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The chemical composition and fluxes of atmospheric wet deposition at four sites in South Africa



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HIGHLIGHTS

- Significant impacts of anthropogenic activities on rain chemistry are indicated.
- Contributions from marine and crustal sources are reflected in rain chemistry.
- More rainfall events with low pH occur at sites nearby anthropogenic sources.
- Increased S- and N-deposition, and rain events with lower pH from 1984 to 2014.
- Rainfall chemistry reflects increased anthropogenic sources and population growth.

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ABSTRACT

South Africa is the economic hub of southern Africa and is regarded as an important source region of atmospheric pollutants. A nitrogen dioxide (NO₂) hotspot is clearly visible from space over the South African Mpumalanga Highveld, while South Africa is also regarded as the 9th largest anthropogenic sulphur (S) emitting country. Notwithstanding the importance of South Africa with regard to nitrogen (N) and S emissions, very limited data has been published on the chemical composition of wet deposition for this region. This paper presents the concentrations of sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), calcium (Ca²⁺), magnesium (Mg²⁺), nitrate (NO₃⁻), chloride (Cl⁻), sulphate (SO₄²⁻) and water-soluble organic acids (OA) in the wet deposition samples collected between 2009 and 2014 at four South African IDAF (IGAC DEBITS Africa) sites, which are regarded as regional representatives of the north-eastern interior. Also, wet deposition fluxes of the ten ions are calculated and presented in this paper. The results show that the total ionic concentrations and fluxes of wet deposition were much higher at the two sites closer to anthropogenic emissions, while the pH of wet deposition at these two sites were lower compared to that of the two sites that were less impacted by anthropogenic emissions. The major sources of the ten ions included marine, terrigenous (crust), fossil fuel combustion, agriculture and biomass burning. Significant contributions from fossil fuel combustion were determined for the two sites in close proximity to anthropogenic source regions. The results of back trajectory analysis, however, did indicate that the two remote sites are also affected by air masses passing over the source region through anti-cyclonic recirculation. The largest contributions at the two sites distant from the anthropogenic source regions were marine sources, while the impact of biomass burning was also more significant at the remote sites. Comparison to previous wet deposition measurements at the South African IDAF sites indicated increases in the wet deposition fluxes of S and N, and more wet deposition events with lower pH. This could be ascribed to a significant increase in anthropogenic activities and population growth in this part of South Africa with an associated increase in energy demand.

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Abbreviations	
%PCL	percentage precipitation covering length
%TP	percentage total precipitation
AF	Amersfoort
ARL	Air Resources Laboratory
C	carbon
Ca ²⁺	calcium
CH ₃ COO ⁻	acetic acid
C ₂ H ₅ COO ⁻	propionic acid
Cl ⁻	chloride
CO ₂	carbon dioxide
C ₂ O ₄ ²⁻	oxalic acid
COO ⁻	formic acid
DEBITS	Deposition of Biogeochemical Important Trace Species
DQO	data quality objectives
EC	electrical conductivity
EF	enrichment factor
GAW	Global Atmosphere Watch
HDPE	high-density polyethylene
H ₂ S	hydrogen sulphide
HYSPPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
IC	ion chromatography
IDAF	IGAC DEBITS Africa
IGAC	International Global Atmospheric Chemistry
IQR	interquartile range
ID	ion difference
K ⁺	potassium
LIS	inter-laboratory comparison study
LT	Louis Trichardt
Mg ²⁺	magnesium
NCEP	National Centre for Environmental Prediction
NF	neutralisation factor
N, Na ⁺	sodium, nitrogen
NH ₄ ⁺	ammonium
NO ₂	nitrogen dioxide
NO ₃ ⁻	nitrate
NO _x	nitrogen oxide and nitrogen dioxide
NOAA	National Oceanic and Atmospheric Administration
OA	organic acid
PCA	principle component analysis
pA	acidity potential
S	Sulphur
SK	Skukuza
SO ₂	sulphur dioxide
SO ₄ ²⁻	sulphate
VT	Vaal Triangle
VWM	volume weighted mean
WMO	World Meteorological Organisation.

1. Introduction

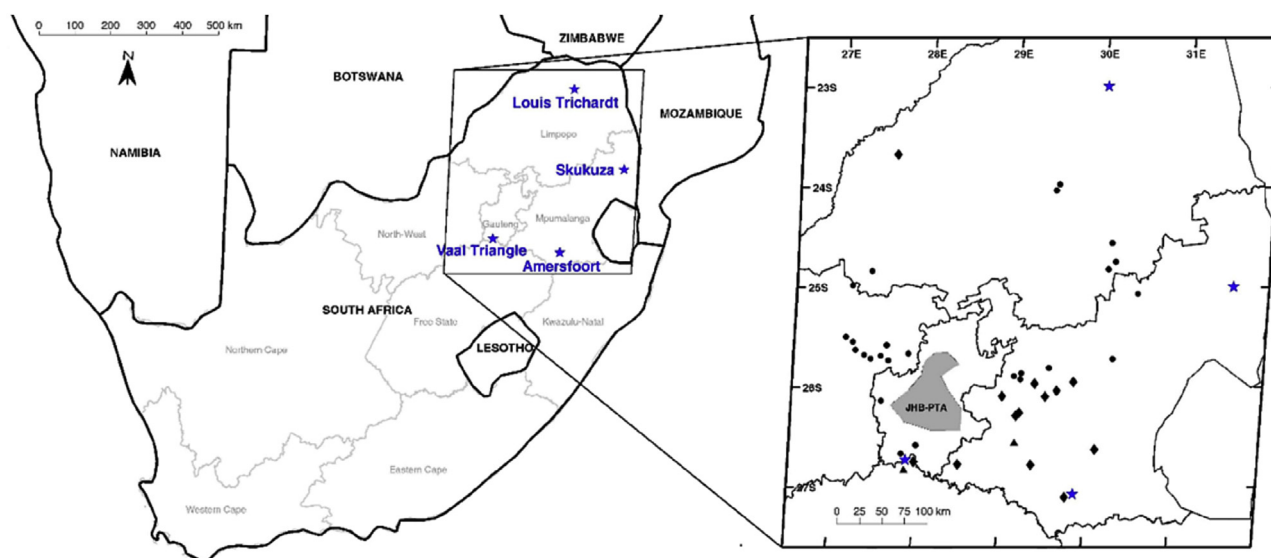
The chemical composition of wet deposition reflects various interacting physical and chemical mechanisms in the atmosphere, which include emission and source amplitude, atmospheric transport processes, atmospheric chemical reactions and removal processes (Galy-Lacaux et al., 2009). Precipitation chemistry also provides a general picture of changes in the composition of the atmosphere caused by anthropogenic activities, as well as changes in meteorology and climate (Vet et al., 2014). The importance of the chemical composition of wet deposition as a source of nutrients, e.g. nitrogen (N), sulphur (S), carbon (C) and base metals, is widely recognised (Duce et al., 2009), while precipitation could also be a source of toxic species. Although it can be a very difficult task, it is important to establish atmospheric budgets of key chemical compounds to understand the functioning of ecosystems and biogeochemical cycles (Dentener et al., 2006; Davidson et al., 2012). Vet et al. (2014) recently presented a comprehensive global assessment on precipitation chemistry and the deposition of biogeochemically important species, which emphasised the importance of wet deposition measurements.

Acid rain was identified as a problem in the 1960s when impacts were observed on aquatic ecosystems and forests (Möller, 1999), acidification of the environment (Gorham, 1998), as well as damages to buildings and sculptures (Ozga et al., 2011; Dolske, 1995). Wet deposition delivers acidic compounds to the surface of the earth, which adversely affect soil, vegetation, coastal waters and continental waters (Bravo et al., 2000). The main cause of this human-induced environmental problem has been the emission of S and N compounds into the atmosphere from sources such as energy production, transport, industry and agriculture. A global assessment of wet deposition pH performed in 2002 by utilising models estimated that Europe, China and eastern North America had the lowest pH values (Rodhe et al., 2002), which was attributed mainly to higher sulphate concentrations. However, nitric acid has also increasingly become an important contributor to the acidity of

rainwater in many regions of China and North America (Xiao, 2016).

The potential adverse environmental impacts related to increased anthropogenic emissions into the atmosphere necessitate the execution of long-term atmospheric measurement programmes. Comprehensive assessments on air quality (Monks et al., 2009) and atmosphere-biosphere interactions (Fowler et al., 2009) indicated the importance of long-term atmospheric chemistry measurements. From these assessments, current and emerging policy requirements could be identified, as well as the need for appropriate data to address related research questions (Vet et al., 2014). The Deposition of Biogeochemically Important Trace Species (DEBITS) task of the International Global Atmospheric Chemistry (IGAC) programme was initiated in 1990 in collaboration with the Global Atmosphere Watch (GAW) network of the World Meteorological Organisation (WMO) to investigate long-term concentrations and deposition (wet and dry) of biogeochemical species (mainly C, N and S species) in the atmosphere in the tropics (Lacaux et al., 2003). The DEBITS programme is currently continuing within the new IGAC structure or DEBITS II (Pienaar, 2005). The African component of this initiative is known as IGAC DEBITS Africa (IDAF) and consists of ten strategically positioned deposition sites in southern and western Africa that are representative of important African ecosystems (<http://idaf.sedoo.fr/spip.php?rubrique45>).

South Africa is regarded as an important source region of biogeochemical and anthropogenic atmospheric pollutants. An NO₂ hotspot is clearly visible over the South African Mpumalanga Highveld (Lourens et al., 2012), with the borders of the Mpumalanga Province indicated in Fig. 1. South Africa is also regarded as the 9th largest atmospheric S-emitting country (Stern, 2006), while biomass burning (mostly wild fires) plumes from this area are known to affect Australia and South America (Wenig et al., 2003). Maritz et al. (2015) also indicated the significant influence of biomass burning on the concentrations of atmospheric organic compounds. Furthermore, South Africa is regarded as the economic hub of southern Africa. Notwithstanding the importance of South



Site	Coordinates	Elevation	Description
Amersfoort (AF)	27°04'13"S 29°52'02"E	1628 m amsl	Semi-arid, regional savannah, impacted by anthropogenic activities, ~200 km south-cast of the Johannesburg metropolis and 50-100 km south-east of the major industrial activities on the Mpumalanga Highveld.
Vaal Triangle (VT)	26°43'29"S 27°53'05"E	1320 m amsl	Semi-arid, regional savannah, situated in the highly industrialised Vaal Triangle area, impacted by emissions from various industries, such as petrochemical, pyro-metallurgical, power plants, high levels of traffic and waste generated by high population density. Site is ~100 km south, south-west of Johannesburg.
Louis Trichardt (LT)	22°59'10"S 30°01'21"E	1300 m amsl	Semi-arid, regional savannah, rural site predominantly used for agricultural purposes, ~400 km north-east of Johannesburg.
Skukuza (SK)	24°59'35"S 31°35'02"E	267 m amsl	Semi-arid savannah, regional background site surrounded by natural bushveld in a protected area, ~30 km from nearest low level anthropogenic pollution sources, mainly informal settlements.

Fig. 1. Locations of the South African IDAF sites. The enlarged section indicates the Johannesburg-Pretoria metropolitan area with a grey shade, DEBITS sites are indicated with a star, petrochemical industries with a triangle, coal-fired power stations with a diamond and pyrometallurgical industries with a circle. Additionally, provincial borders are indicated on the main map. Synoptic description, location, elevation and brief description of the South African IDAF sites are also presented.

Africa with regard to N and S emissions, as well as the need for long-term monitoring programmes, very limited data has been published on the chemical composition of wet deposition for this region (Laakso et al., 2012).

Mphepya et al. (2004, 2006) reported on the wet deposition chemistry of samples collected at three South African IDAF sites, i.e. an industrially influenced site (Amersfoort) and a rural background site (Louis Trichardt) in South Africa from 1986 to 1999, as well as a site at Skukuza in the Kruger National Park from 1999 to 2002. These studies estimated that the chemical composition of wet deposition at these sites is controlled by mainly five source groups, i.e. marine, terrigenous, nitrogenous, biomass burning and anthropogenic (fossil fuel) sources. Due to logistical reasons, wet deposition collection did not continue beyond the above-mentioned periods at South African IDAF sites until 2009. However, the collection of wet deposition events recommenced in 2009 and is currently ongoing. Therefore, the major objectives of this study were to: (1) monitor the chemical composition of wet

deposition and determine wet deposition fluxes of sulphur and nitrogen at the four South African IDAF sites from 2009 to 2014, (2) determine the major sources of ionic species, and (3) investigate whether there have been significant changes of ionic concentrations/fluxes in wet deposition from 1986 to 2014.

2. Sampling sites and methods

2.1. Site descriptions

Wet deposition samples were collected from January 2009 to December 2014 at four sites in the interior of South Africa operated within the IDAF network, i.e. Amersfoort (AF), Vaal Triangle (VT), Louis Trichardt (LT) and Skukuza (SK). The South African IDAF sites are presented within a regional context in Fig. 1. AF, LT and VT are located on the South African Highveld, while SK is situated in the South African Lowveld. AF, LT and SK have been described by Mphepya et al. (2004, 2006) and Martins et al. (2007), while VT has

not been previously introduced. A brief description of each site is also presented in Fig. 1.

2.2. Regional climate and air mass transport

Laakso et al. (2012) recently presented a synopsis of the interaction of pollutants over the interior of South Africa with specific reference to the regional climate, recirculation patterns and inversion layers. The meteorology in South Africa is characterised by strong seasonal variability. The predominant atmospheric circulation pattern over the interior of South Africa is governed by the anti-cyclonic subtropical recirculation, especially during winter (June, July, August) with frequent easterly disturbances during summer (December, January, February) (Tyson et al., 1996; Garstang et al., 1996; Laakso et al., 2012). This dominant high pressure system, together with the low heat capacity of the soil, creates inversion layers that considerably reduce vertical mixing (Garstang et al., 1996). These inversions, in conjunction with the recirculation, contribute significantly to the build-up of pollutants over the interior of South Africa, especially in the cold winter months when more pronounced inversion layers trap pollutants at several different heights near the surface of the earth (Tyson et al., 1996).

Rainfall is also strongly seasonal, with rainfall over the central and northern parts of South Africa occurring almost exclusively from mid-spring up to early autumn (mid-October to March), mostly in the form of convective rainfall (Laakso et al., 2012; Kruger, 2006; Hewitson and Crane, 2006). The lack of rain events and associated wet removal of pollutants during the dry period (April to mid-October), together with the additional occurrences of large-scale wild fires during the dry season (Vakkari et al., 2014) and increased household combustion for space heating (Venter et al., 2012) during the cold winter months, also leads to higher levels of most pollutant species during the dry season. In Fig. S1, the rainfall events for AF, VT, LT and SK for the sampling period, as well as the total annual rainfall depths are presented. These rain depths were measured with standard funnel rain gauges (Bahati) at each of the South African IDAF sites, which were recorded by the site operators after a single rain event occurred. Therefore, it is assumed that the percentage precipitation covering length (%PCL), i.e. the percentage of rain event depths measured with the rain gauge is 100% (WMO, 2004). From these figures, the strong seasonality of rainfall is evident at all the South African IDAF sites, with most rainfall occurring between mid-spring and early autumn. In general, annual rainfall in this semi-arid region is characterised by relatively large inter-annual variations in the rainfall depth and, for the studied period, it ranged between 576 and 912 mm at AF, 818 and 1227 mm at VT, 482 and 985.5 mm at LT, and 474.5 and 782 mm at SK.

The air mass history for each site for the entire sampling period was determined by calculating back trajectories with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) 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. All back trajectories were calculated for 96 h, arriving every hour at a height of 100 m throughout the entire measurement period. These individual trajectories were overlaid with a fit-for-purpose Matlab program on a map area divided into $0.2^\circ \times 0.2^\circ$ grid cells. The colour of each grid cell depends on the number of trajectories passing over it, with dark red indicating the highest percentage of back trajectory overpasses. In Fig. 2, separate dry and wet period overlay back trajectory maps for each of the

South African IDAF sites are indicated. The overlay back trajectories obtained at all the South African IDAF sites clearly indicate the dominant anti-cyclonic circulation pattern of air masses over the interior of South Africa. These overlay back trajectories were further used to visually indicate possible source areas affecting the sites.

2.3. Sample collection

Wet deposition samples, which only included rainwater samples, were collected according to the field protocols of the WMO for precipitation chemistry measurements (WMO, 2004). Wet deposition samples were collected on an event basis with an automated wet-only sampler (Aerochem Metrics, model 301) that exposes the collection vessel, which consists of a plastic bag fitted into a high-density polyethylene (HDPE) bucket, only when it starts raining. The device is equipped with a conductivity sensor that detects the onset of rainfall and activates a mechanism that opens the lid. The afore-mentioned conductivity sensor is also heated to facilitate evaporation of the water on the sensor, thereby ensuring that the lid closes shortly after the rain event had stopped. The advantages of automated wet-only sampling include limiting the contamination of wet deposition by dust and other unwanted materials before and after the events, as well as minimising the delays associated with manual operation. The wet deposition samples were collected in the plastic bags that were placed inside the HDPE bucket. In order to avoid contamination of the sampling plastic bags during long dry periods, these bags were changed once a week. Furthermore, the lid of the HDPE bucket also seals tightly to prevent any air contamination. After a rain event, the plastic bags containing the samples were removed from the collection vessels as soon as possible, but at least within 24 h after an event ended. Thereafter, 45 mL of the collected wet deposition was transferred from the plastic bag into two 50 mL sample bottles, i.e. polyethylene bottles, by cutting open one of the corners of the plastic bag. If wet deposition volumes ≤ 45 mL were collected for rain events with low rain depths, the total wet deposition sample was transferred to only one sampling bottle. The samples were frozen (temperature ranged between 0 and -10°C) at the site by a site operator. These frozen samples were collected once a month at the sites and transported in a frozen state using a portable deep-freeze to the laboratory and stored frozen in the analytical laboratory until they were analysed. There were no field blank determinations conducted due to logistical difficulties associated with performing such activities at these remote sites.

2.4. Chemical analyses

Prior to analysis, samples were unfrozen overnight and analysed as soon as possible. After unfreezing the samples, 25 mL of aliquots were used for immediate conductivity and pH measurements, after which the remaining sample was filtered through a $0.2\ \mu\text{m}$ filter in preparation for chemical analysis. An HI 255 combined meter (Hanna Instruments) was used for pH and conductivity measurements with a low ionic strength electrode. A three-point pH calibration procedure was followed according to the manufacturer's specifications with pH 4.01, 7.01 and 10.01 buffer solutions.

The chemical composition of wet deposition samples collected at each of these sites was determined using a Dionex ICS 3000 ion chromatograph (IC). The species measured included inorganic cations and anions, i.e. sodium (Na^+), ammonium (NH_4^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), nitrate (NO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}), as well as water-soluble organic acids (OA), including formic- (COO^-), acetic- (CH_3COO^-), propionic- ($\text{C}_2\text{H}_5\text{COO}^-$) and oxalic acid ($\text{C}_2\text{O}_4^{2-}$). Standard stock solutions for each ion species analysed were obtained from Industrial Analytical.

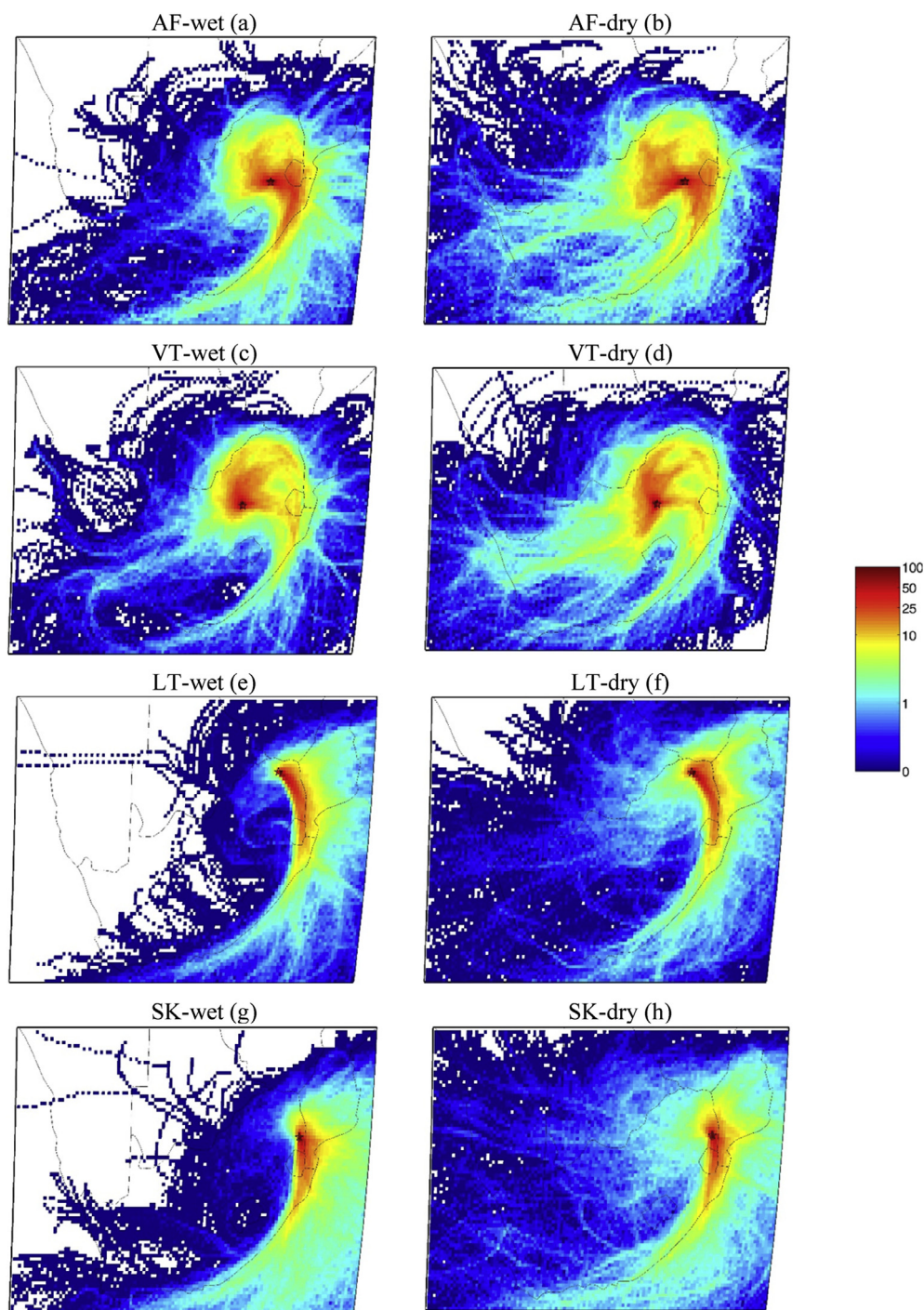


Fig. 2. Overlay back-trajectory analyses for air masses arriving at AF (a) and (b), VT (c) and (d), LT (e) and (f), and SK (g) and (h) between 1 January 2009 and 31 December 2010 during the wet and dry seasons.

Analyses of anions and organic acids were performed with an ASRS 2 mm column, using gradient automated eluent (methane sulfonic acid) generation mode (1.5 mM up to 32 mM) and a flow of 0.25 mL/min to achieve optimal separation of the various anions. Cation analyses were conducted on a CSRS ultra 2 mm column, at fixed eluent (potassium hydroxide) concentration of 25 mM and a flow of 0.45 mL/min. The detection limits of the IC for the species analysed were 1 ppb for Na^+ , K^+ , Mg^{2+} and F^- , 2 ppb for Ca^{2+} , 4 ppb for NH_4^+ , 11 ppb for Cl^- , 28 ppb for NO_3^- and 31 ppb for SO_4^{2-} in aqueous solution.

2.5. Data quality

The WMO Data Quality Objectives (DQOs) presented in the WMO precipitation chemistry guidance manual (WMO, 2004) were the foundation on which data quality was ensured. All collected wet deposition events were visually inspected to exclude any visible contamination, e.g. any plant materials or insects. If any contamination was observed, it was recorded and the sample was filtered through a 0.2 μm filter (Sigma Aldrich) prior to the chemical analysis. The analytical techniques, i.e. IC, pH and conductivity

measurements were also verified by participating in the bi-annual inter-laboratory comparison study (LIS) organised by the WMO. In Fig. 3, the results of the 50th LIS study in 2014 are presented. According to the WMO inter-comparison results, the recovery of each ion in standard samples was between 95 and 105%. Data quality was further ensured by calculating the ion difference (ID) for each sample in order to consider the ionic balance by using the following equation (WMO, 2004):

$$\text{ID}\% = 100 \times \frac{[\text{CE} - \text{AE}]}{[\text{CE} + \text{AE}]} \quad (1)$$

where AE is the total of the anions in μeqL^{-1} and CE is the total of the cations in μeqL^{-1} . Acceptance ranges for the ID are presented in the WMO report (2004) and were applied to all the wet deposition events collected in this study. Only samples that passed WMO criteria were included in the calculations and statistical evaluation presented in this paper.

Table 1 presents the total number of samples collected and chemically analysed, as well as the number of samples that passed the WMO ID% criteria and collected samples discarded due to analytical errors or not being of sufficient volume for complete analyses. The number of wet deposition samples collected included all the events for which rain depth was measured. All these rain events had rain depths of more than 0.2 mm. According to exposure sheets received with each of the wet deposition samples, no incidences were reported where collected wet deposition samples had to be excluded due to instrumental or operational failures during the entire sampling period. Furthermore, exposure sheets also indicated that all the wet deposition samples collected represent a single rain event and do not contain an accumulation of several rain events. The numbers of samples that did not have sufficient volumes for complete analysis were 1, 8, 8 and 20 at AF,

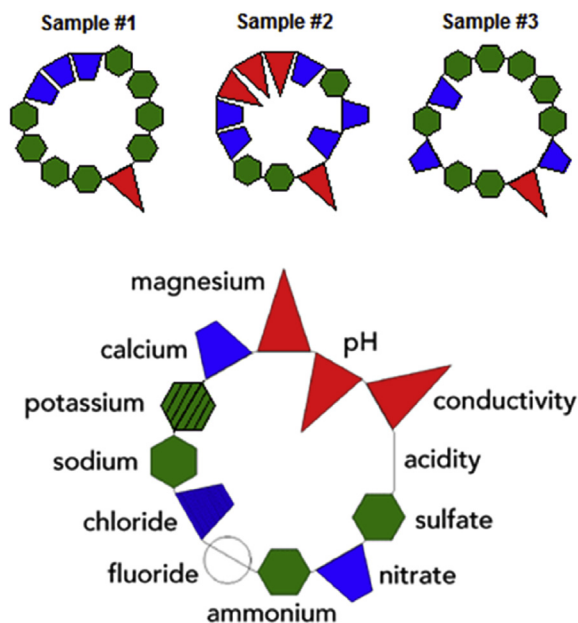


Fig. 3. Results of the LIS 50 study in 2014 indicated by ring diagrams with a legend for the ring diagram included. The green hexagon indicates that the results are good (measurements are within the interquartile range (IQR), defined as the 25th to 75th percentile or middle half (50%) of the measurements), the blue trapezoid indicates that results are satisfactory (measurements are within the range defined by the median \pm IQR/1.349) and the red triangle indicates that the results are unsatisfactory (measurements are outside the range defined by the median \pm IQR/1.349). IQR/1.349 is the non-parametric estimate of the standard deviation, sometimes called the pseudo-standard deviation (QA/SAC-Americas, 2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

VT, LT and SK, respectively. The percentage of the samples that passed the WMO ID% criteria and were not discarded due to analytical errors listed in Table 1 represents wet deposition samples that were in the WMO percentage total precipitation (%TP) acceptance range, i.e. the %TP at all the sites for each of the sampling years were $\geq 70\%$, which is considered to be good (WMO, 2004). The %TP is the percentage of total rainfall depth measured that was associated with valid precipitation chemistry data.

2.6. Calculations and statistical evaluation

The annual volume weighted mean (VWM) concentrations in μeqL^{-1} of each ion were calculated using the following equation (Laouali et al., 2012):

$$\text{VWM}(\mu\text{eqL}^{-1}) = \frac{\sum_{i=1}^N c_i p_i}{\sum_{i=1}^N p_i} \quad (2)$$

where c_i is the concentration of a given ion in the i th sample, p_i is the rainfall depth (mm) during the i th sampling period and N is the total number of samples with valid concentrations for the ion. The total number of samples (N) that were used to calculate the VWM for each site is presented in Table 1. The H^+ concentrations were calculated from the measured pH values. The annual wet deposition fluxes, expressed in $\text{kg ha}^{-1} \text{yr}^{-1}$, were calculated by multiplying the annual VWM ionic concentrations with the total annual rainfall depth at each site and the molar mass (equivalent weight) of the specific ion. The mean fluxes of wet deposition for the six-year sampling period were calculated by using the average annual rainfall from 2009 to 2014 of each of the sites presented in Table 1. The total annual rainfall amount includes all rain events in the year and not only the events used to calculate the VWM ionic concentrations as specified by the WMO precipitation chemistry guidance manual (WMO, 2004).

Various methods, e.g. empirical calculations, statistical evaluations, back trajectory analysis and modelling can be used to estimate the contribution of different sources to the chemical content of wet deposition (Keene et al., 1986; Delmas, 1981; Chao and Wong, 2002; Mphopya et al., 2004; Bao-Zhu et al., 2015). Although no single method is absolute, in combination, relatively accurate estimations can be made.

Contributions of sea salt to ionic concentrations of wet deposition are commonly estimated by calculating the excess concentrations of K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} with respect to sea salt using Na^+ as a reference. Keene et al. (1986) presented reference ratios of these species with regard to Na^+ in seawater. The sea salt fractions of any of these species, X, with respect to Na^+ are

$$[\text{X}]_{\text{marine}} = [\text{Na}^+]_{\text{rain}} \times [\text{X}/\text{Na}^+]_{\text{seawater}} \quad (3)$$

where $[\text{X}]_{\text{marine}}$ is the sea salt contribution of X in μeqL^{-1} , $[\text{Na}^+]_{\text{rain}}$ is the concentration of Na^+ in rain (μeqL^{-1}) and $[\text{X}/\text{Na}^+]_{\text{seawater}}$ is the seawater concentration ratio (Keene et al., 1986).

The non-sea salt fraction of X can then be calculated by:

$$[\text{X}]_{\text{nss}} = [\text{X}]_{\text{rain}} - ([\text{Na}^+]_{\text{rain}} \times [\text{X}/\text{Na}^+]_{\text{seawater}}) \quad (4)$$

where $[\text{X}]_{\text{rain}}$ is the concentration of species X in wet deposition, and $[\text{X}]_{\text{nss}}$ is the non-sea salt contribution of species X in μeqL^{-1} . The enrichment factors (EF) with regard to the reference X/Na^+ ratio were calculated by (Quiterio et al., 2004; Chao and Wong, 2002):

$$\text{Seawater EF}_x = \frac{[\text{X}/\text{Na}^+]_{\text{rainwater}}}{[\text{X}/\text{Na}^+]_{\text{marine}}} \quad (5)$$

Table 1
Summary of wet deposition samples collected at South African IDAF sites from 2009 to 2014.

Site	Amersfoort							Vaal Triangle						
	2009	2010	2011	2012	2013	2014	Total	2009	2010	2011	2012	2013	2014	Total
Number of events collected (N)	55	60	49	50	63	46	323	88	93	73	70	60	61	445
Number of events not passing the WMO ID% criteria	6	13	14	13	5	0	51	15	19	21	6	1	4	66
Number of events discarded due to analytical errors	0	0	0	0	1	1	2	1	1	0	2	4	0	8
Collected rainfall	696	767.4	426	431.75	743.25	736	3800.4	793	954.5	607	815.5	754.1	1222	5146.1
Total rainfall	720	912	576	613.25	821.25	736	4378.5	895.5	1083	818	901	814.1	1227	5738.6
Average rainfall							729.75							956.43
% TP	96.67	84.14	73.96	70.40	90.50	100	86.80	88.55	88.13	74.21	90.51	92.63	99.58	89.68
Site	Louis Trichardt							Skukuza						
	2009	2010	2011	2012	2013	2014	Total	2009	2010	2011	2012	2013	2014	Total
Number of events collected (N)	31	25	32	20	20	29	157	42	49	45	29	50	42	257
Number of events not passing the WMO ID% criteria	9	1	8	2	0	0	20	1	8	3	0	1	0	13
Number of events discarded due to analytical errors	0	0	1	5	2	0	8	2	3	2	9	4	0	20
Collected rainfall	775	492	469.5	352	754.7	985.5	3828.7	604.5	582.5	451.8	443	749.3	492	3323.1
Total rainfall	901.5	504	696.5	482	799.7	985.5	4369.2	611.8	616.6	522.8	474.4	781.8	492	3499.4
Average rainfall							728.2							583.23
% TP	85.97	97.62	67.41	73.03	94.37	100	87.63	98.81	94.47	86.42	93.38	95.84	100	94.96
Number of events collected from 2009 to 2014 at all the sites														1182
Number of events not passing the WMO ID% criteria from 2009 to 2014 at all the sites														150
Number of events discarded due to analytical errors														38
% TP														89.77

where EF_x is the enrichment factor of species X and $[X/Na^+]_{rain}$ is the ratio of species X with regard to Na^+ in wet deposition. EFs must be evaluated carefully since EFs are considered to be a simplified method to determine the marine contribution to wet deposition composition (Reimann and De Caritat, 2005).

Within the South African context, SO_4^{2-} can be viewed as a reference ion for anthropogenic activities. Two approaches can be followed in order to estimate the anthropogenic contribution to SO_4^{2-} concentrations in wet deposition. The first method to estimate the anthropogenic contribution is to subtract the marine contribution (by using Equation (3)) from the determined VWM values for SO_4^{2-} . The excess SO_4^{2-} ($[SO_4^{2-}]_{nss}$) can be attributed to either terrigenous or anthropogenic sources. The contribution of anthropogenic sources to SO_4^{2-} in wet deposition can be inferred by assuming that the SO_4^{2-} contribution from anthropogenic sources is in excess of that supplied by gypsum (Delmas, 1981). Ca^{2+} is a typical lithospheric element and can be used as a reference element for continental crust (Ding et al., 2013). Therefore, an estimation of the anthropogenic SO_4^{2-} contribution can be calculated using the following equation (Delmas, 1981):

$$[SO_4^{2-}]_{anthropogenic} = [SO_4^{2-}]_{nss} - 0.47[Ca^{2+}]_{nss} \quad (6)$$

It has been shown in studies in West Africa (Galy-Lacaux et al., 2009) and by global deposition models (Vet et al., 2014) that the SO_4^{2-} concentration in wet deposition is low in the absence of anthropogenic or volcanic activities. The annual VWM concentrations for SO_4^{2-} at four regionally representative IDAF sites in West Africa were determined to be $7.0 \mu eq.L^{-1}$, which is in agreement with global model estimates. Therefore, an estimation of the anthropogenic contribution to SO_4^{2-} in wet deposition can be made by subtracting this value from the SO_4^{2-} VWM values determined, which was the second method applied to estimate anthropogenic SO_4^{2-} .

The contribution of biomass burning to the chemical content of wet deposition can be estimated by the nss- K^+ fraction and water-soluble OA in wet deposition as reference species (Helas and Pienaar, 1996). However, since K^+ is also a significant component of soil dust, the biomass burning contribution is mostly estimated by using only the acidic contribution of OA to the total acidity (Galy-

Lacaux et al., 2009).

Sulphuric, nitric and organic acids together can be defined as the acidic potential (Laouali et al., 2012). Neutralisation of sulphuric and nitric acids by bases that consist of base cations (e.g. Mg^{2+} , Ca^{2+} and NH_4^+) and anions (e.g. carbonates and bicarbonates) can be evaluated by calculating the neutralisation factors (NF) with the following equation (Laouali et al., 2012; Possanzini et al., 1988):

$$NF_x = X / (NO_3^- + SO_4^{2-}) \quad (7)$$

where X is the base cation of interest, i.e. Mg^{2+} , Ca^{2+} and NH_4^+ .

Statistical evaluations, i.e. principal component analysis (PCA) and Spearman correlations were performed. PCA was performed in order to identify possible similar sources of chemical species that influence the chemical composition of wet deposition samples, while correlations between chemical species could also indicate similar origin and/or air masses from the same origin.

3. Results and discussion

3.1. Ionic composition and acidity of wet deposition

The VWM ionic concentrations and fluxes of wet deposition, as well as the averaged pH and averaged electrical conductivity (EC) values determined at all the IDAF sites in the interior of South Africa from 2009 to 2014 are presented in Table 2. The VWM concentrations of COO^- , CH_3COO^- , $C_2H_5COO^-$ and $C_2O_4^{2-}$ were combined, which are presented as a total for water-soluble OA.

SO_4^{2-} was the most abundant ionic species measured at the four sites. Since S emissions in southern Africa are mostly attributed to anthropogenic activities, it is evident that these activities have a major influence on the atmospheric chemical processes in the region. The reported values of SO_4^{2-} at VT and AF are much higher than that reported for other IDAF sites in Africa (Galy-Lacaux et al., 2009) and, with the exception of eastern North America, eastern Europe and East Asia, even than most other regions in the world (Vet et al., 2014). The sites closer to industrial sources had larger VWM concentrations of SO_4^{2-} . For example, SO_4^{2-} concentrations were four times higher at AF and VT than at LT and SK (Fig. 1).

Table 2The EC, pH, ionic concentrations ($\mu\text{Eq L}^{-1}$) and fluxes ($\text{kg ha}^{-1} \text{yr}^{-1}$) of wet deposition at the four South African IDAF sites from 2009 to 2014.

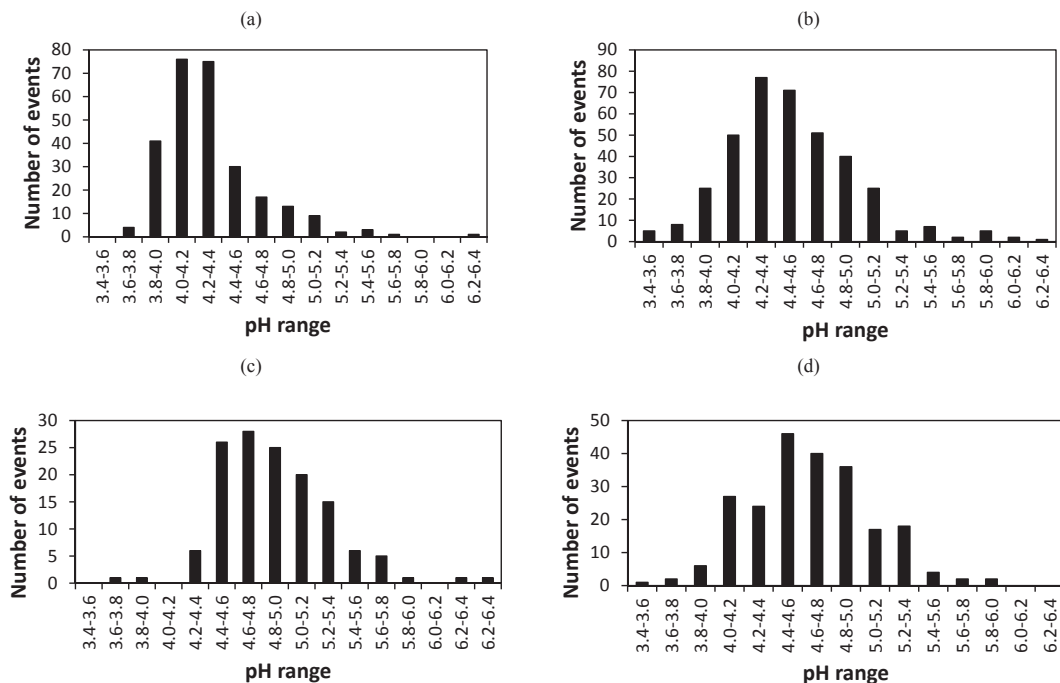
	Amersfoort 2009–2014		Vaal Triangle 2009–2014		Louis Trichardt 2009–2014		Skukuza 2009–2014	
	VWM values	Fluxes	VWM values	Fluxes	VWM values	VWM values	Fluxes	
pH	4.32		4.51		4.89		4.66	
EC	42.6		33.6		13.1		22.9	
H^+	61.18	0.45	44.64	0.43	15.24	0.11	22.24	0.13
Na^+	17.79	2.98	3.50	0.77	7.75	1.30	13.17	1.77
NH_4^+	28.50	3.75	29.06	5.01	10.85	1.42	12.80	1.35
N in NH_4^+		2.91		3.89		1.11		1.04
K^+	7.35	2.10	1.41	0.53	5.12	1.46	2.08	0.48
Mg_2^+	5.54	0.49	4.55	0.53	1.93	0.17	3.27	0.23
Ca_2^+	16.39	2.40	16.18	3.10	6.25	0.91	4.69	0.55
NO_3^-	33.40	15.11	22.97	13.62	7.49	3.38	13.20	4.77
N in NO_3^-		3.41		3.08		0.76		1.08
Cl^-	17.96	4.65	4.52	1.53	10.83	2.80	15.73	3.25
SO_4^{2-}	67.21	23.56	55.00	25.27	12.37	4.33	18.66	5.23
S in SO_4^{2-}		7.87		8.44		1.44		1.75
OA	14.64 (13.24 ^a)	5.57	12.51 (11.49 ^a)	6.10	12.14 (11.10 ^a)	4.54	9.69 (8.69 ^a)	2.93

^a Dissociated fractions of the organic acids are indicated in brackets.

The second and third most abundant species at AF were NO_3^- and NH_4^+ , respectively. These two species were also the second and third most abundant species at VT, with NH_4^+ levels being higher than NO_3^- . Similar to SO_4^{2-} , NO_3^- and NH_4^+ concentrations were also higher (2–3 times) at AF and VT than at LT and SK. This may also reflect that AF and VT were more affected by anthropogenic emissions. However, since the difference is smaller for NO_3^- and NH_4^+ compared to that of SO_4^{2-} , it also indicates that more source groups contribute to the concentrations of NO_3^- and NH_4^+ than to the SO_4^{2-} concentrations at the different sites. The significantly higher VWM concentrations of SO_4^{2-} and NO_3^- measured at AF and VT are in accord with NO_2 and SO_2 concentrations being higher at AF and VT than at LT and SK. The second most abundant species at LT was OA, which is an indicator of biomass burning.

It is also evident that AF and VT, the two sites closer to

anthropogenic emissions, had lower average pH values (4.32 and 4.51, respectively) and higher H^+ concentrations (61.18 and 44.64 $\mu\text{Eq/L}$, respectively), while LT and SK had higher mean pH values (4.89 and 4.75, respectively) and lower VWM H^+ concentrations (15.24 and 22.24 $\mu\text{Eq/L}$, respectively). Table 2 shows that the average pH values at all the sites were in the range of 4.32–4.89, much lower than 5.60, which is the pH of unpolluted rainwater in equilibrium with atmospheric carbon dioxide (CO_2). The observed acidity is mainly due to the large influence of NO_x and SO_2 industrial emissions on the industrialised Mpumalanga Highveld and the Vaal Triangle, as well as organic acid contributions from biomass burning that is being recirculated over the interior of South Africa (Laouali et al., 2012; Laakso et al., 2012; Tyson et al., 1996). Average pH values determined at the South African IDAF sites are much lower compared to the pH of rainwater in western African countries

**Fig. 4.** The pH distribution of wet deposition samples collected during individual rain events between 2009 and 2014 at AF (a), VT (b), LT (c) and SK (d).

where the acidity is predominantly associated with organic species from emitted biogenic processes and biomass burning, with calcium carbonate/bicarbonate acting as a major buffering agent for acidity in rain (Galy-Lacaux et al., 2009; Laouali et al., 2012). These values are also lower than the average global values reported by Vet et al. (2014) and are therefore clearly influenced by anthropogenic activities in southern Africa.

The pH frequency distributions at the four South African IDAF sites are presented in Fig. 5. Although the pH distribution of individual wet deposition rain events were quite different among the four sites, over 94% of rain events observed at each site had pH lower than 5.60. At AF, 17% and less than 1% of rain events had pH <4.00 and >6.00, respectively. The largest number of rain events had pH values between 4.0 and 4.4 at AF. The highest frequency of rain events was at VT at pH values between 4.2 and 4.6, while 10.2% of rain events had pH values lower than 4.0 and 0.8% were higher than 6.00. At LT, the pH values of individual rain events ranged predominantly between 4.4 and 5.0. 1.5% of rain events at LT were below 4.0, while 2.2% were higher than 6.0. 4% of rain events at SK were lower than 4.0 and 0.9% were higher than 6. The largest number of rain events had pH values ranging between 4.4 and 5.0.

The acidity potential (pA) can be defined as the sum of the potential acidic compounds, i.e. sulphuric acid (anthropogenic SO_4^{2-}), nitric acid (NO_3^-) and organic acids (OA) (Mphepya et al., 2004; Laouali et al., 2012), which is presented in Table 3. The measured acidity (H^+ , measured) at all the sites is considerably less than the total H^+ concentration estimated, which can be attributed to neutralisation. NFs can be calculated to evaluate the neutralisation of sulphuric and nitric acids by bases consisting of cations (e.g. Ca^{2+} , NH_4^+ and Mg^{2+}) associated with anions (e.g. oxides, carbonates) by using Equation (7), which are presented in Table 4 for the four South African IDAF sites. It is evident that NH_4^+ is the major ionic species present in wet deposition that neutralises the strong acids, with Ca^{2+} being the second most important species. Mphepya et al. (2004, 2006) also attributed the lower pA compared to measured acidity to neutralisation.

The calculated potential contribution of the mineral acids (sulphuric and nitric acid) at AF and VT is 84% and 87%, respectively, which forms the greatest part of free acidity at these sites affected by industrial and other anthropogenic activities. The potential contribution of mineral acids also dominated wet deposition collected at SK, which contributed 77% of the free acidity, indicating the impacts of air masses passing over the industrialised Mpumalanga Highveld (Fig. 2(g and h)). Although the potential contribution of mineral acids at LT was 58%, a much larger contribution of organic acids, i.e. 42% was calculated at LT, which can partially be attributed to the larger relative contribution of biomass burning at LT.

3.2. Wet deposition fluxes of ions

The wet deposition fluxes of the species determined at the four sites correspond with the relative concentrations of these species in the wet deposition, i.e. species with higher VWM concentrations had higher wet deposition fluxes. The wet deposition flux of S was seven to eight times higher at AF ($7.87 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and VT ($8.44 \text{ kg ha}^{-1} \text{ yr}^{-1}$) compared to depositions thereof at LT ($1.44 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and SK ($1.75 \text{ kg ha}^{-1} \text{ yr}^{-1}$). The total wet deposition flux of N was approximately three times higher at AF ($6.32 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and VT ($6.97 \text{ kg ha}^{-1} \text{ yr}^{-1}$) than total wet N deposition at LT ($1.87 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and SK ($2.12 \text{ kg ha}^{-1} \text{ yr}^{-1}$). N is considered to be an important source of nutrients in ecosystems, while levels above a certain critical load, which depends on the specific ecosystem, can be considered to be contributing to pollution and eutrophication of the environment (Josipovic et al., 2011).

3.3. Sources of ionic species

3.3.1. Principle component analysis (PCA) and correlations of ionic species

Linkages between different chemical species and similar sources can be statistically explored by performing principal component analysis (PCA) and Spearman correlation calculations, which are presented in Fig. 5. PCA was applied as an explorative tool in this study. From a statistical perspective the datasets were not large enough for definitive source apportionment with PCA. For PCA, the dataset was subjected to Box-Cox transformation in an effort to eliminate some possible artefacts, e.g. auto-correlations. There are no well-defined rules for the number of factors to be retained. In general, factors that are either meaningful or with eigenvalues larger than one are kept (Hosiokangas et al., 1999). Three meaningful factors were determined for AF and VT, while two meaningful factors were determined for LT and SK. The factors identified explained 83.3%, 85.7%, 78.8% and 65.9% of the variances of the datasets for AF, VT, LT and SK, respectively.

Based on the results of PCA and Spearman correlation analyses, the main sources influencing the wet deposition composition at AF included terrigenous (crustal), marine, fossil fuel combustion and agricultural sources. The first PCA factor is loaded with all the ionic species normally associated with terrigenous (crustal) sources. The second PCA factor includes Na^+ and Cl^- that are linked to a marine source, which is also strongly indicated by the Spearman correlation between these two ions. The third factor is associated with the acidity (H^+), which is expectedly related to known anthropogenic species (NH_4^+ , NO_3^- and SO_4^{2-}) for this region, which is related mainly to fossil fuel combustion and agricultural activities. These linkages are also supported by the Spearman correlations between H^+ and these species. The contribution from biomass burning is not evident from these statistical analyses. Surprisingly, no correlation for OAs was indicated by either of these two methods.

The PCA analysis for VT yielded a more complex result. While it is clear from the third PCA factor that the acidity at VT is strongly associated with NO_3^- and SO_4^{2-} , the first and second factors seem to represent mixtures of marine, terrigenous (crustal) and fossil fuel sources. The Spearman correlations are slightly more indicative of different sources. At VT, the acidity is also strongly correlated with NO_3^- and SO_4^{2-} , while a weaker relation to NH_4^+ is observed as indicated by Spearman correlations. The strong Spearman correlation between Na^+ and Cl^- is again evident. The difficulty in separating signals from different sources at this site is expected, since this site is surrounded by different industries and other diverse anthropogenic sources.

For LT and SK, PCA analysis resulted in only two identifiable factors. One of these factors included ionic species associated with marine and terrigenous (crustal) sources (factor 1 at LT and factor 2 at SK), with the strong marine influence at these two sites reflected in this factor. The second factor was associated with the acidity and fossil fuel combustion and agricultural sources (factor 2 at LT and factor 1 at SK). The OAs are at both these sites well correlated with the acidity, which was not the case for AF and VT. This is indicative of the relevant importance of OAs from biomass burning in Africa to acidity at sites that are not strongly influenced by anthropogenic sources.

In addition to identifying different source regions, evidence for the neutralisation of acidic species, as discussed in section 3.1, is also provided by the good Spearman correlations between SO_4^{2-} and NO_3^- , and the cations Ca^{2+} , NH_4^+ and Mg^{2+} , as well as the correlations between these acidic ions and cations obtained with PCA as indicated in Fig. 5.

In combination, from these different calculations and correlations, the major source groups identified were marine, terrigenous

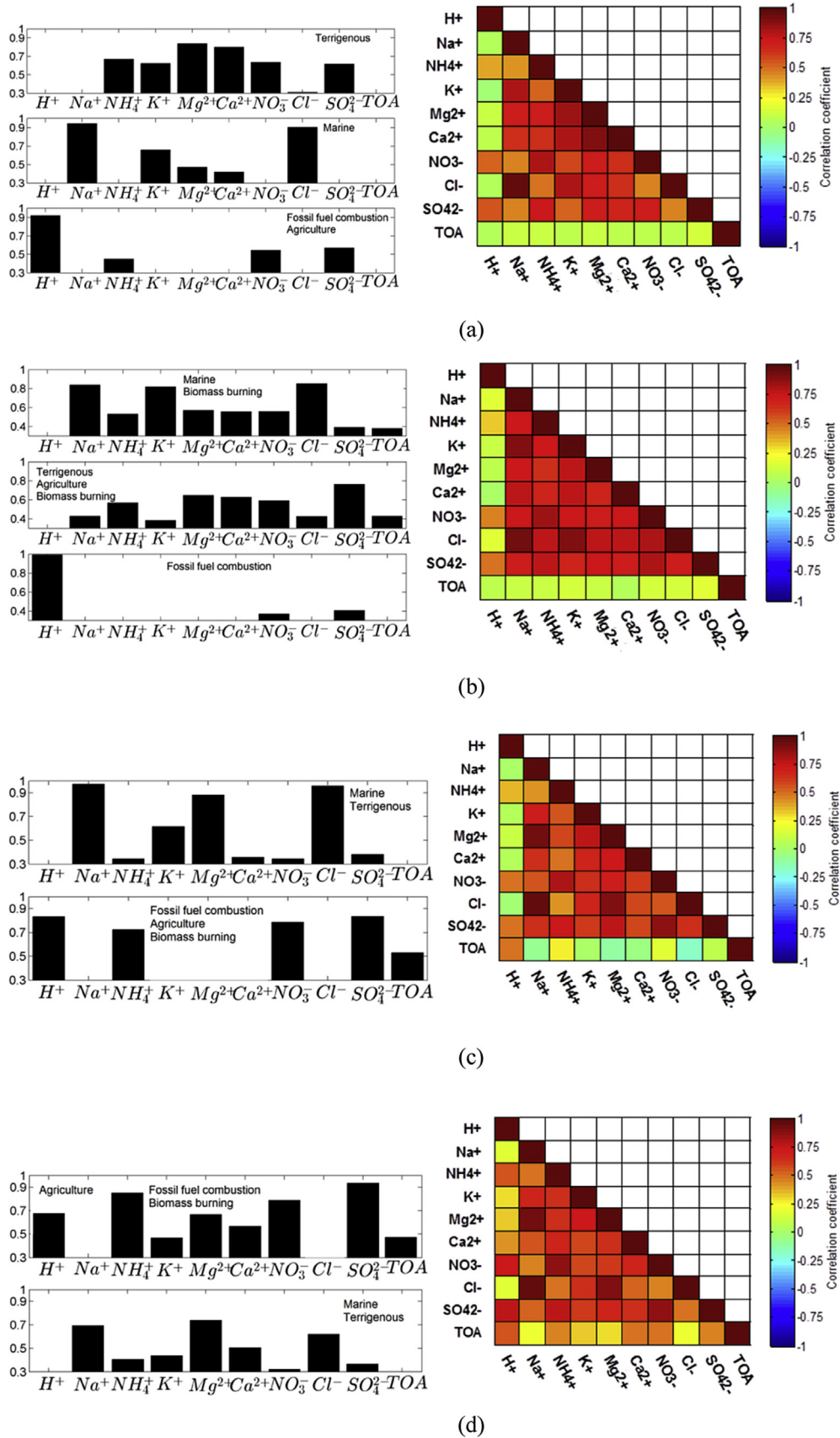


Fig. 5. Major sources of the ions and correlation between each two ions in the wet deposition samples collected in (a) AF, (b) VT, (c) LT, and (d) SK during the period from 2009 to 2014.

Table 3
Contributions of mineral and organic acids to total acidity.

	AF 2009–2014		VT 2009–2014		LT 2009–2014		SK 2009–2014	
	μeqL^{-1}	%	μeqL^{-1}	%	μeqL^{-1}	%	μeqL^{-1}	%
Sulphuric acid	56.8	55	54.5	61	7.6	29	15.1	41
Nitric acid	33.7	32	23.0	26	7.5	29	13.2	36
Organic acids	13.1	13	11.5	13	11.1	42	8.7	23
Total H ⁺ , estimated pA	103.5	100.0	89.0	100.0	26.2	100.0	37.0	100.0
H ⁺ , measured	61.2	56	44.6	50	15.2	58	22.2	61

Table 4
Acid neutralisation factors (NFs) of wet deposition calculated for each of the South African IDAF sites for 2009 to 2014.

Site	NF _{Ca2+}	NF _{Mg2+}	NF _{NH4+}
Amersfoort	0.19	0.07	0.32
Vaal Triangle	0.21	0.06	0.38
Louis Trichardt	0.41	0.13	0.72
Skukuza	0.17	0.12	0.45

(crustal), fossil fuel combustion, agriculture and biomass burning. The contributions to the chemical content of deposition and the atmospheric chemical characteristics of wet deposition will be explored in the following section.

3.3.2. Source contributions

Equations (3) and (4) in Section 2.6 were used to estimate the marine (sea-salt fraction) and non-marine (non-sea-salt fraction) contributions for Ca²⁺, SO₄²⁻, Mg²⁺, K⁺, and Cl⁻. An estimation of these source contributions was calculated by assuming Na⁺ was completely of marine origin. The non-marine contributions for Ca²⁺, Mg²⁺, K⁺ and Cl⁻ were considered to be terrigenous (crustal), while the non-marine SO₄²⁻ was divided into terrigenous and anthropogenic source contributions with the two methods described in Section 2.6. Furthermore, it can be assumed that anthropogenic sources of SO₄²⁻ are predominantly fossil fuel combustion in this part of South Africa. NO₃⁻ and NH₄⁺ can be associated with different sources, which include anthropogenic sources and biogeochemical processes. At the West African IDAF sites, NO₃⁻ and NH₄⁺ could mainly be associated with natural sources (Galy-Lacaux et al., 2009). However, it can be assumed for the South African IDAF sites that NO₃⁻ is predominantly associated with fossil fuel combustion, while NH₄⁺ is mainly related to agriculture. The biomass burning contribution could be related to OA VWM concentrations. In Fig. 6, a summary of the estimations of the source group contributions to the chemical content of wet deposition at South African IDAF sites is presented.

Marine contributions. In Table 5, the ratios of K⁺, Mg²⁺, Ca²⁺, Cl⁻ and SO₄²⁻ in relation to Na⁺ are presented. In addition, the EFs calculated with Equation (5) with regard to the reference seawater ratios, according to Keene et al. (1986), are also listed. The Cl⁻/Na⁺ ratios at all the sites were close to the seawater ratio (1.161), with the EFs being close to 1. In addition, a strong correlation is observed between Na⁺ and Cl⁻ at all the sites (Fig. 5). Since southern Africa is surrounded by the Atlantic and Indian Oceans, the oceans can be considered to be the major sources of Na⁺ and Cl⁻. It also indicates that marine air masses affect all the sites, as indicated by overlay back trajectories in Fig. 2, especially at LT, SK and AF. The Mg²⁺/Na⁺ ratios were also close to that of seawater (0.227) at LT and SK, with strong correlations observed between Na⁺ and Mg²⁺, and Cl⁻ and Mg²⁺ at these two sites. This indicates that the ocean is also a strong source of Mg²⁺ at these sites. The lesser marine influence at AF and, especially, VT is reflected by the Mg²⁺/Na⁺ ratio being

higher than the seawater ratios thereof. The relatively weaker correlation between Na⁺ and Mg²⁺, and Cl⁻ and Mg²⁺ at these two sites compared to the correlations thereof at LT and SK also supports this conclusion. The much higher Mg²⁺ at VT might be attributed to the proximity of several large pyrometallurgical smelters (Fig. 1), since it is well known that fly ash of such smelters has elevated levels of Mg. The higher Mg²⁺ at AF can also be ascribed to being regionally affected by large point sources as indicated in Figs. 1 and 2(a and b).

The marine contribution to the various sites was calculated according to the VWM concentrations and the ratio of Na⁺ to the various other ions in seawater (using the ratios from Keene et al., 1986 in Table 5), from the data listed in Tables 2 and 5 by determining the sum of the marine contributions in relation to the total ionic content at the sites (e.g. $([\text{Na}^+] + [\text{K}^+] + [\text{Mg}^{2+}] + [\text{Ca}^{2+}] + [\text{Cl}^-] + [\text{SO}_4^{2-}])_{\text{seawater}} / [\text{Total VWM ionic concentrations}]$). From these calculations, the marine contribution during the study period was estimated to be 22% at AF, 6% at VT, 28% at LT and 37% at SK (Fig. 6).

Terrigenous (crustal) contributions. The terrigenous (crustal) contribution to the chemical composition of wet deposition is linked to African soil dust species, e.g. calcite, dolomite, gypsum and other key minerals such as illite, smectite and palygorskite. In wet deposition, the correlations between Ca²⁺, Mg²⁺ and SO₄²⁻ are used as an indication of this source strength. These species are relatively well correlated at all the sites, as indicated in Fig. 5. Soil dust is considered to be a major constituent of the regional aerosol load of the South African atmosphere (Piketh and Prangley, 1999; Van Zyl et al., 2014), which can originate from natural soil erosion or dust emitted from industrial activities. Mphepya et al. (2004) also indicated that an additional source of Ca²⁺ and SO₄²⁻ at South African IDAF sites, especially at AF, could be coal combustion. Coal combustion is a major source of SO₄²⁻, while Ca is a major element in fly ash (Mahlaba et al., 2011).

The terrigenous (crustal) contributions to each of the sites were calculated by subtracting the marine contributions from the total VWM concentrations, while an anthropogenic contribution was additionally subtracted from SO₄²⁻. The sum of the terrigenous (crustal) contributions in relation to the total ionic content (e.g. $([\text{K}^+] + [\text{Mg}^{2+}] + [\text{Ca}^{2+}] + [\text{Cl}^-] + [\text{SO}_4^{2-}])_{\text{terrigenous}} / [\text{Total VWM of ionic concentrations}]$) could then be determined. The terrigenous (crustal) contributions to the total ionic content during the study period were estimated to range between 14 and 15%, 15 and 19%, 19 and 24%, and 9 and 13% at AF, VT, LT and SK, respectively, depending on the method applied to calculate the anthropogenic SO₄²⁻ contribution (source contributions presented in Fig. 6 were based on calculations from the second method). Terrigenous (crustal) sources contribute relatively significantly to the chemical composition of wet deposition in southern Africa. This is not surprising, since southern Africa is a semi-arid region in which rainfall is mostly associated with convective events.

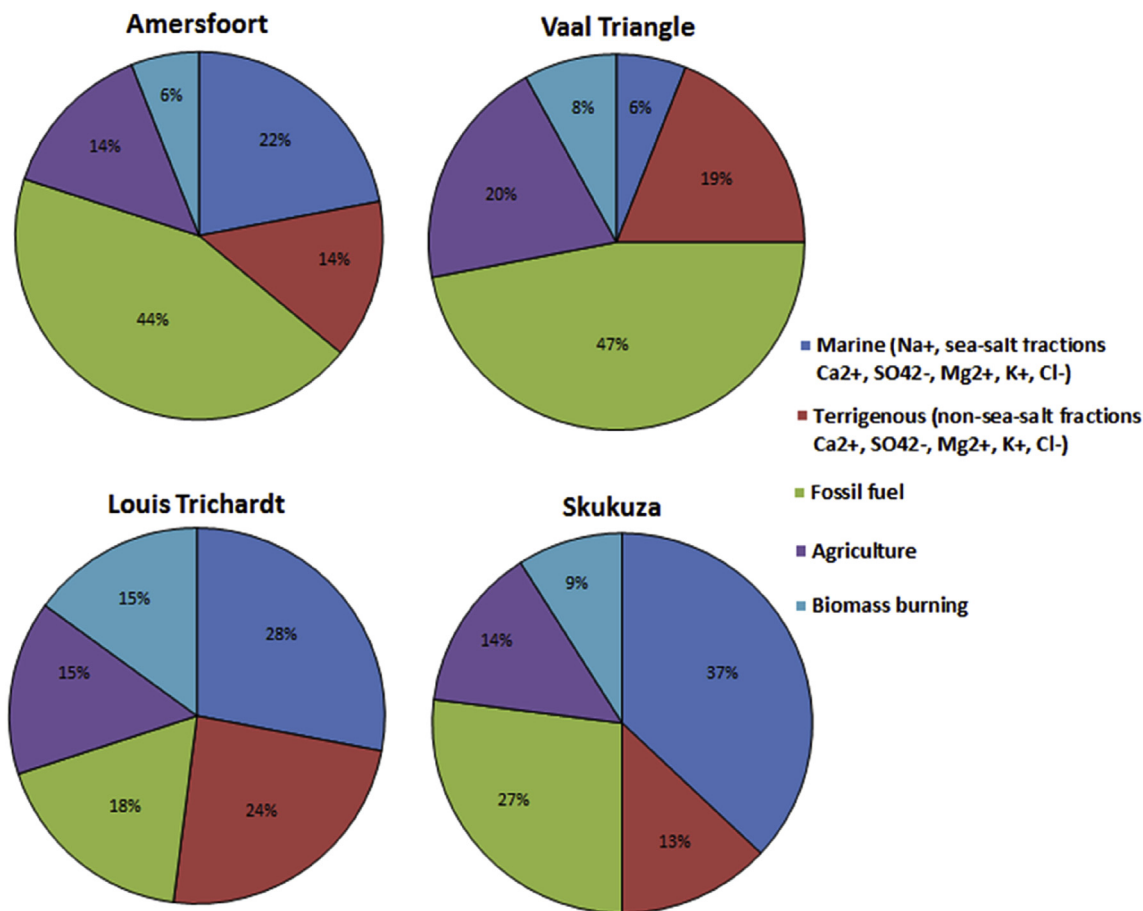


Fig. 6. Estimations of contributions to the chemical content of wet deposition at the South African IDAF sites.

Table 5

Comparison of wet deposition and seawater ratios and corresponding enrichment factors (EF) at South African IDAF sites for the period from 2009 to 2014.

Ions	Seawater ^a	Amersfoort 2009 to 2014	Vaal triangle 2009 to 2014	Louis Trichardt 2009 to 2014	Skukuza 2009 to 2014
Ca ²⁺ /Na ⁺	0.044	0.895	4.627	0.806	0.356
EF _(Ca2+)		20.4	105.4	18.4	8.1
SO ₄ ²⁻ /Na ⁺	0.121	3.429	15.727	1.595	1.417
EF _(SO42-)		28.3	130.0	13.2	11.7
Mg ²⁺ /Na ⁺	0.227	0.308	1.302	0.249	0.248
EF _(Mg2+)		1.4	5.7	1.1	1.1
K ⁺ /Na ⁺	0.022	0.412	0.404	0.660	0.158
EF _(K+)		17.8	18.3	30.0	7.2
Cl ⁻ /Na ⁺	1.161	1.002	1.291	1.397	1.194
EF _(Cl-)		0.9	1.1	1.2	1.0

^a Seawater ratios from Keene et al. (1986).

Fossil fuel combustion contributions. SO₄²⁻ in wet deposition results from emissions of gaseous sulphur dioxide (SO₂) (and hydrogen sulphide (H₂S) to a lesser extent) and particulates containing SO₄²⁻. In the north-eastern interior of South Africa, where the South African IDAF sites are situated, SO₂ and SO₄²⁻ are primarily emitted through anthropogenic activities, i.e. fossil fuel combustion (coal-fired power stations and petrochemical plant) and biomass burning (household combustion). As described previously, the non-marine SO₄²⁻ was divided into terrigenous and anthropogenic (fossil fuel combustion) source contributions with two methods described in

section 2.6, i.e. estimating anthropogenic SO₄²⁻ by calculating the excess of that supplied by gypsum (Equation (6)) and a method where a baseline SO₄²⁻ concentration is subtracted from the total SO₄²⁻ VWM concentration. These results are presented in Table 6.

It follows from Table 6 that the estimated anthropogenic contribution to SO₄²⁻ concentrations in wet deposition is approximately 86, 99, 72 and 80% at AF, VT, LT and SK, respectively as calculated with Equation (6). The second method, where the global background concentration of 7 µeq.L⁻¹ was subtracted from the total SO₄²⁻ VWM concentrations, estimated that 90, 87, 43 and 62%

of the SO_4^{2-} at AF, VT, LT and SK, respectively were of anthropogenic origin. The anthropogenic source contribution to SO_4^{2-} with these two methods differs somewhat for each of the sites and needs further exploration. Long-term tracer studies that quantify the anthropogenic contribution are probably the best methodology to follow. However, these types of studies are very expensive and not really feasible within the South African IDAF network. In terms of the present study, however, it is evident that both methodologies indicate a very strong anthropogenic influence on SO_4^{2-} at AF and VT of similar magnitude (~90%). The discrepancies between the two methods for LT and SK are probably related to an under-estimation of sources of gypsum at LT and VT.

NO_3^- is the final product of multiphase reaction processes of gaseous NO_x , atmospheric particles and cloud water (Galy-Lacaux et al., 2009; Mphepya et al., 2004). Gaseous NO_x is primarily emitted as nitrogen oxide (NO) from natural, e.g. biogenic emissions and biomass burning (naturally occurring wild fires), as well as anthropogenic sources, e.g. biomass burning (household combustion) and fossil fuel combustion (coal-fired power stations and vehicular emissions). However, according to reports on NO_2 emissions in this region from anthropogenic sources (Collett et al., 2010; Lourens et al., 2011; Pretorius et al., 2015), it is expected that a relatively significant fraction of NO_3^- can be considered to be of anthropogenic origin, i.e. fossil fuel combustion emissions from coal-fired power, plants, petrochemical industries, traffic and household combustion.

The large impacts of fossil fuel combustion at AF and VT are evident from the large contribution of the fossil fuel combustion source groups indicated in Fig. 6, i.e. 44% at AF and 47% at VT. As mentioned before, the Vaal Triangle is a highly industrialised area with various large point sources (Fig. 1). AF is situated in close proximity to the industrialised Mpumalanga Highveld where nine coal-fired power stations, a petrochemical plant and a number of pyrometallurgical smelters are located (Fig. 1). In addition to these large point sources in the Mpumalanga Highveld, traffic emissions and household combustion also contribute to elevated levels of atmospheric pollution (Helas and Pienaar, 1996). The AF and VT sites are also situated in regions that have been declared national priority areas by the South African government, i.e. the Highveld Priority Area and the Vaal Triangle Air-shed Priority Area, respectively (Government Gazette, 2007, 2005). The declaration of these regions as priority areas indicates that they are relatively highly polluted by anthropogenic activities. Furthermore, AF is also ~200 km west from the Johannesburg-Pretoria conurbation with a population of more than 10 million people (Fig. 1) (Lourens et al., 2012). The 96-h overlay back trajectories for 2009 and 2010 presented in Fig. 2(a and b) for AF clearly indicate the impacts of air masses passing over the Johannesburg-Pretoria conurbation and the Mpumalanga Highveld with AF being frequently affected by air masses moving over the south-eastern to north-eastern sector. The overlay back trajectories for VT (Fig. 2(c and d)) indicate that, in addition to local point sources in the Vaal Triangle, VT is also the

affected by regional atmospheric pollution and the Johannesburg-Pretoria conurbation.

Although LT and SK have a smaller contribution from the fossil fuel combustion source groups (Fig. 6), overlay back trajectories for LT (Fig. 2(e and f)) and SK (Fig. 2(g and h)) indicate that these sites are also affected by air masses moving over the strongly anthropogenically affected source regions. Although these overlay back trajectory patterns are only for 2009 and 2010, they clearly demonstrate the general anti-cyclonic recirculation pattern of air masses over this part of southern Africa (Van Heerden and Taljaard, 2015). The concentration profile of species associated with fossil fuel combustion pollution also indicates that polluted air masses are diluted as the air masses travel further from the source region to SK and LT. This is reflected in the concentrations of SO_4^{2-} and NO_3^- being slightly higher at SK compared to LT (Table 2).

Agricultural contributions. Atmospheric NH_4^+ results from emissions of gaseous ammonia (NH_3) and particulates containing NH_4^+ . The major sources of NH_3 include bacterial decomposition of urea in animal excreta and from natural or fertilised soils (Schlesinger and Hartley, 1992), wild fires and household combustion of wood (Delmas et al., 1991; Brocard et al., 1996). In addition, the production of fertilisers and petrochemical plants can also be considered a significant source of NH_3 . It is evident from Fig. 6 that the agricultural source group contributions were similar at AF, LT and SK, which can be attributed to regional farming activities in the north-eastern interior of South Africa. A larger agriculture contribution is observed at VT, which is expected due to large-scale industrial production of fertilisers in this area.

Biomass burning contributions. Biomass burning can be considered to originate from natural and anthropogenic sources. In this paper, the concentrations of the total dissociated organic acids were used as a proxy for the contribution of biomass burning, i.e. wild fires. It is evident from Fig. 6 that the largest contribution of biomass burning was at LT. The widespread regional atmospheric influence of biomass burning in southern Africa is evident (Sinha et al., 2004) from the biomass burning source group estimations determined at all the South African IDAF sites.

3.4. Inter-annual variability and seasonal variations

The total annual VWM concentrations and fluxes of the ten ions showed significant changes from 2009 to 2014 as indicated in Fig. 7. Over the 2009 to 2014 period, the total annual VWM concentrations of the ten ions at VT and LT changed quite significantly on an inter-annual basis, while it were fairly similar at SK. At AF the total ionic concentrations were similar from 2009 to 2013, with relatively higher concentrations during 2014. It was expected that rainfall depth and the proximity of anthropogenic sources should have a strong influence on the VWM ionic concentrations. However, it is not the case in this instance, since these sites represent in each of these circumstances an anthropogenic impacted and a remote site. It is clear that the total VWM ionic concentrations therefore depend on a large number of factors. This observation is supported by the comparable relatively low VWM ionic concentrations measured at VT in 2010 and 2011 despite 2010 being a wet year (1083 mm) and 2011 being a relatively dry (818 mm) year. The total VWM ionic concentrations are in both instances lower compared to other years. The relatively dry year, 2011, at VT is characterised by a significantly larger VWM concentration for Ca^{2+} that could be ascribed to more soil dust during a dryer period. The larger VWM concentration for NH_4^+ for the same period and site is probably due to an anthropogenic source in the region that had a more pronounced influence during a dry period. In 2009, a

Table 6

Estimation of SO_4^{2-} sources in μeqL^{-1} . Terrigenous and anthropogenic values in brackets were calculated with the second method (assumption of background concentration of $7 \mu\text{eqL}^{-1}$), while the other terrigenous and anthropogenic values were calculated with the first method (excess of that supplied to gypsum).

Site	Total/ μEqL^{-1}	Marine/ μEqL^{-1}	Non-marine/ μEqL^{-1}	
			Terrigenous	Anthropogenic
Amersfoort	67.2	2.2	7.3 (4.8)	57.7 (60.2)
Vaal Triangle	55.0	0.4	0.1 (6.6)	54.5 (48.0)
Louis Trichardt	12.4	1.0	2.6 (6.0)	8.9 (5.4)
Skukuza	18.7	1.6	2.0 (5.4)	15.1 (11.7)

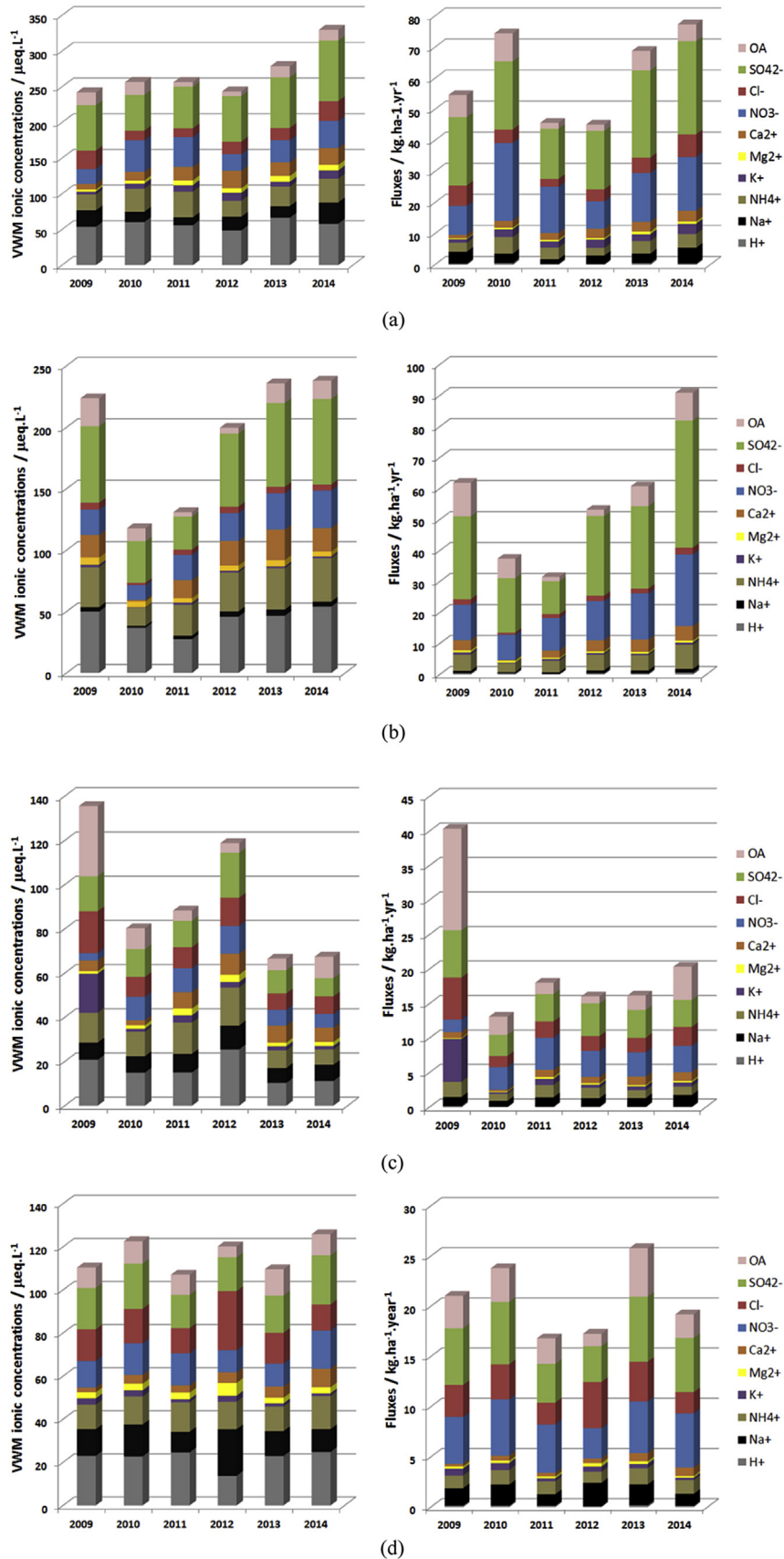


Fig. 7. The annual VWM concentrations and fluxes of wet deposition of each ion observed between 2009 and 2014 at (a) AF, (b) VT, (c) LT and (d) SK.

significantly higher OA VWM concentration was determined at LT, which indicated that the site was more frequently affected by biomass burning events during that year. This also illustrates the inter-annual variability of sources affecting the South African IDAF sites. The relatively large contribution of Na^+ and Cl^- to the total VWM ionic concentrations at SK in 2012 can likely be attributed to increased frequency of cold fronts from the southern oceans passing over South Africa from the south-west during the winter months as indicated in Fig. 2(g and h).

From Fig. 7, it follows that the rainfall depth plays a very important role on the wet deposition fluxes, which is illustrated by the inter-annual wet deposition fluxes' variability correlating with the inter-annual changes in rainfall depth. Furthermore, it is evident that, although the four sites are from a global perspective relatively in close proximity, large inter-annual variations in the ionic concentrations and fluxes of wet deposition occur between these sites, which emphasises the importance of a good spatial coverage when establishing regions that are environmentally at risk. The wet deposition fluxes show inter-annual differences of up to 300% (e.g. at VT when comparing the total wet deposition fluxes in 2010 and 2014), which is mainly due to large fluctuations in the rainfall depth.

It is expected that the chemical composition of wet deposition would be different for each of the seasons due to the meteorological and environmental changes such as rainfall depth, land cover, vegetation growth, biomass burning and anthropogenic activities (e.g. more household combustion for space heating during colder months). The seasonal variability is presented in Fig. 8.

As can be expected, it is clear from Fig. 8 that the ionic concentrations and fluxes of wet deposition closely correlate with the rainfall depth, i.e. significantly higher VWM ionic concentrations during the dry season and much higher wet deposition fluxes during the rainy season. This observation is in agreement with the occurrence that large rainfall events are normally associated with lower VWM ionic concentrations due to the cleansing of the atmosphere by rain drops. It is expected that atmospheric concentrations of these species will increase during the dry season due to the decrease in wet removal thereof, with dry deposition and chemical transformation being the main removal mechanisms. Strong variations in the chemical composition between different seasons are evident. This might be ascribed to the very large influence of anthropogenic activities, especially at the VT and AF sites. The dry winter season in South Africa is characterised by increased atmospheric pollutant concentrations due to the existence of more pronounced inversion layers trapping pollutants near the surface of the earth, while increases in emissions from household combustion for space heating also occur during winter. For SK (Fig. 8(d)), a strong marine signal (Na^+ and Cl^-) is obvious during the dry months of June, July, August and September, which can be linked to the meteorological conditions prevailing during these months, i.e. more cold fronts from the southern oceans passing over the country from the south-west (compare Fig. 3(g and h)). These increased Na^+ and Cl^- VWM concentrations associated with a cold front from the southern ocean passing over the country are also observed at LT and AF during the dry season (compare Fig. 3 (a and b) and (e and f)), while even VT indicates slightly higher Na^+ and Cl^- VWM concentrations during the dry season (compare Fig. 3 (c and d)). It was expected to also observe a strong seasonal signal for biomass burning (OA) from July to September at LT, but it was not observed. This can possibly be attributed to the influence of biomass burning for space heating and cooking, which is common in South Africa. A strong NH_4^+ signal is observed at this site for September and October, which can probably be linked to the beginning of the growth season (spring) and an increase in temperatures.

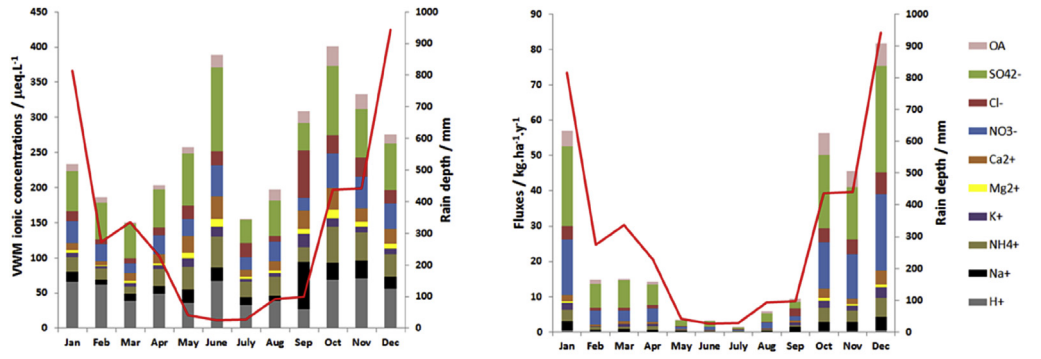
3.5. Comparison to previous measurements

In Fig. 9 and Table 7, the average annual ionic concentration, fluxes and pH values of wet deposition determined at AF, LT and SK in this investigation are compared to previous sampling periods at these sites (Mphepya et al., 2004, 2006). Ionic concentrations and fluxes of wet deposition for the VT site are also included in order to assist in the contextualisation of the results.

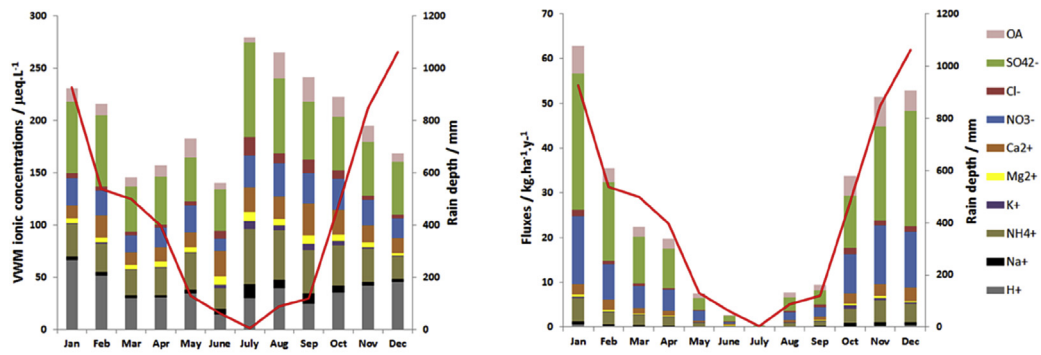
As shown in Fig. 9, it is evident that the total VWM ionic concentration and flux of wet deposition at AF were much higher during 2009–2014 than during 1985–1999. The total VWM ionic concentration increased by a factor of approximately 1.25, while the total wet deposition flux increased by a factor of approximately 1.71. Ionic concentrations are considered to be a better indication of change in the atmospheric chemical composition between these two periods, since wet deposition fluxes also depend on the rainfall amount. The increase in the VWM concentrations of SO_4^{2-} , NO_3^- and NH_4^+ observed at AF can be attributed to increased anthropogenic activities and population growth. Electricity consumption can be considered to be a good indicator of the afore-mentioned increase in anthropogenic activities. As mentioned, the Mpumalanga Highveld holds nine coal-fired power stations, which generate approximately 90% of the electricity in South Africa (Fig. 1) (Burton and Winkler, 2014). Electricity consumption in South Africa increased with 131 024 GWh from 1993 to 2006 (Inglesi-Lotz and Blignaut, 2011). In addition, South Africa also experienced a period of economic growth from 2000, which also coincided with increases in production, especially in the pyrometallurgical industries (e.g. ICDA, 2012). Although, from a very low base compared to SO_4^{2-} and NO_3^- , an increase in the VWM concentrations of Na^+ , Cl^- and K^+ is also observed, with the Na^+ and Cl^- ions almost two times higher during the period from 2009 to 2014. Since Na^+ is commonly assumed to be purely of marine origin and Cl^- is highly correlated with Na^+ , this increase can only be attributed to an increase in marine air masses passing over AF (e.g. a slight change in rainfall patterns). However, this explanation must be substantiated through further investigation. Ca^{2+} and Mg^{2+} were slightly lower during 2009–2014. As Ca^{2+} and Mg^{2+} are considered to be mainly from crustal sources, this observation can be attributed to lower levels of atmospheric dust and higher average rainfall amounts during 2009–2014 than during 1986–1999.

The total VWM concentrations of the ten ions at LT during 1986–1999 and 2009–2014 were similar. The total wet deposition flux of the ten ions shows an increase for the 2009 to 2014 period when compared to the 1986 to 1999 period (Table 7), which can be ascribed to a significant increase in the average annual rainfall. Therefore, although SO_4^{2-} and NO_3^- show an increase in wet deposition fluxes between the two periods, the ionic concentrations of the species were actually slightly lower for the 2009 to 2014 period. The NH_4^+ concentration was marginally higher during 2009–2014. As mentioned previously, LT is a regional background site that is removed from the industrial activities in the interior of South Africa. The wet deposition chemistry results determined at LT for the two periods therefore indicate that the increase in total VWM ionic concentrations observed for wet deposition over the industrialised interior of South Africa over the 2009 to 2014 period did not have a similar impact on wet deposition chemistry at LT.

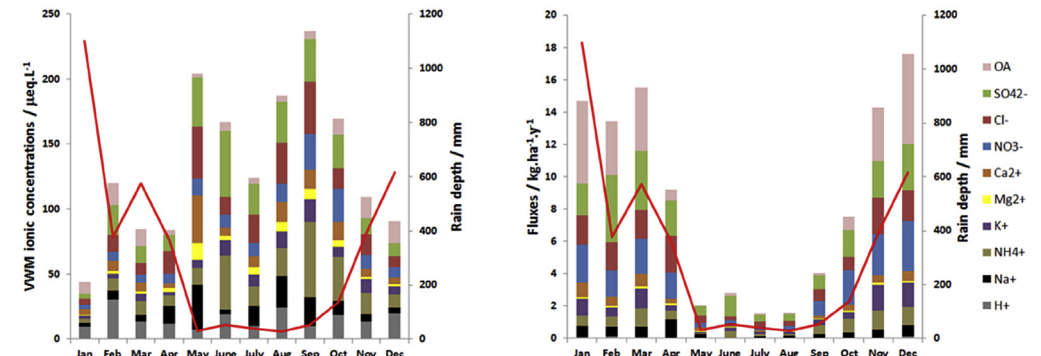
The total VWM ionic concentration of the measured ions at SK increased from 1999 to 2002 to 2009 to 2014, with the wet deposition flux being similar for the two periods due to lower rainfall amounts during the 2009 to 2014 period. The VWM concentrations of SO_4^{2-} , NO_3^- and NH_4^+ measured during the 2009 to 2014 period were also higher at SK, although to a lesser extent than at AF. The observation that SO_4^{2-} was the species with the highest VWM concentration for both periods at this site indicates that although



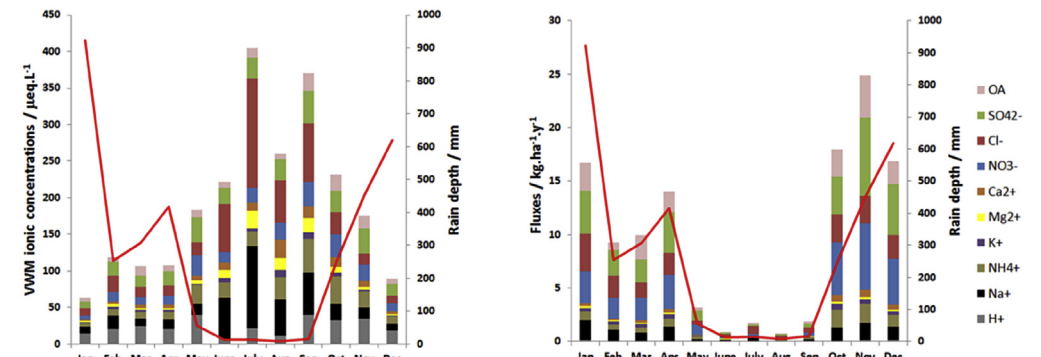
(a)



(b)



(c)



(d)

Fig. 8. Seasonal variations in the ionic concentrations and fluxes of wet deposition at (a) AF, (b) VT, (c) LT and (d) SK between 2009 and 2014. The red lines present monthly rain depths. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

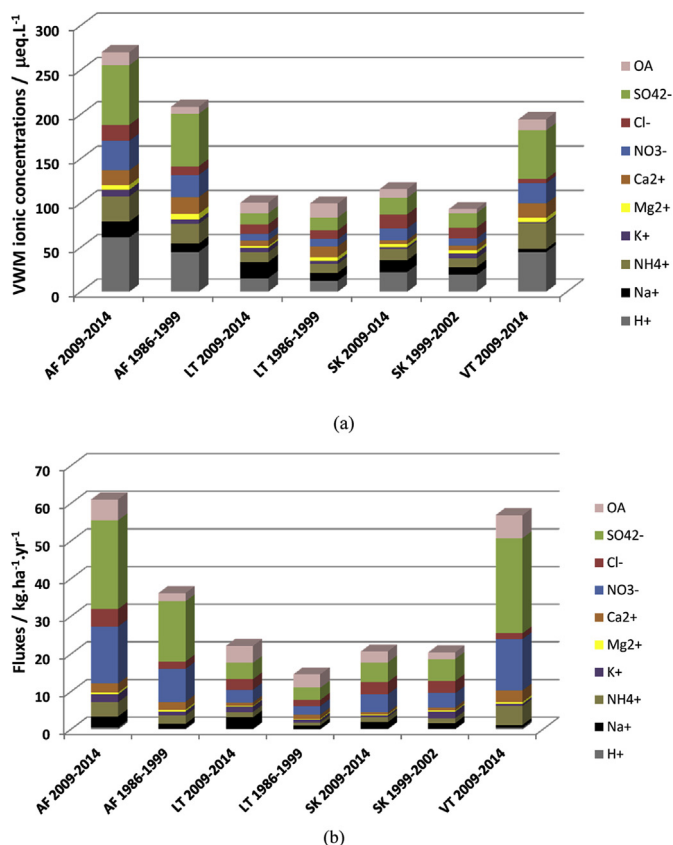


Fig. 9. (a) Ionic concentrations and (b) average annual fluxes of wet deposition determined between 2009 and 2014 at AF, VT, LT and SK, between 1986 and 1999 at AF and LT (Mphepya et al., 2004), and between 1999 and 2002 at SK (Mphepya et al., 2006).

SK is also considered to be a regional background site, it is affected by anthropogenic pollution from the industrialised Highveld. This is also indicated by the overlay back trajectories in Fig. 2(g and h).

Wet deposition flux of S at AF increased from 5.33 kg ha⁻¹ yr⁻¹ during 1986–1999 to 7.87 kg ha⁻¹ yr⁻¹ during 2009–2014, while the N flux increased from 3.66 kg ha⁻¹ yr⁻¹ to 6.01 kg ha⁻¹ yr⁻¹ (Table 7). In addition to higher VWM concentrations measured for SO₄²⁻, NH₄⁺, and NO₃⁻, this increase can also partially be ascribed to the increase of rainfall amount (by a factor of 1.3). At Louis

Trichardt, wet deposition fluxes of S and N increased from 1.07 to 1.44 kg S ha⁻¹ yr⁻¹ and from 1.15 to 1.87 kg N ha⁻¹ yr⁻¹, respectively. S deposition was slightly lower at SK, while N deposition was marginally higher.

Annual average pH did show significant differences among 1986–1999, 1999–2002 and 2009–2014 at all the sites (Table 7). However, the pH distribution of wet deposition samples (Fig. 4) indicates a higher percentage of the rain with lower pH during 2009–2014. During 1986 to 1999, the highest frequency of rain events was between 4.3 and 4.5 at AF, with only 8% of rain events having pH values lower than 4.0 (Mphepya et al., 2004). At LT, the largest number of rain events had pH values ranging between 4.6 and 5.0 during 1986–1999. No rain samples had pH values lower than 4, while 6% of rainfall events had pH values higher than 6.0 (Mphepya et al., 2004). A comparison of these two sampling periods at AF and LT indicates significant increases in rain events with lower pH values. A comparison of the 2009 to 2014 sampling period and the 1999 to 2002 sampling period at SK indicates a 2% increase in rain events with pH values lower than 4.0, with rain events higher than 6.0 remaining almost the same. The pH distribution of wet deposition samples indicated pH values ranging between 4.4 and 5.4 with the highest number of rain events having pH values of 5.2 for the 1999 to 2002 sampling period (Mphepya et al., 2006). A large shift in the frequency distribution is observed at SK for the 2009 to 2014 sampling period with more rainfall events with lower pH values and the peak number of events observed between 4.4 and 4.6.

The potential contributions of mineral acids at AF and LT calculated by Mphepya et al. (2004) were 90 and 50%, respectively, while Mphepya et al. (2006) calculated that mineral acids contributed 81.5% at SK. Lower potential acidic contributions of mineral acids were calculated for the 2009 to 2014 period at AF and SK, which can possibly be ascribed to an increase in household combustion over the Mpumalanga Highveld that can be associated with an increase in organic acids. However, at LT, a decrease in the acidic contribution of organic acids is observed, which can possibly be attributed to an increased contribution from anthropogenic emissions.

4. Conclusions

The work presented here is the first comprehensive analysis of wet deposition in South Africa after the work presented by Mphepya et al. (2004, 2006). The value and necessity of long-term deposition monitoring programmes are clearly indicated by the paper and by comparison to previous reported results. The

Table 7

Annual mean pH and wet deposition fluxes of S and N observed from 2009 to 2014 at AF, VT, LT, and SK, from 1986 to 1999 at AF and LT, and from 1999 to 2002 at SK.

	Amersfoort 2009–2014 ^a	Amersfoort 1986–1999 ^b	Louis Trichardt 2009–2014 ^a	Louis Trichardt 1986–1999 ^b	Skukuza 2009–2014 ^a	Skukuza 1999–2002 ^c	Vaal triangle 2009–2014 ^a
pH	4.32	4.35	4.89	4.91	4.66	4.75	4.51
NH ₄ ⁺ flux (kg N ha ⁻¹ yr ⁻¹)	2.91	1.76	1.11	0.63	1.04	1.02	3.89
NO ₃ ⁻ flux (kg N ha ⁻¹ yr ⁻¹)	3.41	1.97	0.76	0.52	1.08	0.85	3.08
SO ₄ ²⁻ flux (kg S ha ⁻¹ yr ⁻¹)	7.87	5.33	1.44	1.07	1.75	1.96	8.44
N	323	437	157	223	257	146	445
Total collected rainfall (mm)	3800.4	7321.3	3828.7	6012.2	3323.1	2249.5	5146.1
Average annual rainfall (mm)	729.75	563.2	728.2	462.5	583.23	749.8	956.43

N = total number of rain events.

^a This study.

^b Mphepya et al. (2004).

^c Mphepya et al. (2006).

calculation of the annual VWM ionic concentrations and fluxes of wet deposition for all the South African IDAF sites considered in this paper indicated that concentrations of the species largely from human emissions (including SO_4^{2-} , NH_4^+ and NO_3^-) were much higher during 2009–2014 than during 1986–1999 and 1999–2002. By comparing inter-annual results reported in this paper, it is evident that it is speculative to draw conclusions from the rainfall events for just one season. The large differences between sites also emphasise the importance of regionally representative spatial information.

The VWM ionic concentrations of species emitted by anthropogenic activities were much higher at VT and AF, than at SK and LT. The concentrations of maritime species were higher at SK and LT. The results of back-trajectory analyses confirm that air pollutants released from anthropogenic sources would transport to rural regions.

Several empirical and statistical methods were used to determine the major sources of the ten ions in wet deposition. The major five sources are marine, terrigenous, fossil fuel combustion, agriculture and biomass burning. Empirical methods indicated that marine was the largest contributor to Na^+ , Cl^- , and Mg^{2+} at SK and LT, lower at AF and very low at VT. PCA and clustering of the chemical composition data confirmed these observations and provided a theoretical tool to identify different source groups. Terrigenous (crustal) contributions were confirmed with the empirical methods and PCA. The five-year dataset allowed for the identification of different inter-annual and seasonal trends that further enhance the knowledge on atmospheric chemical processes in southern Africa. From the results presented, it is clear that anthropogenic (fossil fuel combustion and agriculture) sources dominate the chemical composition of wet deposition at VT and AM, while also significantly influencing wet deposition chemistry at relatively remote sites (SK and LT). Although the empirical and statistical methods applied in this study could adequately identify source group contributions, it is recommended that in future studies more advanced methods such as positive matrix factorisation should be utilised in wet deposition studies from which the contribution of each source to each ion could be more accurately established (Qiao et al., 2015).

An overall increase of wet deposition fluxes of species associated with anthropogenic activities in South Africa, i.e. SO_4^{2-} , NO_3^- and NH_4^+ , was observed at the South African IDAF sites when the 2009 to 2014 results were compared to previous data reported by Mphopya et al. (2006, 2004). This increase can most likely be ascribed to the increase in anthropogenic activities in South Africa. Concurrently, the annual H^+ concentration increased since the previous reports, which is reflected in a shift to more acidic rain events at all the South African IDAF sites. Acidic potential calculations indicated that only 22–42% of the measured H^+ concentrations were neutralised by alkaline species at the various sites.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2016.07.033>.

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