



Spatio-temporal variability of anions in wet precipitation of Cuiabá, Brazil

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ABSTRACT

Spatio-temporal variability in the ionic chemical composition of atmospheric precipitation samples was investigated at twenty-six points in Cuiabá city, Brazil, during three rainfall events from October 2009 to February 2010. All samples were analyzed for pH, electrical conductivity and ions: chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}). The spatial dependence and variability of the rainwater's ionic composition were evaluated through semivariograms and kriging. A large proportion of the samples were characterized as acid rain: 80.77% of samples in October, 80.77% in December, and 65.38% in February. The average concentrations of Cl^- , F^- , NO_3^- , SO_4^{2-} and PO_4^{3-} were 4.43, 0.29, 3.78, 1.00 and $0.02 \mu\text{eq L}^{-1}$, respectively. A strong correlation was observed between NO_3^- and SO_4^{2-} indicating a common anthropogenic origin of these anions. Maps generated by geostatistical techniques indicated that the highest anion concentrations occurred at the beginning of the rainy season in the industrial district and during periods of lower rainfall in the city center, indicating the important role of local emission sources.

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1. Introduction

Atmospheric deposition is a major source of chemical constituents for many ecosystems and its composition is strongly affected by human activity. Recent increases in the emission of airborne pollutants, mainly sulfur dioxide (SO_2), nitrogen oxides (NO_x), volatile organic compounds (VOCs) and aerosols, have been caused by increases in the urban population and the concomitant increases in transport and other forms of energy use (Migliavacca et al., 2005a; Fontenele et al., 2009). Indeed, urban areas are particularly susceptible to problems related to atmospheric deposition of particles, due in large part to the

high density of both vehicles and industrialized areas within most modern metropolitan areas (Fornaro and Gutz, 2006).

Fuel combustion and industrial processes are not the only source of air pollutants (Fornaro, 2006). In many regions, especially tropical lowlands in the developing world, forest fires may also release significant quantities of particulates into the atmosphere. Such fires are major sources of anthropogenic emissions of gases and aerosols during the dry season in central and northern Brazil (Lioussé et al., 2004), causing damage to ecosystems and reducing air quality in both rural and adjoining urban settlements.

Much of the damage caused by airborne pollutants (particles and gases such SO_2 and NO_x) is a consequence of their incorporation into water droplets (wet deposition) formed during precipitation – the most effective mechanism for removing compounds from the atmosphere (Singh et al., 2007). Such incorporation occurs by two main processes: within the cloud ('in cloud') where solid particles, known as "Aitken particles", serve as cloud condensation nuclei and below cloud through adsorption to cloud droplets and fog

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('below-cloud') (André et al., 2007; Singh et al., 2007). Atmospheric deposition is a major component of cycling and redistribution of various chemical species on the surface and therefore plays a fundamental role in continental and coastal biogeochemical processes.

Although originating from a series of complex chemical reactions, the hydrochemistry of precipitation is largely determined by atmospheric emissions and is thus directly related to natural and anthropogenic activities in the region (Singh et al., 2007). A quantitative and qualitative assessment of rainfall depositions is therefore an important prerequisite for a better understanding of the influence of anthropogenic activities on these biogeochemical processes. Such an understanding is also practically important, since high levels of toxic depositions could have a negative impact on stocks, native fauna and flora, human health, and on any exposed materials (Leal et al., 2004; Souza et al., 2006).

Given the highly geographically localized nature of many sources of emissions (e.g. traffic and industrial areas) and the highly seasonal nature of other sources (e.g. forest fires) it follows that levels and chemical characterization of pollutants in wet deposition should show strong spatio-temporal patterns. However, existing studies of the chemical composition of precipitation in Brazil have not specifically assessed spatial variability (e.g. Mello, 2001; Flues et al., 2002; Rocha et al., 2003; Fornaro and Gutz, 2003; Migliavacca et al., 2004; Leal et al., 2004; Migliavacca et al., 2005a; Migliavacca et al., 2005b; Fornaro and Gutz, 2006; Pelicho et al., 2006; Pauliquevis et al., 2007; Rodrigues et al., 2007; Teixeira et al., 2008; Fontenele et al., 2009). Mapping the spatial and temporal distribution of common pollutants in rainfall could considerably increase our understanding of the complex relationship between pollutant sources and the areas most affected by the return of ions to the surface through precipitation. Unfortunately, accurate spatial analysis of the chemical composition of precipitation across large areas such as cities is practically difficult and frequently prohibitively expensive. For these reasons scientists have been obliged to create geostatistical models that are able to accurately estimate values at unsampled locations based on data collected from a small number of strategically located sampling points (Lophaven et al., 2004). The widespread availability of such models is a consequence of recent advances in geostatistics, a branch of applied mathematics concerned with the analysis and prediction of regionalized phenomena (Cressie, 1993). In this case, precipitation can be considered as a regionalized variable because its ionic composition varies in space due to spatial differences in the type and rate of emission of local sources (Al-Khashman and Tarawneh, 2007).

The aim of this study was to analyze the spatio-temporal variability in pH, electrical conductivity and the concentration of chloride anions (Cl^-), fluoride (F^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}) of precipitation through semivariograms and kriging enabling a safe valuation of those phenomenons in Cuiabá City, Mato Grosso State, Brazil.

2. Study area

Cuiabá city is the state capital of Mato Grosso, located in the central part of Brazil (15°35'56"S 56°06'01"W) near the

border of the Pantanal wetland and Amazonia. Its average altitude is 174 m above sea level, and has total area of 3538.17 km² and an urban area of 254.57 km². The conurbation between Cuiabá city and the city of Várzea Grande forms the urban sprawl Cuiabá–Várzea Grande, with an estimated population of around 790,000 inhabitants, of which 550,000 are from Cuiabá. There are approximately 225,000 motor vehicles within this area (Brasil, 2009) and it is the largest commercial and services center in the state. The city has an industrial district with 183 industries currently operating including representatives from the following sectors: rubber, food and animal products, wood processing, concrete artifacts and ceramics, chemicals and gases, metallurgical products and fertilizer production (Mato Grosso, 2010).

The climate in Cuiabá is semi-humid tropical – classified as Aw (tropical savanna climate) according to the climatic classification of Köppen – with a rainy season from October to April and dry season from May to September, with annual rainfall of 1500 mm. In the rainy season the stronger winds are predominantly from the north due to the convergence zone of the South Atlantic. The monthly average air temperature ranges between 21.9 °C and 31.3 °C (Maitelli, 1994).

3. Material and methods

3.1. Collection of precipitation samples

The sampling network for collection of precipitation samples comprised of 26 locations in the urban city and neighboring points (Fig. 1). Sampling locations were chosen to provide a systematic coverage of the area that included densely populated districts, the outskirts of the town, green areas, industrial zones, areas near roads and streets with heavy traffic of vehicles. Other factors taken into account included logistics (security and access), predominant wind direction, and the distance from obstacles that could interfere in sampling (Migliavacca et al., 2005a; Singh et al., 2007).

A total of 78 wet precipitation samples were collected at 26 locations from three rainfall events in October 2009, December 2009 and February 2010. Rainfall samples were collected manually using a PVC funnel (diameter 23 cm) fitted to polyethylene container, 2 m above ground. The sampling funnel was uncovered only during precipitation events thereby avoiding contribution from dry fall out. The sampling bottles and funnels were thoroughly washed with deionized water until the reading of the electrical conductivity of the water fell below 2 $\mu\text{S cm}^{-1}$ and were dried before use (Astm, 2008). The sample collectors were deployed just before the onset of rainfall and were withdrawn immediately after the rain had stopped. Two aliquots of each sampling location were collected. All the samples were immediately transferred to the laboratory where the unfiltered samples were assessed for pH and electrical conductivity (EC), and aliquots for the analysis of major anions were filtered through cellulose acetate membrane with a pore size of 0.22 μm (Sartorius, Germany). The filtered samples were stored at low temperature (4 °C) in a refrigerator and the analysis of anions was completed within a five day period.

The monthly precipitation data (1996–2010) were provided by the National Institute of Meteorology, station 9th District Meteorological Cuiabá/MT (15°37'S; 56°06'W).

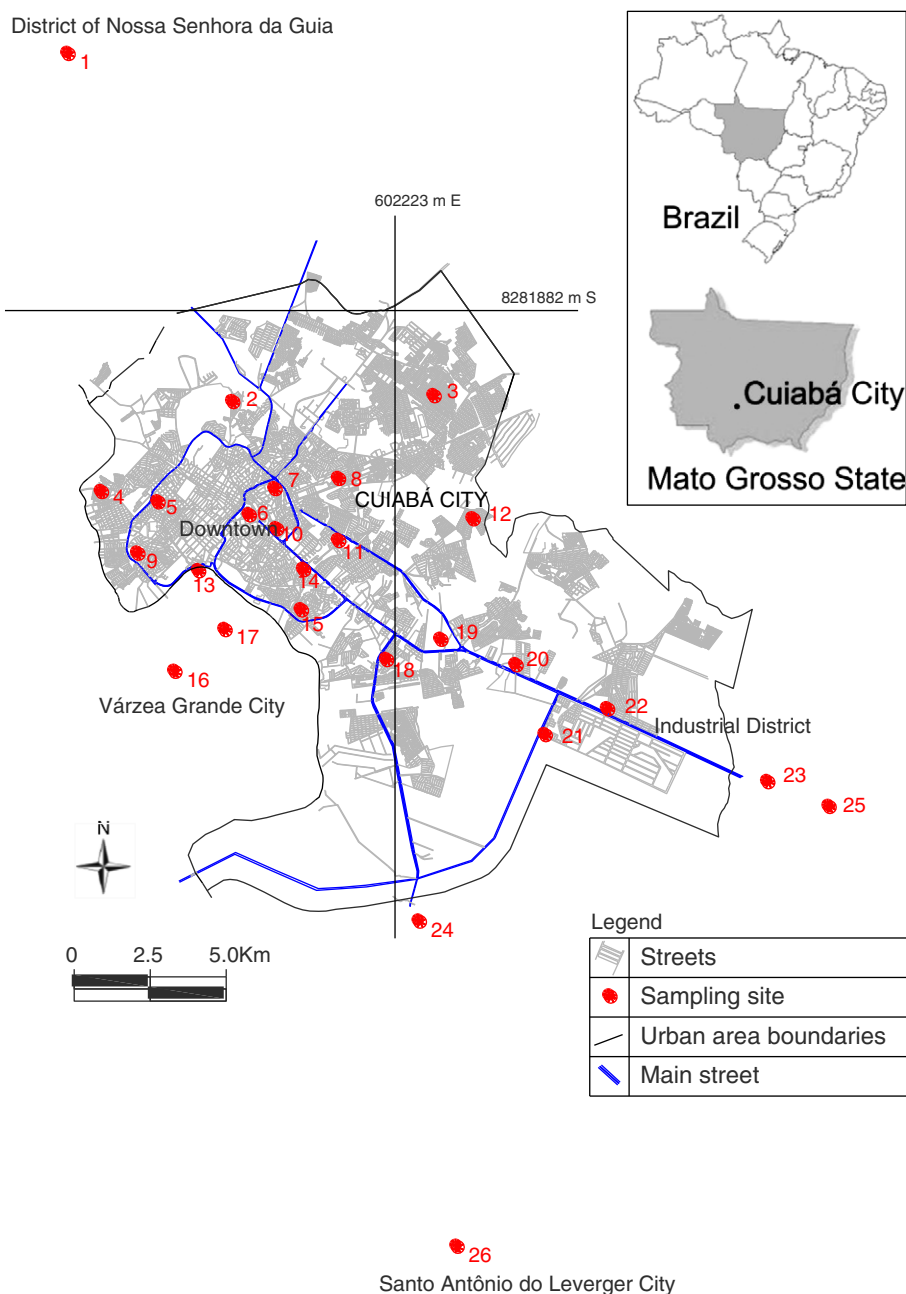


Fig. 1. Location map of the sampling network (26 locations) in the urban city and neighboring points in the Cuiabá city, Mato Grosso state, Brazil.

3.2. Chemical analysis

The pH and electrical conductivity of the samples were determined using unfiltered aliquots from each sampling location that were analyzed immediately on arrival at the laboratory. The pH measurements were performed with a calibrated pH-meter (model mPA-210, Tecnozon, Brazil) and electrical conductivity was measured with a conductivity meter (model mCA-150, Tecnozon, Brazil).

The chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), and phosphate (PO_4^{3-}) – were determined with ion chromatography (Dionex ICS 90, USA). The analytical

conditions were as follows: anion column (IonPac AS14A), flow rate 1 mL min^{-1} , eluent of NaHCO_3 (0.8 mmol L^{-1}) and Na_2CO_3 (6.4 mmol L^{-1}) and regenerant solution of sulfuric acid (25 mN). The equipment was calibrated with standard solutions of anions at the following concentrations: 50, 100, 200, 500 and $1000 \mu\text{g L}^{-1}$. The detection limits were: $1.74 \mu\text{g L}^{-1}$ for Cl^- ; $1.63 \mu\text{g L}^{-1}$ for F^- ; $7.38 \mu\text{g L}^{-1}$ for NO_3^- ; $6.78 \mu\text{g L}^{-1}$ for SO_4^{2-} ; and $16.07 \mu\text{g L}^{-1}$ for PO_4^{3-} . The detection limits (DL) were calculated using the linear coefficient of the calibration curve, which corresponds to the signal of the blank sample (a) plus three times the standard deviation (SD), i.e., $\text{DL} = a + 3(\text{SD})$ according to Leal et al. (2004).

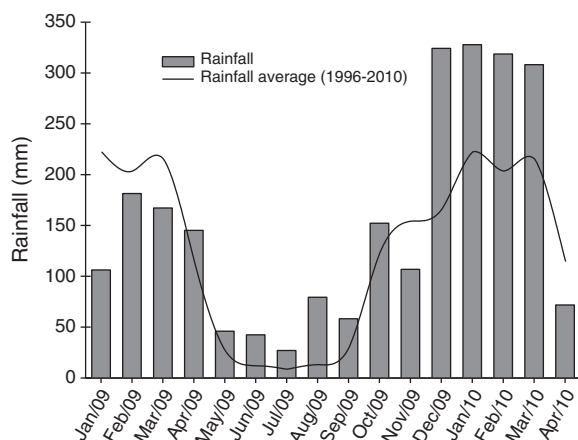


Fig. 2. Monthly accumulated precipitation from January 2009 to April 2010 Cuiabá city, Mato Grosso state, Brazil. The solid line is the average rainfall from 1996 to 2010.

3.3. Geostatistical analysis

Geostatistical analysis was applied to the chemical variables' data set to estimate the spatial variability and the influence of natural and anthropogenic sources on the chemistry of the atmospheric wet precipitation in the study area. The conceptual basis of geostatistics (the theory of regionalized variables) was developed by Matheron and was based on observations of Krige – hence the use of the term “kriging” to refer to a group of geostatistical techniques to interpolate the value of a random field. Here, a regionalized variable is a numerical function with spatial distribution, ranging from one location to another with apparent continuity, but these variations cannot be represented by a simple mathematical function (Burrough and McDonnell, 1998). Atmospheric variables with geographic coordinates, such as the chemical composition of precipitation, are considered regionalized variables that can vary continuously in geographical space. The semi-variance (or the structure function) is the tool that was used to represent the scale and structure of spatial variability (Mesev, 2007) and is represented by the following Eq. (1):

$$\hat{\gamma}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [z(x_i) - z(x_i + h)]^2 \quad (1)$$

Table 1

Average (\pm standard deviation, sd), minimum and maximum of ionic concentrations ($\mu\text{eq L}^{-1}$), pH, electric conductivity (EC, $\mu\text{S cm}^{-1}$) in precipitation, sampled in October, December/2009 and February/2010 in Cuiabá, Brazil.

Month	Descriptive statistic	pH	EC	Cl^-	F^-	NO_3^-	SO_4^{2-}	PO_4^{3-}
October	Average	5.26	6.41	4.27	0.12	5.20	1.09	0.04
	\pm sd	–	4.77	2.33	0.26	4.37	0.45	0.19
	Minimum	4.85	3.05	1.4	0	1.90	0.68	0
	Maximum	6.39	28.87	13.20	1.03	23.85	2.77	0.98
December	Average	5.20	7.22	4.72	0.59	3.27	1.03	0.01
	\pm sd	–	2.69	3.15	1.46	1.27	0.88	0.03
	Minimum	4.88	3.85	0.43	0	1.52	0.47	0
	Maximum	5.90	16.40	13.05	4.87	6.00	4.93	0.13
February	Average	5.50	5.81	4.30	0.15	2.87	0.88	0
	\pm sd	–	2.88	2.65	0.27	1.67	0.42	0
	Minimum	4.95	2.80	1.07	0	1.47	0.46	0
	Maximum	5.92	15.26	11.09	0.93	8.69	2.31	0

where $\hat{\gamma}$ is the estimated semivariance for each distance (lag) between pairs of points, $N(h)$ is the number of pairs of measured values $z(x_i)$, $z(x_i + h)$, separated by distance h (Burrough and McDonnell, 1998). The adjusted variogram model describes the spatial patterns and predicts the values of the chemical variables at the unsampled locations through kriging. In this study, a spherical model was fitted by the method of restricted maximum likelihood, and data were interpolated by ordinary kriging. The best model and fitting method were evaluated through cross validation. The statistical software package R and geostatistical analysis package geo-R (Ribeiro and Diggle, 2001) were used throughout the analysis.

4. Results and discussion

4.1. Seasonality of precipitation

The accumulated precipitation from January 2009 to April 2010 is shown in Fig. 2. During the dry season (May to September 2009) the total precipitation was 253 mm. Due to the low level of precipitation in the dry season particles accumulate in the atmosphere, increasing the rate of wet deposition in the rainy season. During the sampling period (October 2009 to February 2010) the accumulated precipitation was 1229.6 mm. The monthly rainfall during the rainy season (October 2009 to February 2010) increased progressively and, from December, the monthly precipitation was higher than 300 mm. The accumulated precipitation during the rainy season was 48% higher than average meteorological conditions for Cuiabá (1084 mm), probably due to El Niño event of 2009 (Melo and Nobre, 2009).

4.2. Variation of chemical composition

Five ionic species, pH and electrical conductivity were measured for each sample over the three sampling periods (Table 1). The average relative abundance of ionic species in precipitation was: $\text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{F}^- > \text{PO}_4^{3-}$. The NO_3^- and SO_4^{2-} showed a decline in average concentrations during the sampling period (October–February). The F^- and PO_4^{3-} were not detected in all of the precipitation samples. The NO_3^- was the most abundant of the anions, with an average percentage contribution (46.24%) that was higher than SO_4^{2-} (30.17%) in October. However, in the other two sampling periods the average percentages were similar: SO_4^{2-} (33.99%)

and NO_3^- (34.74%) in December, and SO_4^{2-} (33.77%) and NO_3^- (35.34%) in February. The relative contribution of Cl^- was lower than NO_3^- and SO_4^{2-} throughout the study period: 21.74%, 28.65% and 30.32%, in October, December and February, respectively. F^- and PO_4^{3-} ions had the lowest percentage contributions, averaging 0.29% and 1.55%, in October, 1.95% and 0.66%, in December and 0.57% and 0% in February, respectively.

pH values below of 5.60 were obtained for 80.8% (October), 80.8% (December) and 65.4% (February) of the samples (Fig. 3). Values below 5.6 for rain water are considered acidic, representing a balance of pure water and atmospheric CO_2 (Mello, 2001; Migliavacca et al., 2005b). In October, a maximum pH of 6.39 was recorded, which may be related to the fires that occur at the end of the dry season (August and September) or at the beginning of the rainy season in both in rural and urban areas. The maximum values of pH and electrical conductivity were higher in October than in December and February, indicating that the salts dissolved in the precipitation were basic. Once again this may be due to fires generating increased concentrations of Ca and Mg related to release of oxides ash (Kauffman et al., 1994). The average value of pH indicated that Cuiabá tended toward slightly acidic precipitation (below 5.6), in contrast to other metropolitan areas that are frequently characterized by pH values below 5.0 (Fornaro and Gutz, 2003; Basak and Alagha, 2004; Cao et al., 2009).

A predominance of this anion may be the result of oxidation of nitrogen oxides (NO_x) emitted by the burning of fossil fuels used in vehicles and which are suspended in the atmosphere during the dry period. Leal et al. (2004) observed that NO_3^- anions were among the most abundant anions in precipitation in the city of São Paulo, Brazil. Their study suggests that a staggering 96% of NO_x were emitted by 6 million vehicles, of which 81% are diesel engines. In other regions of Brazil, the SO_4^{2-} are the most abundant in samples of precipitation (Teixeira et al., 2008), indicating that sulfuric acid (H_2SO_4) is the main compound responsible for the acidity of precipitation. Sulfates are derived from the combustion of fossil fuels and biomass. Sulfates need to be carefully controlled because they contribute to the formation of particulate matter, cause acid precipitation and can damage to vegetation after even short periods of exposure (Cetesb, 2009).

The contribution of Cl^- was lower than other anions, probably because Cuiabá is located far from the ocean. By contrast, in coastal areas the concentration of Cl^- is typically high due to the influence of sodium chloride salts from the marine environment (Mello, 2001; Teixeira et al., 2008).

F^- and PO_4^{3-} can occur in precipitation samples due to resuspension of soil dust containing fertilizer or because of industrial emissions. However, the territory immediately within and surrounding Cuiabá has a few agricultural activities, mainly horticulture, with small areas planted (Mato Grosso, 2008), which explains the few samples found to contain these anions.

The average concentrations of anions in precipitation from Cuiabá differ markedly from those recorded in other sites (Table 2). Anion concentrations tend to be higher in cities with a high population density, many industries, and large volume of vehicles (Fornaro and Gutz, 2003; Basak and Alagha, 2004; Mouli et al., 2005; Pelicho et al., 2006; Cao et al., 2009), as well as those that use coal for domestic heating (Basak and Alagha, 2004), or which are located in a region without a

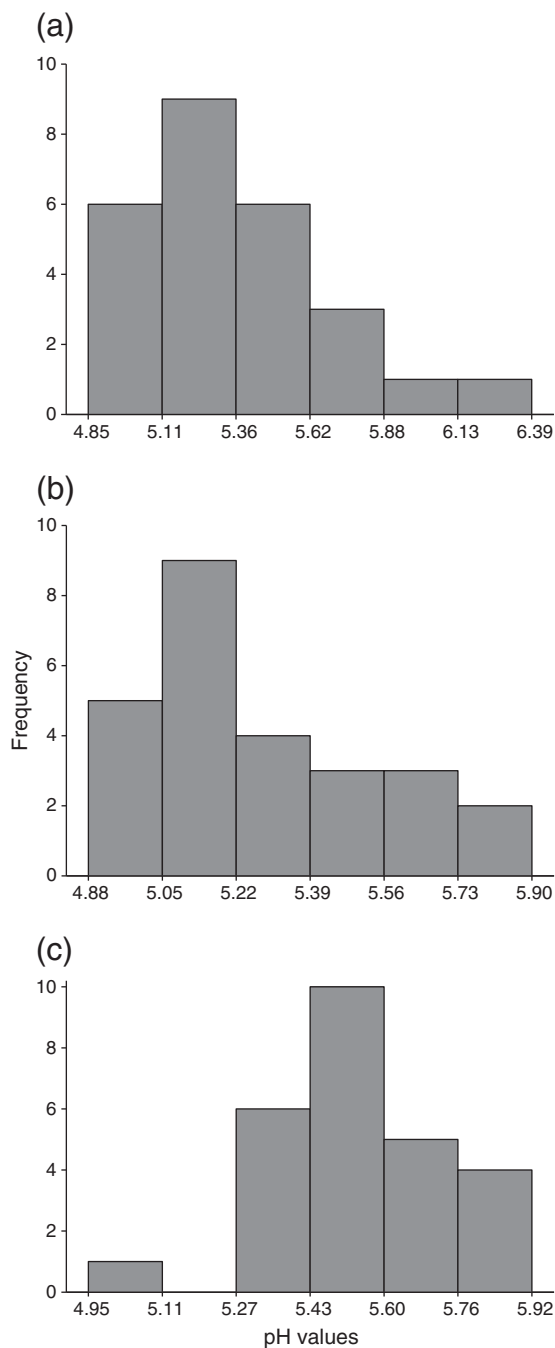


Fig. 3. pH frequency distribution of precipitation sampled in (a) October, (b) December and (c) February in Cuiabá city, Mato Grosso state, Brazil.

power plant (Migliavacca et al., 2005a), or which are under the influence of specific geographical conditions such as México city which is located on a volcanic plateau (Báez et al., 2007).

Low concentrations of anions of precipitation compared with other regions were anticipated in the present study because Cuiabá has a relatively high volume of precipitation, removing particles and gases in the atmosphere, and because the local power plant (in operation since August 2007) runs on natural gas. Moreover, this plant only operates when the

Table 2pH, electrical conductivity (EC, $\mu\text{S cm}^{-1}$) and of ionic concentrations ($\mu\text{eq L}^{-1}$) in precipitation, sampled in site of the others sites.

Site	pH	EC	Cl^-	F^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Reference
São Paulo City, Brazil	4.77	–	4.7	–	15.6	4.75	–	FORNARO e GUTZ (2003)
Istanbul City, Turquia	4.81	–	124.8	–	33.4	115.2	–	BASAK e ALAGHA (2004)
Petra Region, Jordan	6.85	160.60	80.60	–	35.70	53.20	–	AL-KHASHMAN (2005a,b)
Tirupati City, Índia	6.78	–	33.91	4.72	40.84	127.96	–	MOULI et al. (2005)
Candiota Region, Brazil	5.33	7.78	11.8	4.90	5.21	21.2	–	MIGLIAVACCA et al. (2005a)
Londrina City, Brazil	5.51	15.70	9.00	–	10.60	3.87	–	PELICO et al. (2006)
México City, México	5.08	–	9.56	–	42.62	61.94	–	BÁEZ et al. (2007)
Guangzhou City, China	4.49	–	86.80	12.70	53.40	163.30	–	CAO et al. (2009)
Maolan area, China	5.40	–	5.14	0.90	3.01	40.35	–	HAN et al. (2010)
Cuiabá City, Brazil	5.30	6.48	4.40	0.29	3.80	1.01	0.05	Present study

demand for electricity cannot be supplied by hydroelectric plants. In general, power plants emit SO_2 , NO_x ($\text{NO} + \text{NO}_2$) and particulate matter, and their secondary products which are formed from photochemical reactions between chemical species in the primary atmosphere (Lora, 2002). Researchers have estimated that power plants with natural gas emit a combined total of about 0.68 g/kWh of NO_x (Schaeffer and Szklo, 2001). Considering the capacity of the power plant in Cuiabá is 480 MW, the estimated emissions would be approximately 326.4 kg/h of NO_x when operating at maximum capacity.

In the dry season Cuiabá city is probably strongly impacted by pollutants that come from fires in the surrounding landscape that are used to clear native vegetation for pastures and crops. In the rainy season, due to the high volume of precipitation, these chemical constituents are quickly removed from the atmosphere – a process which can be observed in the clear decrease of concentrations of anions present in precipitation from October to February.

4.3. Correlation matrix

Correlation analysis was performed to determine the association between the ionic constituents in the precipitation

and to distinguish the possible common sources of these components. The analysis was performed separately for the three sampling months: October, December and February. In October, electrical conductivity was correlated, in descending order, with NO_3^- , SO_4^{2-} and Cl^- . These anions also demonstrated some significant correlations with each other: Cl^- and NO_3^- , Cl^- and SO_4^{2-} , NO_3^- and SO_4^{2-} (Table 3). A significant correlation between NO_3^- and SO_4^{2-} ($r=0.86$) has been previously recorded in samples from Petra in Jordan (Al-Khashman, 2005a). This association was attributed to the accumulation of these ions in the atmosphere during the rainy season and to the anthropogenic and agricultural activities around the study area (Al-Khashman, 2005a). In the present study the significant correlation between NO_3^- and SO_4^{2-} can probably be attributed to the co-emission of their precursors SO_2 and NO_x (Cao et al., 2009). In December there was a significant correlation between electrical conductivity and $\text{NO}_3^-/\text{SO}_4^{2-}$, as well as between NO_3^- and SO_4^{2-} – although the value of the correlation coefficient (r) was lower than that recorded in October. In February there was a significant correlation between electrical conductivity and NO_3^- and between NO_3^- and SO_4^{2-} . In all three sampling periods (October, December and February) there was no signif-

Table 3Matrix of Pearson correlation between pH, electric conductivity and ionic concentrations in precipitation, sampled in October, December/2009 and February in Cuiabá, Brazil. Bold numbers represent significant correlations ($p \geq \pm 0.5$).

Month		H^+	EC	Cl^-	F^-	NO_3^-	SO_4^{2-}	PO_4^{3-}
October	H^+	1.00						
	EC	–0.19	1.00					
	Cl^-	–0.10	0.79	1.00				
	F^-	0.09	0.08	–0.16	1.00			
	NO_3^-	–0.14	0.96	0.75	0.19	1.00		
	SO_4^{2-}	–0.12	0.88	0.73	0.21	0.94	1.00	
December	PO_4^{3-}	–0.06	–0.05	0.003	–0.09	–0.02	0.01	1.00
	H^+	1.00						
	EC	0.29	1.00					
	Cl^-	–0.27	0.15	1.00				
	F^-	–0.12	0.02	–0.11	1.00			
	NO_3^-	0.30	0.70	0.14	0.04	1.00		
February	SO_4^{2-}	0.26	0.55	0.16	0.32	0.64	1.00	
	PO_4^{3-}	–0.12	0.22	0.38	–0.17	0.31	0.14	1.00
	H^+	1.00						
	EC	–0.42	1.00					
	Cl^-	–0.11	0.25	1.00				
	F^-	–0.20	0.19	0.01	1.00			
	NO_3^-	–0.22	0.58	0.20	0.51	1.00		
	SO_4^{2-}	–0.38	0.50	0.37	0.45	0.87	1.00	
	PO_4^{3-}	–	–	–	–	–	–	–

icant correlation between H^+ and electrical conductivity, Cl^- , F^- , NO_3^- , SO_4^{2-} or PO_4^{3-} . Such a lack of correlation has been observed in several other studies (Basak and Alagha, 2004; Cao et al., 2009), probably because significant quantities of H^+ are neutralized by natural constituents found in precipitation of the region.

4.4. Ratio of SO_4^{2-}/NO_3^-

Sulfate and nitrate anions, commonly present in precipitation, contribute to acidification and the SO_4^{2-}/NO_3^- ratio may indicate that anthropogenic sources have altered atmospheric precipitation (Al-Khashman, 2005a; Migliavacca et al., 2005b). The SO_4^{2-}/NO_3^- ratios in the three sampling periods (October, December and February) were 0.76, 0.94 and 1.01 (averaging 0.91). The lowest ratio was recorded in October, thereafter there was an increasing trend until February due to high concentrations of NO_3^- at the beginning of the rainy season, decreasing during the course of sampling and they became nearly equal to the SO_4^{2-} concentration in February (ratio = 1.01).

The SO_4^{2-}/NO_3^- ratios obtained in this study tend to be lower than those recorded in other sites (Table 4). Marginally higher, SO_4^{2-}/NO_3^- ratios have been recorded in Eshidiya (1.91) (Al-Khashman, 2005a), Candiota (1.63) (Migliavacca et al., 2004) and Ankara (1.60) (Topçu et al., 2002). Eshidiya is located near a phosphate mine in Jordan and experiences a desert climate with low precipitation of about 50 mm per year (Al-Khashman, 2005a). The Candiota region of southern Brazil (420 km from the city of Porto Alegre) is heavily involved in the coal mining industry, limestone extraction, cement fabrication and also possesses a coal-fired energy plant (Migliavacca et al., 2004). Finally, in the rural area of Ankara (Turkey), the measurement was taken from a site (Cubuk) located about 50 km from the city where there are no major settlements or industrial activities (Topçu et al., 2002). However, many sites have recorded much higher ratios, e.g. San Jose, Costa Rica (18.6) (Herrera et al., 2009), Guaíba, Brazil, (8.70) (Migliavacca et al., 2005b) and Lucknow, India (3.56) (Singh et al., 2007). San Jose forms a metropolitan area along with Heredia and Belen where the main driver of the high ratio is probably the emission of sulfur dioxide from a nearby volcano, followed by the high sulfur content of diesel fuel used in Costa Rica (Herrera et al., 2009). The Guaíba region in southern Brazil is mainly characterized by the presence of fixed or mobile emission sources, including vehicles (diesel and gasoline), an oil refinery, a petrochemical industry, steel, leather and two thermoelectric plants (Migliavacca et al., 2005b). Lucknow in India also has characteristics of an industrialized

city with diverse industrial units and about 750 million vehicles (light and heavy, gasoline and diesel) (Singh et al., 2007).

4.5. Spatial variability

After adjusting for semivariograms for pH, electrical conductivity and chloride anions (Cl^-), nitrate (NO_3^-) and sulfate (SO_4^{2-}), the data were successfully interpolated using ordinary kriging (Figs. 4–6). F^- and PO_4^{3-} were not assessed because data were of insufficient quality.

In October, the maps of the anions (Cl^- , NO_3^- , SO_4^{2-}) and electrical conductivity show a similar spatial pattern, with increasing concentrations in the Industrial District in the south-east of the study area. The maximum concentration of Cl^- ($13.20 \mu eq L^{-1}$), NO_3^- ($23.85 \mu eq L^{-1}$), SO_4^{2-} ($2.77 \mu eq L^{-1}$) and maximum electrical conductivity ($28.87 \mu S cm^{-1}$), so as the highest pH value (6.39) were observed at site 23, and the lowest pH value (4.85) at site 19 – both of which are located in the Industrial District.

In December, in contrast to the previous month, the maps of both the anions and the electrical conductivity were dissimilar. The highest concentrations of Cl^- ($13.05 \mu eq L^{-1}$) being observed at site 20 in the Industrial District, the highest concentration of NO_3^- ($6.00 \mu eq L^{-1}$) was at site 6 in down town Cuiabá, and the highest concentration of SO_4^{2-} ($4.93 \mu eq L^{-1}$) was at site 4 in the northwest of the city. Electrical conductivity ($16.40 \mu S cm^{-1}$) was highest at site 17 in the west of the study area. The lowest pH (4.88) was found at site 8 near the down town area.

February was similar to December in that the maximum concentrations were spread across the study area: Cl^- ($11.09 \mu eq L^{-1}$) at site 1 in the District of Nossa Senhora da Guia, NO_3^- ($8.69 \mu eq L^{-1}$), SO_4^{2-} ($2.31 \mu eq L^{-1}$) and electrical conductivity ($15.26 \mu S cm^{-1}$) at a site in the center of Cuiabá, and the lowest pH value (4.95) at site 4 northwest of the city.

In this study, similar spatial patterns of Cl^- , NO_3^- , SO_4^{2-} , pH and electrical conductivity were observed in October, with maximum values in the Industrial District. However, it was expected that high concentrations of ions diminished the pH, or increase the acidity of precipitation, because the ions Cl^- , NO_3^- and SO_4^{2-} can form chloric, nitric and sulfuric acids, respectively. On the other hand, in this site, the maximum concentrations of ions, maximum value of electrical conductivity and pH were detected probably indicating that this area was over the influence of biomass burning. This occurs when the value of electrical conductivity and pH increase together, due to increased release of cations bound to oxides in the ash (Kauffman et al., 1994). In December and February, the highest concentrations of anions were concentrated in the city center, implicating local emission sources such as vehicles in streets with high traffic flow.

Spatial patterns of NO_3^- and SO_4^{2-} in October showed high visual correspondence, a finding confirmed by significant correlation between the anions ($r = 0.94$, $p < 0.05$). However, the maps of ion concentrations Cl^- , NO_3^- and SO_4^{2-} , electrical conductivity and pH for December and February did not show the same spatial pattern, indicating that local urban sources, such as vehicular emissions, are influencing the spatial pattern.

Table 4
 SO_4^{2-}/NO_3^- ratio in wet precipitation at various sites in the others sites.

Site	SO_4^{2-}/NO_3^-	Reference
Ankara, Turkey	1.60	Topçu et al. (2002)
Candiota, Brazil	1.63	Migliavacca et al. (2004)
Eshidiya, Jordan	1.91	Al-Khashman (2005a)
Guaíba, Brazil	8.70	Migliavacca et al. (2005b)
Lucknow, India	3.56	Singh et al. (2007)
San Jose, Costa Rica	18.6	Herrera et al. (2009)
Cuiabá, Brazil	0.91	Present study

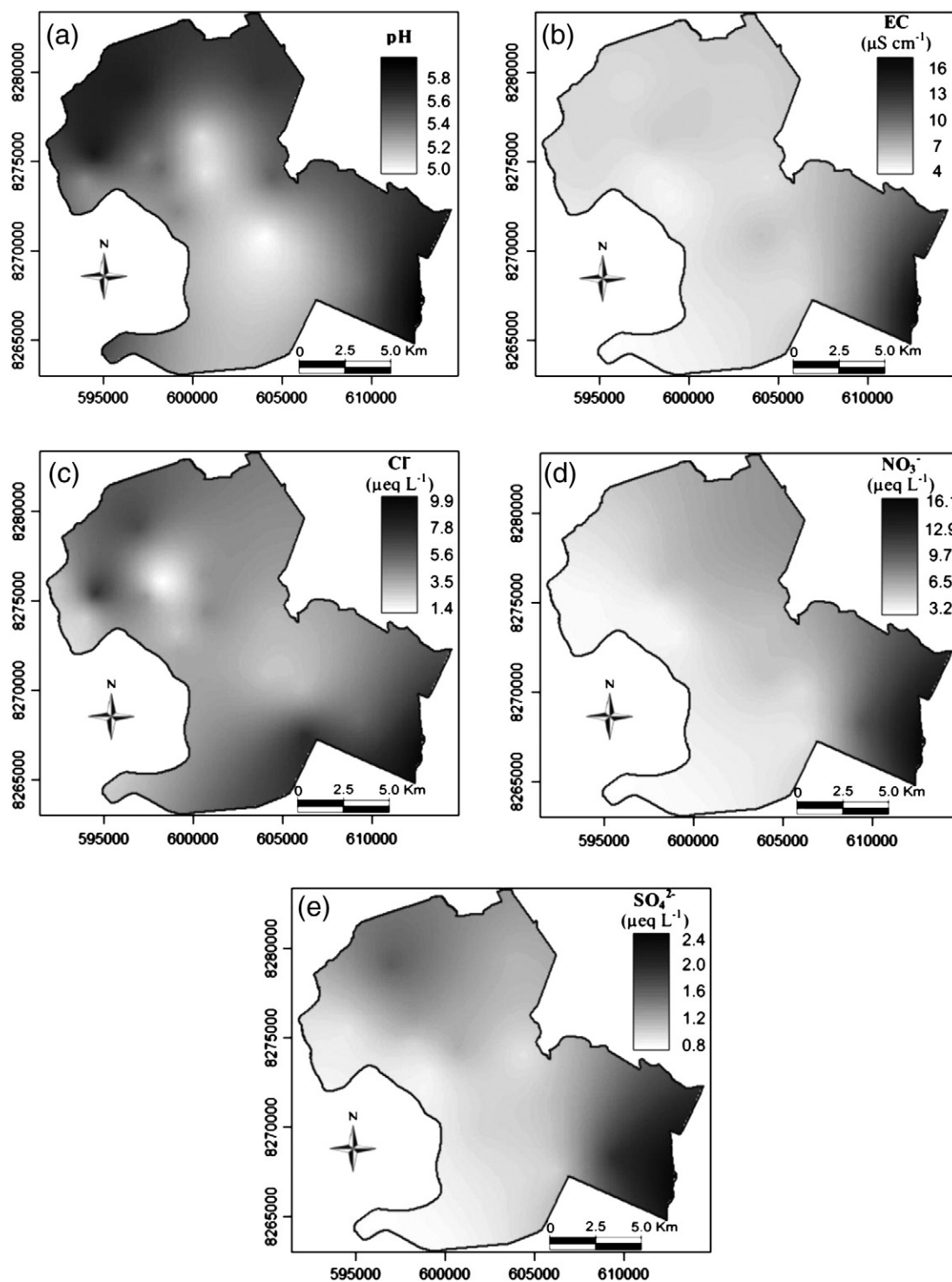


Fig. 4. Spatial variability of (a) pH, (b) electrical conductivity (EC, $\mu\text{S cm}^{-1}$), (c) chloride (Cl^- , $\mu\text{eq L}^{-1}$), (d) nitrate (NO_3^- , $\mu\text{eq L}^{-1}$) and (e) sulfate (SO_4^{2-} , $\mu\text{eq L}^{-1}$) in precipitation, sampled in October/2009 in Cuiabá, Brazil.

5. Summary and conclusions

Our investigation of the anionic composition of precipitation over three rainfall events in the city of Cuiabá indicated

that the rainfall is slightly acidic at the beginning of the rainy season and approaches to limits' neutral water by end of the season. The quantitative analysis and identification of spatial patterns confirmed the removal of accumulated

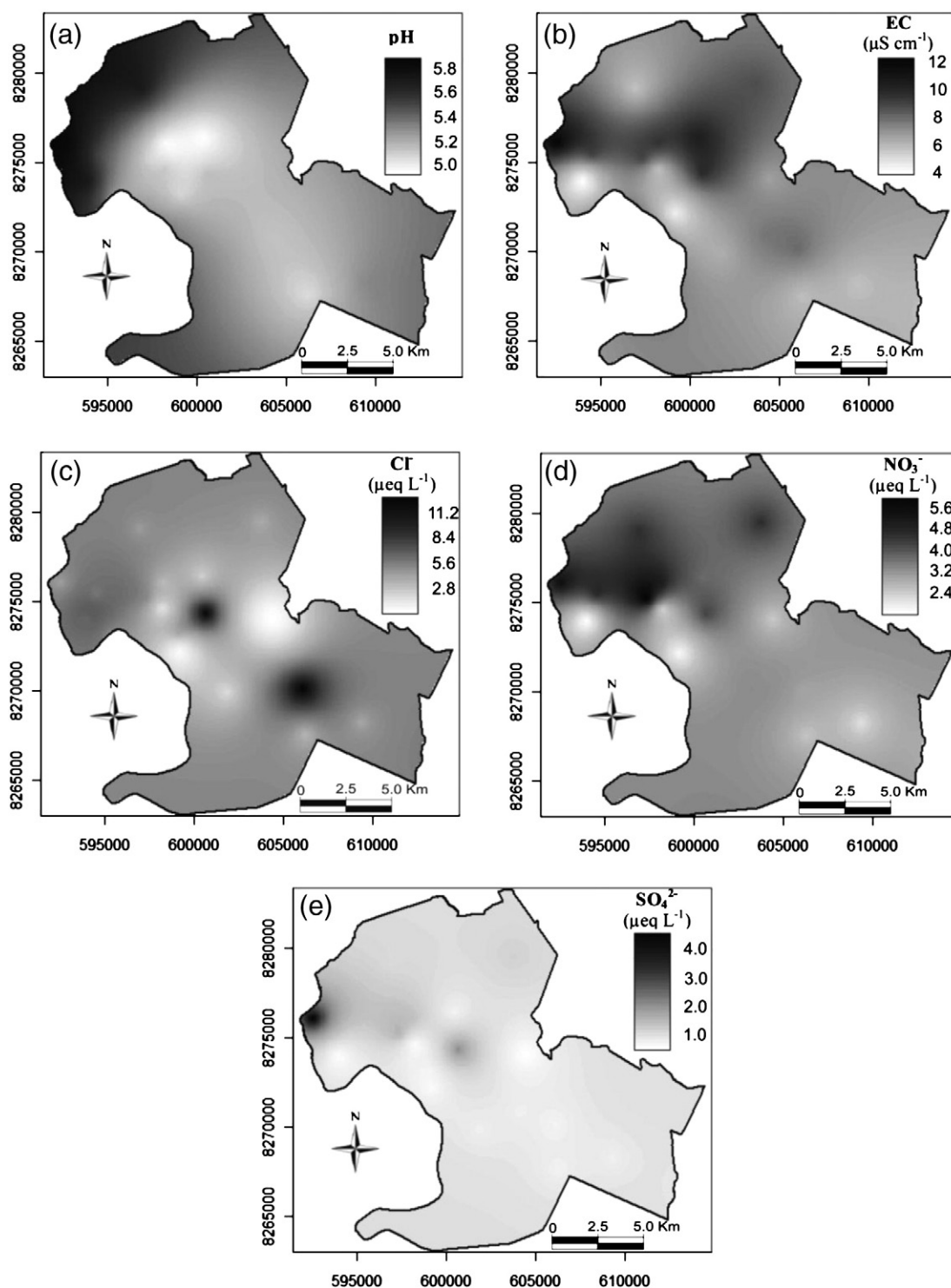


Fig. 5. Spatial variability of (a) pH, (b) electrical conductivity (EC, $\mu\text{S cm}^{-1}$), (c) chloride (Cl^- , $\mu\text{eq L}^{-1}$), (d) nitrate (NO_3^- , $\mu\text{eq L}^{-1}$) and (e) sulfate (SO_4^{2-} , $\mu\text{eq L}^{-1}$) in precipitation, sampled in December/2009 in Cuiabá, Brazil.

particles that accumulate in the atmosphere during a typical dry season due to the intense fires that occur when the native vegetation is burnt.

With the use of geostatistics it was possible to construct detailed maps of the spatial variability of the chemical and

physical–chemical composition of precipitation in the urban area of Cuiabá. However, to provide maximum benefits for urban planning these techniques must be extended to other regions of the country – as seen in the United States and Europe that have strong monitoring networks that provide

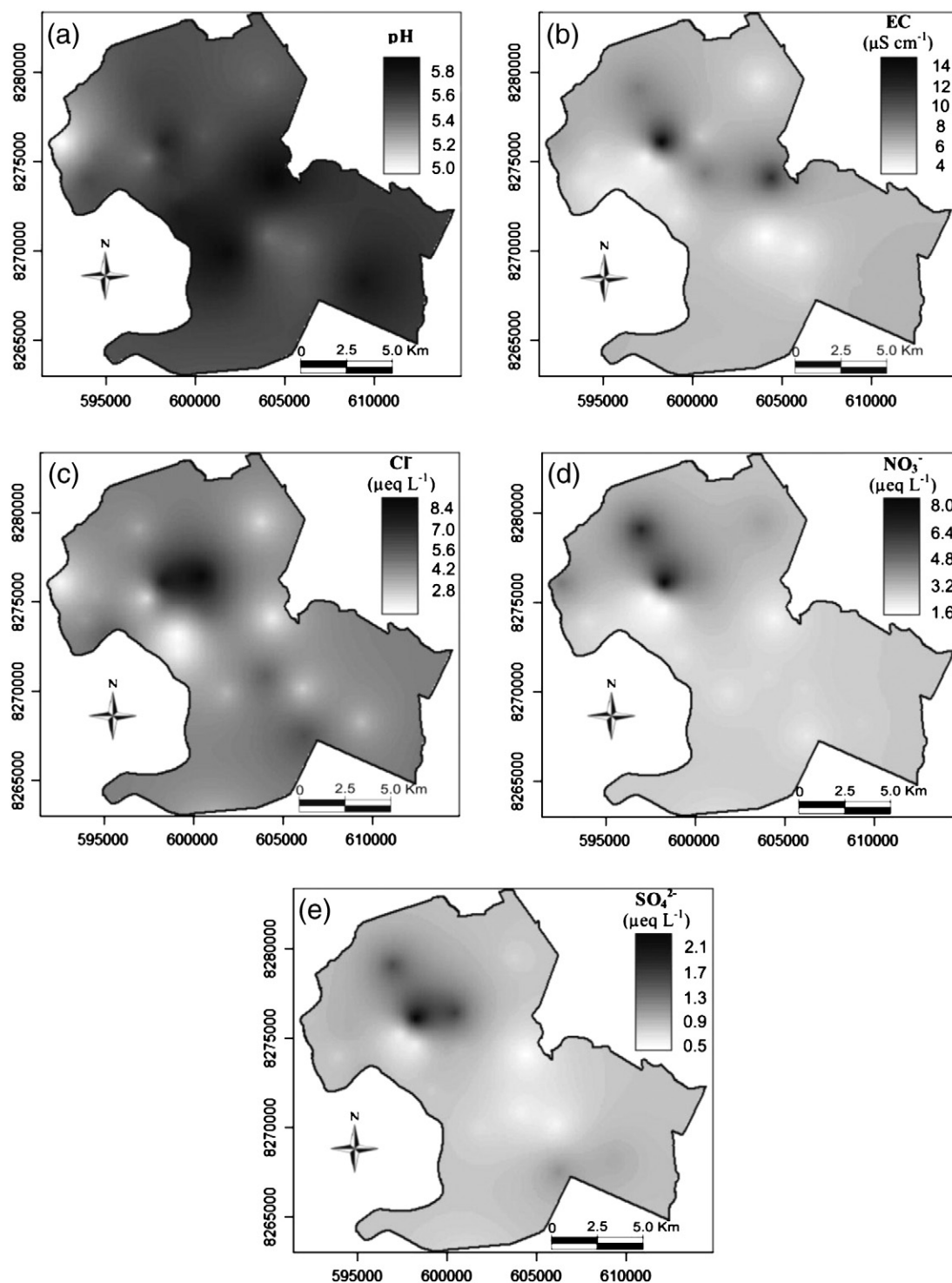


Fig. 6. Spatial variability of (a) pH, (b) electrical conductivity (EC, $\mu\text{S cm}^{-1}$), (c) chloride (Cl^- , $\mu\text{eq L}^{-1}$), (d) nitrate (NO_3^- , $\mu\text{eq L}^{-1}$) and (e) sulfate (SO_4^{2-} , $\mu\text{eq L}^{-1}$) in precipitation, sampled in February/2010 in Cuiabá, Brazil.

a detailed analysis of the relationship between sources of gas and particle emissions and the spatial patterns of deposition of chemical compounds by precipitation.

The sampling grid used within the study was sufficient to characterize the spatial variability in the chemical constituents

of precipitation in all sampling periods. This was verified by the experimental semivariograms and the observation that in the first period (October) the highest concentrations of anions were detected in Industrial District and in the last period (February) they were recorded near the city center. This

study can be used to help design future monitoring networks in Brazil using the knowledge that pollution sources outside of urban industrialized areas, such as streets with high traffic flow, can also significantly contribute to geographically localized changes in atmospheric deposition.

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