the tubes were sealed with Swagelok® brass 1/4″ caps and stored in a fridge at temperatures below 18 °C before they were transported to the field for sampling. VOC samples were collected on Tenax-TA and Carbopack-B adsorbent tubes (6.3 mm ED × 90 mm, 5.5 mm ID) by using a constant flow type automated programmable sampler. A needle valve attached to the pump was used to keep the flow constant, while magnetic valves were used to direct flow to a specific sample tube. After a specific tube was sampled, the tube was automatically sealed off and the next tube selected for sampling. The flow of the pump was calibrated each week. A sampling flow between 100 and 110 mL min^{-1} was used throughout the study. Hellén et al. (2002) reported no breakthrough for Tenax-TA and Carbopack-B tubes when sampling for four hours at a flow rate of 100 mL min^{-1}. Once a week, the tubes were removed from the automated sampler and closed with Swagelok® caps. Each tube was separately wrapped in aluminium foil and stored in a container for transport to the laboratory. Tubes were stored in the laboratory in a freezer within a clean environment to minimise pre-analysis elution and breakdown of the sampled compounds. For each month, a field blank was analysed to compensate for the possibility of contamination from sample handling and storage. The total concentration of aromatic hydrocarbons in all field blanks was found to be < 0.076 ppb. Actual concentrations of all species reported in this paper were significantly higher than blank values and also well above the detection limit for each species. Blank values were subtracted from exposed samples.

The analyses and preparation of the adsorbent tubes were done by the Finnish Meteorological Institute. The instrumental setup was a thermal desorption instrument (Perkin–Elmer TurboMatrix™ 650, Waltham, USA) connected to a gas chromatograph (Perkin–Elmer® Clarus® 600, Waltham, USA) with a DB-5MS (60 m, 0.25 mm, 1 µm) column and a mass selective detector (Perkin–Elmer® Clarus® 600 T, Waltham, USA).

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The sample tubes were desorbed at 300 °C for 5 min and cryofocused in a Tenax cold trap (–30 °C) prior to injection of the sample into the column by rapidly heating the cold trap (40 °C min^{-1}) to 300 °C. A three-point calibration curve was obtained by using liquid standards dissolved in methanol. Standard solutions were injected into adsorbent tubes and were flushed with nitrogen (100 mL min^{-1}) for ten minutes in order to evaporate the methanol. The tubes containing the standards were desorbed and analysed with the same method used for the sampled tubes. Thirteen aromatic hydrocarbons were detected and quantified during this study.

2.2.2 Ancillary measurements

Trace gas measurements continuously conducted at Welgegund were used to assist in the interpretation of aromatic hydrocarbon results obtained. These were measured by utilising a Thermo-Electron 43S sulphur dioxide (SO_2) analyser (Thermo Fisher Scientific Inc., Yokohama-shi, Japan), a Teledyne 200AU NO_x analyser (Advanced Pollution Instrumentation Inc., San Diego, Cam USA), an Environment SA 41M O_3 analyser (Environment SA, Poissy, France) and a Horiba APMA-360 CO analyser (Horiba, Kyoto, Japan). A more detailed description of additional parameters monitored at Welgegund is given by Beukes et al. (2014) and Petäjä et al. (2013).

2.2.3 Air mass back trajectory analysis

Individual hourly back trajectories were calculated with the HYSPLIT 4.8 model, 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 US National Weather Service's National Centre for Environmental Prediction (NCEP) and archived by the ARL (Air Resources Laboratory, 2012). Each hourly arriving back trajectory was calculated for 96 h (4 days) backwards. An arrival height of 100 m was chosen, since aromatic hydrocarbons are mainly emitted within the lowermost layer of the troposphere. Furthermore, the orography in HYSPLIT is not very well defined, and therefore lower arrival heights could result in larger error margins on individual trajectory calculations. Back trajectories were calculated for the start, middle and end of each measurement period, i.e. three-hourly arriving back trajectories calculated for each two-hour sample.

3 Results and discussion

3.1 Contextualising aromatic hydrocarbon concentrations measured at Welgegund

The monthly median aromatic hydrocarbon concentrations determined in this study ranged between 0.01 and 3.1 ppb. As previously mentioned, benzene is currently the only VOC listed as a criteria pollutant in the NAAQS (Lourens et al., 2011; Government Gazette, 2009), with an annual average limit of 1.6 ppb (2015 standard). The Welgegund annual median benzene concentration was 0.13 ppb, which is well below the SA standard. The highest benzene concentration measured was 8.7 ppb, which indicated that the site is occasionally significantly impacted by pollution sources. Liu et al. (2000), who conducted a study in a relatively non-polluted area in the northeast of China, reported an average benzene concentration of 9.4 $\mu g\,m^{-3}$ (2.94 ppb). Lourens et al. (2011) reported an annual median of 0.91 ppb in the Mpumalanga Highveld and the Vaal Triangle, which is higher than the annual median value measured at Welgegund. This can be attributed to the measurement sites in the Mpumalanga Highveld and the Vaal Triangle being closer to the large point sources than Welgegund. In another investigation, van der Walt (2008) measured benzene levels in a South African metropolitan area and reported an annual mean of 1.8 ppb. A comparison of the benzene concentrations measured at Welgegund with these studies indicates that Welgegund can be considered as a regional background site, which is on occasion impacted by major plumes from different sources.

Toluene was the most abundant aromatic hydrocarbon species, with an annual median concentration of 0.63 ppb – nearly five times higher than the benzene annual median concentration. This was not unexpected, since toluene levels are usually two to four times higher than benzene concentrations (Borbon et al., 2002; Na and Kim, 2001; Brocco et al., 1997). Liu et al. (2000) and Lourens et al. (2011) also reported toluene concentrations to be substantially higher than that of benzene. Considering that toluene also has negative effects on human health, as well as that it is a precursor for O_3 and secondary organic aerosol formation, it should be considered to be included in future South African air quality legislation.

The second and third most abundant aromatic hydrocarbons measured were styrene and (m, p)-xylene with annual median concentrations of 0.66 and 0.50 ppb, respectively. o-Xylene and ethyl benzene had annual median concentrations of 0.20 and 0.25 ppb, respectively. The other aromatic hydrocarbons measured had annual median concentrations that were significantly lower. This does not necessarily mean that their emission sources were lower, since the ambient concentrations are determined by the emission rate and their atmospheric lifetimes (Parra et al., 2006).

3.2 Temporal variations

Although samples were collected during daytime and night-time in order to identify possible diurnal influences, results indicated no statistically significant differences in the concentrations of aromatic hydrocarbons measured during daytime and night-time. This indicates that there are no major local sources such as traffic that would result in a distinct diurnal pattern. Therefore, no distinction was made in subsequent sections based on daytime or night-time sampling.

The monthly temporal variations of the measured aromatic hydrocarbon species are presented in Fig. 2. These figures indicate the median, mean, 25th and 75th percentiles, as well as ±2.7 of the quartiles for each species (Matlab, 2010). The number of samples collected per month (N) is also provided. In general, no distinct seasonal pattern is observed for any of the species measured. The results indicate relatively high values during February 2011 and March 2011 for all the aromatic hydrocarbon species, with the exception of benzene. If these higher values coincided with a seasonal cycle, it would have been expected that similar higher values would have been observed in the corresponding months in the next year, which was not the case. The reason for these higher levels of aromatic carbons observed during these two months will be explored in Sect. 3.3. No seasonal patterns for BTEX were observed in a previous investigation conducted in the Mpumalanga Highveld and Vaal Triangle (Lourens et al., 2011).

3.3 Influence of source regions

Since no distinct seasonal cycles could be identified for the measured aromatic hydrocarbon species (Fig. 2), the possible influence of air masses passing over different source regions on the concentration of these species was explored. Since VOC were collected for only four two-hour sampling periods per week, the allocation of hourly back trajectories to air masses passing over all of the source regions defined by Beukes et al. (2014) was statistically not significant. Therefore, it was decided to group the Johannesburg–Pretoria megacity, the Vaal Triangle and the Mpumalanga Highveld source regions together, since these source regions were identified by Beukes et al. (2014) as the regions with the highest anthropogenic impacts. In this paper, this combined source regions will be referred to as Area I. The western BIC, the eastern BIC and the anti-cyclonic source regions that lie on the anti-cyclonic recirculation path of air masses moving towards Welgegund (Beukes et al., 2014) were grouped together and are referred to as Area II. Lastly, the Regional Background source region was kept as defined by Beukes et al. (2014). In Fig. 3, the different source regions considered in this study are presented.

For the entire VOC measurement period, 582 back trajectories were generated. Back trajectory sets, i.e. three trajectories per sampling period, were classified as passing over the different source regions defined in Fig. 3. For the two anthropogenically influenced source regions, i.e. Area I and II, only back trajectory sets that had passed over one of these source regions were considered. Therefore, back trajectory sets that had passed over both these source regions were not considered in further discussions on the influence of source regions. Back trajectory sets were allocated as passing over the Regional Background if such trajectories did not pass over either Area I or II, or both Area I and II. Taking this into consideration, 86 % of all back trajectory sets could be classified as passing over just one of the three source regions defined.

In Fig. 4, the back trajectories of air masses passing over the different source region are presented. 39 % of the VOC samples were collected during periods when air mass back trajectory sets had passed over Area II, while 33 % and 14 % of VOC samples were collected when air mass back trajectory sets passed over the Regional Background and Area I, respectively. The reason for the lower percentage of air masses passing over Area I can be attributed to the persistence of the anti-cyclonic circulation pattern over the interior of South Africa, which favours the arrival of air masses at Welgegund from the north to north-eastern sector.

In Fig. 5, the monthly fractional distribution of VOC samples collected during periods when air mass back trajectory sets had passed over the different source regions is presented. In this figure, air masses that had passed over multiple source regions were defined as mixed. The monthly fractional distribution (Fig. 5) can possibly be used to explain the lack of seasonal pattern observed for the aromatic hydrocarbon species (Fig. 2). During February 2011, more than 60 % of the air masses that arrived at Welgegund passed over Area I, which consists of the Johannesburg–Pretoria metropolitan conurbation, the Vaal Triangle and the Mpumalanga Highveld. According to Lourens et al. (2012), the Johannesburg–Pretoria megacity is relatively heavily polluted, while both the Vaal Triangle and the Mpumalanga Highveld source regions have been included in areas declared as pollution hotspots (national priority areas) by the SA government (Government Gazette, 2005, 2007). Considering the high frequency of air masses arriving at Welgegund after passing over Area I during the initial period of the study (Fig. 5), the relatively high aromatic hydrocarbon levels measured in February 2011 and March 2011 (Fig. 2) can be related to the relatively polluted air masses arriving during this period. Conversely, during the rest of the study, most of the air masses that arrived at Welgegund passed only over Area II and the Regional Background, which corresponds with lower concentrations measured (Fig. 2). It is therefore postulated that the monthly seasonal cycles presented for the aromatic hydrocarbon species (Fig. 2) are not directly related to seasonal patterns in emissions, but rather depend on the origin of the air masses sampled. Any monthly differences are likely to be a result of month-to-month differences in air mass trajectories. The afore-mentioned postulation is strengthened by a slight concentration increase of most of the aromatic hydrocarbon species observed during August and September 2011 (Fig. 2), which correlated with an increase in frequency of the arrival of air masses that had passed over Area I (Fig. 5).

The aromatic hydrocarbon concentrations measured for air masses passing over the three source regions are presented in Fig. 6. As expected, aromatic hydrocarbon concentrations were in general significantly higher for air masses that passed over Area I, which are considered to be more polluted. Air masses that passed over Area II and the Regional Background had much lower aromatic hydrocarbon levels, and were in the same order. The large point sources in Area II are mainly pyrometallurgical smelters (Fig. 2) that produce metals from ores by means of reducing processes (e.g. ferrochromium, as indicated by Beukes et al., 2010, 2012). Aromatic hydrocarbon emissions are not usually associated with these activities and so the relatively low values are expected. In addition, the large point sources in Area II are on average further away from Welgegund than the large point sources in Area I. This longer travelling time will result in the increased oxidation of the aromatic hydrocarbon species. Aromatic hydrocarbons measured in air masses from the Regional Background can possibly be attributed to smaller cities and agricultural activities in this region, but may also be associated with natural emissions (e.g. Heiden et al., 1999).

3.4 Interspecies correlation: an indication of sources

Several authors (Hoque et al., 2008 and references therein) have performed correlation analyses to determine the possible source(s) for aromatic hydrocarbons. In this section, Pearson's correlation analyses were applied to correlate the concentrations of the different aromatic hydrocarbons measured to each other, as well as to trace gas concentrations for air masses passing over each of the three source regions defined. These correlations are graphically presented in Fig. 7.

For air masses that had passed over Area I, relatively good correlations ($r > 0.8$) between the aromatic hydrocarbons were observed, except with benzene. The correlations of benzene with the other aromatic hydrocarbons were less significant, i.e. $r > 0.6$. This indicates that all the aromatic hydrocarbons, except maybe benzene, could be from similar sources. Karl et al. (2009) used aircraft flux measurements to show that toluene to benzene ratios can vary greatly (< factor of 3 to > factor of 15) on a spatial scale of tens of kilometres, indicating differences associated with various sources within a region, indicating that a high correlation between benzene and toluene will not always be the case. Large coal-fired power stations and petrochemical operations in source Area I, together with vehicle emissions, are expected to be the dominant sources of aromatic hydrocarbons in this source region. Venter et al. (2012) recently indicated that household combustion, which is a very common occurrence in especially semi- and informal settlements, could also contribute significantly. None of the aromatic hydrocarbons correlated with any of the inorganic gaseous species, except benzene that had a correlation coefficient of 0.612 with CO. Benzene also showed a negative correlation with O_3. Both the correlation with CO and the negative correlation with O_3 indicate that benzene was mainly present in fresher plumes arriving at Welgegund. The partial correlation of benzene with CO indicates that incomplete combustion sources such as vehicle emissions, household combustion and biomass combustion may be the dominant benzene emissions sources in Area I.

With the exception of benzene and toluene, the other aromatic carbons in air masses that had passed over Area II correlated relatively well ($r > 0.73$) with each other. Although benzene and toluene did not correlate with the other aromatic hydrocarbons, they correlated relatively well ($r = 0.74$) with each other. Therefore, it seems that the sources of benzene and toluene were related, while the sources of the other aromatic hydrocarbons were related. However, neither benzene nor toluene correlated with CO, as was the case for benzene in air masses that had passed over Area I. Incomplete combustion sources were therefore unlikely to be the main sources of these two species. The nature of large point sources in Area II is dramatically different to that of Area I. Virtually no large combustion point sources occur in Area II, since pyrometallurgical operations mainly focusing on reductive smelting are dominant.

For air masses that had passed over the Regional Background, benzene correlated well ($r = 0.92$) with toluene. However, in contrast to air masses that had passed over Areas I and II, not all of the remaining aromatic hydrocarbon species correlated with one another. Only a few significant correlations existed, e.g. ethylbenzene, styrene, (m, p)-xylene and o-xylene, correlated well ($r > 0.8$) with each other. This indicates that the sources of benzene and toluene were again linked, but that the sources of the other aromatic hydrocarbon species were not necessarily linked. Furthermore, the lower concentrations measured in air masses that had passed over the Regional Background resulted in more uncertainty, which could lead to lower correlations.

3.5 Interspecies ratios: an indication of sources and aging

In addition to interspecies correlations, interspecies ratios can also be used as an indicative method to determine possible sources for aromatic hydrocarbon and the age of air masses (Hoque et al., 2008 and references therein). The interspecies ratios of the atmospheric concentrations of aromatic hydrocarbons with benzene are presented in Table 1. Since most of the aromatic hydrocarbons are more reactive than benzene, the toluene / benzene (T / B), (m, p)-xylene / benzene ((m, p)-X / B), o-xylene/benzene (o-X / B) and (m, p)-xylene / ethylbenzene ((m, p)-X / EB) ratios can provide information on the distance from emission sources and the estimated photochemical age of the air mass (Monod et al., 2001; Derwent et al., 2000). The atmospheric T / B ratio, for instance, is usually high close to anthropogenic emissions and will decrease with an increase in distance from the sources (Lee et al., 2002). A value of 2.7 for the T / B ratio is usually an indication of fresh emissions originating from traffic (Brocco et al., 1997).

As indicated in Table 1, the highest aromatic hydrocarbon ratios were observed for plumes passing over Area I, whereas lower ratios were detected in plumes passing over Area II and the Regional Background. The ratios (calculated from the average concentrations) for plumes passing over Area I were 6.51, 7.31, 2.84, 2.55 and 2.87 for (T / B), ((m, p)-X / B), (o-X / B) ((m, p)-X / EB) and (EB / B), respectively. These ratios indicate the influence of anthropogenic activities in this area, as well as the closer proximity of especially the Johannesburg–Pretoria megacity that is part of Area I to the Welgegund monitoring station.

The ratios for plumes passing over Area II were 2.38, 1.97, 0.76, 2.20 and 0.89 for (T / B), ((m, p)-X / B), (o-X / B) ((m, p)-X / EB) and (EB / B), respectively. As mentioned previously, although anthropogenic activities are also present in this source area, the major industrial activities in this area are not usually associated with high emissions of VOCs. Additionally, sources in Area II are also further away from the measurement site compared to sources in Area I. The ratios therefore also indicate aged air masses, which might be transported by the dominant anti-cyclonic circulation pattern of air masses from the industrial hub of South Africa. Therefore, it is likely that most of the aromatic hydrocarbons in air masses that had passed over Area II had undergone photochemical degradation.

For air masses passing over the Regional Background, the aromatic hydrocarbon interspecies ratios were 2.66, 2.05, 0.85, 2.19 and 0.93 for (T / B), ((m, p)-X / B), (o-X / B) ((m, p)-X / EB) and (EB / B), respectively. These ratios compared well with the ratios calculated for Area II, which also indicate no local sources of atmospheric aromatic hydrocarbons.

According to literature, the use of solvents (e.g. in paint) is thought to be a major non-traffic source of aromatic hydrocarbons. Brocco et al. (1997) stated that toluene, ethylbenzene, and o, m, p-xylene (TEX) make up the largest portions of solvents. In Fig. 8, the concentration ratios of TEX / total aromatics for air masses that had passed over the three sources regions are illustrated. The ratios show a seasonal pattern with the maximum values in summer and minimum in winter. This is similar to the observation made by Rappenglück and Fabian (1999) who reported that the evaporation of solvents makes a greater contribution to atmospheric VOCs during summer. It is therefore clear that aromatic hydrocarbons originating from solvents make a contribution to aromatic hydrocarbons in air masses that had passed over all three source regions, including the Regional Background. However, the magnitude of this contribution was not determined from this data.

3.6 O_3 formation potential of aromatic hydrocarbons

While the evaluation of aromatic hydrocarbons on a concentration (ppb) basis is of interest in order to assess human exposure to toxic compounds such as benzene, it is also of interest to examine the relative importance of these pollutants pertaining to their role in the production of O_3 (Carter, 1994). Beukes et al. (2014), Laakso et al. (2013) and Venter et al. (2012) indicated that O_3 is currently the most problematic pollutant in South Africa. Tropospheric O_3 impacts on air quality, food security (Zunckel et al., 2006) and regional climate change (Fry et al., 2013). Therefore, the relative contributions of aromatic hydrocarbons to photochemical O_3 formation in air masses that had passed over the three source regions were examined. Several reactivity scales can be used to estimate O_3 formation for specific hydrocarbons. One method that determines the ability of aromatic hydrocarbons to produce O_3 entails calculating the product of the average concentration and the maximum incremental reactivity coefficient (MIR) of each compound, i.e. O_3 formation potential = VOC × MIR (Carter, 1994). The MIR scale has been used to assess O_3 formation potential for aromatic hydrocarbon in numerous previous studies (Hoque et al., 2008; Na et al., 2005; Grosjean et al., 1998).

The ranking of the aromatic hydrocarbon species according to air mass origin for O_3 formation potential is provided in Table 2. As indicated (Table 2), the highest contribution of aromatic hydrocarbon concentrations to O_3 formation potential were observed for plumes passing over Area I. The O_3 formation potential for air masses that had passed over Area II and the Regional Background was in the same order of magnitude. Based on the O_3 formation potential values, xylenes ((m, p)-xylene plus o-xylene) are the dominant contributor to O_3 formation for air masses that have passed over Area I, with 1,2,4-trimethylbenzene the second largest contributor. The O_3 formation potential of benzene was the lowest, even though it is considered to be the most hazardous species of the atmospheric aromatic hydrocarbons. As previously stated, the use of solvents (e.g. in paint) is thought to be a major non-traffic source of aromatic hydrocarbons, with toluene, ethylbenzene and o, m, p-xylene (TEX) making up the largest portion of solvents (Brocco et al., 1997). It was also shown that the ratio of TEX / total aromatic hydrocarbons followed a typical seasonal pattern demonstrating the contribution from solvents (Fig. 8) in all three source regions. From Table 2 it is evident that TEX contributes significantly to O_3 formation relative to the other species considered in this paper. The contribution of the evaporation of solvents to O_3 formation as a fraction of the overall aromatic hydrocarbons O_3 formation potential therefore seems to be significant.

4 Conclusions

The monthly median aromatic hydrocarbon concentrations at Welgegund ranged between 0.01 and 3.1 ppb. Benzene is the only VOC listed as a criteria pollutant in the NAAQS, and had an annual median of 0.13 ppb, which was well below the SA standard. Toluene was the most abundant aromatic hydrocarbon species, with an annual median concentration of 0.63 ppb.

No statistically significant differences in the concentrations of aromatic hydrocarbons measured during daytime and night-time were found, which indicated the lack of local sources. Additionally, no distinct seasonal patterns were observed for any of the species measured. The possible influence of air masses passing over different source regions on the concentration of these species was therefore explored. The Johannesburg–Pretoria megacity, the Vaal Triangle and the Mpumalanga Highveld were grouped together as Area I, while the western BIC, the eastern BIC and the anti-cyclonic source regions were grouped together as Area II. Lastly, the Regional

Background source region excluded any area with significant anthropogenic activities. Results indicated that the lack of well-defined seasonal cycles could be attributed to the origin of the air masses sampled. Aromatic hydrocarbon concentrations were in general significantly higher for air masses that passed over Area I, which is likely to be more polluted. Air masses that passed over Area II and the Regional Background had much lower aromatic hydrocarbon levels, and were of the same order.

Interspecies correlations indicated that all the aromatic hydrocarbons, except benzene, originated from similar sources in Area I. Benzene most likely originated from incomplete combustion sources in Area I. For Area II, benzene and toluene were found to originate from similar sources, while all the other aromatic hydrocarbons were emitted by related sources. In contrast to Area I, benzene did not originate from incomplete combustion sources in Area II. For air masses that had passed over the Regional Background, benzene and toluene were again linked, but the sources of the other aromatic hydrocarbon species were not necessarily linked.

Interspecies ratios showed that the highest aromatic hydrocarbon ratios were observed for plumes passing over Area I, whereas lower ratios were detected in plumes passing over Area II and the Regional Background. These ratios indicate the influence of anthropogenic activities in especially Area I and also the closer proximity of especially the Johannesburg–Pretoria megacity in Area I to the Welgegund monitoring station, i.e. less aged plumes.

The concentration ratios of TEX / total aromatics for air masses that had passed over the three sources regions indicated a seasonal pattern with the maximum values in summer and minimum in winter. Aromatic hydrocarbons originating from solvents, which are expected to be higher in the heat of summer, therefore make a significant contribution to the total aromatic hydrocarbons in air masses that pass over all three source regions.

The highest contributions of aromatic hydrocarbon concentrations to O_3 formation potential were observed for plumes passing over Area I, with air masses that had passed over Area II and the Regional Background in the same order of magnitude.

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Xylenes ((m, p)-xylene plus o-xylene) were the dominant contributor to O_3 formation for air masses that have passed over Area I, with 1,2,4-trimethylbenzene being the second largest contributor. The O_3 formation potential of benzene was the lowest.

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Table 1. The aromatic hydrocarbon ratios for the specific source regions.

	Area I	Area II	Regional Background	Automotive exhaust
toluene/benzene	6.51	2.38	2.66	2.7[a]
(m, p)-xylene/benzene	7.31	1.97	2.05	1.8[b]
o-xylene/benzene	2.84	0.76	0.85	0.9[c]
ethylbenzene/benzene	2.87	0.89	0.93	
1,3,5-TMB/benzene	1.27	0.15	0.13	
styrene/benzene	5.66	2.23	2.44	
propylbenzene/benzene	0.62	0.07	0.07	
(m, p)-xylene/ethylbenzene	2.55	2.20	2.19	
o-xylene/ethylbenzene	0.99	0.85	0.91	

[a] Brocco et al., 1997; Guicherit, 1997;
[b] Stevenson et al., 1997;
[c] Guicherit, 1997

Table 2. Ozone formation potential of the aromatic hydrocarbon concentrations of air masses passing over the three source regions.

	Area I			Area II		Regional Background	
	Mean	MIR coefficient	O_3 formation potential	Mean	O_3 formation potential	Mean	O_3 formation potential
benzene	0.228	0.42	0.096	0.335	0.141	0.299	0.125
toluene	1.482	2.70	4.001	0.796	2.148	0.796	2.148
ethylbenzene	0.653	2.70	1.762	0.300	0.809	0.279	0.753
(m, p)-xylene	1.665	8.20	13.653	0.661	5.418	0.612	5.014
styrene	1.288	2.20	2.834	0.746	1.641	0.730	1.607
o-xylene	0.647	6.50	4.208	0.254	1.651	0.253	1.645
propylbenzene	0.142	2.10	0.298	0.025	0.053	0.021	0.043
1,3,5-TMB	0.289	10.10	2.916	0.051	0.512	0.038	0.381
1,2,4-TMB	1.073	8.80	9.444	0.196	1.728	0.146	1.289
1,2,3-TMB	0.518	8.90	4.608	0.101	0.900	0.076	0.674

Note: TMB = trimethylbenzene

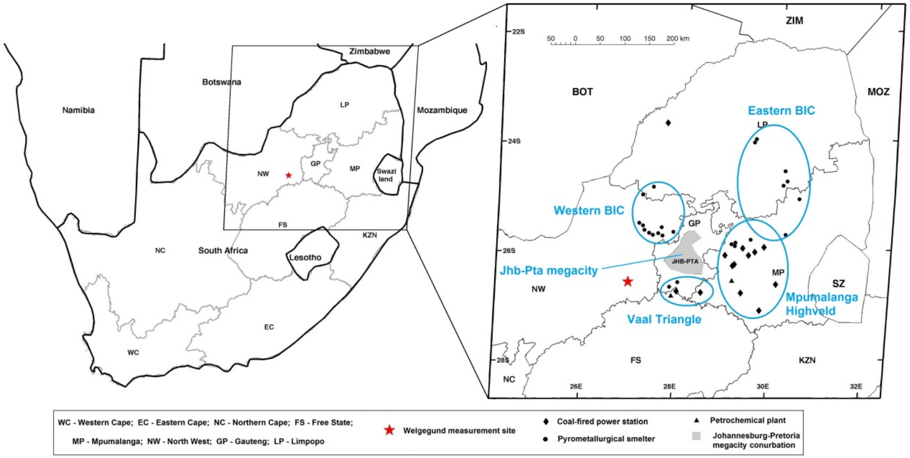

Fig. 1. Southern African map, indicating the location of the Welgegund measurement station, large point sources in the industrial hub of South Africa and anthropogenic source regions impacting Welgegund.

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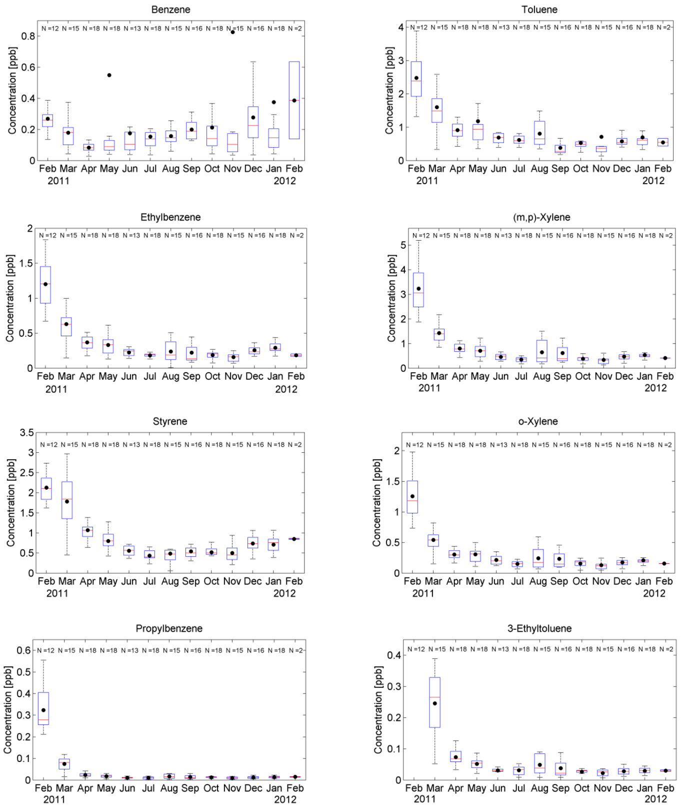

Fig. 2a. Monthly annual variation of aromatic hydrocarbon concentrations measured during the one-year sampling period. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ±2.7σ or 99.3 % coverage, if the data has a normal distribution (MATLAB, 2010). The values displayed near the top of the graphs indicate the number of samples (N) analysed for each month.

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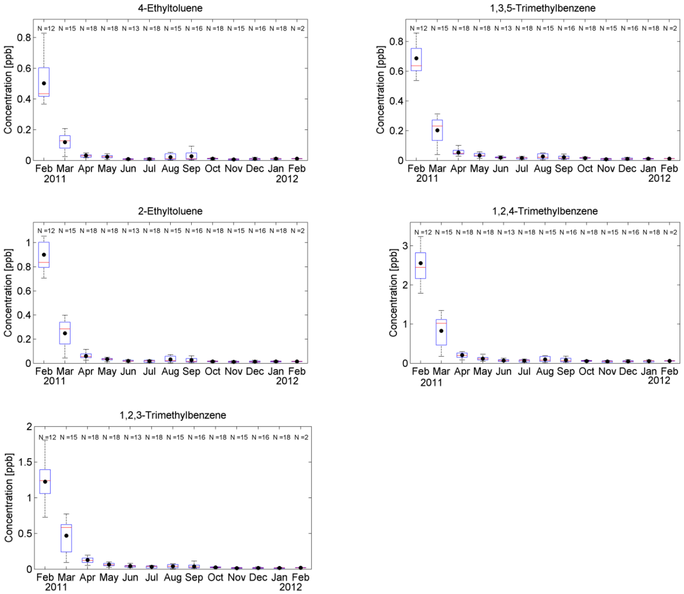

Fig. 2b. Continued.

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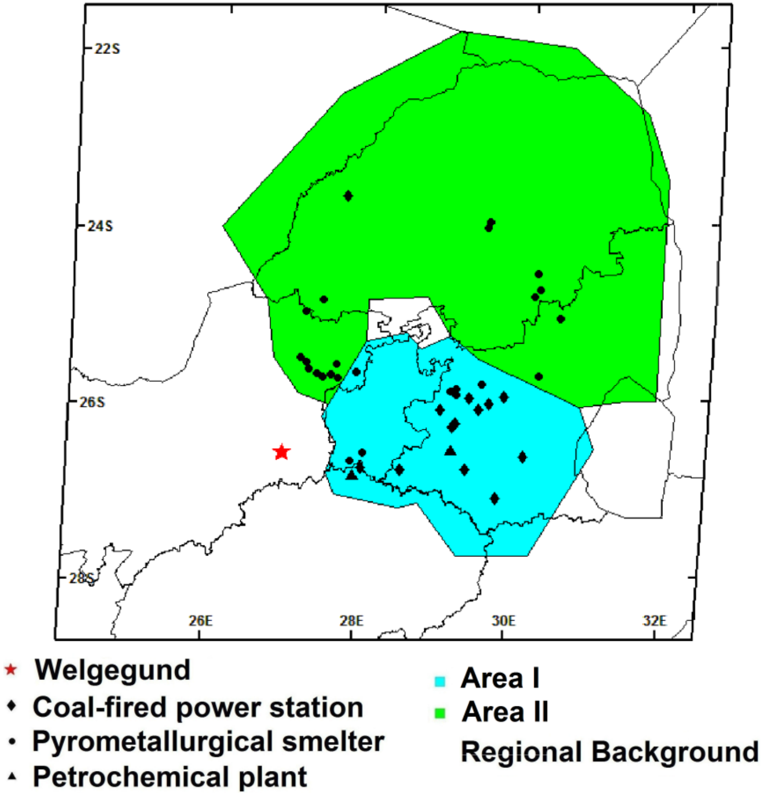
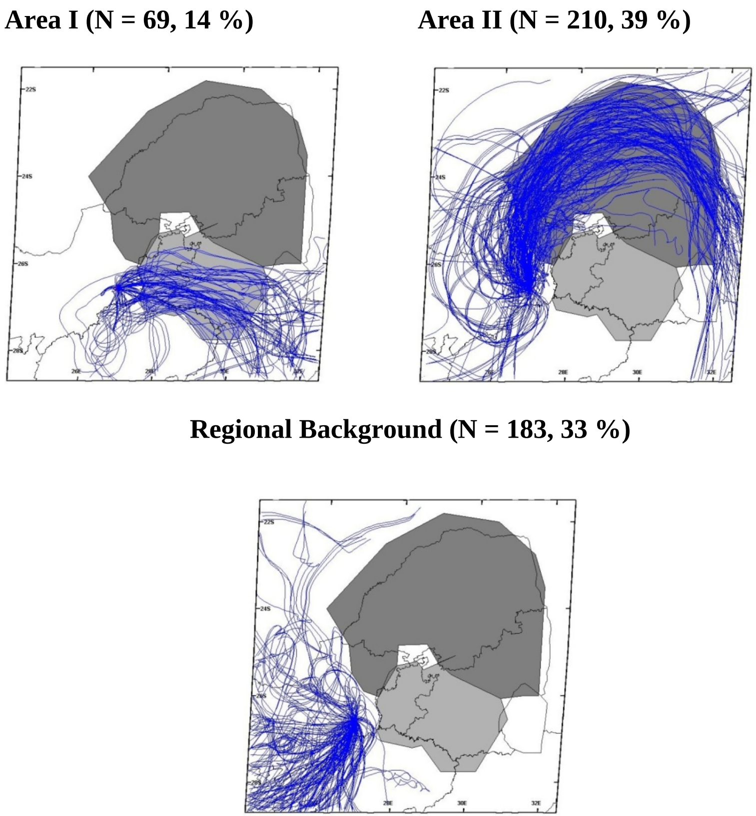


Fig. 3. Map of the north-eastern part of South Africa indicating the location of the Welgegund measurement station, large point sources in the industrial hub of South Africa and the source regions defined in this study.


Area I (N = 69, 14 %)

Area II (N = 210, 39 %)

Regional Background (N = 183, 33 %)

Fig. 4. Graphical representations of back trajectories allocated as passing over the defined source regions. The percentage of the trajectories allocated as passing over a specific source region and the number of trajectories it represents are provided in brackets.

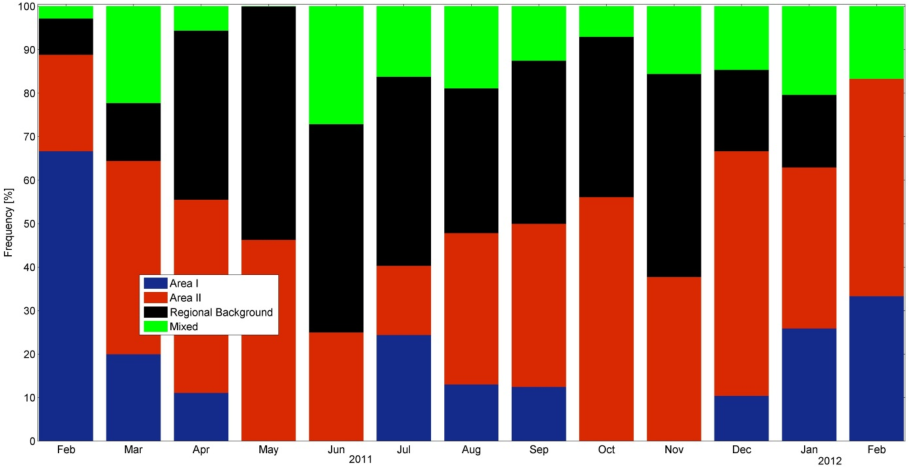


Fig. 5. Monthly fractional distribution of VOC samples allocated according to air mass back trajectory sets after passing over the defined source regions.

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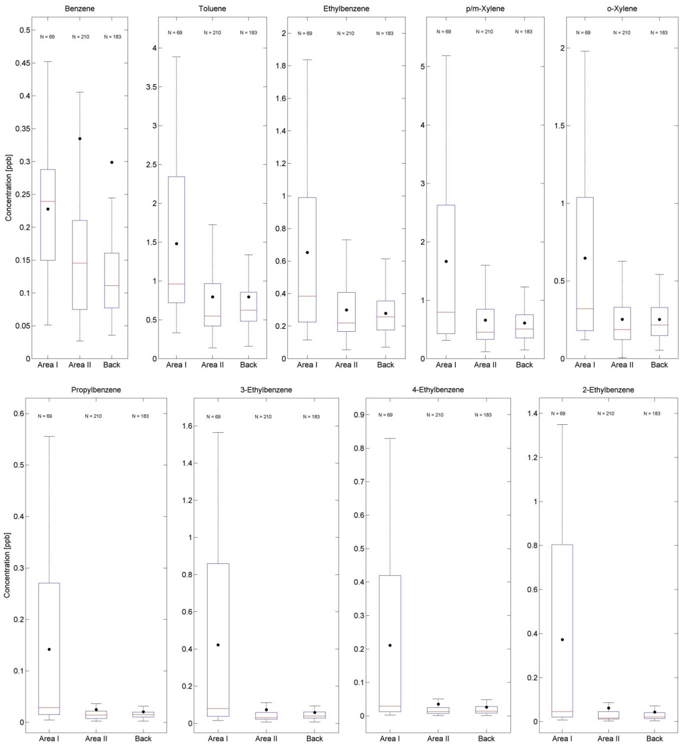

Fig. 6a. BTEX concentrations measured in air masses arriving at Welgegund, after they had passed over the defined source regions. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ±2.7σ or 99.3 % coverage, if the data has a normal distribution (MATLAB, 2010). The values displayed near the top of the graphs indicate the number of samples (N) analysed for each source area.

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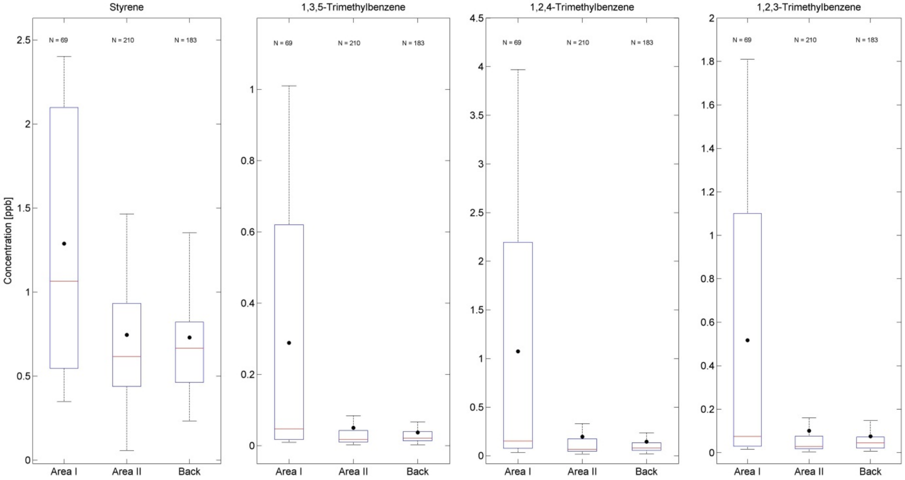
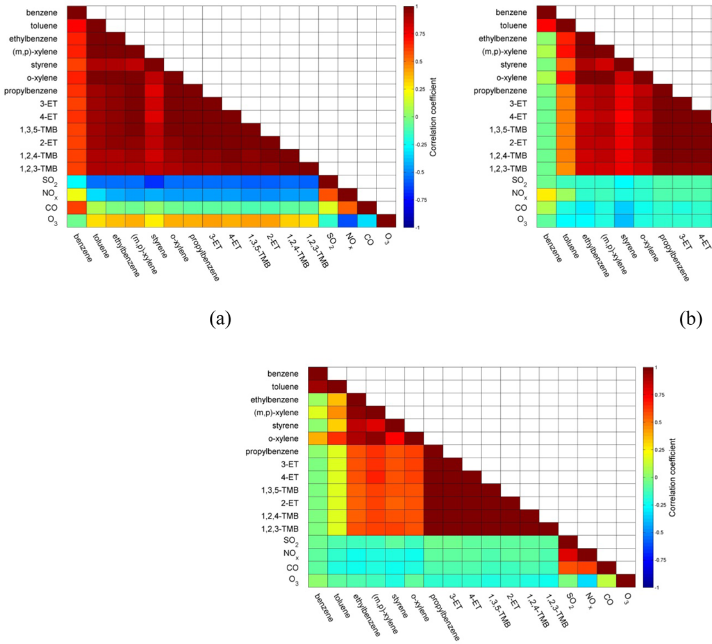


Fig. 6b. Continued.



(a)

(b)

(c)

Fig. 7. Correlation analysis for aromatic hydrocarbons with one another and with inorganic trace gases, in samples that were collected when back trajectory sets had passed over Area I **(a)**, Area II **(b)** and the Regional Background **(c)**.

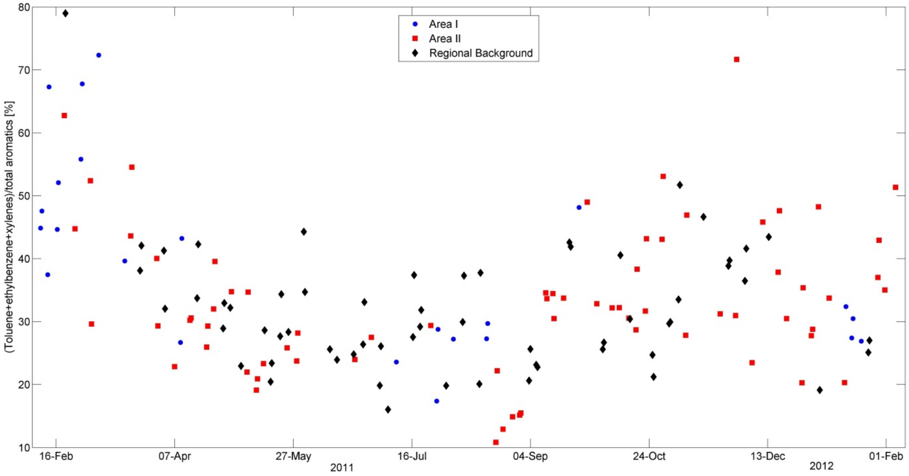


Fig. 8. Temporal variation of the concentration ratios of the sum of toluene, ethylbenzene and xylenes (TEX) to total aromatics from air masses arriving at Welgegund after passing over the three source regions.