Temporal assessment of volatile organic compounds at a site with high atmospheric variability in the North-West Province

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Abstract

Volatile organic compounds (VOCs) are emitted into the atmosphere from biogenic and anthropogenic sources with atmospheric lifetimes ranging from minutes to months, depending on the specific VOC compound considered. It is estimated that biogenic VOCs (BVOCs) (e.g. isoprenes, terpenes) make up 90% of the global atmospheric VOC budget. However, in highly industrialised regions, anthropogenic VOCs (e.g. benzene, toluene, ethylbenzene and xylene, combined abbreviated as BTEX) might dominate. VOCs have various reversible and irreversible effects on human health. They also have environmental impacts that range from changes in the population of terrestrial and aquatic ecosystems to the extinction of vulnerable species. VOCs are precursors for the formation of ozone (O_3) during solar radiation initiated reactions in the presence of NO_x. Tropospheric O_3 is considered a pollutant, with negative impacts on human health, ecosystems and food security. O_3 is also a short-lived greenhouse gas. Through reactions with radical species, VOCs lead to the formation of higher molecular weight organic compounds, which produce carbon monoxide (CO), peroxyacytyl nitrate (PAN) and ultimately secondary organic aerosol (SOA) particles. SOA particles impact directly on air quality and visibility, as well as directly and indirectly on the radiation balance of the earth that contributes to the regulation of climate.

Notwithstanding the importance of atmospheric VOCs, limited data is available for VOCs in South Africa. In this study, a comprehensive dataset of BVOC and anthropogenic VOC species was obtained at the Welgegund measurement station in the North West Province, South Africa. Measurements were conducted from 9 February 2011 to 4 February 2012. Samples were collected on Tenax-TA and Carbopack-B adsorption tubes twice a week for two hours during day time and two hours during night time. The first 1.25m of the stainless steel sampling inlet was heated to 120ºC to remove O_3 that could lead to sample degradation. Analyses of the sampled adsorption tubes were conducted by thermal desorption, cryo-focusing, re-desorption, followed by gas chromatography separation and analysis with a mass selective detector (GC-MS).

The results indicated that toluene was the most abundant aromatic hydrocarbon and heptane the most abundant alkane. Benzene is currently the only VOC listed as a criteria pollutant in the South African Air Quality Act with an annual average standard of 1.6ppb. The annual

median benzene concentration was 0.13 ppb, while the highest daily benzene concentration measured was 8.7 ppb. No distinct seasonal cycles were identified for anthropogenic VOC species measured, i.e. aromatic hydrocarbons and alkanes. However, air mass history analysis indicated that air masses that passed over the Mpumalanga Highveld, the Vaal Triangle and the Johannesburg-Pretoria conurbation (collectively referred to as Area I) had significantly higher concentrations of these anthropogenic VOCs compared to air masses that passed over the western and eastern Bushveld Igneous Complex, and a region over which air masses typically followed an anti-cyclonic movement pattern (collectively referred to as Area II). Anthropogenic VOC levels in air masses that passed over the regional background (areas with no large point sources) had levels similar to air masses that had passed over Area II. Relatively good interspecies correlations ($r > 0.8$) between most of the aromatic hydrocarbons in air masses that had passed over Area I, with the exception of benzene, indicated that these species had common sources. Benzene, however, correlated well with CO, indicating that sources associated with incomplete combustion were most likely the origin of benzene in air masses that had passed over Area I.

The interspecies concentration ratios for plumes passing over Area I indicated that this source region is relatively close to the Welgegund monitoring station and air masses that passed over this source region were substantially influenced by anthropogenic activities. The concentration ratios for plumes that passed over Area II and the Regional Background indicated that these were aged air masses. Furthermore, the concentration ratios of toluene, ethylbenzene and o,m,p-xylene (TEX) to the total aromatic concentration for air masses that passed over the various source regions showed a greater contribution to the total VOC concentration during periods of higher temperature, i.e. summer. This proved that the evaporation of solvents contributes significantly to VOC levels during the months with higher temperatures.

The relative contribution of aromatic hydrocarbons to photochemical O_3 formation in air masses that passed over the various source regions indicated the highest contribution was observed for air masses that passed over Area I, with Area II and the Regional Background in the same order of magnitude.

The annual temporal variations of the measured BVOCs indicated that 2-methyl-3-buten-2-ol (MBO) and isoprene exhibited distinct seasonal patterns, i.e. higher values in summer and lower values in winter. The monoterpenes (MT) and the sesquiterpenes (SQT) did not follow

distinct seasonal patterns. BVOC concentrations correlated relatively well to seasonal variations in temperature, photosynthetically active radiation (PAR), rainfall, relative humidity (RH) and CO_2 flux. This proved that biogenic activity is responsible for BVOCs emitted. The most abundant MT was α-pinene, while β-caryophyllene was the most abundant SQT with annual median concentrations of 0.468 ppb and 0.022 ppb, respectively. Pollution roses for isoprene showed a dominance of sources from the north-west to the north-east, as well as the south-east. These directions correlated to areas where pockets of the savannah biome are located.

Keywords: Volatile organic compounds (VOCs), aromatic hydrocarbons, biogenic VOCs, BTEX, Welgegund

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