

Supplementary Material

to the manuscript entitled

PM_{2.5}, soot and geographical origin of air masses in Cape Town, South Africa

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Supplementary text

S1. Inductively coupled plasma-optical emission spectrometry

A Varian 710-ES inductively coupled plasma-optical emission spectrometer was used to determine the concentrations of the selected elements in composite samples. The 710-ES has a wavelength range of 177-785 nm and low detection limits ($1 \mu\text{g.L}^{-1}$).

Standard and control solutions were prepared in 100 mL volumetric flasks. Volumetric flasks were cleaned by rinsing three times with Milli-Q water. Elemental extraction was performed in 100 mL beakers. Five beakers were cleaned with a dilute solution of nitric acid (HNO_3 , 5 wt. %). 250 mL of the HNO_3 solution was prepared by transferring 90-100 mL of Milli-Q water to a clean 250 mL volumetric flask then adding 14 mL of 69% HNO_3 (Merck Millipore, part number: 1018322500, lot: 1041704) before making up to the mark with Milli-Q water. 40-50 mL of the acid solution was added to the beakers and boiled for 10 minutes on a hotplate. After 10 minutes, the beakers were removed and allowed to cool to ambient temperature. Once cooled, the residual acid solutions were discarded and beakers rinsed three times with Milli-Q water.

Three working standards and a control (or check standard) were prepared using Custom multi-element standard solution 1586 (part number: VHG-ZLGC-1586-500), 1000 mg.L^{-1} sodium (Na^+) standard (part number: VHG-INAW1K-500) and 1000 mg.L^{-1} calcium (Ca^{2+}) standard (part number: VHG-ICAW1K-500) manufactured by VHG Labs. Standard solution 1586 contained 24 elements in a 5 wt. % HNO_3 /0.2 wt. % hydrofluoric acid (HF) matrix. Metal concentrations in the standard solution are shown in the table below.

Table S1: Composition of VHG Labs multi-element standard solution 1586

Element	Concentration	Element	Concentration	Element	Concentration
	n		n		n
Al	100	Cu	100	P	100
As	100	Fe	100	K	1000
Ba	100	Pb	100	Si	100
Be	100	Li	100	Sr	100
B	100	Mg	100	Ti	100
Cd	100	Mn	100	V	100
Cr	100	Mo	100	Zn	100
Co	100	Ni	100		

Working standards were prepared by pipetting 2.0, 5.0 and 10 mL of standard solution 1586 (lot: 10059633-1), 1.0, 2.5 and 5.0 mL of 1000 mg.L^{-1} Ca^{2+} (lot: 73924) and 1.0, 2.5 and 5.0 mL of Na^+ (lot: 30701264) standards into three 100 mL volumetric flasks, and making up to the mark with Milli-Q water. A control solution was prepared by pipetting 2.0 mL of standard solution 1586 (lot: 10059633-2) and 1.0 mL of the 1000 mg.L^{-1} Ca^{2+} (lot: 73925) and Na^+ (lot: 30701265) into a fourth 100 mL volumetric flask, and making up to the mark with Milli-Q water. Solution preservation was not performed because analysis was carried out immediately.

Hot acid extraction using a mixture of dilute nitric acid and hydrochloric acid (or aqua regia) (3 wt. % HNO₃/8 wt. % HCl) as per EPA Compendium Method IO-3.1 (1999) was used to extract metals from samples. 100 mL of aqua regia was prepared by transferring 40-50 mL of Milli-Q water to a clean 100 mL volumetric flask then adding 3.5 mL of 69% HNO₃ and 22 mL of 32 % HCl (Kimix, part number: n/a, lot: NO6244980) before making up to the mark with Milli-Q water. Four composite samples and blank filter were cut into two halves with a scalpel. One half of each sample was placed exposed side face-down into four separate beakers containing 15 mL of aqua regia (blank was placed in a fifth beaker). The beakers were covered with watch glasses and acid solutions refluxed for 15 minutes (at 120-130 °C) using a hotplate. After 15 minutes, the beakers were removed and allowed to cool to ambient temperature. Once cooled, 10 mL of each solution was decanted into five 15 mL centrifuge tubes. Sample preservation was not performed because samples were analysed immediately.

Pre-analysis checks were done on specific components to ensure that they were clean and ‘fit-for-use’ prior to analysis. These checks were important because of the number of samples analysed on a weekly basis and sensitivity of the instrument.

Instrument operations were performed in accordance with procedure *Elemental analysis using the Varian 710-ES Inductively Coupled-Plasma Optical Emission Spectrometer* (compiled by the ENS group) using ICP Expert II software. Three optimisation steps were carried out during instrument setup: torch alignment, drift and select wavelength (λ) intensity calibrations. Torch alignment was done using a 5.0 mg.L⁻¹ Mn solution. The intensity was > 300,000 counts (expected). Instrument drift was checked with Milli-Q water and was acceptable (if drift is erratic, check the torch). Finally, selective λ intensity calibration was done using the 5.0 mg.L⁻¹ working standard solution (if intensities are too low, calibration will abort. Check gas supply and repeat). When setup was complete, the instrument was standardised. The operating conditions of the spectrometer are shown in the table below.

Table S2: 710-ES operating conditions

Condition	Unit	Value
Ar pressure	kPa	550 (\pm 50)
RF power	kW	1.2
Nebuliser pressure	kPa	200
Plasma gas flow rate	L.min ⁻¹	15
Auxillary gas flow rate	L.min ⁻¹	1.2
Pump speed	rpm	6
Replicate read time	s	5
Sample delay time	s	45
Stabilisation time	s	15
Rinse time	s	30

Working standards, control and samples were analysed in triplicate without background correction. The sample introduction needle was rinsed with dilute HNO₃ (2 wt. %) and Milli-Q water between acquisitions to prevent cross-contamination between samples. Linear and quadratic standardisation equations were used when the concentration of the highest standard

was $\leq 10 \text{ mg.L}^{-1}$ and $> 10 \text{ mg.L}^{-1}$ respectively (see the table below). Standard deviation $< 3 \%$ was considered acceptable (if $\geq 3 \%$, results were nullified and samples rechecked).

Table S3: Elements, emission wavelengths and standardisation equations

Element	Emission λ	Standardisation equation	Element	Emission λ	Standardisation equation
Al	394.4	Linear	Mg	280.3	Linear
As	193.7	Linear	Mn	257.6	Linear
Be	313.0	Linear	Mo	202.0	Linear
Cd	214.4	Linear	Ni	221.6	Linear
Ca	315.9	Quadratic	P	213.6	Linear
Cr	267.7	Linear	K	769.9	Quadratic
Co	238.9	Linear	Si	250.7	Linear
Cu	327.4	Linear	Na	568.3	Quadratic
Fe	238.2	Linear	Sr	407.8	Linear
Pb	220.4	Linear	Ti	336.1	Linear
Li	670.8	Linear	Zn	213.9	Linear

If the concentration of an element in the control (first check) deviated by 30 % or more from the expected value, sample analysis was aborted and standardisation repeated. If the problem persisted, the instrument was shut down and further actions taken. If the concentration of an element in the control (second check) deviated by 30 % or more, the result (of that particular element) was nullified and sequence repeated. The control values of all elements tested were within acceptable limits.

S2. Ion chromatography

A Dionex ICS-1600 ion chromatograph was used to determine the concentrations of the selected anions in composite samples. The ICS-1600 is designed for solid IC performance and ease-of-use with electrolytic suppression and front panel control.

Working standards, control and eluent solutions were prepared in volumetric flasks. Volumetric flasks were cleaned by rinsing three times with Milli-Q water. Extraction of anions from samples was performed in 100 mL beakers. Like the volumetric flasks, beakers were cleaned by rinsing with Milli-Q water three times. Milli-Q rinsing was preferred to chemical cleaning to prevent unwanted contamination. Dedicated glassware was used so there was no need for a chemical cleaning regime.

Three working standards and a control were prepared using anion calibration standard 59 (part number: IV-STOCK-59) manufactured by Inorganic Ventures Incorporated. The calibration standard contained seven anion species in a water matrix. Anion concentrations in the calibration standard are shown in the table below.

Fig. 3.15: Dionex ICS-1600 High-Performance Liquid Chromatograph (left) and schematic representation of the anion analysis process [Images: own (left) and Thermo Scientific (right)]

Table S4: Composition of Inorganic Ventures anion calibration standard 59

Anion	Concentration (mg.L ⁻¹)	Anion	Concentration (mg.L ⁻¹)
Br ⁻	1000	NO ₂ ⁻	1000
Cl ⁻	1000	PO ₄ ³⁻	1000
F ⁻	1000	SO ₄ ²⁻	1000
NO ₃ ⁻	1000		

2, 5 and 10 mg.L⁻¹ working standards were prepared by pipetting 0.2, 0.5 and 1 mL of calibration standard (lot: H2-MEB537138) into three dedicated 100 mL volumetric flasks, and making up to the mark with Milli-Q water. A 5 mg.L⁻¹ control was prepared by pipetting 0.5 mL of calibration standard (lot: H2-MEB537139) into a fourth 100 mL volumetric flask, and making up to the mark with Milli-Q water. Because standards and control solutions were prepared 10 minutes before analysis, preservation was not required.

Warm water extraction as proposed by D. Jenke (1983) was used to extract anions from samples. 1 cm² sub-samples were cut from the remaining halves of the four composite samples and blank filter (see section 3.2.2.3.4) with a scalpel. With flat-nosed tweezers, the sub-samples were placed into five separate 100 mL beakers containing 15 mL of Milli-Q water (pre-heated to 50-60 °C). Each beaker was covered with a watch glass. D. Jenke (1983) indicated that 15 minutes of sonicating was sufficient. Because of the unavailability of an ultrasonic bath, the heated solutions were agitated (by swirling) for 15 minutes whilst maintaining temperatures between 50-60 °C. After 15 minutes, the beakers were allowed to cool to ambient temperature. Once cooled, 10 mL of each solution was transferred to five separate 15 mL centrifuge tubes. Chemical preservation was not performed to prevent contaminant ingress, instead, samples were refrigerated overnight at 4-6 °C.

2.0 L of sodium carbonate/sodium bicarbonate eluent (4.5 mM Na₂CO₃/1.4 mM NaHCO₃) was prepared by pipetting 20 mL of Na₂CO₃ (0.45 M)/NaHCO₃ (0.14 M) AS22 eluent concentrate (Thermo Scientific, part number: 063965, lot: 170512) into 700-800 mL of Milli-Q water and stirring well before making up to the mark in a 2.0 L volumetric flask.

Tubing and connectors were checked for leaks before start-up. Once checks were completed, the instrument was primed. Priming is a process of manually expelling trapped gases that can alter the conductivity of an eluent thus impacting retention times. Once priming was completed, the priming valve was shut and the instrument started-up. It took approximately 30-45 minutes for the instrument to stabilise with a baseline conductivity of < 0.1 µS.cm⁻¹.

Instrument operations were performed in accordance with procedure *Anion analysis using the Dionex ICS-1600 Ion Chromatograph* (compiled by the ENS group) using Chromeleon software. The operating conditions of the chromatograph are shown in the table below.

Table S5: ICS-1600 operating conditions

Condition	Unit	Value
Pump pressure	kPa	13,700 (\pm 500)
Suppressor current	mA	50
Column heater temperature	$^{\circ}$ C	35
Eluent flow rate	mL.min ⁻¹	1.2
Sample volume	μ l	25
Sample run time	s	900
Rinse time	s	60

Samples were injected into the chromatograph by an autosampler (Dionex AS-DV). An Dionex AS22 separator column was installed. A Milli-Q water rinse step of the sample introduction, between acquisitions, prevented cross-contamination between samples. Linear standardisation equations were used (see the table below). Standard deviation < 3 % was considered acceptable (if \geq 3 %, results were nullified and samples rechecked).

Table S6: Anions, retention times and standardisation equations

Anion	Retention time (minutes)	Standardisation equation	Anion	Retention time (minutes)	Standardisation equation
F ⁻	2.38	Linear	NO ₃ ⁻	5.09	Linear
Cl ⁻	3.30	Linear	PO ₄ ³⁻	6.93	Linear
NO ₂ ⁻	3.91	Linear	SO ₄ ²⁻	7.88	Linear
Br ⁻	4.57	Linear			

The same acceptance criteria (applicable to ICP-OES) applied to IC. If the concentration of an anion in the control (first check) deviated by 30 % or more from the expected value, sample analysis was aborted and standardisation repeated. If the problem persisted, the instrument was shut down and further actions taken. If the concentration of an element in the control (second check) deviated by 30 % or more, the result (of that particular anion) was nullified and sequence repeated. The control values of all anions tested were within acceptable limits

S3. Selecting City of Cape Town ambient air quality monitoring (AAQM) stations for correlation purposes

Six AAQM stations were selected to provide adequate coverage around the study site (Kraaifontein). These were (latitude, longitude):

- Atlantis (-33.5623, 18.4805)
- City Hall (-33.9251, 18.4237)
- Goodwood (-33.9024, 18.5651)
- Somerset-West (-34.0774, 18.8318)
- Tableview (-33,8196, 18.5143)

- Wallacedene (-33.8570, 18.7259)

The AAQM stations at Wallacedene, Goodwood, Tableview, City Hall and Somerset-West are within a 30 km radius of the study site in Kraaifontein. The PM₁₀, NO₂, SO₂, O₃ data collected at these five monitoring sites were used to indicate potential local sources of ambient PM within a 30 km radius of the study site.

Atlantis is situated between the study site and Saldanha and would have given an indication of overall contribution by ore refineries.

Wallacedene (3 km from the study site) was the only station that monitored PM₁₀. The station gave an indication of overall contribution by dwellers and other sources east of the site.

City Hall (27 km), Goodwood (14 km), Tableview (18 km) and Wallacedene stations had monitored for NO₂. Wallacedene had insufficient data hence overall contribution by sources east of the study site could not be determined. The stations at City Hall, Goodwood and Tableview would have given an indication of overall contribution by sources west of the site

Atlantis (37 km), City Hall, Goodwood, Somerset-West (29 km), Tableview and Wallacedene stations had monitored for SO₂. Overall contribution by local sources to the north of the study site could not be determined because Atlantis station was “out-of-bounds”. City Hall and Tableview stations would have given an indication of overall contribution by sources west of the site (Goodwood had insufficient data). Somerset-West and Wallacedene stations would have given an indication of overall contribution by sources south and east of the site respectively.

Atlantis Goodwood and Wallacedene stations had monitored for O₃. As mentioned before, overall contribution by local sources to the north of the study site could not be determined because Atlantis station was “out-of-bounds”. Goodwood station would have given an indication of overall contribution by sources west of the site while Wallacedene station would have given an indication of overall contribution by sources east of the site.

The station at Atlantis (37 km NNW of the study site) provided data for the north. This station monitored for two air pollutants: O₃ and SO₂. Atlantis was situated between the study site and Saldanha, correlation between study data and data collected by this station would have given an indication of overall contribution by ore refineries to PM_{2.5} collected in filter samples. O₃ is regarded as the most important indicator of photochemical air pollution but because O₃ data had fluctuated considerably and to determine the impact of sources NNW of the study site stability of data was important hence SO₂ was selected for correlation purposes. Besides being the most abundant air pollutant, SO₂ data was far more stable than that of O₃. SO₂ is a known by-product of the refining processes.

O₃ is a strong oxidising agent that oxidises air pollutants nitrogen dioxide (NO₂) and SO₂ into nitrates (NO₃⁻) and sulphates (SO₄²⁻), two major chemical constituents of PM. These chemical reactions deplete O₃ in the atmosphere thus correlations between itself and PM_{2.5} concentrations and absorption coefficients should be negative.

The five remaining stations were all within a 30 km radius of the study site thus any correlation with data collected by these stations was considered local source contribution: Wallacedene (3 km ESE of the study site), Goodwood (14 km WSW of the study site), Tableview (18 km WNW of the site), City Hall (27 km WSW of the site) and Somerset-West (29 km SSE of the site).

Correlation between study data and data collected by AAQM stations was important for determining the effects of long-range transport on PM_{2.5} collected in filter samples. Air quality information was used to determine potential sources of ambient PM in the region. O₃ is an atmospheric gas and strong oxidising agent but the pollutant of interest was SO₂. O₃ is regarded as the most important indicator of photochemical air pollution but because O₃ data had fluctuated considerably and to determine the impact of sources NNW of the study site stability of data was important hence SO₂ was selected for correlation purposes. SO₂ is a known by-product of the refining processes. Because Atlantis was situated between the study site and Saldanha, correlation between study data and data collected by this station would have given an indication of overall contribution by ore refineries to PM_{2.5} collected in filter samples.

S4. 24-hour air pollution the levels measured by City of Cape Town

The mean PM₁₀ level measured at the Wallacedene AAQM station (3 km from PM_{2.5} sampling site) for the 1-year study period was 36.4 µg.m⁻³, which was below the yearly SA NAAQS (40 µg.m⁻³) (Department of Environmental Affairs, 2005), but exceeded the yearly WHO air quality guideline (20 µg.m⁻³) nearly two-fold (World Health Organization, 2005) (Table S7). The PM₁₀ levels exceeded the daily WHO air quality guideline (50 µg.m⁻³) on 22 of the 121 days; mostly in autumn and winter (World Health Organization, 2005). The PM₁₀ levels exceeded the daily SA NAAQS (75 µg.m⁻³) on 2 days in autumn and winter (Department of Environmental Affairs, 2005). These exceedances indicate that the population of Cape Town may experience various health outcomes due to outdoor PM₁₀ exposure, as indicated previously, although the mean PM₁₀ level measured at the Wallacedene AAQM station was lower than the mean in 598 cities in 24 countries (56.0 µg.m⁻³) (Lui et al 2019). The PM_{2.5}:PM₁₀ ratio in this study is 0.38, which is similar to that of the Pretoria study site (0.32) reported by Snider et al. (2016). The ratios of the other study locations reported by Snider et al. (2016) ranged from 0.39 to 0.69 with a mean of 0.50.

The mean NO₂ levels fluctuated from 2.9 µg.m⁻³ at the Somerset West AAQM station (37 km from PM_{2.5} sampling site) to 28.9 µg.m⁻³ at the City Hall AAQM station (27 km away), which were lower than the mean in 652 cities in 24 countries (30.4 µg.m⁻³) (Lui et al 2019). (Table S7). The NO₂ levels did not exceed the yearly SA NAAQS (40 µg.m⁻³) nor the yearly WHO air quality guideline (40 µg.m⁻³) (Department of Environmental Affairs, 2005; World Health Organization, 2005). There is no daily SA NAAQS or WHO air quality guideline for NO₂. NO₂ is a precursor for nitrate, which has been reported to increase mortality (Atkinson et al. 2015). The World Health Organization published in 2013 the Review of Evidence on Health Aspects of Air Pollution (REVIHAAP) report (World Health Organization, 2013). The REVIHAAP report concluded that health effects reported in numerous epidemiological studies were observed when PM₁₀, NO₂, SO₂ and ground-level O₃ levels were below the WHO air quality guidelines, hence the need to update the 2005 World Health Organization air quality guidelines.

The mean SO₂ levels varied from 3.2 µg.m⁻³ at the Somerset West AAQM station to 9.7 µg.m⁻³ at the Goodwood AAQM station (14 km away), which were lower than the mean (20.2 µg.m⁻³) reported by Lui et al 2019 (Table S7). The SO₂ levels did not exceed the daily SA NAAQS (125 µg.m⁻³) (Department of Environmental Affairs, 2005). The SO₂ levels never exceeded the

daily SA NAAQS ($50 \mu\text{g}\cdot\text{m}^{-3}$) nor the daily WHO air quality guideline ($20 \mu\text{g}\cdot\text{m}^{-3}$) (World Health Organization, 2005)). There is no yearly WHO air quality guideline for SO_2 . SO_2 is a precursor for sulphate, which lead to an increase mortality (Atkinson et al. 2015). Sulphate also leads to a substantial increase in the bioavailable metals and soot in $\text{PM}_{2.5}$ (World Health Organization, 2013).

The mean ground-level O_3 levels fluctuated from $27.1 \mu\text{g}\cdot\text{m}^{-3}$ at the Goodwood AAQM station to $48.6 \mu\text{g}\cdot\text{m}^{-3}$ at the Somerset West AAQM station, which were lower than the mean ($65.4 \mu\text{g}\cdot\text{m}^{-3}$) reported by Lui et al 2019. (Table S7). There is no daily or yearly SA NAAQS or WHO air quality guideline for ground-level O_3 (Department of Environmental Affairs, 2005; World Health Organization, 2005). The maximum 8-hour average WHO air quality guideline is $100 \mu\text{g}\cdot\text{m}^{-3}$.

The levels of PM_{10} , NO_2 , SO_2 and O_3 varied by the hour of the day and indicated possible sources (Figures S9 to S12).

The morning peak for PM_{10} recorded at the Wallacedene AAQM station on weekdays was more prominent in winter than in summer, which may be due to both traffic and biomass burning for space heating during winter (Figure S9). The morning peak for PM_{10} on weekends was also more prominent in winter than in summer, but the peak in summer was shifted later. This later peak may be due to residents leaving home later during weekends in summer, whilst in winter residents spend more time at home during weekends. The winter evening peaks on weekdays and weekends may be due to both traffic and biomass burning for space heating. The summer afternoon peaks on weekdays and weekends may also be due to both traffic and biomass burning for barbequing.

NO_2 levels at the Goodwood and Tableview AAQM stations had a morning and afternoon peak, which are most likely due to traffic (Figure S10). The City Hall AAQM station is located in the city centre of Cape Town with persistent traffic from morning to late evening. The NO_2 levels recorded at the City Hall AAQM increased from 5am and remained high throughout the day and decreased from 19:00 onwards.

The hourly SO_2 levels at Wallacedene and Tableview AAQM stations were higher than those at the City Hall, Somerset West and Atlantis AAQM stations (Figure S11). No clear morning or afternoon traffic peak was observed from the SO_2 levels recorded at the City Hall, Somerset West and Atlantis AAQM stations. The conversion of SO_2 to SO_4^{2-} is promoted by the coexistence of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), which may be an explanation for the lack of morning and afternoon peaks in the city centre of Cape Town as NO_x is generated continuously by the persistent traffic (He et al. 2014). A prominent SO_2 morning peak was observed at the Wallacedene AAQM station, which may be an indication of traffic. A possible reason for the absence of a clear SO_2 afternoon peak at Wallacedene AAQM station is that SO_2 is converted quicker to SO_4^{2-} during the afternoon when sunlight is brightest (He et al. 2014). A large oil refinery is located near the Tableview AAQM station (White et al. 2009). It is assumed that SO_2 emissions occur continuously throughout the day at the oil refinery, hence the persistent high SO_2 levels at the Tableview AAQM station. The afternoon dip in SO_2 levels detected at the Tableview AAQM station may be due to the conversion of SO_2 to SO_4^{2-} .

Ground-level O_3 is formed by a series of complex photochemical reactions between NO_x and volatile organic compounds in the presence of sunlight, hence the afternoon peaks observed at Atlantis and Goodwood AAQM stations (Figure S12). The highest O_3 levels are not always

found in city centres where the pollutants that form O₃ are emitted. When NO emitted by traffic is high, O₃ formation is inhibited. The hourly ground-level O₃ levels in the small town of Atlantis were as expected higher than those at the Goodwood AAQM station, located in Cape Town.

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S5. Correlation between 24-hour air pollutant levels and meteorological conditions

PM_{2.5} and temperature had a negative correlation in winter and spring, although insignificant (Table S9). In summer and autumn, the correlation between PM_{2.5} and temperature was positive, but still insignificant. Soot and temperature had a negative correlation in autumn and winter and a positive correlation in spring and summer, with only the latter being significant ($p < 0.05$) (Table S9). A possible reason for stronger correlations in colder climatic conditions may be that ammonium salts are then more frequent in tropospheric PM (Bencs et al. 2010). Relative humidity, wind speed and precipitation all had mostly negative correlations with PM_{2.5} and soot levels; with varying significance. Lui et al. (2019) reported that on average, the correlation coefficient between PM_{2.5} and temperature was -0.25 and -0.17 with relative humidity in 652 cities in 24 countries.

NO₂ and SO₂ had negative correlations with temperature during the 1-year study period (Table S11), as was the case with PM_{2.5} and soot (Table S9). In contrast, PM₁₀ and ground-level O₃ had positive correlations with temperature. As with PM_{2.5} and soot (Table S9), relative humidity, wind speed and precipitation had mostly negative correlations with PM₁₀, NO₂, SO₂ and O₃ levels (Table S11). Lui et al. (2019) reported that on average, the correlation coefficient between PM₁₀ and temperature was -0.23 and -0.21 with relative humidity.

References

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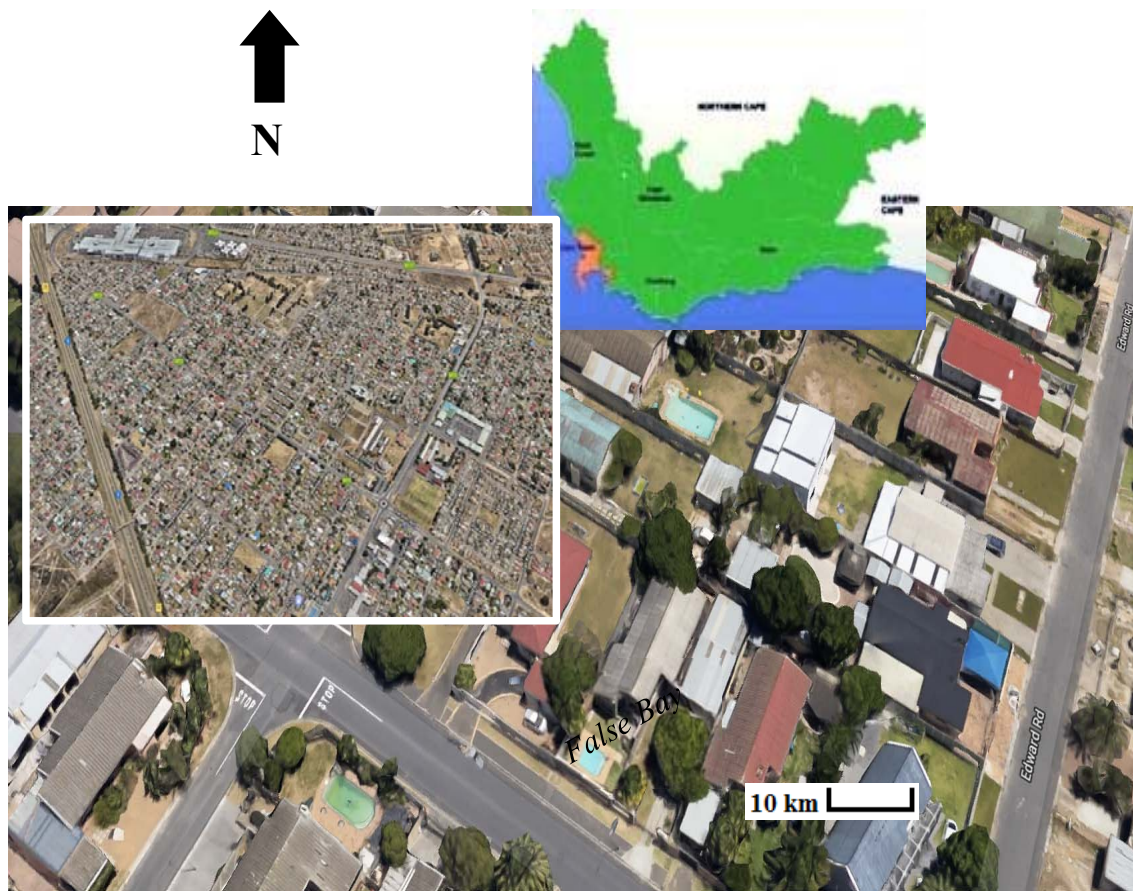


Figure S1 Location of the $PM_{2.5}$ sampling site. The sampling site (yellow arrow) was on the roof of a house in Kraaifontein, Cape Town, South Africa 3 m above ground level. An aerial photograph of the western parts of Kraaifontein (top-left) shows the proximity of the sampling site to the N1 freeway (pink marker) (Images: Google Maps).

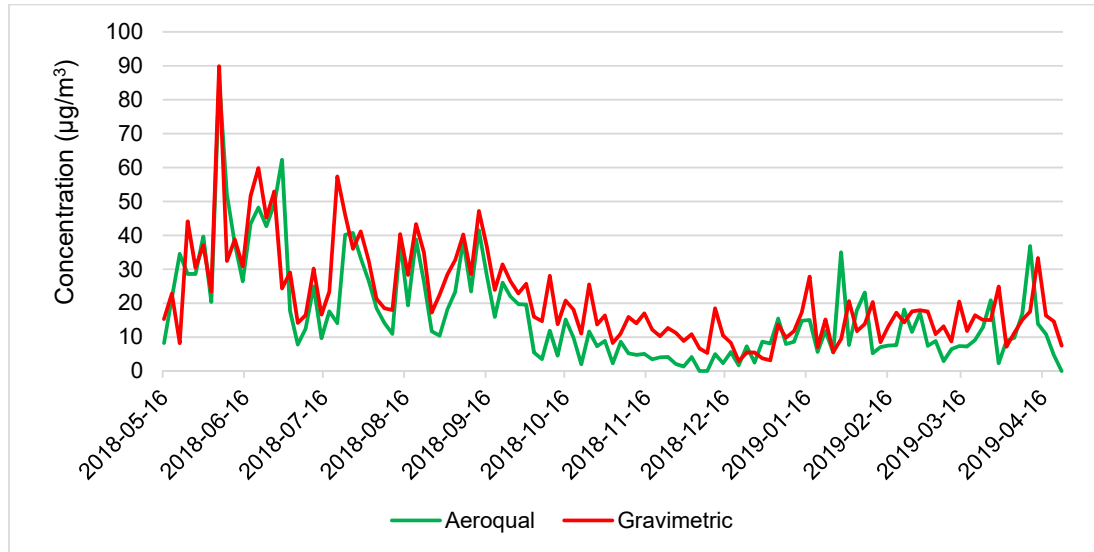


Figure S2 PM_{2.5} levels measured by the gravimetric filter-based methods and the online continuous sampling instrument (Aeroqual) at the School of Health Systems and Public Health, University of Pretoria during 16 May 2018 to 23 April 2019. (Source Mwase, 2020)

Mwase NS. Human health risks of inhalable exposure to PM_{2.5} Pretoria, South Africa. MSc (Epidemiology) dissertation. University of Pretoria. 2020

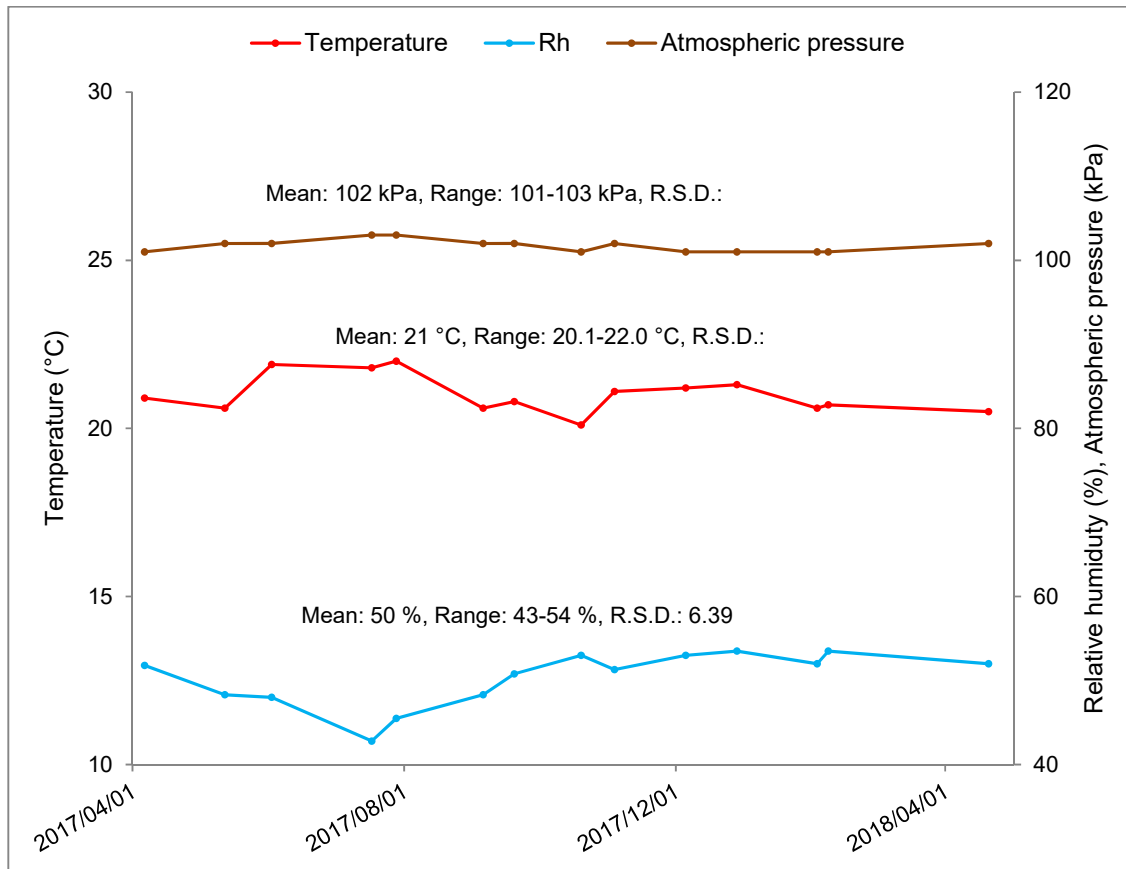


Figure S3 Weighing room laboratory conditions at the School of Health Systems and Public Health, University of Pretoria
R.S.D. is relative standard deviation

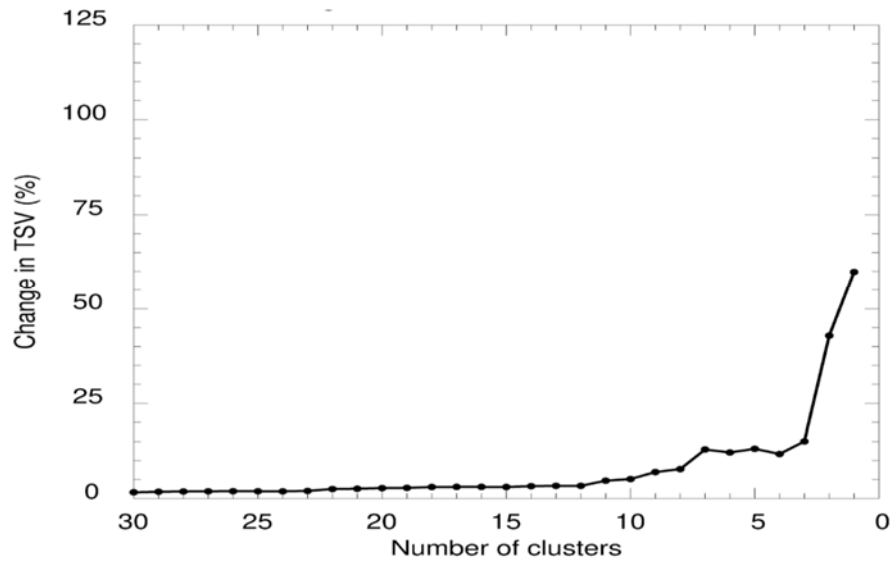


Figure S4 Total spatial variance (TSV) plot to determine the optimum number of pre-dominating transport clusters for the 1-year study period

The possible number of transport clusters (geographical origins of air masses) was 3, 4, 5 or 6. Refer to Figure S5.

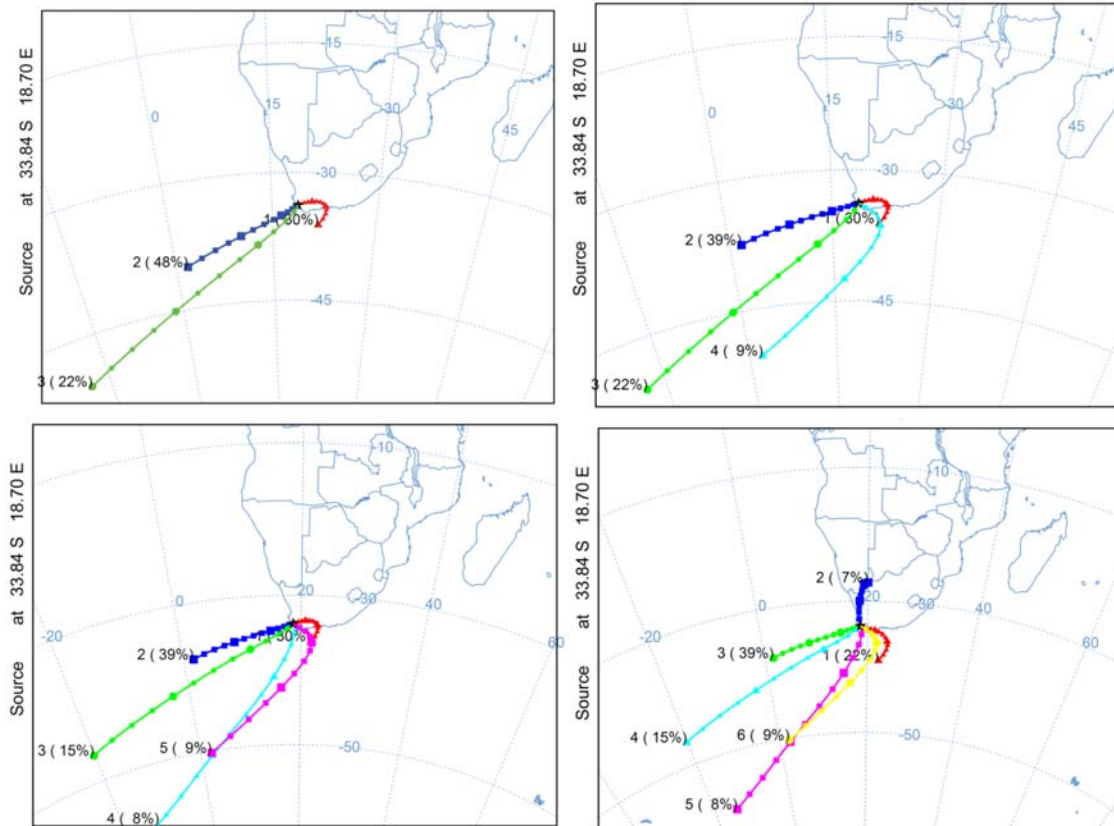


Figure S5 Number of potential geographical origins of air masses during April 2017 to April 2018 in Cape Town, South Africa

When the number was specified as 6 then clusters 5 and 6 did not separate. We selected the optimum number of transport clusters as 4.

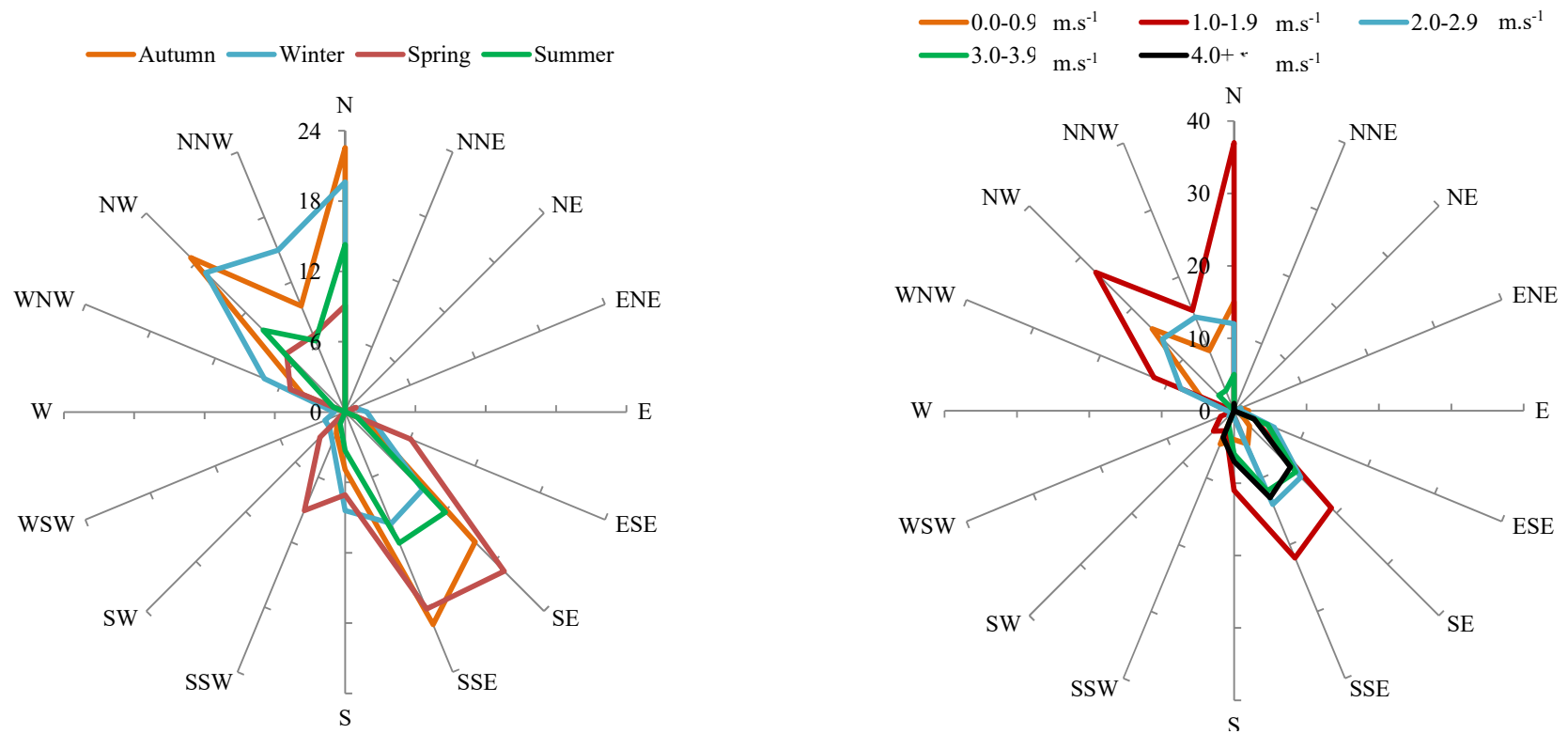


Figure S6 Seasonal wind frequency (left) and mean wind velocities (right) for the 1-year study period.

Autumn (16/04/2017 to 30/05/2017 and 01/03/2018 to 18/04/2018), winter (01/06/2017 to 31/08/2017), spring (01/09/2017 to 30/11/2017) and summer (01/12/2017 to 28/02/2018)

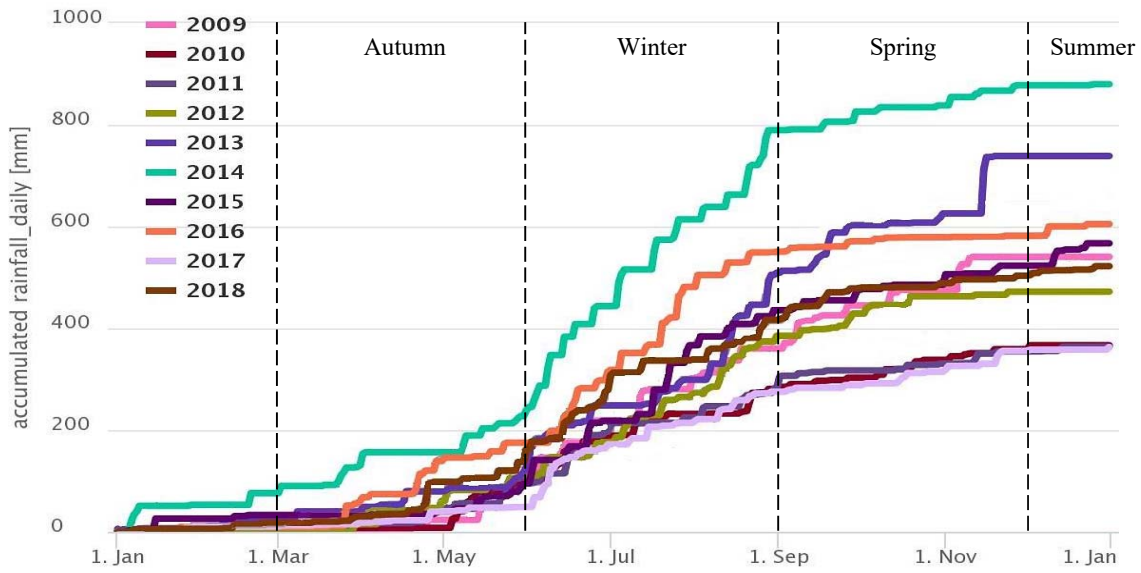


Figure S7 Accumulated rainfall for Cape Town for ten year period (2009-2018). Data generated by the City of Cape Town weather station in Tygerberg (approx. 11 km from the PM_{2.5} sampling site in Kraaifontein, Cape Town, South Africa) <http://www.csag.uct.ac.za/current-seasons-rainfall-in-cape-town/>

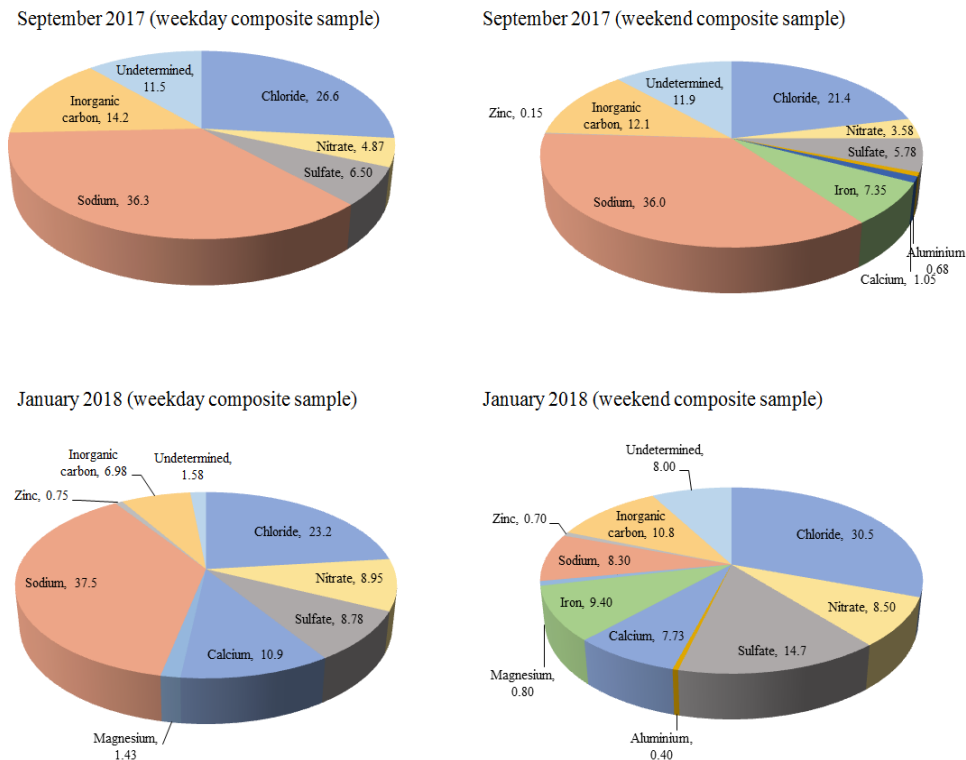


Figure S8 Chemical composition (in wt. %) of 96-hour PM_{2.5} samples on weekdays and weekends during the 22 days in September 2017 and January 2018 in Kraaifontein, Cape Town, South Africa

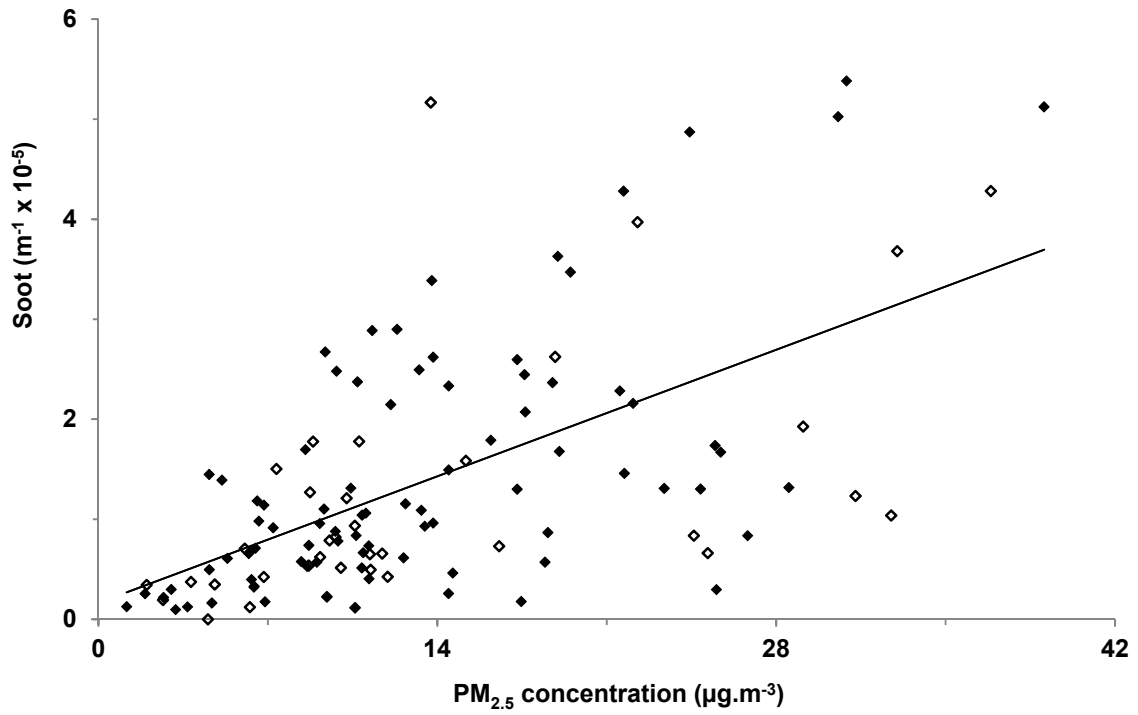


Figure S9 Correlation between soot and PM_{2.5} levels on 121 days during 18 April 2017 to 16 April 2018 in Kraaifontein, Cape Town, South Africa

Weekday samples are shown as solid diamonds and weekend samples (which include public holidays) as clear diamonds.

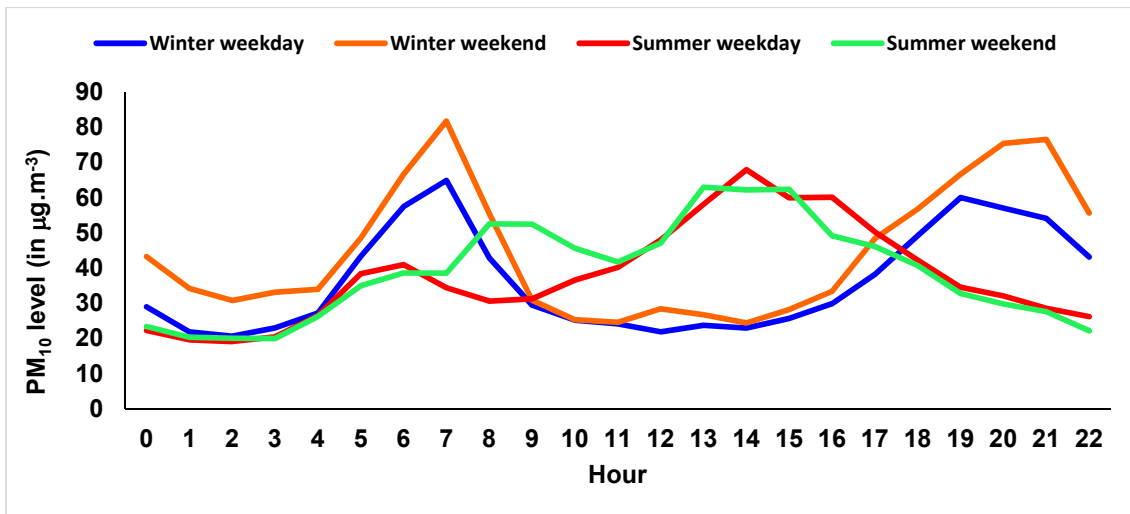
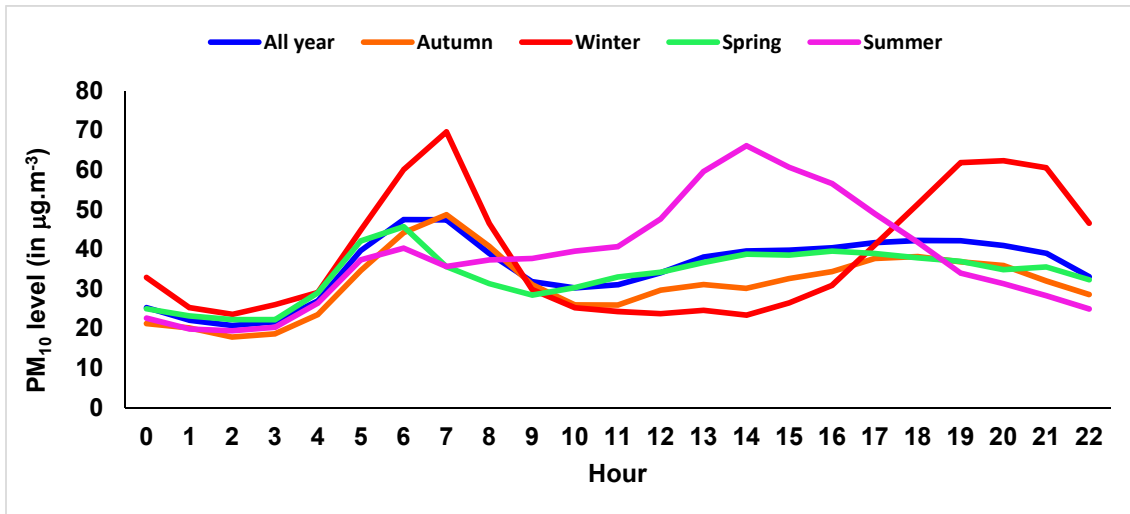


Figure S10 PM₁₀ levels measured at Wallacedene air quality monitoring station, Cape Town; by hour of the day during 18 April 2017 to 16 April 2018 (121 days)

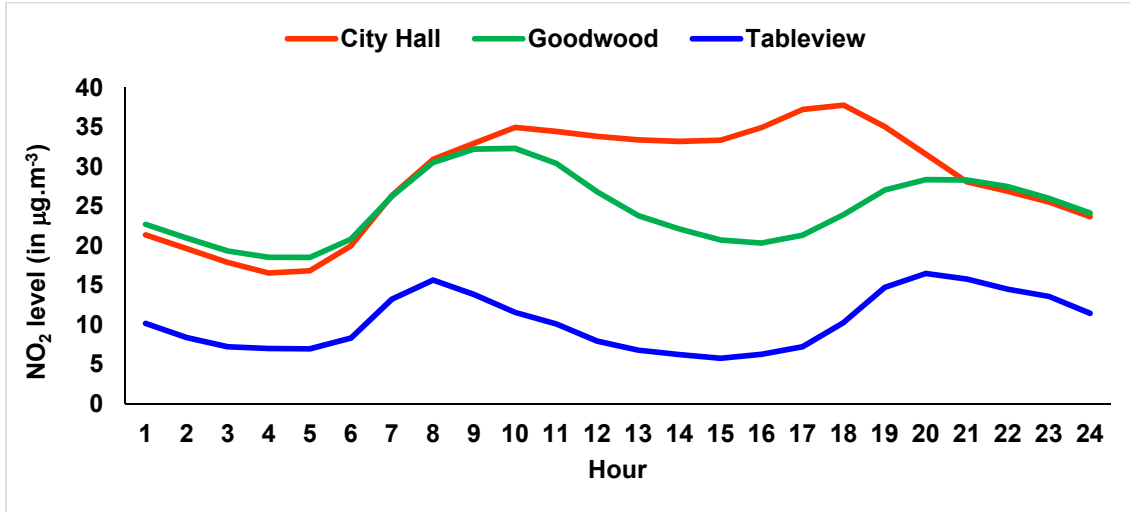


Figure S11 NO₂ levels measured at the City Hall, Goodwood and Tableview air quality monitoring stations, Cape Town; by hour of the day during 18 April 2017 to 16 April 2018 (121 days)

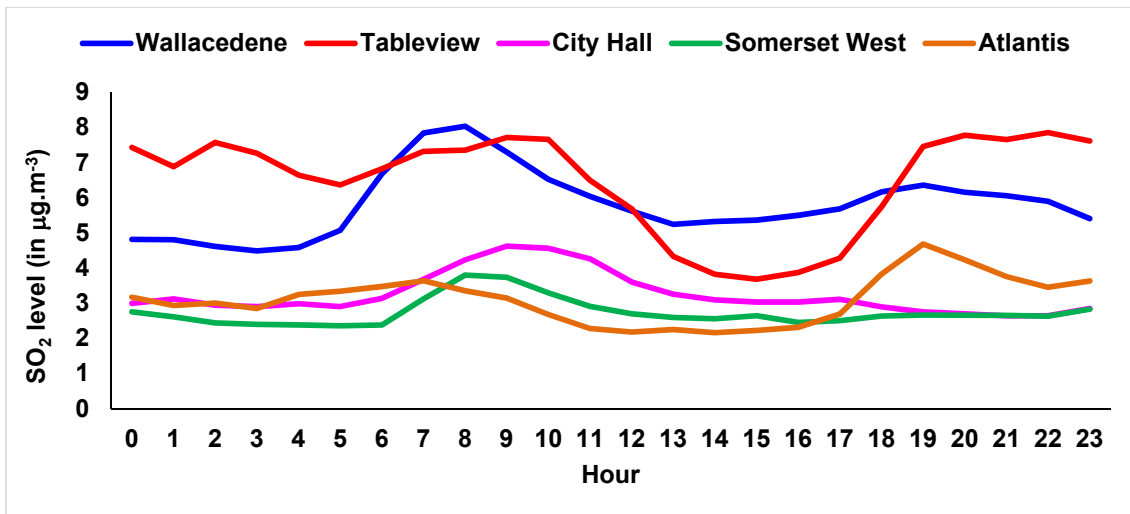


Figure S12 SO₂ levels measured at the Atlantis, City Hall, Tableview, Somerset West and Wallacedene air quality monitoring stations, Cape Town; by hour of the day during 18 April 2017 to 16 April 2018 (121 days)

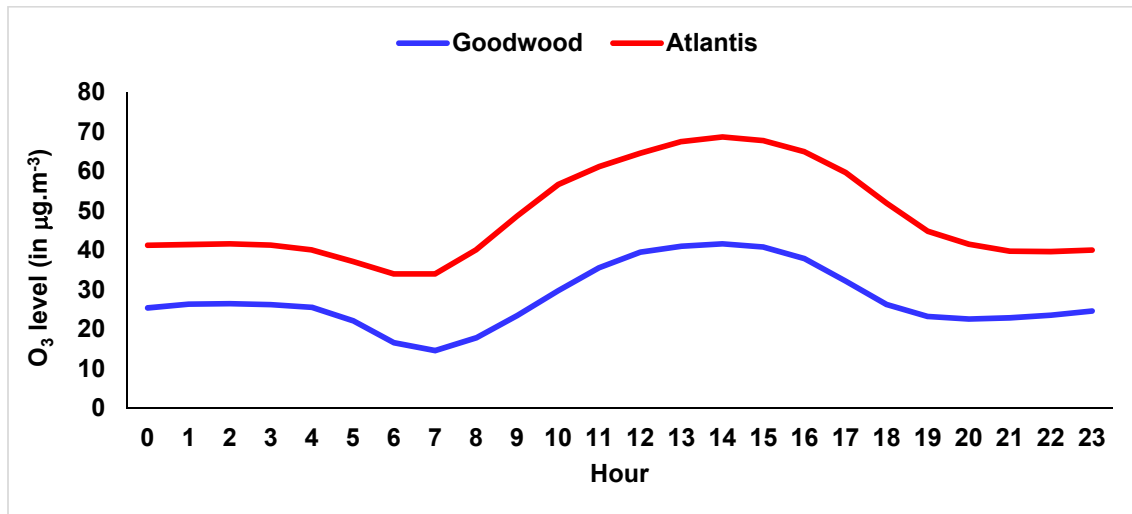


Figure S13 Ground-level O₃ levels measured at Goodwood and Atlantis air quality monitoring stations, Cape Town; by hour of the day during 18 April 2017 to 16 April 2018 (121 days)

Table S7 Frequency of geographical origin of air masses on 121 days during 18 April 2017 to 16 April 2018 in Cape Town, South Africa

	Entire year		Autumn		Winter		Spring		Summer	
	n	%	n	%	n	%	n	%	n	%
Indian-Ocean	35	28.9	16	51.6	4	13.3	7	23.3	8	26.7
Atl-Ocean-WSW	48	39.7	9	29.0	14	46.7	12	40.0	13	43.3
Atl-Ocean-SW	29	24.0	4	12.9	11	36.7	7	23.3	7	23.3
Atl-Ocean-SSW	9	7.4	2	6.5	1	3.3	4	13.3	2	6.7
Total	121	100	31	100	30	100	30	99.9	30	100

Table S8 Descriptive statistics of 24-hour PM₁₀, NO₂, SO₂, O₃ and meteorological conditions on 121 days during 18 April 2017 to 16 April 2018 in Cape Town, South Africa, by geographical origin or air mass

Variable	N	N missing	Minimum	Mean	Median	Maximum	Std Dev
Indian-Ocean							
PM ₁₀ (µg.m ⁻³)	32	3	11.3	42.6	37.2	96.7	22.6
NO ₂ (µg.m ⁻³)	34	1	8.3	23.4	21.7	44.0	9.7
SO ₂ (µg.m ⁻³)	35	0	2.0	5.4	4.8	13.2	2.6
O ₃ (µg.m ⁻³)	34	1	15.8	36.6	32.7	72.3	13.7
Temperature (°C)	35	0	13.3	19.7	19.7	25.3	2.6
Relative humidity (%)	35	0	37.3	66.3	67.3	83.0	10.4
Wind speed (m.s ⁻¹)	35	0	1.1	3.5	3.1	7.8	1.7
Precipitation (mm)	35	0	0.0	0.0	0.0	0.7	0.1
Atl-Ocean-WSW							
PM ₁₀ (µg.m ⁻³)	46	2	5.0	30.5	28.8	63.3	14.7
NO ₂ (µg.m ⁻³)	47	1	7.3	19.5	18.7	36.9	6.7
SO ₂ (µg.m ⁻³)	48	0	1.2	4.6	3.9	14.3	2.4
O ₃ (µg.m ⁻³)	47	1	13.1	34.7	34.4	67.0	11.1
Temperature (°C)	48	0	12.1	17.4	16.7	25.1	3.6
Relative humidity (%)	48	0	52.2	71.2	71.6	90.7	9.2
Wind speed (m.s ⁻¹)	45	3	1.0	3.4	3.3	7.7	1.5
Precipitation (mm)	48	0	0.0	1.0	0.0	11.4	2.3
Atl-Ocean-SW							
PM ₁₀ (µg.m ⁻³)	25	4	13.4	37.8	37.0	66.1	14.7
NO ₂ (µg.m ⁻³)	27	2	9.8	20.3	20.3	34.8	6.6
SO ₂ (µg.m ⁻³)	28	1	2.6	5.3	4.9	11.3	2.2
O ₃ (µg.m ⁻³)	27	2	15.8	34.7	37.0	46.7	7.3
Temperature (°C)	28	1	9.2	16.0	16.2	24.0	4.2

Variable	N	N missing	Minimum	Mean	Median	Maximum	Std Dev
Relative humidity (%)	28	1	50.2	66.4	66.1	89.0	8.4
Wind speed (m.s ⁻¹)	25	4	1.0	4.2	4.9	8.1	1.9
Precipitation (mm)	29	0	0.0	0.9	0.0	7.8	2.2
Atl-Ocean-SSW							
PM ₁₀ (µg.m ⁻³)	9	0	25.1	40.8	41.5	62.1	11.3
NO ₂ (µg.m ⁻³)	9	0	13.5	17.7	17.0	25.0	3.9
SO ₂ (µg.m ⁻³)	9	0	3.5	4.9	4.1	11.1	2.4
O ₃ (µg.m ⁻³)	9	0	26.1	41.3	39.3	58.3	12.4
Temperature (°C)	9	0	11.1	17.5	15.8	23.1	3.9
Relative humidity (%)	9	0	53.4	61.2	58.8	75.8	8.3
Wind speed (m.s ⁻¹)	9	0	2.0	4.3	4.1	7.0	1.5
Precipitation (mm)	9	0	0.0	0.5	0.0	4.1	1.4

NO₂, SO₂, O₃ levels averaged across the ambient air quality monitoring sites

Table S9 Correlation between PM_{2.5} and soot levels and meteorological conditions on 121 days during 18 April 2017 to 16 April 2018 in Cape Town, South Africa

	Entire year		Autumn		Winter		Spring		Summer	
	PM _{2.5}	Soot	PM _{2.5}	Soot	PM _{2.5}	Soot	PM _{2.5}	Soot	PM _{2.5}	Soot
Soot	0.596*	1.000	0.750*	1.000	0.818*	1.000	0.546*	1.000	0.427*	1.000
Temperature	-0.216*	-0.306*	0.121	-0.135	-0.223	-0.139	-0.163	0.215	0.221	0.568*
Relative humidity	-0.170	-0.115	-0.434*	-0.386*	-0.209	-0.418*	-0.032	-0.196	-0.372*	-0.429*
Wind speed	-0.312*	-0.598***	-0.296	-0.614*	-0.464***	-0.447***	-0.334	-0.365***	0.057	-0.108
Precipitation	-0.078	-0.230*	-0.176	-0.339	-0.161	-0.329	-0.100	-0.285	-0.069	-0.258

For number of missing values: temperature (1), relative humidity (1), wind speed (7)

* $p < 0.05$

Table S10 24-hour mean PM₁₀, NO₂, SO₂ and O₃ levels (in µg.m⁻³) measured at six municipality ambient air quality monitoring stations on 121 days during 18 April 2017 to 16 April 2018 in Cape Town, South Africa

Variable	N	N missing	Minimum	Mean	Median	Maximum	Std Dev
Wallacedene							
PM ₁₀	112	9	5.0	36.4	35.2	96.7	17.7
NO ₂	16	105	8.7	25.6	25.2	48.8	13.5
SO ₂	111	10	1.2	6.0	5.6	13.5	2.7
O ₃	107	14	11.7	31.3	30.3	58.4	10.7
Goodwood							
NO ₂	65	56	11.4	24.5	22.3	48.5	8.4
SO ₂	44	77	2.2	9.7	6.7	28.9	6.9
O ₃	57	64	14.5	27.1	25.7	42.0	6.7
Tableview							
NO ₂	111	10	1.6	10.8	9.3	35.0	7.2
SO ₂	99	22	0.5	6.9	4.1	38.9	6.7
City Hall							
NO ₂	100	21	9.4	28.9	27.8	69.3	11.3
SO ₂	79	42	0.1	3.5	2.4	15.4	2.9
Somerset West							
SO ₂	99	22	1.0	2.9	2.8	6.8	1.1
Atlantis							
SO ₂	83	38	0.4	3.2	2.9	8.2	1.9
O ₃	78	43	24.4	48.6	48.4	94.5	12.3

Table S11 Correlation between PM₁₀, NO₂, SO₂, O₃ levels and meteorological conditions on 121 days during 18 April 2017 to 16 April 2018 in Cape Town, South Africa

	PM₁₀	NO₂	SO₂	O₃
Temperature	0.072	-0.105	-0.009	0.112
Relative humidity	-0.445*	-0.208*	-0.328*	-0.132
Wind speed	-0.159	-0.636*	-0.321*	0.352*
Precipitation	-0.248*	-0.069	-0.226*	-0.055

NO₂, SO₂, O₃ levels averaged across the ambient air quality monitoring sites

For number of missing values: temperature (1), relative humidity (1), PM₁₀ (9), NO₂ (4), SO₂ (1), O₃ (4)

* p < 0.05