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Evaluation of the rainwater acidity of a rural region due to a coal-fired power plant in Brazil

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Abstract

Rainwater samples (73) of a rural region surrounding a coal plant in the northeast of Paraná State (Brazil) were evaluated. Samples of bulk and wet deposition were analysed during a 1-year period (June 1999–June 2000). A large number of rain samples (51) presented pH values below 5.6 (volume weight mean (VWM) was $\text{pH} = 4.7 \pm 0.7$), indicating that the region rainwater was slightly acidic. The anions and cations concentrations in rainwater samples showed a high sulphate concentration ($69 \mu\text{eq l}^{-1}$), followed by sodium, calcium and ammonium (35 , 32 and $30 \mu\text{eq l}^{-1}$, respectively). The analysis of different data of the region indicates that one probable source of the high sodium concentration is fly ash, after the coal burning process. Due to a large contribution of these cations to the sulphate neutralization action, the rainwater of this region displays only a moderate acidity, which does not cause significant environmental impact. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Acid rain; Rainwater; Coal power plant; Ionic composition

1. Introduction

With a fast economic development, Brazil energy consumption has increased significantly in the last decade. Coal combustion has become an interesting alternative of energy generation. In order to implement new coal-fired power plants, economical and environmental cost–benefit evaluations have to be established (Saldanha, 1988).

Brazilian coal presents high amounts of ash and sulphur; its use is convenient only when the coal plant is built near the coal mine, so that the transportation cost is limited. Therefore, just the south region of Brazil, where coal mines are located, can be benefited with this kind of energy generation (IAIC, 1994).

For energy generation, the coal combustion is processed in furnaces at 1700°C . In the combustion

process, most part of the mineral matter of the coal is melted. The heavy ash fraction is deposited at the bottom of the furnaces, so it is called bottom ash. Light ash is carried through the furnaces by the gases flowing toward the chimney. Depending on the emission control system of the chimney, most part of the ash is collected and the leftover (fly ash) is released into the atmosphere. The amount of ash released into the atmosphere is variable, with releases of around 10% in old plants, while in modern plants, with sophisticated emission control equipment, they can be reduced to 0.5% (UNSCEAR, 1988).

Together with the fly ash emission, large amounts of gases considered as acid precursors, such as SO_2 and NO_x , are released into the atmosphere, and contribute to the acid precipitation in the region.

Rain is the most effective scavenging factor for removing particulate and dissolved organic gaseous pollutants from the atmosphere. The scavenging of the atmosphere pollutants affects the chemical composition

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and the pH of rainwater. The degree of acidity depends on the neutralization by certain rainwater components such as ammonia and calcium carbonate and/or hydroxide (Warneck, 1988; Kulshrestha et al., 1995a, b).

The chemicals present in the atmosphere influence the water cycle of the atmosphere whereas the material deposited by the rain affects soil, superficial water and vegetation. The composition of the rainwater depends on the local emission, on the pollutants transport, on the sea level elevation and on the drop size, which in turn influences the rainout (in-cloud scavenging) and the washout (below-cloud scavenging). The different climate conditions also influence the trace substances concentration in the rain (Baron and Denning, 1993).

Acid rain presents a pH lower than 5.6, which is the value expected on the basis of the equilibrium of pure water and atmospheric CO_2 (Charlson and Rodhe, 1982; Likens, 1976; Seinfeld, 1986). To investigate the effect caused by the activity of a coal-fired power plant on the rainwater quality of the region, this work has evaluated the rain events in the period of 1 year. The chosen site for this study was a rural region around a coal plant located in the town of Figueira, in the northeast region of Paraná State, Brazil. Electrostatic filters were installed in 1997, 2 years before the present work was carried out. The rainwater samples were collected from June 1999 to June 2000. The data allowed us to observe the regional variability of the majority of ions concentrations in rainwater and evaluate their contribution to the acidity of the rain.

2. Local description

The evaluation of the rainwater was carried out in the town of Figueira, located northeast of the Paraná State (latitude $23^\circ 52'$ and longitude $50^\circ 24'$), where the coal-fired power plant of 10 MW has been operating since 1963. The climate context is (Cfb) mesothermic humid subtropical, with temperatures between 11°C and 26°C . The average relative humidity is 67% and the average annual precipitation in the last 10 years has been 1398 mm. The precipitation in the sampling period (June 1999 to June 2000) was of 1148 mm, but only 180 mm was analysed in this study. Despite the fact that rain samples were not so numerous, they were distributed homogeneously in the sampling period, and so they could be considered representative. The predominant vegetation is *cerrado* (tropical savanna) and the relief is slightly hilly, with average heights of 600 m. The soil is classified as yellowish-red podzolic, considered acidic, with low base saturation and high exchangeable aluminum and high activity clay. Figueira has the coal exploration and the power plant as its principal economic activity (Morrone and Daemon, 1985).

3. Materials and methods

For the rainwater sampling two collection points were defined: (a) near the coal plant and (b) at the workers houses. The (b) point is located 5 km away from the plant in a no-preferential wind direction. Two 17 cm-diameter sampling bottles of poly(ethylene terephthalate) (PET) were set up in each collection point on a grounded 1 m-high support. The sampler (I) collected samples of rainwater with wet and dry deposition (bulk sample), while the sampler (II), which was placed on the support prior to the rainfall, collected the only wet deposition (wet-only sample). After each rain event, an aliquot of 150 ml was taken from each sampler and stored at freezing temperature to conserve its integrity and the total volume is noted down. A number of 30 events were sampled, and a total of 73 samples of rainwater were collected. Immediately after samples defrosting, a Digimed pHmeter model 330 with a glass-body combination electrode and an Orion Conductivity Meter determined the pH and conductivity (25.0°C), respectively. In all samples, the cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) and anions (SO_4^{2-} , NO_3^- , Cl^-) concentrations were determined by ion chromatography (IC), using a Dionex DX-120 Ion Chromatography system coupled to a Water-100 integrator. The separation of cations was achieved through a cationic column (HPIC-CS14 Dionex) with an elution solution of 10 mmol l^{-1} metasilicic acid, at a flow rate of 0.86 ml min^{-1} . For anions, an anionic column (HPIC-AS14-Dionex) was used and elution was carried out with a $1.0\text{ mmol l}^{-1}\text{ Na}_2\text{CO}_3/3.5\text{ mmol l}^{-1}\text{ NaHCO}_3$ solution, at a flow rate of 1.2 ml min^{-1} .

4. Results and discussion

To verify whether major components had been measured in the rainwater analysis, two kinds of quality control were applied. Linear regression analysis between measured anions (Σ^-) and cations (Σ^+) gives $r = 0.7$ and slope = 0.5 ($\Sigma^+ > \Sigma^-$), which indicates that anions HCO_3^- and organics (formate and acetate) are probably present but were not measured. On the other hand, linear regression analysis between the measured and the calculated conductivity gives $r = 0.9$ and slope = 1, which indicates that practically the majority of the ions were analysed.

The results obtained for the pH and for the cations and anions concentration in the 73 rainwater samples, their average concentration, median, volume weight mean (VWM), range and standard deviation are presented in Table 1. The data of the anions and cations concentration show a high relative standard deviation (from 76% to 191%), indicating a great variability in the cations and anions concentration in each rain event. The

Table 1
Rainwater (73 samples) chemical composition data ($\mu\text{eq l}^{-1}$) of a rural region surrounding the coal plant in the city of Figueira (PR), Brazil

	Median	Average (\pm sd) ^a	VWM	Range	Range ^b
pH	5.0	4.7 (0.7)	4.9	4–6.6	5.4–7.8
Cond ^c	22.5	23.8 (18)		5–116	
H ⁺	9	18 (25)	14	0.4–115	0.0–3.7
Na ⁺	20	37 (42)	35	0.4–192	5.1–4074
NH ₄ ⁺	13	29 (48)	30	0.5–269	8.3–847
K ⁺	8	11 (11)	10	0.3–48	1.3–498
Mg ²⁺	5	12 (23)	12	0.3–117	1.0–390
Ca ²⁺	15	33 (46)	32	1.9–246	36.9–2011
Cl ⁻	13	17 (13)	16	1.3–70	2.8–443
NO ₃ ⁻	11	17 (25)	13	1.0–155	1.6–376
SO ₄ ⁻	49	74 (84)	69	4.4–608	11.4–1287

^asd = standard deviation.

^bAlastuey et al., 1999.

^c $\mu\text{S cm}^{-1}$.

highest concentration is observed for SO₄⁻, followed by Na⁺, Ca²⁺ and NH₄⁺. The burning process of the local coal, with a high content of pyrite (7%), results in the emission of large amounts of SO₂ into the atmosphere (IAIC, 1994).

A comparison between the values (Table 1) obtained for the cations and anions concentration in the present study and a similar study carried out in a coal-fired power plant in Spain (Alastuey et al., 1999) shows that our values are 2–3 times lower. This result is likely to depend on the size of the Figueira coal plant (10 MW), rather smaller than Spain plant (1050 MW), for which higher concentrations are expected. An evaluation of the higher ion concentration of the Spanish plant shows higher concentrations for calcium ions in the rainwater, around 8 times higher than in the present work. Here the major ion concentration is sulphate, which explains the differences in pH in the two cases. A high concentration of sulphate tends to lead to a higher acidity in the rainwater. In a study carried out by Piccolo et al. (1988), it was observed that the rainwater pH of a region close to Bahia Blanca estuary (Argentina), adjacent to a fossil-fuelled power plant of 600 MW, ranged between 6.5 and 7.2 in a 1-year sampling period (1984–1985). The values of pH are proved to be clearly related to the weather condition. The highest values of pH were observed under the influence of continental air masses, which traveled over the pampas soil (mainly composed of sand, CaCO₃ and little organic matter), introducing large amounts of alkaline cations (Ca²⁺, Mg²⁺ and K⁺). In the Bahia Blanca estuary the mean values observed for the alkaline cations were 2.6 mg l⁻¹ of Ca²⁺, 0.5 mg l⁻¹ of Mg²⁺ and 0.8 mg l⁻¹ of K⁺, which represented around the double of the mean values obtained in the present work: 0.7 \pm 0.9 mg l⁻¹ of Ca²⁺, 0.2 \pm 0.3 mg l⁻¹ of Mg²⁺ and 0.4 \pm 0.4 mg l⁻¹ of K⁺.

Table 2
SO₄⁻/NO₃⁻ ratios in some cities of Brazil

	SO ₄ ⁻ ($\mu\text{eq l}^{-1}$)	NO ₃ ⁻ ($\mu\text{eq l}^{-1}$)	Ratio SO ₄ ⁻ /NO ₃ ⁻	Reference
Porto Alegre	125	7.3	17.2	Luca et al., 1991
São Paulo	34.6	26.1	1.3	Paiva et al., 1997
Belo Horizonte	25.1	12.0	2.1	Figuerêdo, 1999
Figueira	69	13.0	5.3	This work

Another important comparison can be made with the data from industrialized urban and large vehicles fleet regions in Brazil. Measurements of the SO₄⁻ and NO₃⁻ concentrations were carried out in some industrialized cities of Brazil, such as: (a) Porto Alegre, a metropolitan area with several sources of atmospheric pollution, especially oil refineries, petrochemical industries, steel and metallurgical mills, coal-fired power plant, etc., (b) Belo Horizonte, with pollutant sources like oil refineries, iron and steel industries, sulfuric acid plant, etc. and (c) São Paulo, the largest industrial city of Brazil with vehicles fleet of about 5.5 million of light vehicles. The data are presented in Table 2. The lowest SO₄⁻/NO₃⁻ ratio (Table 2) is obtained for São Paulo, where the emission control of SO₂ has started in the early 1980s, and the high concentration of NO_x from the vehicles emission resulted in an increase of NO₃⁻ concentration (CETESB, 2000).

Fig. 1 presents the profile of the cations monthly VWM of the rain events collected in sampler I + II, at the sampling points (a) and (b). The visual evaluation shows that Ca²⁺ and NH₄⁺ are the predominant cations in the rainwater of the Figueira region, in most rain events. In some events, high concentrations of Na⁺ and Mg²⁺ are observed.

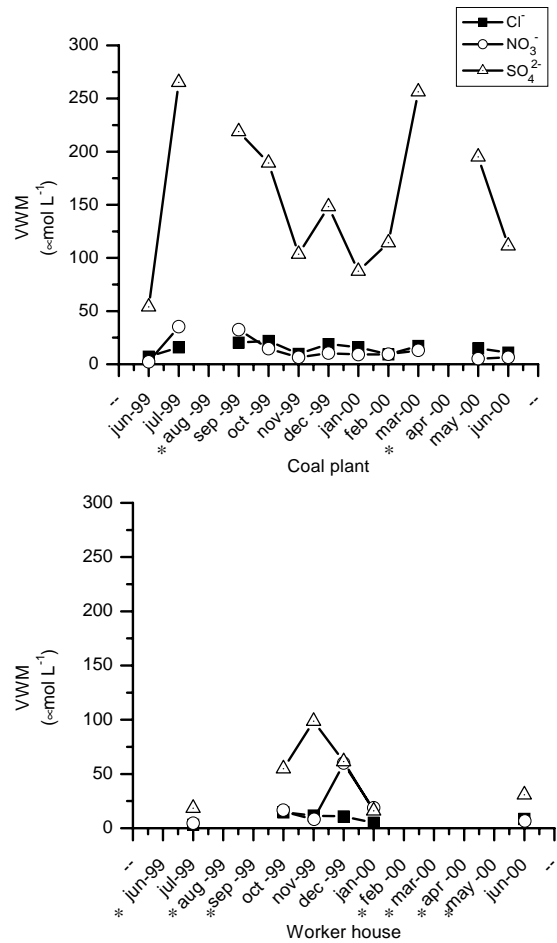
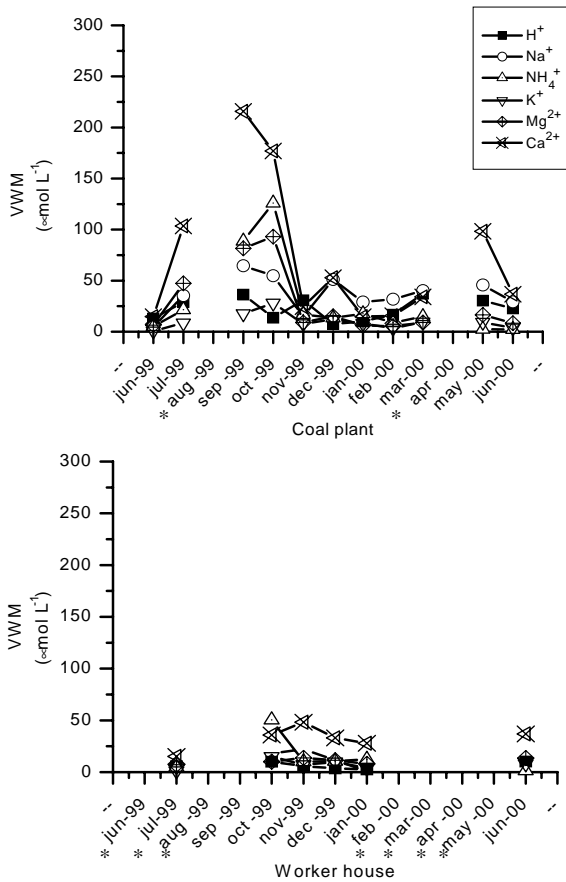


Fig. 1. Variation of the monthly VWM cations in rainwater for the two collection points and for samplers I (bulk deposition)+II (wet-only deposition). *Month without collection; only April presented no precipitation.

Fig. 2. Variation of the monthly VWM anions concentrations in rainwater for the two collection points and for samplers I (bulk deposition)+II (wet-only deposition). *Month without collection; only April presented no precipitation.

Fig. 2 presents the profile of the anions monthly VWM of the sampling rainwater. The profile shows a clear predominant concentration of sulphate in all events. The local atmosphere was responsible for the high sulphate concentration.

Comparing the sampling points (a) coal plant and (b) workers houses (Figs. 1 and 2), a significant difference in the concentration is observed, point (b) having lower values. Point (b) is not located in the main wind direction, where the coal plant could cause greater influence and major contamination due to the emission of particulate and gases. The high sulphate level in the sampling point (b) indicates that the site really is largely affected by the coal plant emission. Although the point (b) is located in a position less influenced by the coal plant, the sulphate concentration is still high. At the sampling point (a), different sulphate concentrations are obtained in sampler (I) and (II), unlike sampling point (b). The higher sulphate concentration in sampler (I) could be associated with higher particulate contents in

the atmosphere near the coal plant, bound to adsorb the sulphate (HouBao et al., 1999).

Fig. 3 is the histogram for 73 rain samples. The region rainwater pH ranges from 4.0 to 6.6, presenting an average value of 4.7 ± 0.7 , with a variation coefficient of 15%. A large number of rain samples (51 samples, 70%) presents $\text{pH} \leq 5.6$, indicating that the region rainwater is slightly acidic.

The high sulphate concentration in the rainwater composition could lead to a very high acid level. The pH values obtained in rainwater samples are not as low as expected, indicating that alkaline species (NH_3 and calcium carbonate or hydroxide) are probably neutralizing the sulphate acid action.

To find out the predominant alkaline cations (Ca^{2+} , Na^+ , Mg^{2+} or NH_4^+) and acid anions (SO_4^{2-} , NO_3^- or Cl^-) in the rainwater, a triangular diagram (Fig. 4) was

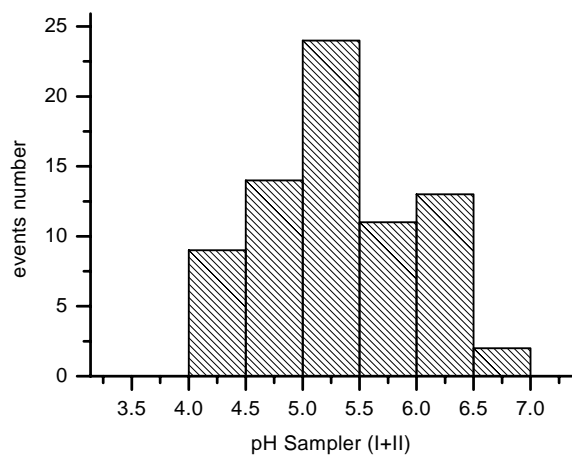


Fig. 3. Histograms of pH values for sampler I (bulk deposition) + II (wet-only deposition).

drawn, showing the relative proportion of these cations and anions (Beverland et al., 1998). An examination of the cations (Ca^{2+} , Mg^{2+} and NH_4^+) triangle (Fig. 4a) reveals that both Ca^{2+} and NH_4^+ are predominant in rainwater samples. Since a high Na^+ concentration was observed in some rainfalls, the cations (Ca^{2+} , Na^+ and NH_4^+) triangle was also plotted (Fig. 4b). The analysis of this triangle shows scattered points, which does not allow to identify which alkaline cations contributed more to the rainwater neutralization. In the case of the anions (SO_4^{2-} , NO_3^- and Cl^-) triangle (Fig. 4c), it was clearly concluded that sulphate is the major ion contributor to the acid rain composition.

To verify which cations (Ca^{2+} , Na^+ , Mg^{2+} or NH_4^+) more frequently neutralize the sulphate, Kulshrestha et al. (1995a) suggested the use of a neutralizer factor (NF), using the ratio of cations over anions [Ca^{2+} or Mg^{2+} or $\text{NH}_4^+/\text{NO}_3^- + \text{SO}_4^{2-}$]. As in this study the rainwater presents insignificant NO_3^- concentration, we decided to calculate the $\text{Ca}^{2+}/\text{SO}_4^{2-}$, $\text{NH}_4^+/\text{SO}_4^{2-}$, $\text{Mg}^{2+}/\text{SO}_4^{2-}$ and $\text{Na}^+/\text{SO}_4^{2-}$ ratios for each rainwater sample; the average values are listed in Table 3. The average of the ratios $\text{Ca}^{2+}/\text{SO}_4^{2-}$, $\text{NH}_4^+/\text{SO}_4^{2-}$ and $\text{Na}^+/\text{SO}_4^{2-}$ are similar, which means an equal contribution of the three cations to the neutralization of the sulphate, confirmed by the triangle in Fig. 4d and e.

It is well known that a high concentration of calcium in the rainwater might depend on the use of fertilizer or of soil neutralizers (frequently CaCO_3), on the soil composition itself, through re-suspension, or on the deposition of the coal plant fly ash.

According to Blume (1992), high concentrations of NH_4^+ found in rainwater could be related to gaseous ammonia (NH_3) introduced into the atmosphere, mainly by cattle breeding (80%), fertilizer use (17%) and industrial processes. The Figueira region is an

Table 3
NF of the major ions in the rainwater samples

	$\text{Ca}^{2+}/\text{SO}_4^{2-}$	$\text{NH}_4^+/\text{SO}_4^{2-}$	$\text{Mg}^{2+}/\text{SO}_4^{2-}$	$\text{Na}^+/\text{SO}_4^{2-}$
Minimum	0.1	0.01	0.02	0.04
Maximum	6.3	4.4	1.37	3.63
Average	0.59	0.56	0.19	0.53
sd	0.8	0.74	0.24	0.54

sd = standard deviation.

agricultural and cattle breeding area and therefore a potential NH_3 source.

To detect the sources of the ions present in the rainwater, a Pearson correlation matrix with all cations and anions concentrations data was built. The correlation coefficient of various parameters was entered in Table 4. The higher correlations are obtained for $\text{Mg}^{2+} \times \text{Ca}^{2+}$ (0.9), $\text{K}^+ \times \text{Mg}^{2+}$ (0.8), $\text{K}^+ \times \text{Ca}^{2+}$ (0.8), $\text{NH}_4^+ \times \text{K}^+$ (0.8), $\text{NH}_4^+ \times \text{Mg}^{2+}$ (0.8), $\text{NH}_4^+ \times \text{Ca}^{2+}$ (0.7), indicating that the presence of these cations is mainly due to the re-suspension of soil particulate and fertilizer use. For $\text{Ca}^{2+} \times \text{SO}_4^{2-}$ (0.7), $\text{SO}_4^{2-} \times \text{Cl}^-$ (0.7), $\text{Na}^+ \times \text{Cl}^-$ (0.8), good correlations are also found. Considering the neutralized factor of $\text{Ca}^{2+}/\text{SO}_4^{2-}$ (0.59), the triangular diagram (Fig. 4d) and the correlation $\text{Ca}^{2+} \times \text{SO}_4^{2-}$ (0.7), it can be concluded that carbonate and/or hydroxide calcium compounds might be important acid rain neutralizers in the Figueira region.

A high sodium concentration (Tanner, 1999; Khemani et al., 1994; Liljestrand and Morgan, 1980) had been previously observed in rainwater near coastal sites, where the sodium was of marine origin and Na^+/Cl^- ratios were close to 0.86. The high correlation for $\text{Na}^+ \times \text{Cl}^-$ (0.8) can be an indicator of the marine origin of Na^+ and Cl^- . To verify this hypothesis, the Na^+/Cl^- rate was calculated. According to Alastuey et al. (1999), this value should be 0.86 in order to confirm the marine source of Na^+ and Cl^- in the rainwater. The average value obtained for the Na^+/Cl^- rate is 1.97, much higher than the value established in the literature, showing that these ions are probably not of marine origin.

According to literature data (Sha et al., 1996; Acker et al., 1998), in most rains of the world the cations that are mainly responsible for the sulphate neutralization are calcium and ammonium. In the present case, sodium plays an important role in the neutralization, although the sodium is not of marine origin, as concluded in the above paragraph.

An analysis of different data of the studied region shows that one probable source of sodium is the adsorbed sodium in the fly ash, after the coal burning process. Results of the fly ash leaching tests (700 mg kg^{-1} of Na) and the ash X-ray Fluorescence

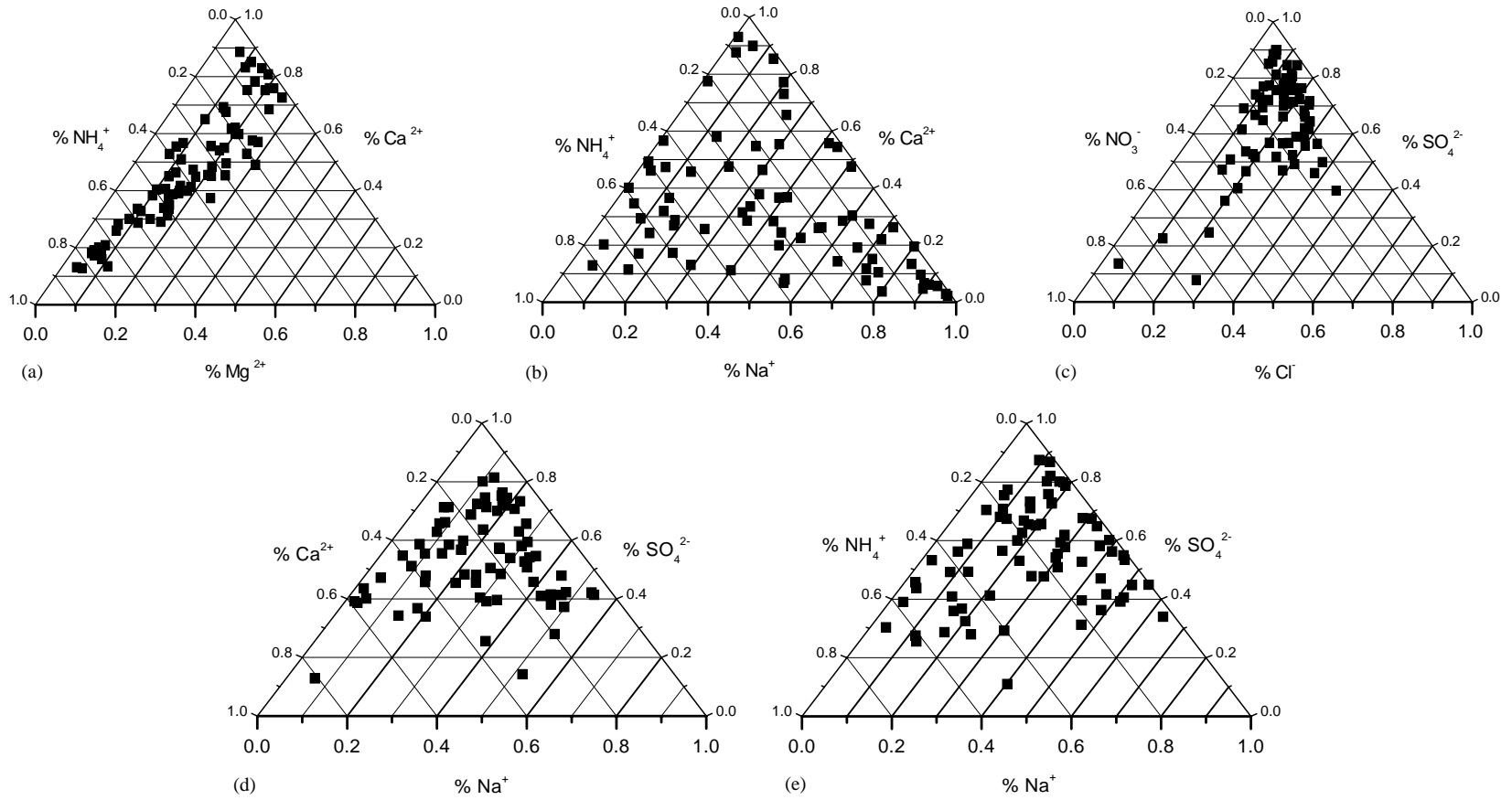


Fig. 4. Triangular diagrams of major ions relative percentage.

Table 4
Correlation coefficients values for cations and anions

	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻
Na ⁺	0.1							
NH ₄ ⁺	0.1	0.3						
K ⁺	0.1	0.5	0.8					
Mg ²⁺	-0.1	0.5	0.8	0.8				
Ca ²⁺	0.1	0.5	0.7	0.8	0.9			
Cl ⁻	0.2	0.8	0.3	0.6	0.5	0.5		
NO ₃ ⁻	0.1	0.3	0.1	0.3	0.4	0.5	0.4	
SO ₄ ²⁻	0.2	0.6	0.3	0.5	0.6	0.7	0.7	0.5

analysis, with average contents of 0.76% (5638 mg kg⁻¹ of Na) for Na₂O and 107 mg kg⁻¹ for Cl⁻, confirmed the presence of high sodium and chloride concentration. This evidence and the high correlation between Na⁺ × Cl⁻ (0.8) confirm the origin of these ions in the rainwater of the Figueira region.

5. Conclusion

The cations and anions analysis in the rainwater samples within a 1-year period (June 1999–June 2000) show high sulphate content, followed by ammonium, calcium and sodium. The high sulphate concentration was expected due to the presence of SO₂ in the local atmosphere.

The two sampling points (a) coal plant and (b) workers houses show significant differences, that might be explained by differences in the collecting points site. The (b) point is located off the main wind direction, where the coal plant is less likely to have some influence, but the sulphate concentration remains high (69 µeq l⁻¹ and range of 4.4–608 µeq l⁻¹) compared with the rainwater of other industrialized regions of Brazil, like São Paulo, with a sulphate concentration of 5–89 µeq l⁻¹ (Paiva et al., 1997). This shows that the Figueira region is greatly influenced by the coal-fired power plant.

A large number of rain samples (51 samples, 70%) presents pH ≤ 5.6, indicating that the region rainwater is slightly acidic.

The high sulphate concentration in the rainwater composition is potentially responsible for very high acid level of the rainwater. The pH values obtained in the rainwater samples are not as low as expected, indicating that alkaline species, such as Ca²⁺, Na⁺ or NH₄⁺, are probably neutralizing the sulphate acid action.

It was clearly observed that the cations (Ca²⁺, Na⁺ and NH₄⁺) act as sulphate neutralizers in each rain event sample. Due to the substantial contribution of these cations to the sulphate neutralization action, the rainwater of this region is only slightly acidic, which does not cause a significant environmental impact.

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