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Chemical speciation and phase fractionation of N, S and Cl compounds in the atmosphere of Reconcavo, Bahia, Brazil

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ABSTRACT

Studies of chemical speciation and phase fractionation of atmospheric inorganic compounds of N, S and Cl have been undertaken in the atmosphere of the Reconcavo Baiano. The objectives were to determine the enrichment of the clean air masses coming from the Atlantic by different chemical species resulting from NO_2 SO_2, HCl and NH_3 emissions from the industrial areas at the Reconcavo and to estimate the changes in air quality regarding between 2008 and 2010. The following sampling devices were used: passive samplers (PS) and continuous analyzers for NO_2 and SO_2; diffusion tubes coated with citric acid for ammonia and NaF for strong acids (HCl, HNO_3 and H_2SO_4), the latter in a thermodiffusion system with a back-up filter for collection of the thermically stable (140 °C) ammonium salts and other particles <2 μm. In parallel, Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ suspended particles fractionated by size on Nuclepore membrane with a Berner cascade impactor (0.06 to >14.9 μm). The analytical methodology for the discontinuous measures included ion chromatography (SO_2 as SO_4^{2-} in the PS, anions of the PM and as representants of the acids in the gas phase) and molecular spectrophotometry using the Griess–Saltzman method (λ = 540 nm) and indophenol method (λ = 630 nm) for determination of NO_2 and NH_3, respectively. Clean air masses from the Atlantic (13 nmol m^{-3} HCl, 2.9 nmol m^{-3} HNO_3, 1.6 nmol m^{-3} H_2SO_4, 9.8 nmol m^{-3} SO_2, 16 nmol m^{-3} NO_2 and 84 nmol m^{-3} NH_3) are slighted enriched in the gas and particulate phase with respect to HNO_3 and H_2SO_4, respectively, by emissions of the industrial complex. However, enrichment occurs for HCl, SO_2, NO_2 and NH_3. In the area of industrial complex influence hydrochloric acid predominates over the other two strong acids, as expected, due to its direct emission from the petrochemical waste incinerator. Ammonium chloride is the predominant gas to particle transformations. During the period of 2008–2010 a decrease varying between 18 and 49% is observed on the levels of almost all compounds in Lamarão do Passé, downwind from an oil refinery but not in Camaçari, downwind from the industrial complex, where all other compounds presented an increased in their concentrations with the exception of HNO_3 and HCl.

1. Introduction

The Reconcavo Baiano is the region comprising the All Saints Bay area (1052 km^2), the largest bay on the Brazilian coast and the lands around them (between 13° S and 38° W). The area has been the scene of an industrial boom and includes the largest industrial complex in the Southern Hemisphere, making the bay the main recipient of the atmospheric pollution load of the anthropogenic activities in the region [1].

The chemical behavior of atmospheric trace constituents (gaseous and particles) is very complex and depends on a number of physical, chemical, meteorological and geographical factors. In many times, substances that are emitted directly into the atmosphere from natural or anthropogenic sources undergo transformations – gas–particle conversion, for example – generating more toxic substances than their precursors, resulting in greater damage to the flora, fauna, and human heritage where they are deposited [2].

Air pollutants can be deposited by different processes on the soil, forests and surface water, also reaching the groundwater and, consequently, may cause damage to ecosystems. Industrial activities and inappropriate land use are considered the most important causes for the continuing process of change in the atmosphere composition, due to the emissions of gaseous pollutants such as sulfur dioxide, nitrogen oxides and ammonia, among others [3].

Nitrogen is certainly the most important nutrient that governs the growth and reproduction of living organisms, and is significant in limiting the incorporation of the atmospheric carbon in plant biomass, exerting a strong influence on the carbon cycle in natural ecosystems, and consequently on the climate changes. There are two major demands that drive the current disruption of the nitrogen

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cycle: the fossil fuel consumption for energy production, leading to emissions of nitrogen oxides into the atmosphere, and the need to feed a growing number of people worldwide, resulting in ammonia emissions, generated from agriculture [4,5].

Nitrogen compounds emitted into the atmosphere by natural and anthropogenic sources may be transformed through atmospheric reactions, forming nitric acid, nitrates and other nitrogen compounds [6,7]. The deposition of these compounds changes the amount of N and may result in changes in the cycle that leads to the N saturation in natural ecosystems, causing relative mineral imbalances such as the scarcity of Mg, K, and P with respect to N, severe yellowing of trees and accumulation of free amino acids. The extra contribution of N to terrestrial and aquatic systems can result in several harmful consequences for the environment, such as the decline of forest and of crop productivity and biodiversity loss [8–10].

Oxidized species of nitrogen ($NOx = NO + NO_2$) may indirectly contribute to global warming by participating in complex reactions with volatile organic compounds, leading to the formation of tropospheric ozone. In addition, NO_2 can participate in the atmosphere in a series of photochemical reactions, for example, in the formation of "smog" photochemical, which reduces visibility. It can also react with moisture in the air to form nitric acid, thus contributing to acid deposition. The reduced species (NH_x = ammonium + ammonia + amines) have a role in nitrogen enrichment and eutrophication of aquatic ecosystems [2,11].

Sulfur compounds in the reduced and oxidized forms can be emitted into the atmosphere by both natural and anthropogenic sources. Andreae and Jaeschke (1992) [12] and Nguyen (2006) [13] estimated the total flux of sulfur compounds (not including marine sulfate) into the atmosphere as 158 ± 30 Tg S yr^{-1}; 8% of this flow comes from volcanoes and geothermal activities, 32% from the biosphere (oceans, soils, plants and mangroves) and 60% from anthropogenic sources (including biomass burning). The SO_2 is the main sulfur compound emitted by these sources (94%). On the other hand, the natural emissions of sulfur compounds (65 ± 25 Tg S yr^{-1}, not including marine sulfate) are predominant in the form of reduced sulfur compounds (RSC). The transformation of these compounds in the troposphere shows a trend toward higher oxidation states, since the RSC easily react with present oxidizing species, resulting in formation of SO_2, which is then oxidized to H_2SO_4 and other sulfates [14], contributing to the acidification of the precipitation – which has an important role in the acidification of lakes and soils – the damage to forests, human health and vegetation, and the corrosion of structures and monuments [2,15]. Sulfate particles are also incorporated into the atmospheric aerosols, where they can act as cloud condensation nuclei (CCN) with possible climatic consequences [16,17].

In 1956, Junge [18] observed that the ratio NO_3^-/Cl^- in the aerosol of the coast of Florida was higher when the wind came from the continent and lower when the wind came from the ocean, assuming that the breeze of the land contained anthropogenic pollutants that react with the particles. Since then, many authors have observed a chloride ion deficit in the aerosol concerning the sodium ion concentration. The authors attributed these observations to reactions with acids, such as sulfuric and nitric acid with NaCl in the marine aerosol, producing gaseous HCl [19–22].

The hydrochloric acid is also directly emitted from urban and industrial incinerators or by the bleaching processes of paper industries, as in the case of emission sources in the area of this study. Until recently, the HCl levels in ambient air were not well established in the literature. Reported values in the range concentration are below the ppb level [22–24].

In Brazil, most studies about nitrogen and sulfur cycles have focused only on the environmental compartments soil/water due to the difficulties involved in atmospheric measurements, especially in the chemical speciation, fractionation of particles of semi volatile species, in the need for continuous data—particularly in remote areas lacking electricity and infrastructure. Thus, there are several studies published in the literature on the atmospheric chemistry of inorganic N and S mainly in the Northern Hemisphere, but very few studies refer to data from the atmosphere of tropical countries. During the last 20 years, studies of chemical speciation and phase fractionation of atmospheric inorganic compounds of N, S and Cl have been undertaken in the atmosphere of the Reconcavo of Bahia, focusing on different chemical aspects [25]: a—understand local processes of acid rain; b—to achieve a grasp of the role of seaspray as scavenger of gaseous acid precursors compounds; [26–28]; c—obtain specific scientific atmospheric information to better support environmental management for government and industries [29].

Starting 2004, the Industrial Complex of Camaçari has been adopting abatement measures for atmospheric emissions, such as substitution of old equipment for modern ones and improvement of production efficiency and thus minimizing losses. Air quality auto-monitoring networks have shown reduction of SO_2, of O_3 and its precursor gases, NO_2 and VOCs (organic volatile compounds). On the other hand, local traffic has increased of about 30%, thus increasing emissions of these gases.

The objectives of this work were to determine the enrichment of the clean air masses coming from the Atlantic by different chemical species resulting from NO_2 SO_2, HCl and NH_3 emissions from the industrial areas at the Reconcavo and to estimate the changes in air quality between 2008 and 2010.

2. Materials and methods

2.1. Measurement sites

Four sampling sites have been selected downwind from the main industrial centers located at the North and Northeast areas of the Reconcavo. One station at the coastline was set as reference of background levels of air masses coming from the east, from the Atlantic Ocean, with no industrial influence. Fig. 1 displays the sampling sites: at the North of the All Saints Bay, Madre de Deus (15.432 inhabitants) and São Francisco do Conde (23,000 inhabitants) both towns at a distance of 1 and 14 km downwind respectively from the oil refinery (RLAM); at the Northeast of the Reconcavo, Camaçari (231,973 inhabitants) and Lamarão do Passé (1,276 inhabitants), at a distance of 1 and 14 km downwind respectively from the largest industrial complex of the Southern Hemisphere; at the east, Itacimirim village, on the coastline and upwind from the industrial activities. Prevailing winds bring air masses from the Atlantic Ocean at least 66.4% of the time (see Fig. 1).

2.2. Sampling

Speciation of strong acids and its ammonium salts, in the gaseous and particulate phase has been accomplished by the combination of thermo diffusion in front of a particle collector using a noncommercial system developed by Niessner and Klockow [30], shown in Fig. 2. The system is composed of a Teflon virtual impactor at the entrance (138 L h^{-1}), separating the particles with an aerodynamic diameter > 2.5 μm (18 L h^{-1}) from the fine particles and the gaseous species; two diffusion tubes of 90 cm × 6 mm each in series coated with 0.1% NaF and connected with a 30 cm diffusion tube coated with sodium carbonate as trap for some sulfur compounds; at the end of the air stream, a membrane filter placed on a filter holder collects the fine particles at a flow rate of 120 L h^{-1}. In the first diffusion tube nitric and hydrochloric acids are collected on the walls. A heating system maintains the temperature of the second 90 cm NaF—denuder at 140 °C. The separated particles by the Teflon virtual impactor are collected in a 37 mm Nuclepore membrane with 0.2 μm pore size. As significant losses can occur in this impactor, this membrane is discarded [31]. Ammonium nitrate and ammonium chloride are thermally unstable and decompose with heat, and its constituents (around 65% in the of NH_4Cl) are collected in the heated diffusion

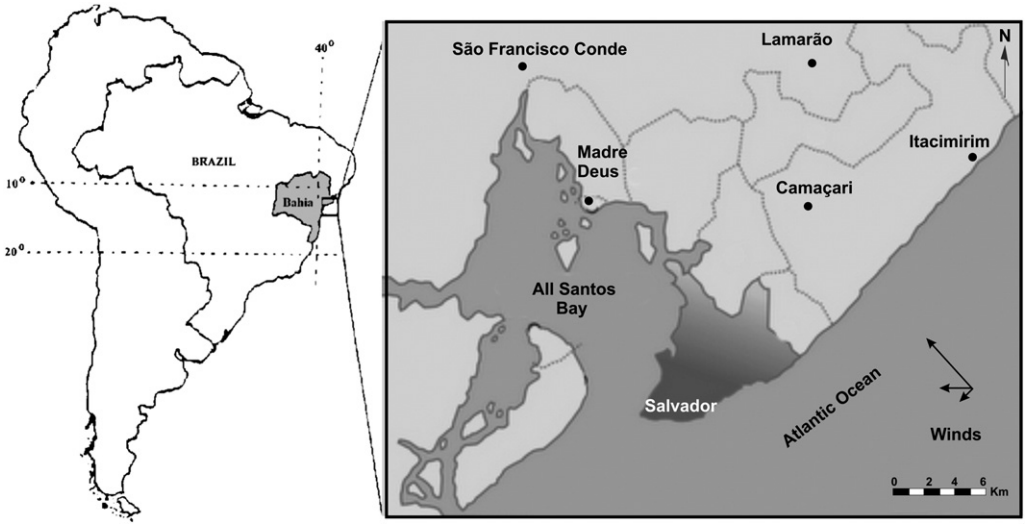

Fig. 1. Map of Reconcavo area showing the sampling stations.

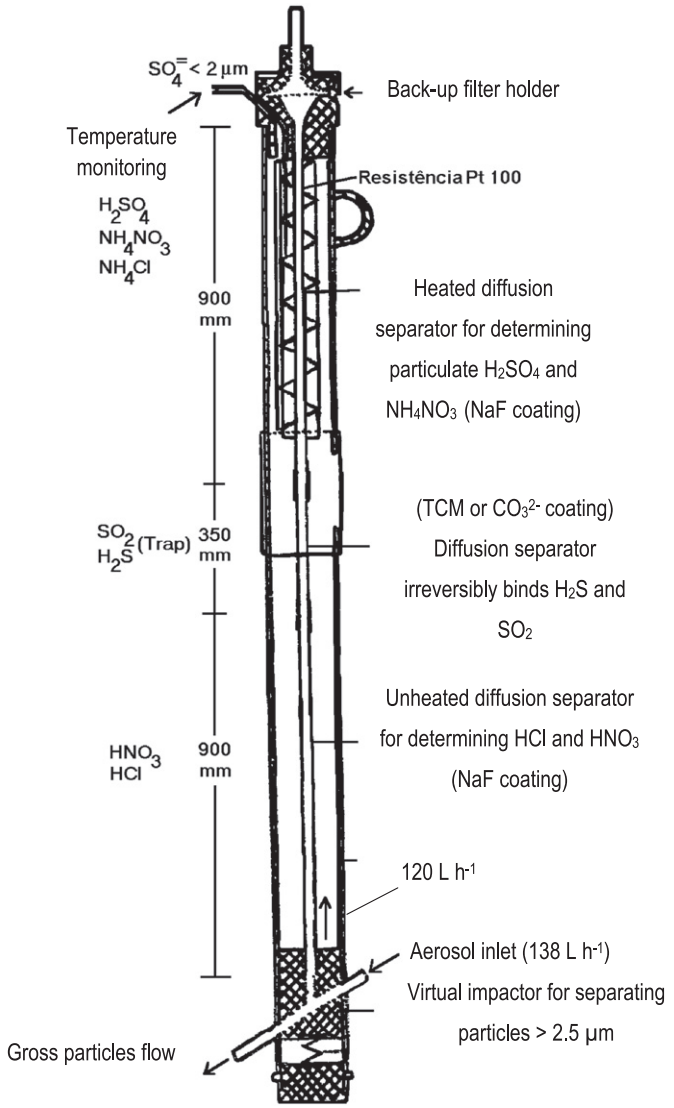

Fig. 2. Speciation of nitric, sulfuric and hydrochloric acids and its salts using thermodiffusion sampling technique.

tube, together with sulphuric acid, whose droplets are completely evaporated and fixed at the coating walls of the denuder. Thermically stable compounds such as NH_4HSO_4, $(NH)_3H(SO_4)_2$, $(NH_4)_2SO_4$, NaCl, $NaNO_3$ and Na_2SO_4 pass the tubes without decomposing nor reacting with the NaF and are collected along with other particles in the membrane filter (Nucleopore, 0.2 µm pore size) in the filter holder. Fig. 2 indicates the compounds sampled at the different stages of the system.

Ammonia is sampled in a separate diffusion tube (90 cm × 6 mm) coated with 0.2% citric acid, without heating at a flow rate of 80–120 L h^{-1} for 24 h [24,32]. After sampling the tubes are closed for transportation to the laboratory for analysis. Field blanks are taken every day. Sealed diffusion tubes were transported to the sampling sites and returned to the lab after the sampling without exposure to check whether contamination occurred during preparation, transportation and analysis.

Continuous monitors manufactured by Environnement, and calibrated with a dynamic gas calibrator (Environnement, Model EV-3M) were used for determination of NO_2 and SO_2 on two sites, Lamarão do Passé and Camaçari, during the sampling campaign of 2008. Passive samplers (triplicate) exposed during 5 days have been used in the 2010 campaign in all sampling stations. The passive samplers used are based on gas molecular diffusion through static air layer developed for use in tropical conditions of high temperatures and high humidity [33–38]. The absorbing medium in the passive samplers was cellulose filter impregnated with a 1.0×10^{-2} mol L^{-1} Na_2CO_3 solution for SO_2 and with a mixture of KI 5.0×10^{-1} mol L^{-1} + KOH 2.0×10^{-1} mol L^{-1} in methanol for NO_2. The performance of the passive samplers used has been calibrated previously for this area by exposing them side by side to continuous analyzers [37]. The relative standard deviation was proved to be 2.6–3.3% for NO_2 and 5.1 to 12% for SO_2. The average accuracy was around 11% for both, and thus within the recommended limit established by the European Union for this type of sampler [39].

Samples of suspended particles fractionated by size have been obtained with Berner cascade impactor [40]. Cut off of aerodynamic diameter sizes (µm) has been defined previously as to provide more information on the fine particle mode and ordered to Hauke-Aeras: 0.06, 0.18, 0.55, 1.7, 5.0, and 14.5 µm. The particles were sampled on Nucleopore membrane (47 mm, 0.2 µm) at air flux of 19.2 L min^{-1} during 24 h.

2.3. Analysis

The diffusion tubes were eluted with 2 mL of deionized water and after several inversions of the tubes with closed end; anions

Table 1
Concentrations in nmol m^{-3} of the chemical species (gaseous and particles) measured in the atmosphere of Reconcavo, Bahia, Brazil.

Atmospheric average concentrations and range, nmol m^{-3}										
HCl	HNO_3	H_2SO_4	NH_3	SO_2	NO_2	NH_4Cl	NH_4NO_3	Other Cl^- <2 μm	Other NO_3^- <2 μm	Other SO_4^{2-} <2 μm
Itacimirim, 2010[a]										
13 ± 2.6 (12–15)	2.9 ± 0.8 (2.0–3.5)	1.6 ± 0.3 (1.4–1.9)	84 ± 8.2 (76–92)	9.8 ± 1.1 (11–9.0)	16 ± 3.7 (39–44)	13 ± 2.1 (12–16)	3.0 ± 0.2 (2.9–3.1)	7.5 ± 20 (48–86)	5.0 ± 0.7 (4.7–6.1)	5.9 ± 0.9 (5.1–6.9)
São Francisco do Conde, 2010[a]										
15 ± 3.3 (12–19)	3.0 ± 0.9 (2.2–4.2)	5.5 ± 4.8 (1.4–12)	186 ± 19 (167–202)	23 ± 2.6 (21–26)	120 ± 6.7 (117–129)	36 ± 17 (13–49)	3.8 ± 0.6 (3.0–4.3)	26 ± 9.2 (14–36)	4.1 ± 0.9 (2.9–5.0)	5.6 ± 2.1 (7.0–2.6)
Madre de Deus, 2010[a]										
13 ± 3.6 (10–17)	1.8 ± 1.4 (0.2–2.7)	8.5 ± 5.9 (1.9–13)	133 ± 37 (101–173)	49 ± 6.2 (44–56)	137 ± 9.0 (172–189)	40 ± 22 (15–57)	5.0 ± 1.4 (3.4–5.9)	30 ± 17 (11–43)	5.0 ± 1.4 (3.4–5.9)	8.5 ± 5.9 (1.9–13)
Lamarão do Passé, 2008[b]										
103 ± 93 (14–382)	12 ± 15 (0.3–98)	1.2 ± 1.5 (0.1–9.7)	193 ± 119 (6.0–516)	74 ± 50 (3.1–193)	138 ± 76 (53–471)	30 ± 54 (4.0–287)	1.2 ± 0.8 (<0.23–4.3)	22 ± 21 (3.3–149)	3.3 ± 1.4 (0.1–8.3)	8.1 ± 5.2 (0.7–27)
Lamarão do Passé, 2010[a]										
13 ± 2.9 (9.9–17)	1.8 ± 1.3 (0.2–3.4)	1.9 ± 3.0 (1.5–8.4)	97 ± 24 (79–114)	53 ± 7.0 (48–58)	84 ± 8.1 (79–90)	19 ± 13 (11–41)	3.5 ± 2.6 (<0.23–7.1)	25 ± 18 (7.0–48)	4.6 ± 1.5 (3.1–7.0)	4.5 ± 2.8 (1.5–8.4)
Camaçari, 2008[b]										
125 ± 58 (27–242)	14 ± 5.0 (6.7–25)	1.2 ± 0.7 (0.7–3.2)	150 ± 154 (3.2–465)	88 ± 98 (2.1–395)	154 ± 53 (52–278)	49 ± 56 (5.0–223)	2.2 ± 2.0 (<0.23–9.1)	20 ± 7.6 (5.3–40)	3.5 ± 1.7 (1.8–9.1)	5.9 ± 7.1 (1.3–30)
Camaçari, 2010[a]										
18 ± 4.6 (13–22)	2.2 ± 2.0 (0.2–4.3)	5.1 ± 5.5 (1.8–12)	203 ± 42 (170–250)	100 ± 5.1 (95–105)	210 ± 1.2 (366–368)	22 ± 11 (15–35)	3.6 ± 1.1 (2.9–5.0)	23 ± 2.8 (21–26)	4.6 ± 0.4 (4.1–4.9)	12 ± 1.6 (10–14)

Values in parenthesis = range.
[a] $n = 5$.
[b] $n = 28$.

(Cl^-, NO_3^-, SO_4^{2-}) corresponding to strong acids and ammonium salts were determined by suppressed ion chromatography. The analysis conditions were the following: anion separation column Dionex Ionpac AS 14 (250 × 4.0 mm), eluent $NaHCO_3$ 1.0 mmol L^{-1}/Na_2CO_3 3.5 mmol L^{-1}, flow 1.0 mL min^{-1} and ion suppresser Altech DS-PLUS. To determine the precision of the analysis (defined as relative standard deviation), each standard solution of chloride, nitrate and sulfate calibration curve was analyzed four times and an average of 98% was obtained for the precision. The accuracy was estimated as 4% from the analysis of artificial rain reference sample: RAIN-97, Environment Canada. The citric acid-diffusion was eluted too with 2 mL of deionized water. Ammonium was determined by molecular spectrophotometry (λ = 630 nm) using the indophenol method. Anions in atmospheric particulate matter sampled with the Berner impactor (Cl^-, NO_3^-, SO_4^{2-}) were also determined by ion chromatography and NH_4^+ by spectrophotometry under the same conditions described above.

After the period of exposure of the passive samplers, SO_2 and NO_2 were absorbed on the impregnated filter as sulfate or nitrite. Each filter of the passive samplers was transferred to a microtube for extraction of

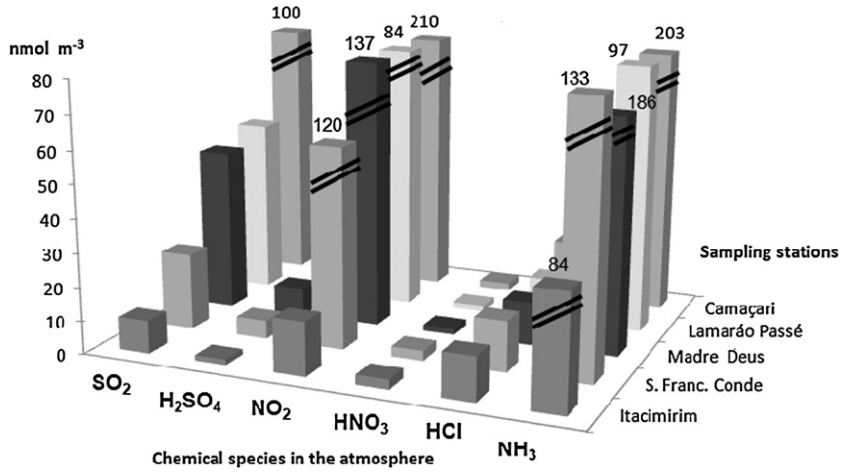

Fig. 3. Strong acids, precursors and ammonia in the atmosphere of Reconcavo, October 2010.

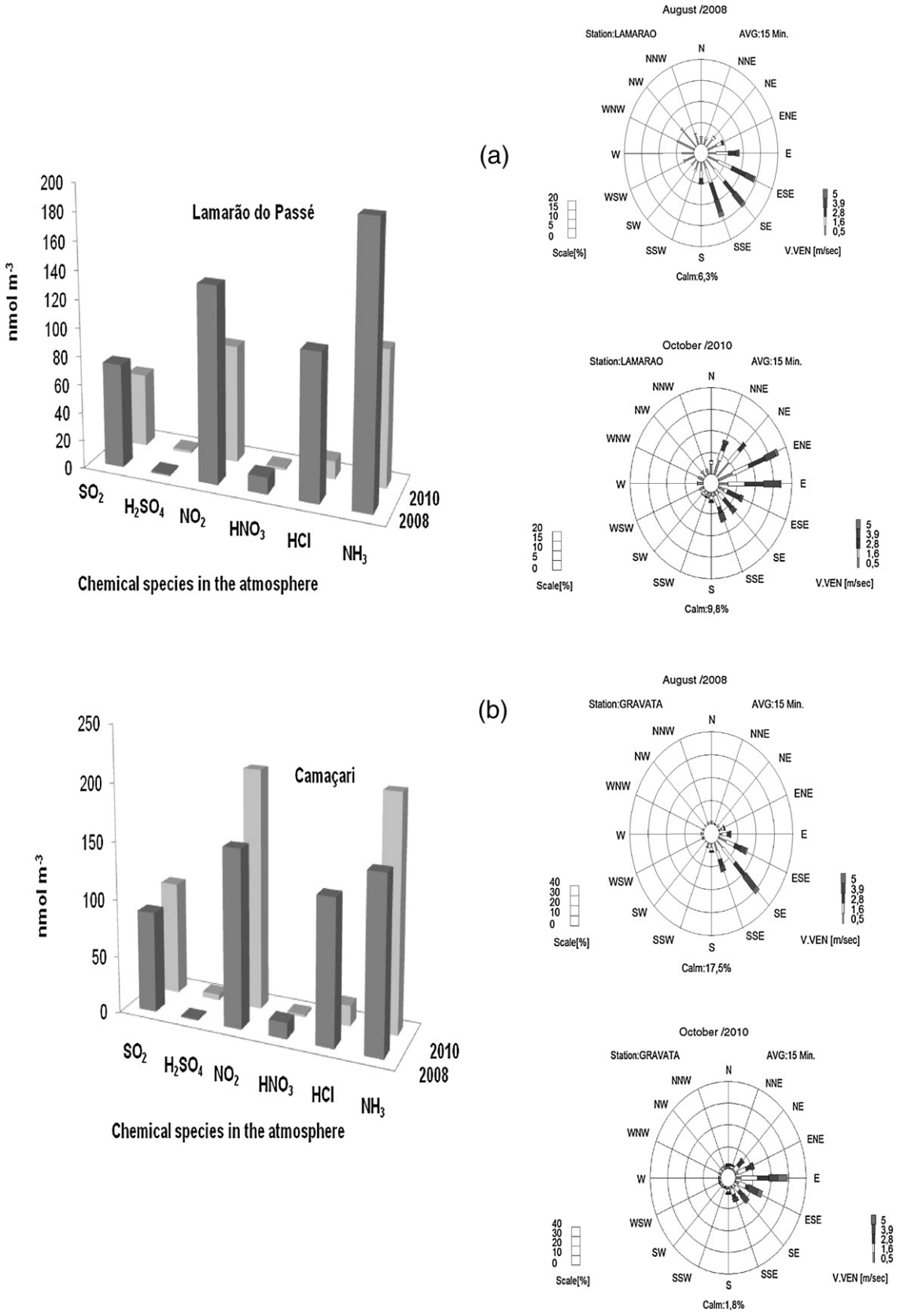

Fig. 4. Strong acids, precursors and ammonia simultaneously measured in the atmosphere of Reconcavo, in 2008 and 2010: (a) Lamarão do Passé; (b) Camaçari.

the anions. Sulfate was extracted with 1.5 mL of a 1.0×10^{-2} mol L^{-1} H_2O_2 solution to ensure complete oxidation to SO_4^{2-} [34] and determined by ion chromatography on the same above conditions for SO_2. Nitrite was extracted with 1.5 mL of deionized water in ultrasonic bath for 15 min and determined by molecular spectrophotometry ($\lambda = 540$ nm) using the modified Griess–Saltzman method for NO_2

[41]. Limits of detection for the measurements using passive samplers were 0.49 ng m^{-3} SO_2 (7.6 nmol m^{-3}) and 0.37 ng m^{-3} NO_2 (8.0 nmol m^{-3}); limits of quantification were 1.6 ng m^{-3} SO_2 (26 nmol m^{-3}) and 1.2 ng m^{-3} NO_2 (27 nmol m^{-3}).

3. Results and discussion

Table 1 shows the species concentrations in nmol m^{-3} (gases and particles) measured in the atmosphere of the Reconcavo of Bahia. Reported data are 24 h average for the species sampled with the thermodiffusion system (strong acids and ammonium salts) and with the continuous monitor (SO_2 and NO_2 in 2008). The results of measurements obtained with passive samplers (SO_2 and NO_2 in 2010) correspond to the average of the 5 days exposure period. In each case the number of samples is indicated in Table 1.

The concentrations of strong acids, their precursors and ammonia in all sites sampled are presented in Fig. 3. Air masses arriving at the coastline of the region from the Atlantic Ocean present the lowest concentrations for all compounds except HNO_3, most probably because NH_3 levels from the sea are lower than from terrestrial areas; thus its neutralization to NH_4NO_3 occurs to a lesser extent than in other sites.

Ammonia and NO_2, followed by SO_2, dominate over the other compounds. In spite of the high relative humidity (>70%), reaction of the two main nitrogen species to form particulate NH_4NO_3 is very limited, to the extent of 1–4%. Concentrations are higher in Camaçari (closest site to the Industrial Complex), followed by Madre de Deus and São Francisco do Conde (downwind from the refinary plume). The highest enrichment factors, expressed as the ratio of average concentrations of the different sites to the one of the background (Itacimirim), are found for NO_2: 13.1 in Camaçari, 8.5 and 7.5 for Madre de Deus and São Francisco do Conde, respectively.

Similar measurements taken in 2008 and 2010 for two sites, Camaçari and Lamarão do Passé, together with the wind rose, are shown in Fig. 4. A decrease varying between 18 and 49% is observed on the levels of almost all compounds in Lamarão, but not in Camaçari, where all other compounds presented an increased in their concentrations with the exception of HNO_3 and HCl. This is consistent with the reduction of industrial emissions [29] and with the large increase in vehicle emissions in Camaçari, where circulated in 2010, 30% more vehicles than in 2008.

In Fig. 5, the concentration of airborne particles <2 μm corresponding to strong acids neutralization products and to other reactions, it shows the predominance of NH_4Cl followed by other chlorides <2 μm, in agreement with the predominance of HCl and NH_3 in the two stations in both periods, shown in Fig. 4. Low concentrations of NH_4NO_3 observed in Fig. 5 are also in agreement with the low atmospheric concentrations of HNO_3 (Fig. 4). In both stations the behavior of SO_2 seems to tend more to the gas–particle reaction to formation of other sulfate <2 μm than to the formation of H_2SO_4 (Fig. 5 and Table 1).

In order to define the size distribution of Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ in the atmospheric particulate matter as gross and fine particles (Fig. 6), the first two and the last four stages of the cascade impactor were added, respectively. In all stations, the influence of marine aerosol can be observed through the high percentage of chloride particles >2 μm. In the other species, the predominance in the fine particles (<2 μm) is notorious, showing the characteristics of the anthropogenic influence in the atmosphere, as previously observed.

Fig. 7 presents simultaneous measurements of the N, S and Cl compounds in the atmosphere of Camaçari, which represents a typical industrial area in the Reconcavo Baiano. This figure was divided into parts, depending on the species that can react with each other and some products of its transformations. Fig. 7a shows great variation in the concentrations of NH_3 (3.2 to 465 nmol m^{-3}), often accompanied by NH_4NO_3. The HNO_3 concentration decreases with the increasing of the NH_3 concentrations, showing the consumption of the acid, combining with the production of NH_4NO_3 in the atmosphere. The NO_2 behavior compared to HNO_3 cannot be highlighted, since their levels remained almost constant throughout the study period. Fig. 7b shows the decrease of the SO_2 concentration associated with the increased H_2SO_4 concentration in some days. The concentration of other SO_4^{2-} <2 μm, products of reactions gas – particle and particle – particle (SO_2 – H_2SO_4 and H_2SO_4 – SO_4^{2-} <2 μm) show fluctuations between 1.3 and 30 nmol m^{-3}. Fig. 7c shows the behavior of NH_3, HCl and certain products of their transformations (NH_4Cl and other chlorides <2 μm) in those sampling station in the same period. Along with the fluctuations in the NH_3 concentrations, as already mentioned, this figure shows, on a smaller scale, fluctuations in the HCl concentrations. It is observed that higher concentrations of NH_3 are associated with higher concentrations of NH_4Cl. The other chlorides <2 μm, showed that their behavior does not seem to follow the fluctuations of the other species reported in this figure.

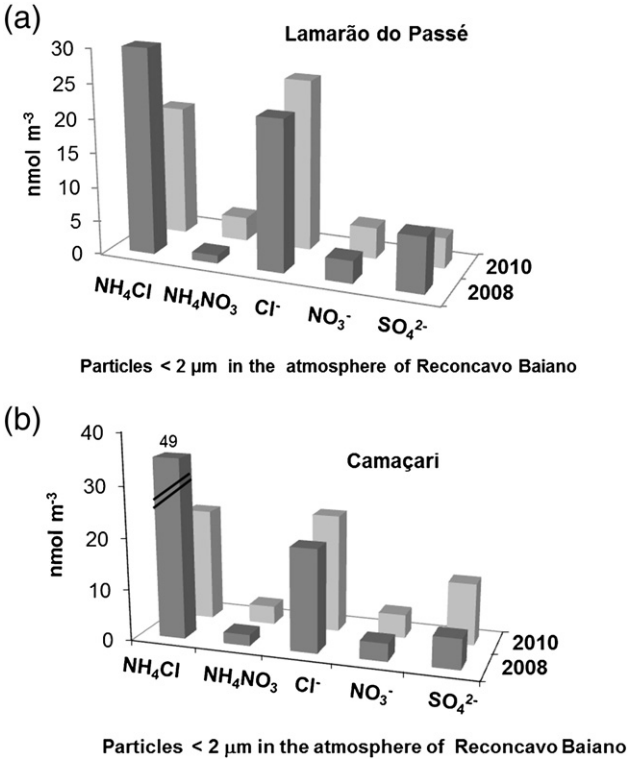

Fig. 5. Concentration of particles <2 μm, transformation products of strong acids and other atmospheric reactions in the Reconcavo in 2008 and 2010: (a) Lamarão do Passé; (b) Camaçari.

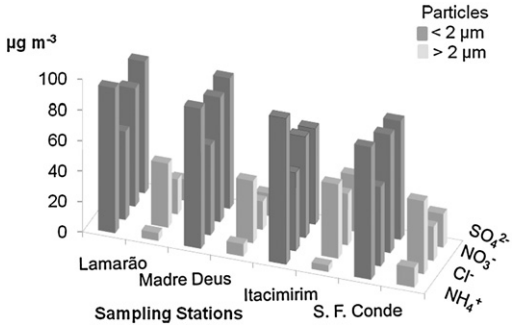

Fig. 6. Percentual distribution of Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ as fine and gross particles in the atmosphere of Reconcavo, in 2010.

Fig. 8 shows the distribution of the particulate matter <2 μm as N, S and Cl species sampled with the thermodiffusion system, differentiating thermally unstable species, sampled in the heated denuder (H_2SO_4, NH_4NO_3 and NH_4Cl) and stable species, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, $(NH_4)_2SO_4$, NaCl, $NaNO_3$ and Na_2SO_4, that are not fragmented at 140 °C and are retained on a back-up filter. This figure compares the behavior of this distribution in the two sampling periods in Camaçari, industrial and urban area with the control station (Itacimirim) in 2010.

In Fig. 8, it can be observed that the particulate matter <2 μm containing S species contributes little to the distribution of fine particles; between them the ammonium salts predominate in both areas, included in the parcel of "other SO_4^{2-}," when compared to H_2SO_4. The NH_4NO_3 also contributes little, as expected, because under the typical environmental conditions of the region (high temperature and relative humidity) this species does not remain in the solid state; in the aqueous phase they can volatilize more easily. In addition, low concentrations of HNO_3 in the studied atmosphere can explain the low production of NH_4NO_3, product of its reaction with NH_3. The NH_4Cl, partially sampled (65%) [31] in the thermodiffusion system (corrected to verify this distribution), represents the predominant specie, which is concomitant with the abundance of the reagents for their formation, HCl and NH_3, in the local atmosphere.

Analysis of hierarchical clustering was done to verify the similarities between the stations and the sampler species, according to Fig. 9, which represents the corresponding dendograms. In the samplers stations (Fig. 9a), four main groupings can be found: grouping 01—Camaçari/2010; grouping 02—Lamarão do Passé and Camaçari/2008; grouping 03—Lamarão do Passé, São Francisco do Conde and Madre

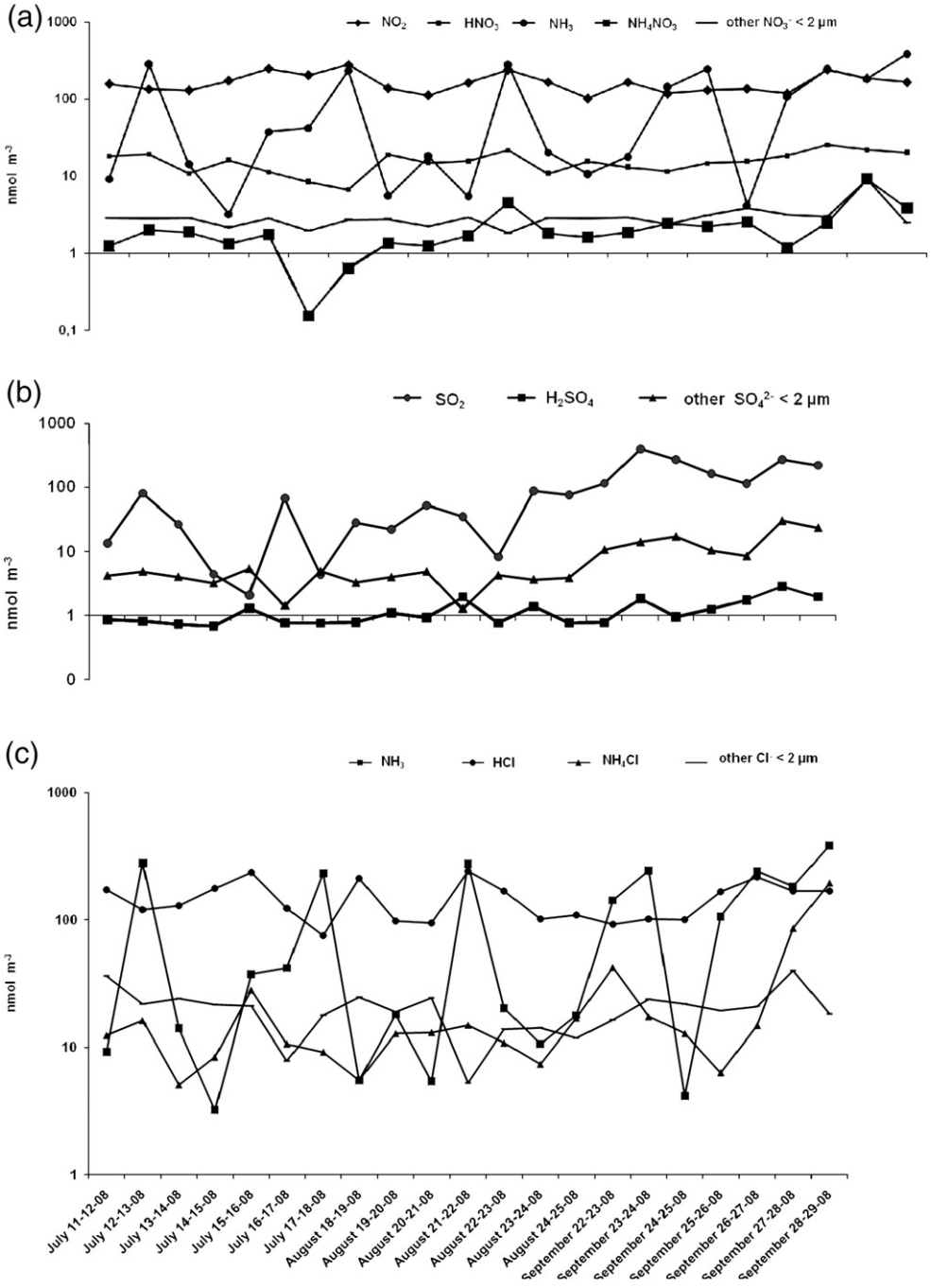

Fig. 7. Behavior of N, S and Cl compounds in the atmosphere of Camaçari, Reconcavo, monitored during 3 months in 2008.

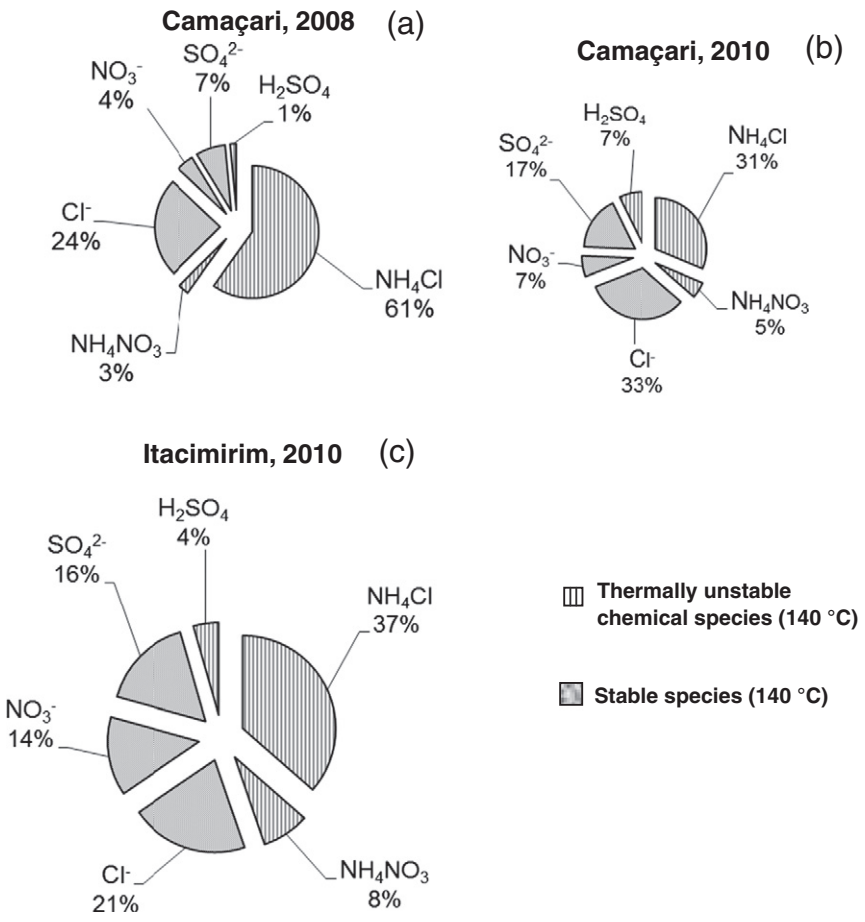

Fig. 8. Comparison of the distribution of N, S and Cl species in the particulate matter <2 μm: (a) Camaçari, 2008, (b) Camaçari, 2010, (c) Itacimirim, 2010.

de Deus/2010; grouping 04—Itacimirim/2010. The samplers of Lamarão and Camaçari/2008 showed the higher similarity on the dendogram, with a shorter Euclidian distance, followed by the samplers that came from the stations of São Francisco do Conde and Madre de Deus/2010. The highest Euclidian distance showed in the samplers of Itacimirim and Camaçari/2010 represents the low similarity between these stations: one control station, in the coast, without industrial activities and little contribution of the emissions of atmospheric pollutants, while Camaçari suffers high influence of the industrial complex as well as vehicle emission sources. In Fig. 9b, five main groupings between the species: in grouping 01, NO_2 and NH_3, relatively abundant in the region's atmosphere and precursor of HNO_3 and of many products of strong acid transformation, respectively; grouping 02 SO_2, which shows itself isolated probably due to it being primarily emitted in the atmosphere of this region by vehicle means; grouping 03, Cl^- <2 μm and NH_4Cl, both byproducts of atmospheric transformation involving HCl in gas and particulates; grouping 04, NO_3^- <2 μm, NH_4NO_3, SO_4^{2-} <2 μm, HNO_3 and H_2SO_4 products of the transformation of nitric acid (gas–particle interaction) and sulfuric acid (particulate–particulate interaction); grouping 05, HCl, which probably predominates in the region's atmosphere since it is predominantly a primary contaminant that comes from the incinerator emissions from industrial residues and other direct sources.

4. Conclusions

Clean air masses from the Atlantic penetrating into the Reconcavo area are enriched by NO_2, NH_3 and SO_2 emissions from the petrochemical complex and the oil refinery. Less than 5% of the NO_2 and NH_3 react forming neither HNO_3 nor NH_4NO_3. However, NO_2 seems to undergo gas to particle transformation by reaction with other compounds, forming other nitrates. Concentrations of SO_2 are lower than NO_2, and 50% or less undergo gas to particle transformation producing equally H_2SO_4 and other sulfates, except for Camaçari, where other sulfates – which include the ammonium salts – predominates.

Among the strong acids determined in the atmosphere of the industrial complex influence area, the hydrochloric acid predominates, as expected, due to their local emissions as primary pollutant. Its concentration range in 2008 presented higher values than those reported for other Brazilian industrial areas [25,42,43]. The decrease on its concentration reaching background levels can be explained by the absence of operation of the industrial liquid waste incinerator during the measures period and differences in winds directions between the two campaigns, as shown by the wind roses.

The simultaneous study of the atmospheric behavior of the species that can react with each other and some of its transformation products shows the following: the consumption of SO_2 is associated with the increasing of the atmospheric H_2SO_4 concentration; the NH_3 fluctuations are associated with the consumption of nitric acid and with increased production of NH_4NO_3; higher concentrations of NH_3 are accompanied by higher concentrations of NH_4Cl in the atmosphere that includes HCl as predominate strong acid.

In relation to the particulate phase <2 μm as products of transformation of strong acids in the atmosphere, NH_4Cl is the predominant species (31 to 60%), followed by other chlorides (21–33%), ammonium sulfate (7–17%) and other nitrates (4–14%), respectively.

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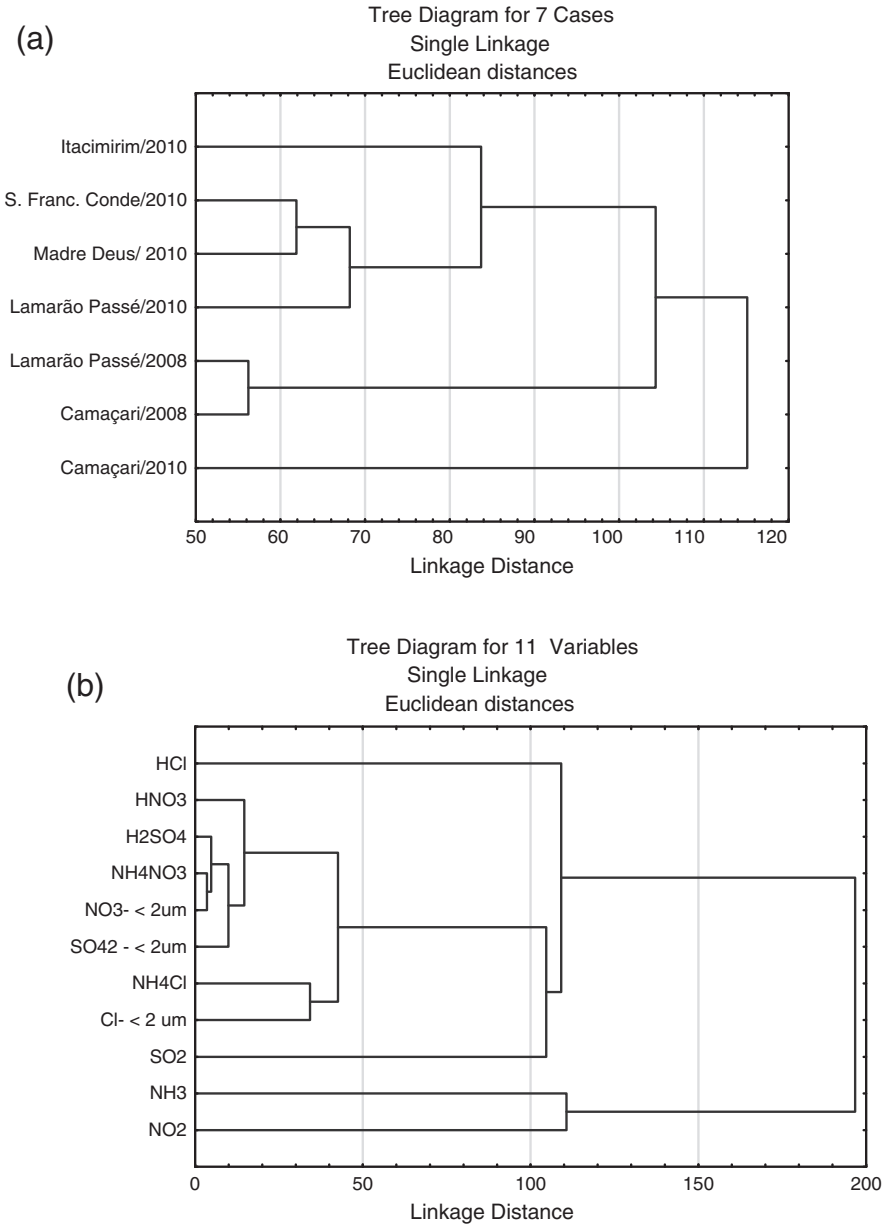

Fig. 9. Dendograms of similarity among: (a) sampling stations, (b) chemical species in the atmosphere. Reconcavo, Bahia, Brazil, 2008/2010.

the students to the Coordination for Graduated Human Resources (CAPES) of the Ministry of Education of Brazil.

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