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Precipitation Chemistry in Semi-Arid Areas of Southern Africa: A Case Study of a Rural and an Industrial Site

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Abstract. Experimental data on the precipitation chemistry in the semi-arid savanna of South Africa is presented in this paper. A total of 901 rainwater samples were collected with automatic wet-only samplers at a rural site, Louis Trichardt, and at an industrial site, Amersfoort, from July 1986 to June 1999. The chemical composition of precipitation was analysed for seven inorganic and two organic ions, using ion chromatography. The most abundant ion was SO_4^{2-} and a large proportion of the precipitation is acidic, with 98% of samples at Amersfoort and 94% at Louis Trichardt having a pH below 5.6 (average pH of 4.4 and 4.9, respectively). This acidity results from a mixture of mineral and organic acids, with mineral acids being the primary contributors to the precipitation acidity in Amersfoort, while at Louis Trichardt, organic and mineral acids contribute equal amounts of acidity. It was found that the composition of rainwater is controlled by five sources: marine, terrigenous, nitrogenous, biomass burning and anthropogenic sources. The relative contributions of these sources at the two sites were calculated. Anthropogenic sources dominate at Amersfoort and biomass burning at Louis Trichardt. Most ions exhibit a seasonal pattern at Louis Trichardt, with the highest concentrations occurring during the austral spring as a result of agricultural activities and biomass combustion, while at Amersfoort it is less pronounced due to the dominance of relatively constant industrial emissions. The results are compared to observations from other African regions.

Key words: acid rain, chemical composition, precipitation chemistry, semi-arid savanna, wet deposition.

1. Introduction

Various sources, for example, natural (marine, biogenic, crustal) and anthropogenic emissions influence the chemical composition of trace elements in the atmosphere. The gases and aerosols from these sources are incorporated into raindrops through various processes during rain events, hence by analysing the chemical composition of rain samples, the chemical species present in the atmosphere can be

identified and quantified to obtain information about the atmospheric constituents. Knowledge of the chemical composition of precipitation is therefore critical in understanding regional and local air pollution and its effects on the eco-systems.

Recent studies in precipitation chemistry have been published for tropical countries (Ayers *et al.*, 2000; Gillett *et al.*, 2000; Williams *et al.*, 1997; Lara *et al.*, 2001). In contrast, there are relatively few studies on the rainwater chemistry of semi-arid countries (Norman *et al.*, 2001; Satsangi *et al.*, 1998; Herut *et al.*, 2000; Mamane and Gottlieb, 1995), and especially in Africa (Turner *et al.*, 1996; Galy-Lacaux and Modi, 1998). Relatively little information is available for South Africa, which has one of the largest industrialised economies in the southern hemisphere and is the only industrialised regional energy producer on the African continent (Siversten *et al.*, 1995).

Eskom, the major power utility in South Africa, has been monitoring rain chemistry on a continuous basis since 1985 (Turner *et al.*, 1996) and, as of 1995, has supported the International Global Atmospheric Chemistry (IGAC) programme DEBITS (Deposition of Biogeochemically Important Trace Species) for Africa IDAF (IGAC DEBITS AFRICA) with wet deposition and passive sampling results from two of its monitoring sites. The main focus of the IDAF programme is to identify the chemical cycles of important nutrient species in the atmosphere, including the emissions from biomass burning, ecosystems and man-induced activities, such as change of land use and industrial emissions. To achieve this, the IDAF project set up 10 monitoring stations in various African ecosystems. The precipitation composition differs significantly in various tropical regions, depending on the dominant sources within the region considered.

In this paper the precipitation chemistry data from two sites on the South African plateau ('Highveld'), characterising industrial (Amersfoort) and rural (Louis Trichardt) environments, respectively, are presented for the period 1986 to 1999, within the context of the IDAF network. The main objectives are to:

- determine the mean chemical composition of rainwater in a rural and an industrial area within the semi-arid savanna of South Africa, based on a large set of quality-checked data;
- identify the potential anthropogenic and natural sources of the chemical content of precipitation;
- determine the seasonal variability and temporal trends of the rainwater composition;
- present a comparative study of precipitation characteristics between the semi-arid regions of Africa, viz., Niger and South Africa.

2. Regional Climate and Sampling Sites

Most of the rainfall over the central and northern parts of South Africa occurs during the summer months from October to March, mostly in the form of convective precipitation, while the southern part (Cape Province) is characterised by

winter rainfall. The predominant circulation type in southern Africa is governed by subtropical recirculation of air over the subcontinent with the average frequency of recirculated air being estimated to be 64% (Tyson *et al.*, 1996). Over the central interior the airflow responsible for the dispersion of pollutants is mostly from north-westerly directions. Details of the climate characteristics and their relevance to the transport of pollutants are summarised in Held *et al.* (1996), while the most common pathways, based on a five-year trajectory climatology, have been identified by Piketh and Prangley (1998).

Figure 1 shows the location of the 10 IDAF stations operating in 2002. The Amersfoort site (No. 9) is located at 27°08' south and 29°49' east in the south-eastern part of the Mpumalanga Province, 1646 m above mean sea level (amsl). This is roughly 200 km south-east of Johannesburg and 50–100 km south-east to south-south-east of the major industrial activities, which also include the main centre of electric power generation in the Mpumalanga Highveld area. Amersfoort falls into a climatological transition region between the Highveld and the nearby escarpment. The nearest representative long-term climatological observations are from Ermelo, about 90 km north-north-east of Amersfoort (SAWB, 1986). The mean annual precipitation there is 755 mm, with January (126 mm) and November (131 mm) having the highest mean monthly rainfall. Rain is recorded on 96.7 days/year (≥ 0.1 mm), of which on average 24 days receive ≥ 10 mm/day. However, from May to August the average monthly rainfall totals are ≤ 20 mm. Surface winds on the South African plateau are mostly driven by orographic features at night (very stable boundary layer), while during daytime the overlying gradient winds will break through (convective boundary layer), resulting in large diurnal and seasonal variations (Held *et al.*, 1996). For the purpose of rain quality one should therefore rather look at winds within the mixing layer (2,500 m amsl; SAWB, 1950), which would be responsible for the dispersion of pollutants. During winter and spring, most winds in the Amersfoort area blow from westerly directions (south-west to north-west, 78%), being slightly more south-westerly in autumn, while during summer only 47% of winds come from the west and 28% from south-easterly directions. Thus, prevailing winds can be expected to frequently transport pollutants from the metropolitan and industrial regions (Gauteng and Mpumalanga) towards this site. This station is representative of a site strongly influenced by industry in a semi-arid area in southern Africa.

The Louis Trichardt site (No. 8) is located at 23°00' south and 30°02' east in the Northern Province, 961 m amsl, roughly 400 km to the north-north-east of Johannesburg. Although the mean annual precipitation is very similar (748 mm) to that at Amersfoort, the distribution of rain differs, viz. only 83.8 days/year with ≥ 0.1 mm are recorded on average, of which 20 days/year receive ≥ 10 mm/day. January is the month with the highest mean total (164 mm), while only 8 mm fall during August. From May to September ≤ 20 mm/month are recorded on average (SAWB, 1986). Winds over the Northern Province (Pietersburg wind rose for 2,500 m amsl; SAWB, 1950) are more uniform in frequency than in the Amersfoort area, but show

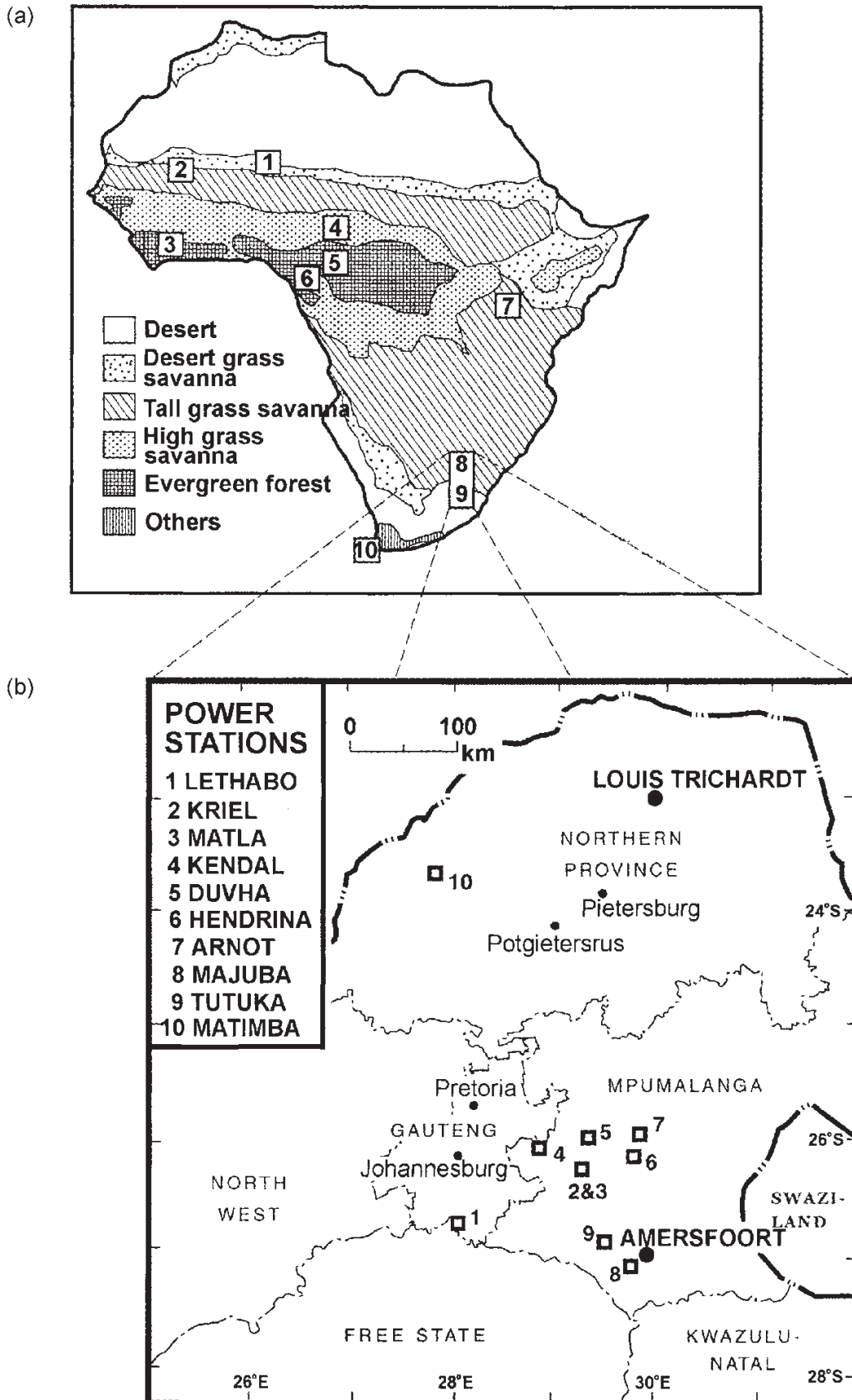


Figure 1. (a) Vegetation and location map of the 10 measurement stations of the IDAF network in 2002 (1. Banizoumbou, Niger; 2. Senpou, Mali; 3. Lamto, Ivory Coast; 4. Ngola, RCA; 5. Bomassa, Congo; 6. Zoétélé, Cameroon; 7. Mount Kenya, Kenya; 8. Louis Trichardt, RSA; 9. Amersfoort, RSA; 10. Cape Point, RSA). (b) The Louis Trichardt and Amersfoort sampling sites, as well as major power stations are shown in the map below (after Galy-Lacaux and Modi, 1998).

a distinct seasonal variation with a more dominant easterly component during summer, veering through south-east in autumn, to predominantly southerly in winter, followed by slightly more frequent northerly-component winds in spring. Winds rarely blow directly from the industrialised region towards this site. However, the site is ideally located to detect any pollution that has been recirculated within the frequently occurring sub-continental anticyclone system. There are no major cities or towns within a 100 km radius. The area is predominantly used for agricultural purposes, such as maize and cattle farming, and therefore it can be assumed that Louis Trichardt represents a rural site in a semi-arid region in southern Africa.

3. Collection Procedure, Chemical Analysis and Data Quality

3.1. COLLECTION PROCEDURE

Rainwater samples were collected on an event basis with an automated wet-only sampler (AeroChometric) that exposes the collector, a high-density polyethylene (HDPE) bucket, only when precipitation is falling. The device is equipped with a sensor that detects the onset of precipitation and activates a mechanism that opens the lid with the first raindrop and closes it just after the rain event. The advantages of automated wet-only sampling are: contamination of rainwater by dust is minimal before and after the events, and the delay in the execution of manual operation is reduced to a minimum. All samples were removed from the collectors as soon as possible, but at least within 24 hours after an event ended. Thereafter, the collected precipitation was divided into two samples in polyethylene bottles. The pH of one of the samples was immediately measured and the other sample was stored in frozen condition until being transported to the laboratory for chemical analysis. Upon arrival at the laboratory, 25 ml of aliquots were taken for immediate conductivity and pH measurements. The remaining sample was filtered through a 0.2 μm filter and the filtrates were chemically analysed.

3.2. CHEMICAL ANALYSIS

The chemical content of rainwater samples was determined by ion chromatography at the chemical laboratory of Eskom TSI. The ion chromatography systems used in this study are presented in Table I, including the main characteristics of the analytical parameters for the determination of mineral ions (sodium, ammonium, potassium, magnesium, calcium, chloride, nitrate and sulphate) and organic ions in rainwater samples. The highest-grade salts commercially available from suppliers were used to prepare stock standards from which appropriate dilutions were made. The analytical precision of organic ion measurements was 10%, while for other ions the precision was 5% or better. H^+ was calculated from the pH measurements using a Radiometer instrument with a combined electrode (ROSS) filled with KCl (3 M) and saturated with AgCl. For pH calibration, two buffer solutions at pH 4.01

and 7.00 were used. After the pH calibration, a buffer solution at pH 6.01 was used as control sample.

3.3. DATA QUALITY

In performing data quality control in the field, an attempt is made to identify and exclude samples, which were obviously contaminated or are questionable. Several methods were used to determine the suitability of a particular sample for inclusion in the database. Firstly, a sample could be visibly contaminated, i.e., if the sample was discoloured or contained insects or other foreign material. The site operator screens the sample to exclude such contaminated samples.

Secondly, the chemical laboratory of Eskom TSI is participating in the World Meteorological Organization (WMO) inter-laboratory comparisons since 1995 (WMO, 1997, 1998, 1999). This program annually evaluated all ion chromatography chemical analysis, pH and conductivity measurements performed in the laboratory and results compared to the reference values. Figure 2 shows the results of the WMO inter-calibration in 1999 for all mineral ions included in the synthetic samples (WMO, 1999). Ion concentrations analysed by the Eskom Laboratory are well correlated with the linear regression coefficient r being close to 1. According to the Eskom WMO intercomparison results, the analytical precision for all the ions species presented in this study is estimated to be better than 5%. Further quality control of the chemical analyses of field samples is performed by calculating either the ionic balance and/or the conductivity test. The latter is specifically used to detect analytical errors, as well as to ensure that major ions had been determined accurately. The calculations are based on the percent ion balance criteria, as described by WMO (EPA, 1994). The criteria has been applied to all precipitation samples in the database and only data that passed the WMO specifications was used in this study.

The total number of precipitation samples collected and chemically analysed during the study period is given in Table II. From July 1986 to June 1999, 655 and 314 rain events were collected at Amersfoort and Louis Trichardt, respectively, with distinct wet (October through March) and dry (April to September) seasons. In total, 588 and 262 samples for Amersfoort and Louis Trichardt, respectively, were sent to the Eskom Laboratory for chemical analysis, while 67 and 52 rain events, respectively, had only sufficient volume for measurements of pH at the field site. Of these samples, 437 and 223, respectively, passed the WMO criteria and were used in this study. The mean annual precipitation during the study period was 755 and 745 mm, respectively at Amersfoort and Louis Trichardt. The total rainfall depth of 5,888 and 4,678 mm, collected at Amersfoort and Louis Trichardt, respectively, can be considered as representative of the entire rainy season (July–June) during which a total of 7,321 and 6,012 mm of precipitation, respectively, was recorded.

Table 1. Ion Chromatography analytical parameters and sequence for chemical analysis of the precipitation samples

Apparatus	Analysis	Columns	Regeneration	Eluant/rate (analysis time)	Calibration	Control standard
Dionex 4000 series gradient mode + automated sampler	Anions + organic acids	AG4A-SC + AS4A-SC	Chemical suppression (regeneration by 0.0125 M H ₂ SO ₄)	NaOH gradient 0.5 mM ↓ 40 mM	Initial solution: 1000 ppm Cl ⁻ , CH ₃ COO ⁻ , HCOO ⁻ 2500 ppm SO ₄ ²⁻ , NO ₃ ⁻	Prepared in-house: CH ₃ COO ⁻ = 3.00 ppm HCOO ⁻ = 1.50 ppm Cl ⁻ = 2.00 ppm NO ₃ ⁻ = 1.00 ppm SO ₄ ²⁻ = 4.00 ppm
	HCOOH					
	CH ₃ COOH					
	Cl ⁻					
	NO ₃ ⁻ SO ₄ ²⁻			1.5 ml/min (26 min)	Dilution factors: 1/500, 1/1000, 1/2000	
Dionex 4000 series manual (loop) injection	Cations	CG 12 + CS 12	Electric suppression (SRS)	20 mM M.S.A. 1 ml/min (12 min)	Initial solution: Na ⁺ , NH ₄ ⁺ , Ca ²⁺ = 1000 ppm K ⁺ , Mg ²⁺ = 500 ppm	Prepared in-house: Na ⁺ , NH ₄ ⁺ = 0.50 ppm K ⁺ , Mg ²⁺ = 0.20 ppm Ca ²⁺ = 0.40 ppm
	Na ⁺					
	NH ₄ ⁺					
	K ⁺					
	Mg ²⁺ Ca ²⁺				Dilution factors: 1/500, 1/1000, 1/2000	

The following steps describe the analysis sequence: 1 – standards (high first, low last), 2 – demineralised water, 3 – control standard, 4– 5 samples and control standard, 5 – repeat step 4 for up to 20 samples. (For more than 20 samples new standards are prepared and run).

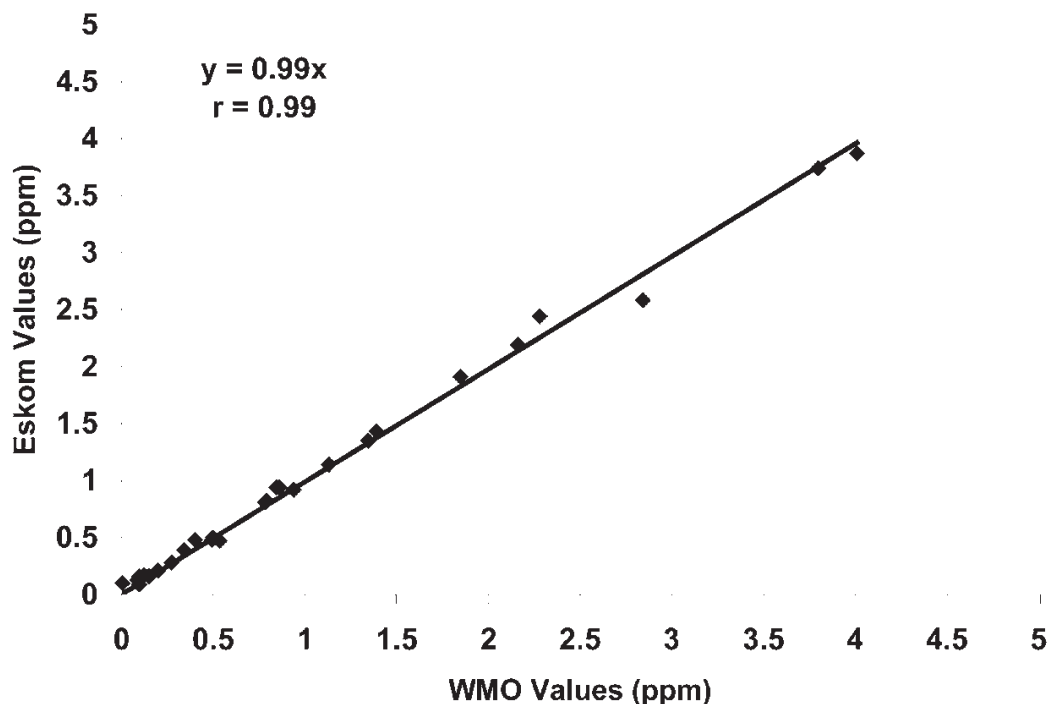


Figure 2. Results of the 21st inter-laboratory comparison of the World Meteorological Organisation (WMO, 1999) for the IC analysis of mineral ions (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-}) at the Eskom Laboratory in 1999.

Table II. Summary of rain samples collected at Amersfoort and Louis Trichardt between July 1986 and June 1999

	Number of events		Precipitation amount (mm)	
	Amersfoort	Louis Trichardt	Amersfoort	Louis Trichardt
Total number of samples collected	655	314	7321	6012
Samples measured for field pH only	67	52	519	521
Samples sent for chemical analysis	588	262	6803	5492
Samples which passed the WMO criteria	437	223	5888	4678

4. Chemical Composition of Precipitation

Table III presents the volume-weighted mean chemical composition, the annual wet deposition and the averaged pH calculated from the volume weighted mean concentration of H^+ for Amersfoort and Louis Trichardt.

Table III. Volume-weighted mean (VWM) chemical composition of precipitation and yearly wet deposition at Amersfoort and Louis Trichardt during 1986–1999. The measurements from Banizoumbou only represent the 1996 rainy season

Ions	Amersfoort		Louis Trichardt		Banizoumbou ^c	
	VWM $\mu\text{eq.l}^{-1}$	Wet deposition ^b $\text{mmol.m}^{-2}.\text{yr}^{-1}$	VWM $\mu\text{eq.l}^{-1}$	Wet deposition ^b $\text{mmol.m}^{-2}.\text{yr}^{-1}$	VWM $\mu\text{eq.l}^{-1}$	Wet deposition $\text{mmol.m}^{-2}.\text{yr}^{-1}$
ph	4.35		4.91		5.7	
H ⁺	44.9	329.0	12.2	73.1	2.1	1.0
Na ⁺	9.3	68.2	9.3	56.1	7.7	3.7
NH ₄ ⁺	22.3	163.4	9.7	58.0	12.9	6.3
K ⁺	4.7	34.1	3.8	22.8	4.7	2.3
Ca ²⁺	18.7	68.6	12.0	36.0	31.2	7.6
Mg ²⁺	6.7	24.5	4.1	12.2	5.6	1.4
NO ₃ ⁻	25.0	183.0	8.0	48.2	12.3	6.0
Cl ⁻	9.8	71.6	10.0	60.1	7.4	3.6
SO ₄ ²⁻	59.1	216.0	14.5	43.6	8.6	2.1
HCOO ⁻	7.5 (6.0) ^a	55.3	12.9 (11.5) ^a	77.6	4.7 (4.5) ^a	2.3
CH ₃ COO ⁻	6.1 (2.0) ^a	44.8	8.2 (4.3) ^a	49.3	3.1 (2.7) ^a	1.5
No. of events	437.0		223.0		29	
Total (mm): total	7321.3		6012.2		489.5	
Annual mean	563.2		462.5		489.5	

^a Dissociated fraction.

^b Wet deposition is calculated by using the annual mean rainfall amount for the period 1986–1999.

^c Galy-Lacaux and Modi (1998).

The volume-weighted composition in $\mu\text{eq.l}^{-1}$ of any ion was computed from the ionic concentration C_n and the depth of the rainfall H_n (mm) of the events collected:

$$\text{Volume weighted mean} = \sum C_n H_n / \sum H_n .$$

The annual wet deposition, expressed in $\text{mmol.m}^{-2}.\text{yr}^{-1}$, is calculated from the total rainfall amount. The period mean pH value at Amersfoort, calculated from the volume-weighted mean concentration of H^+ , is 4.35 (Table III), which indicates an acidic value. However, the pH of individual events showed a very large fluctuation, ranging from 3.5 to 6.2 (Figure 3). The overwhelming majority of precipitation events, viz. 98%, had a pH value below 5.6, which is the pH of unpolluted water equilibrated with atmospheric CO_2 , 8% were below 4.0, while only 1% of the samples showed pH values of above 6.0.

At Louis Trichardt, the annual mean pH was 4.91, which is only a slightly acidic value. As can be seen from Figure 3, the distribution of the pH range is shifted towards higher pH values, with individual events ranging from 4.1 to 6.2. About 94% showed a pH of less than 5.6, but no samples were below 4.0, while about 6% of precipitation events had a pH above 6.0, suggesting a strong presence of alkaline species in these rain samples. The IDAF station of Niger, Banizoumbou, also presents a weak acidity with an average pH = 5.7 (Galy-Lacaux and Modi,1998). Similar results were reported for Haifa in Israel by Mamane and Gottlieb (1995).

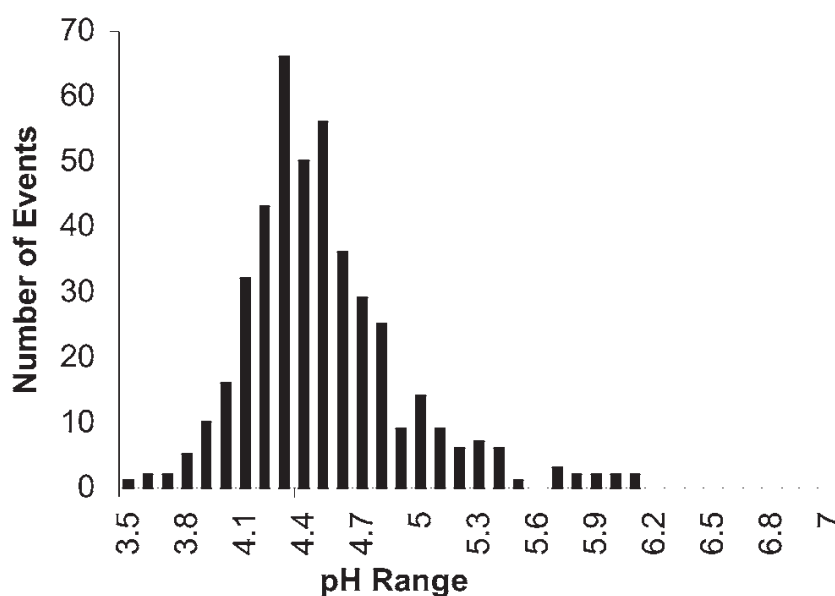
The precipitation at Amersfoort is dominated by the SO_4^{2-} ion ($59.1 \mu\text{eq.l}^{-1}$), with the next most abundant ions being H^+ , NO_3^- , NH_4^+ , and Ca^{2+} with 44.9, 25.0, 22.3, and $18.7 \mu\text{eq.l}^{-1}$, respectively (Table III). These five ions represent 79% of the ionic content of the rainwater samples. At Louis Trichardt, the precipitation is also dominated by SO_4^{2-} , but to a lesser degree than at Amersfoort, with only $14.5 \mu\text{eq.l}^{-1}$. The other abundant ions are H^+ , Ca^{2+} , NH_4^+ , and NO_3^- with concentrations of 12.2, 12.0, 9.7, and $8.0 \mu\text{eq.l}^{-1}$, respectively (Table III). Unlike Amersfoort and Louis Trichardt, Banizoumbou shows a high Ca^{2+} concentration, followed by NH_4^+ and NO_3^- (Galy-Lacaux and Modi,1998).

The chemical composition of precipitation was further studied by calculating correlation coefficients. The ‘Spearman’ method was selected to compute the correlation coefficients at the 95% confidence interval. The correlation coefficients between the different species are examined in order to determine the potential sources that influence the rainwater composition and/or the potential origin of some of the species that are transported in the same air masses.

4.1. MARINE AND TERRIGENOUS CONTRIBUTIONS

The most common method of evaluating the contribution of sea salts to ion concentrations in precipitation is to compare the Cl^-/Na^+ ratio in the precipitation to that in seawater. The sea is considered to be a major source of both ions. At both sites the annual ration of Cl^- and Na^+ are close to the seawater ratio (Table V). The

AMERSFOORT



LOUIS TRICHARDT

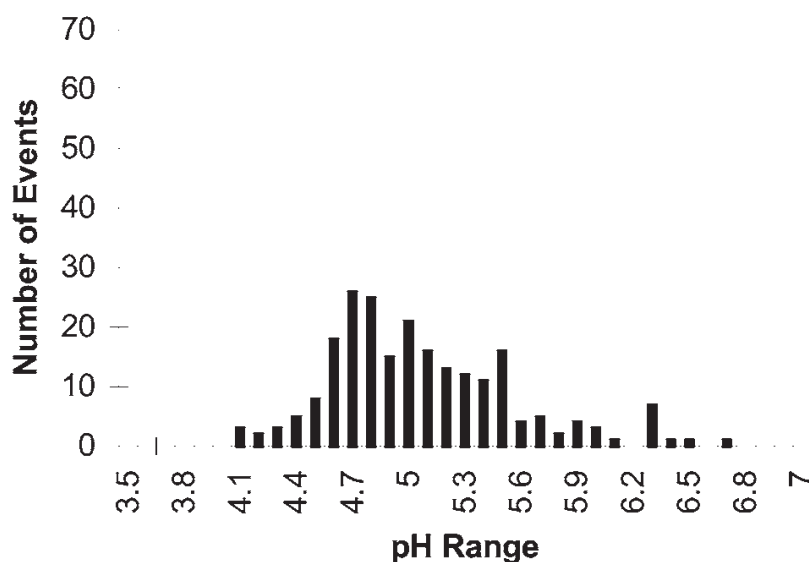


Figure 3. Frequency distribution of rainfall pH values for Amersfoort (top) and Louis Trichardt (bottom) for the 1986–1999 rainy seasons.

relatively strong correlation between the two ions (correlation coefficients of 0.78 and 0.86 for Amersfoort and Louis Trichardt, respectively; Table IV) shows that the marine constituents of the Indian Ocean influence the chemical content of the precipitation. The mean annual ratios of chlorine to sodium ions for Amersfoort and Louis Trichardt (1.054 and 1.075, respectively) were very close to that of seawater (1.161). According to the Cl^-/Na^+ ratio measured, one can calculate the contribution of sea salt particles in the dissolved phase using the following equation:

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

Table IV. Correlation coefficients between some ions in rainwater for the dry season, wet season and annually, 1986–1999. The Spearman' method was used to compute the 95% confidence intervals of the correlation coefficients. Only pairs with correlation above 0.5 were included

Ion pairs	Amersfoort			Louis Trichardt		
	Dry	Wet	Annual	Dry	Wet	Annual
	season	season		season	season	
H ⁺ vs SO ₄ ²⁻	0.87	0.86	0.86	0.75	0.68	0.68
H ⁺ vs NO ₃ ⁻	0.75	0.80	0.79	0.63	0.64	0.63
H ⁺ vs HCOO ⁻					0.65	0.62
H ⁺ vs CH ₃ COO ⁻					0.57	0.53
NH ₄ ⁺ vs SO ₄ ²⁻	0.72	0.78	0.77	0.83	0.63	0.63
NH ₄ ⁺ vs NO ₃ ⁻	0.74	0.75	0.74	0.85	0.75	0.76
Ca ²⁺ vs SO ₄ ²⁻	0.68			0.54		
Ca ²⁺ vs NO ₃ ⁻	0.67					
Mg ²⁺ vs SO ₄ ²⁻	0.64	0.55	0.52	0.53	0.51	0.51
Mg ²⁺ vs NO ₃ ⁻	0.74	0.50	0.52			
Na ⁺ vs Cl ⁻	0.66	0.87	0.78	0.98	0.71	0.86
Mg ²⁺ vs Cl ⁻	0.69		0.52	0.69		0.52
K ⁺ vs Cl ⁻	0.73	0.55	0.59	0.73	0.55	0.59
Ca ²⁺ vs Mg ²⁺	0.71	0.60	0.57	0.59	0.60	0.59
Mg ²⁺ vs Na ⁺	0.65	0.50		0.90	0.65	0.68
SO ₄ ²⁻ vs NO ₃ ⁻	0.80	0.86	0.85	0.71	0.65	0.59
CH ₃ COO ⁻ vs HCOO ⁻	0.67	0.71	0.70	0.64	0.84	0.83
NH ₄ ⁺ vs CH ₃ COO ⁻					0.62	0.59
NH ₄ ⁺ vs HCOO ⁻		0.60	0.55		0.72	0.69

where $[X]_{\text{marine}}$ is the marine contribution for element X in $\mu\text{eq.l}^{-1}$, $[\text{Na}^+]_{\text{rain}}$ is the concentration of sodium ions in rain ($\mu\text{eq.l}^{-1}$), and $[X]/[\text{Na}^+]_{\text{seawater}}$ is the concentration ratio in seawater (Keene *et al.*, 1986). The sum of marine contributions (Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻ and K⁺ ions) to the total ionic content of Amersfoort and Louis Trichardt was 11 and 23%, respectively (calculated from Table III). As shown in Table IV, Mg²⁺ was correlated with Ca²⁺ (0.57 at Amersfoort and 0.59 at Louis Trichardt), as well as with SO₄²⁻ (0.52 at Amersfoort and 0.51 at Louis Trichardt). This positive relationship suggests the importance of the particles eroded from semi-arid regions to the chemical content of precipitation. Soil dust is the major constituent of the regional aerosol loading of the atmosphere over South Africa (Piketh *et al.*, 1999).

Taking into account the marine contribution determined above and adjusting for the contribution of SO₄²⁻ from terrigenous sources, the sum of the potential

Table V. Seasonal and annual ionic ratio in rain

Ions	Sea-water ^a	Amersfoort			Louis Trichardt		
		Dry season	Wet season	Annual	Dry season	Wet season	Annual
K^+/Na^+	0.022	1.108	0.424	0.505	0.324	0.474	0.409
Ca^{2+}/Na^+	0.044	2.598	1.935	2.011	1.080	1.460	1.290
Mg^{2+}/Na^+	0.227	1.108	0.663	0.720	0.408	0.474	0.441
Cl^-/Na^+	1.161	1.853	0.946	1.054	1.080	1.066	1.075
SO_4^{2-}/Na^+	0.121	6.461	6.337	6.355	1.746	1.553	1.559

terrigenous ions ($Ca^{2+} + Na^+ + SO_4^{2-} + Mg^{2+}$) can be estimated for Amersfoort and Louis Trichardt to be 19 and 27% of the total ionic precipitation content, respectively. In contrast, at Banizoumbou, potential terrigenous ions contribute 57% of the total ionic content of which 96% is from Ca^{2+} . This high terrigenous contribution could emphasise the direct influence of soil dust on precipitation chemistry in this region, therefore highlighting the importance of the heterogeneous chemistry between gas and soil particles on precipitation chemistry and the associated indirect terrigenous contributions (Galy-Lacaux and Modi, 1998; Galy-Lacaux *et al.*, 2001). The wet deposition of SO_4^{2-} at Amersfoort and Louis Trichardt is 216.3 and 43.6 $mmol.m^{-2}.yr^{-1}$, respectively (Table III). The SO_4^{2-} concentration in wet deposition measured at Amersfoort is of the same magnitude to that of industrial sites in North American (Dovland and Pederson, 1996). The SO_4^{2-} wet deposition at Louis Trichardt is high in comparison with rural semi-arid savanna eco-system sites in Africa, e.g., Banizoumbou (2.1 $mmol.m^{-2}.yr^{-1}$; Table III).

4.2. NITROGENOUS CONTRIBUTIONS

NO_3^- and NH_4^+ concentrations of 25.0 and 22.3 $\mu eq.l^{-1}$, respectively, in the precipitation at Amersfoort are relatively high compared to Louis Trichardt (8.0 and 9.7 $\mu eq.l^{-1}$, respectively; Table III). NO_3^- in precipitation tends to be highest where air is most polluted with nitrogen oxides. Both Amersfoort and Louis Trichardt sites do not have a high population density, nor numerous vehicles. However, Amersfoort is downwind of the industrial region where NO_x emissions are high. At both sites, NH_4^+ , NO_3^- and SO_4^{2-} , all of which can be attributed to anthropogenic pollution, are highly correlated to each other (Table IV), although the correlations at Louis Trichardt appear to be higher in the dry season than the wet season, while at Amersfoort they are slightly higher during the wet season. The NO_3^- and NH_4^+ concentrations at Louis Trichardt are more or less comparable to those of Banizoumbou (12.3 and 12.9 $\mu eq.l^{-1}$, respectively; Table III). On the African ecosystem scale, the amount of inorganic nitrogen contained in precipitation (Ta-

ble III) at Louis Trichardt, which is representative of a dry savanna region, is comparable to those of the wet savanna of Lamto ($\text{NO}_3^- = 8.9$ and $\text{NH}_4^+ = 16.8 \mu\text{eq.l}^{-1}$; Yoboué, 1991) and the equatorial forest of Dimonika (8.6 and $6.4 \mu\text{eq.l}^{-1}$, respectively; Lacaux *et al.*, 1992). Higher NO_3^- and NH_4^+ concentrations were measured in Gopalpura, India (42.6 and $43.4 \mu\text{eq.l}^{-1}$, respectively; Satsangi *et al.*, 1998).

NH_4^+ is another form in which nitrogen occurs in rainwater. The NH_4^+ component of precipitation results from the incorporation of gaseous NH_3 and particles containing NH_4^+ in clouds and rainwater. Major sources of NH_3 include bacterial decomposition of urea in animal excreta and emissions from natural or fertilised soils (Schlesinger and Hartley, 1992), savanna fires and domestic fuel wood burning (Delmas *et al.*, 1991; Brocard *et al.*, 1996). NH_4^+ wet deposition at Amersfoort and Louis Trichardt is 163.4 and $58.0 \text{ mmol.m}^{-2}.\text{yr}^{-1}$, respectively. These values are higher than at Banizoumbou ($6.3 \text{ mmol.m}^{-2}.\text{yr}^{-1}$) and illustrate the intensity of the NH_4^+ sources in the semi-arid savanna (Table III), possibly due to agricultural activities and the petrochemical plants on the Mpumalanga Highveld, which have been found to emit NH_3 (Van der Walt *et al.*, 1998).

NO_3^- in rainfall is the final result of multiphase reaction processes of nitrogenous gases, atmospheric particles and cloud water. Nitric oxide is the major oxide of nitrogen released from biomass burning. Biogenic NO emissions from South African savannas are equal to the amount of NO generated by biomass burning, but slightly less than those from industry (Otter *et al.*, 2001). Soil texture, soil water content, soil nitrogen status and burning present a high spatial and temporal variability of NO emissions (Matson *et al.*, 1989; Ambus and Christensen, 1994; Levine *et al.*, 1996). The nitrogen compound flux necessary to equilibrate the Amersfoort and Louis Trichardt wet deposition of 163.4 and $58.0 \text{ mmol.m}^{-2}.\text{yr}^{-1}$ (Table III), respectively, is 74 and $25 \text{ ngN(NO) m}^{-2}.\text{s}^{-1}$, respectively. Parsons *et al.* (1996) measured emissions of $3.5 \text{ ngN(NO) m}^{-2}.\text{s}^{-1}$ on the infertile soils in the semi-arid savanna of South Africa. The regional emissions from savanna soils are therefore not sufficient to equilibrate the wet deposition of nitrate measured at Amersfoort and Louis Trichardt. This is contrary to the situation at the Banizoumbou site (Galy-Lacaux and Modi, 1998).

4.3. ACIDIC CONTRIBUTIONS

Like in other parts of the world, acidity is a key aspect of atmospheric chemistry in southern Africa. As can be seen in Table IV, H^+ is highly correlated with SO_4^{2-} and NO_3^- at both sites, although the correlation between H^+ and SO_4^{2-} was slightly higher in the dry season than in the wet season. In general, CH_3COO^- and HCOO^- were highly correlated (0.70 at Amersfoort and 0.83 at Louis Trichardt) at both sites. However, CH_3COO^- and HCOO^- were correlated with H^+ only at Louis Trichardt (Table IV). For this reason it can be concluded, that these species contribute a substantial amount to the acidity of Louis Trichardt's rainwater.

Table VI. Estimation of SO_4^{2-} sources in $\mu\text{eq.l}^{-1}$

Site	Total	Excess	Marine	Terri- genous	Anthropo- genic
Amersfoort	59.1	58.0	1.1	8.8	49.2
Louis Trichardt	14.5	13.4	1.1	5.6	7.8

Table VII. Contribution of mineral and organic acids to the total acidity

	Amersfoort		Louis Trichardt	
	$\mu\text{eq.l}^{-1}$	%	$\mu\text{eq.l}^{-1}$	%
Sulphuric acid	49.2	60	7.8	25
Nitric acid	25.0	30	8.0	25
Organic acids	8.0	10	15.8	50
Total H^+ , estimated	82.2		31.6	
H^+ , measured	44.9		12.2	

The excess SO_4^{2-} can be attributed to either terrigenous sources or anthropogenic pollution. Assuming that the SO_4^{2-} contribution from terrigenous sources is the concentration in excess of that supplied by gypsum (Delmas, 1981)

$$[\text{SO}_4^{2-}]_{\text{anthropogenic}} = [\text{SO}_4^{2-}]_{\text{rainfall}} - 0.47[\text{Ca}^{2+}]$$

and adjusting for the contributions of sulphate from marine and terrigenous sources, one can infer the contribution of the anthropogenic sources (Table VI).

The average acidity at Amersfoort ($44.9 \mu\text{eq.l}^{-1}$) is high compared to that at Louis Trichardt ($12.2 \mu\text{eq.l}^{-1}$; Table III). Assuming that acidity is due to excess SO_4^{2-} , organic acids ($\text{HCOO}^- + \text{CH}_3\text{COO}^-$) and NO_3^- , one can deduce the acidity derived from a mixture of mineral acids (H_2SO_4 , HNO_3) and organic acids (HCOOH , CH_3COOH), as shown in Table VII.

The H^+ ion concentration ($44.9 \mu\text{eq.l}^{-1}$ and $12.2 \mu\text{eq.l}^{-1}$, at Amersfoort and Louis Trichardt, respectively; Table III), measured during the study period, is considerably less than the total contribution estimated from organic and mineral acids. This would imply that only some portion of these ions might have contributed to rain acidity. The mineral acids at Amersfoort represent the greater part of free acidity compared to the contribution from the organic acids. This is contrasted by the fact, that the total organic acid concentration at Louis Trichardt is high compared to that at Amersfoort. This suggests that organic acids dominate the sources of acidity in Louis Trichardt, while mineral acids dominate at Amersfoort,

Table VIII. Source group contribution to precipitation in Amersfoort and Louis Trichardt

	Amersfoort (%)	Louis Trichardt (%)
Marine	11	23
Terrigenous	19	27
Fossil fuel	35	15
Biomass	9	24
Other (H ⁺ and NH ₄ ⁺)	26	11

which is in agreement with previously published data (Turner *et al.*, 1996). The total acidic contribution to the overall volume-weighted mean ion concentrations at Amersfoort and Louis Trichardt is 38 and 30%, respectively (Table III). If all these ions (SO₄²⁻, NO₃⁻ and organic) existed in the form of free acids, the precipitation pH would be 4.09 (Amersfoort) and 4.50 (Louis Trichardt), which is lower by 0.3 pH and 0.4 pH units, respectively, than actually measured (4.35 and 4.91). The relatively large difference indicates that the acids present in the rainwater samples have gone through a significant process of neutralisation.

4.4. SOURCE GROUP ESTIMATION

In order to infer the contribution of each source to the total precipitation content, it was assumed that all the nitrogen oxide originated from fossil fuel combustion and no correction for terrigenous and biomass burning contributions was made, hence the contribution of this source was overestimated. Table VIII shows the estimates of the relative contribution from the different sources to the chemical composition of precipitation at Louis Trichardt and Amersfoort.

These estimates suggest that the fossil fuel sources were the highest contributor to the total precipitation content at Amersfoort. However, at Louis Trichardt, marine, terrigenous and biomass sources contribute more or less equal amounts to the total precipitation content. This is in good agreement with previous estimates (Turner *et al.*, 1996), showing that, at Amersfoort the fossil fuel sources were the biggest contributor to potential acidity, while at Louis Trichardt biomass products predominated.

5. Seasonal Variability and Temporal Trends of Annual Concentrations

Chemical data for precipitation at Amersfoort and Louis Trichardt were analysed in greater detail for possible seasonal patterns. H⁺, nss-SO₄²⁻, NO₃⁻ and NH₄⁺ show a strong seasonal variability at Louis Trichardt, while at Amersfoort the seasonal

variation of precipitation chemistry data is less pronounced, especially for H^+ and nss-SO_4^{2-} (Figure 4). This clearly illustrates the influence of fossil-fuel, as Amersfoort is downwind of the major industrial complexes. At Louis Trichardt, acidity in terms of the H^+ ion concentration generally reaches a maximum in spring (September–November) and a minimum in winter (June–August). The magnitude and ranges of acidity differed considerably between the two sites (Figure 4). Amersfoort had the highest H^+ ion concentration throughout the year, with average monthly values ranging from $27 \mu\text{eq.l}^{-1}$ to $55 \mu\text{eq.l}^{-1}$, while at Louis Trichardt the concentrations were lower, ranging from a monthly average of $5 \mu\text{eq.l}^{-1}$ in July to over $34 \mu\text{eq.l}^{-1}$ in September. The difference in magnitudes and ranges between the stations may be partly due to location, since Louis Trichardt is in a rural environment, while Amersfoort is downwind of the Mpumalanga Highveld industrial source region. During the dry season (May to September) the concentrations of H^+ , nss-SO_4^{2-} , NO_3^- and NH_4^+ are relatively high, especially in August and September, when the influence of local fires and of extensive savanna fires in the southern hemisphere is most pronounced. Thereafter, the concentrations decrease more or less evenly until they reach low values from December to February. The concentrations generally do not fluctuate much during the wet season (October to March). The NH_4^+ concentration shows an interesting seasonal behaviour, with the volume-weighted monthly mean values reaching a sharp peak in September, especially at Louis Trichardt. Since major sources of NH_3 emissions are known to be animal wastes and fertilisers (Schlesinger and Hartley, 1992), the maximum in NH_4^+ concentration may be due to early spring fertilisation at local agricultural sites.

In the dry season, the seasonal ionic ratio is higher at Amersfoort, than during the wet season (Table V), while the wet season ionic ratios are higher at Louis Trichardt than the dry season ionic ratios, except for the Cl^-/Na^+ and $\text{SO}_4^{2-}/\text{Na}^+$ ionic ratios, for which the difference is 0.01 and 0.20, respectively. This indicates the contribution of particles from additional sources like particles emitted by biomass burning of the savanna (Cachier and Ducret, 1991), which influence the content of chloride in the air masses affecting the two sites. Other possible sources could include industry, but this would have to be related to seasonal changes in the transport patterns, as the industrial emissions are more or less constant throughout the year.

The increased concentrations observed during spring are likely the results of a combination of large-scale circulation and source strength (transport and emissions). The strength and the seasonal shift of the Indian Ocean Anticyclone have important effects on the seasonal variation of transport patterns to and from the Highveld, which obviously impact on the removal mechanisms, causing them to also be seasonally dependent (Piketh and Prangley, 1998).

Annual mean concentrations of major ions during 1986–1999 show that during 1986/1987, the H^+ concentration was 87 and $18 \mu\text{eq.l}^{-1}$, at Amersfoort and Louis Trichardt, respectively, whereas the concentration in 1998/1999 had decreased to

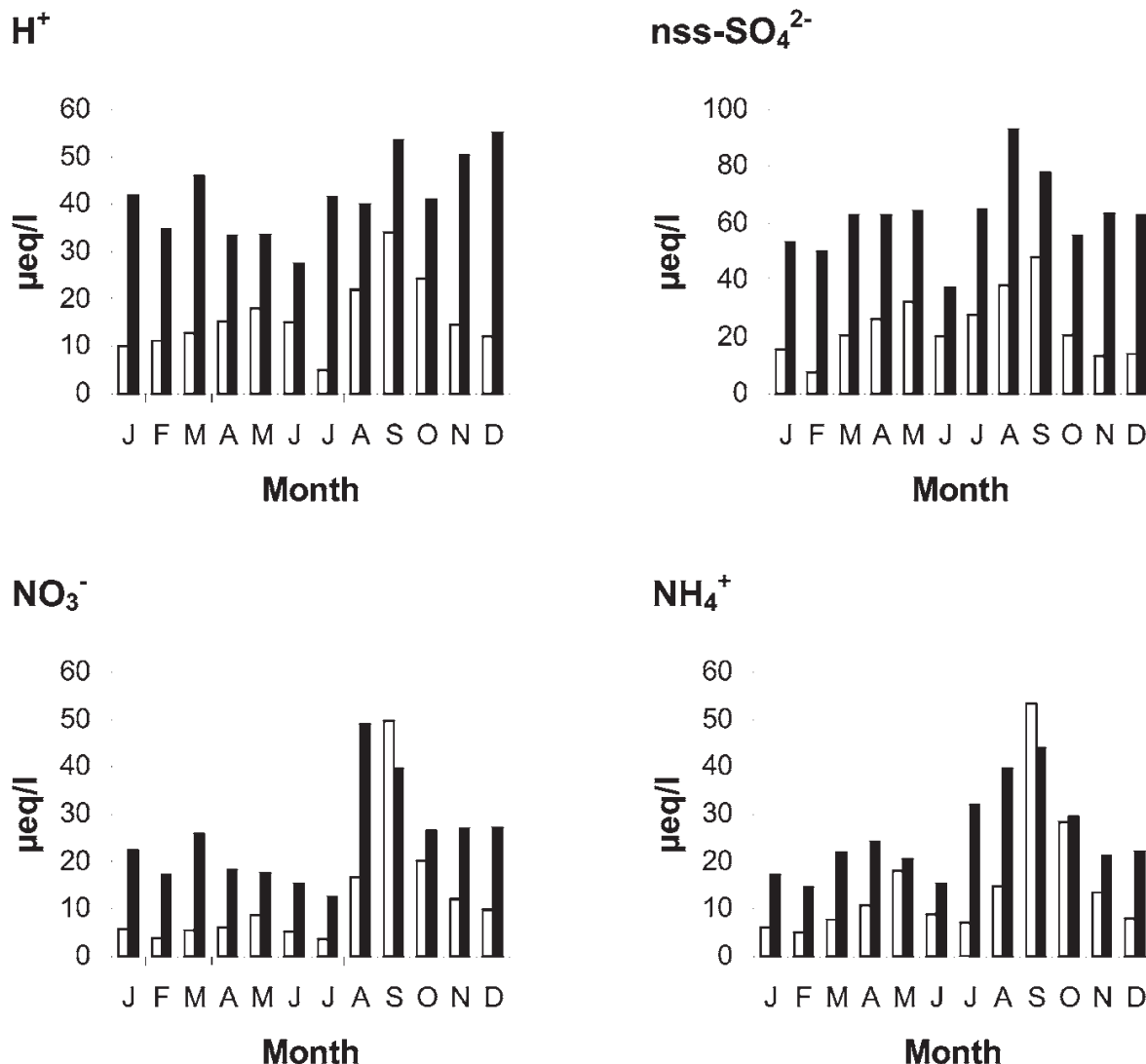


Figure 4. Monthly mean concentration of major ions during 1986–1999, for Amersfoort (black), and Louis Trichardt (white) for the 1986–1999 rainy seasons.

67 and 8 $\mu\text{eq.l}^{-1}$, at the two sites, respectively (Figure 5). Overall, the acidity has clearly decreased during the 13-year period, although with some fluctuations. This might be attributable to the removal/extinguishing of the major burning colliery discard dumps and shut-downs of some of Eskom’s Power Stations, as well as more efficient combustion processes and improved removal of particulate emissions at Eskom’s coal-fired Power Stations.

At Amersfoort, the nss-SO_4^{2-} concentration was higher than that of any other ion by a factor of two during the 13-year period, whereas at Louis Trichardt, the nss-SO_4^{2-} concentration was of the same order of magnitude as that of other major ions. At Louis Trichardt, the nss-SO_4^{2-} concentration fluctuated between 45 and about 65 $\mu\text{eq.l}^{-1}$.

The concentration of nitrate was highest in 1998/1999 at both sites. At Louis Trichardt, the NH_4^+ concentration fluctuated greatly. However, the highest concentration of NH_4^+ was recorded at Amersfoort in 1998/1999, with nss-SO_4^{2-} and NO_3^- also being high. The NH_4^+ ion is biologically converted to nitric acid after deposition, which ultimately makes NH_4^+ an acidifying substance. This implies that the

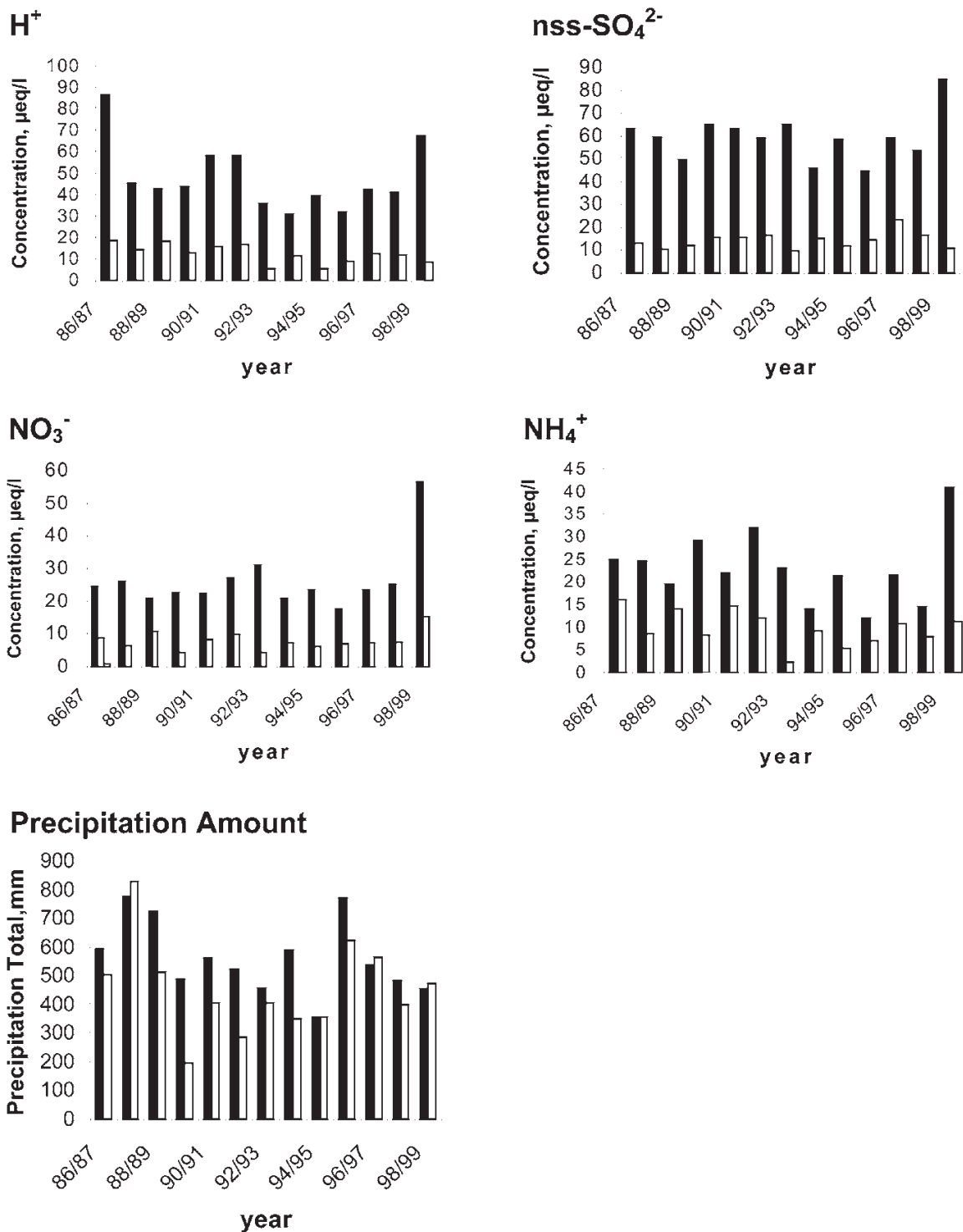


Figure 5. Annual mean concentration of major ions and annual precipitation totals (rain years July–June during the period 1986–1999), for Amersfoort (black), and Louis Trichardt (white).

ecosystem in the Amersfoort area has been acidified during the study period. The ionic concentration in precipitation is largely determined by air concentrations and precipitation amounts. Above average precipitation totals were observed during 1987/1988, 1988/1989 and 1995/1996, which could have resulted in a decrease of concentrations. Despite the increase in precipitation amounts, concentrations of major ions were generally high. Thus, the precipitation amount should not directly be related to the temporal trends in concentrations that subsequently emerge.

6. Discussion

The study of the chemical composition of rainwater and wet deposition in regions representative of rural and industrial areas in South Africa was undertaken for the first time to determine the chemical species present in precipitation during a 13-year period and to examine the relative contributions from various sources. The nature of the chemical species found in precipitation depends on numerous interacting mechanisms, such as the intensity of the sources of the species or of their precursors, the transportation and dynamic transfer in the atmosphere, atmospheric chemistry and the physical characteristics of the atmosphere. The main characteristics of the chemical composition of rain collected at Amersfoort and Louis Trichardt, averaged over 13 years, allow emphasising the following points:

At Amersfoort, the concentrations of nss-SO_4^{2-} and NO_3^- are as high as those in north-eastern U.S.A. and central Europe, typical of regions affected by acid-forming emissions. However, most of the acidity is neutralised by the base cations, Mg^{2+} , Ca^{2+} and NH_4^+ . Therefore, the average pH of precipitation is around 4.35, which is an acid value. At Louis Trichardt, the concentrations of nss-SO_4^{2-} and NO_3^- are comparable with western African sites (Lacaux *et al.*, 1992; Galy-Lacaux and Modi, 1998). As there are no major anthropogenic sources directly affecting Louis Trichardt, this could be attributed to aged aerosol, subject to sub-continental recirculation (Held *et al.*, 1994). Marine, terrigenous, fossil-fuel and biomass sources influence the precipitation composition at Amersfoort and Louis Trichardt. The marine and terrigenous sources are well established by the ratio of Na^+ to Cl^- , being closer to the seawater ratio, and the high Ca^{2+} , SO_4^{2-} , and Mg^{2+} ion concentrations coming from dust dispersed as a result of soil erosion and entrainment of the particles in the atmosphere. It is difficult to discriminate between mineral dust originating from soil erosion and dust emitted by coal-fired power plants, which are very dominant sources for SO_4^{2-} in South Africa (Puxbaum *et al.*, 2000). However, based on the relationship of trace elements, Maenhaut *et al.* (1996) showed that mineral dust at Palmer, a site on the Highveld, about 200 km east of Johannesburg, was mainly soil-derived. Coal combustion could be an additional potential source for the terrigenous compounds, especially Ca^{2+} , which is a major component of fly ash. One can therefore expect, that at Amersfoort high concentrations of Ca^{2+} from fly ash are observed, since it is located downwind of the majority of coal-fired power plants. The NO_3^- and SO_4^{2-} ions are correlated, due to the similarity in their behaviour in precipitation and the co-emission of their precursors SO_2 and NO_x (Saxena *et al.*, 1996), which clearly indicates fossil-fuel source influences.

The other signatures of atmospheric sources are highlighted by the relative high organic (HCOOH and CH_3COOH) and nitrogenous ion contents in the precipitation. The atmospheric sources of HCOOH and CH_3COOH in rain have not yet been properly identified. Likely sources include anthropogenic sources, i.e., vehicular emissions (Talbot *et al.*, 1988) and natural sources e.g., ants (Graedel and Eisner, 1988), plants (Talbot *et al.*, 1990) and soil (Sanhueza and Andreae, 1991), as well

as direct emissions from biomass burning (Talbot *et al.*, 1988) and also oxidation of precursor compounds in the gas phase (Madronich and Calvert, 1990). Particulates and gaseous acids are scavenged by clouds or rain and in-cloud oxidation of aldehydes. Relatively large concentrations of gaseous HCOOH (0.7 ppbv) and CH₃COOH (0.8 ppbv) are present in the atmosphere of the Mpumalanga Highveld (Snyman and Held, 1996) and scavenging of these acids during rainfalls could be a significant source of the HCOO⁻ and CH₃COO⁻ ions in the rain samples at Amersfoort and Louis Trichardt. Furthermore, a statistical correlation between HCOO⁻ and CH₃COO⁻ concentrations was found in both Amersfoort and Louis Trichardt rain samples.

The NH₄⁺ content (22.3 μeq.l⁻¹ for Amersfoort and 9.7 μeq.l⁻¹ for Louis Trichardt) can be attributed to the NH₃ sources associated with agricultural and industrial activities. For instance, NH₄⁺ is a component of fertilisers, but also a product of animal wastes. Regarding the industrial sources, NH₃ can be present in emissions from coal gasification. The NO₃⁻ signatures in precipitation at Louis Trichardt and Amersfoort are not of the same order of magnitude as the natural emissions from semi-arid savanna soils (Parsons *et al.*, 1996; Otter *et al.*, 2001). At Amersfoort, nitrate ion concentrations and deposition values are comparable to levels in Japan (Lee *et al.*, 2000) and European countries (Dovland and Pederson, 1996).

The acidity of precipitation during the study period had an average concentration of 44.9 μeq.l⁻¹ (pH of 4.35) and 12.2 μeq.l⁻¹ (pH of 4.91), for Amersfoort and Louis Trichardt, respectively. It was estimated from the average chemical composition, that this acidity originates from a mixture of inorganic and organic acids. At Amersfoort, 90% of the acidity originates from inorganic sources, of which 60% is in the form of sulphuric acids, while at Louis Trichardt 50% is derived from organic acids, with nitric and sulphuric acids contributing equal amounts (Table VII). The relative contributions of organic acids at these South African sites are higher than in Banizoumbou, but lower than in the tropical and equatorial areas. For example, the organic contribution is of the order of 60–80% of that in the Brazilian Amazon (Andreae *et al.*, 1988; Andreae *et al.*, 1990; Williams *et al.*, 1997), Venezuela (Galloway *et al.*, 1982) and in Australia (Likens *et al.*, 1987).

7. Conclusion

Rain samples from Amersfoort and Louis Trichardt have been analysed for the period 1986–1999 to characterise the chemical composition of precipitation and identify possible sources. The major conclusions from the present study are:

- Mineral acids (H₂SO₄ and HNO₃) seem to be the primary contributors to precipitation acidity in Amersfoort, while at Louis Trichardt both organic (HCOOH and CH₃COOH) and mineral acids contribute equal amounts of acidity.

- Marine, terrigenous, nitrogenous and anthropogenic sources influence precipitation in southern Africa. Fossil-fuel sources are larger contributors to the total precipitation ion content at Amersfoort, while at Louis Trichardt, marine terrigenous and biomass sources contribute equal amounts to the total precipitation ion content.
- Alkaline species, mainly related to terrigenous sources, have been identified as a significant contributor to acid rain neutralisation, especially at Louis Trichardt.
- H^+ , $\text{non-seasalt-SO}_4^{2-}$, NO_3^- and NH_4^+ ions exhibit a seasonal pattern in Louis Trichardt with the highest precipitation concentrations occurring during the austral spring, possibly as a result of increases in local agricultural activities.

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