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Atmospheric particle dry deposition of major ions to the South Atlantic coastal area observed at Baía de Todos os Santos, Brazil

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ABSTRACT

The coastal atmosphere adjacent to large urban areas can be strongly affected by the emission of air pollutants, among them, major ions species. In this study, the chemical composition and sources of carboxylates and other water-soluble ions in fine and coarse aerosols as well as estimates of particle dry deposition fluxes were studied at a tropical coastal site affected by an urban environment. The mean concentrations of the total carboxylates were 78 ng m⁻³ in fine fraction and 81 ng m⁻³ in coarse fraction of particulate matter (PM). The corresponding values for the total inorganic ions were 2143 ng m⁻³ and 4880 ng m⁻³ respectively. Main sources for fine particles were: (i) photochemical formation of carboxylic acids in vapor phase and a posterior gas-to-particle conversion onto sea salt particles; (ii) emissions from anthropic sources with long range transportation processes; and (iii) the interchanging of volatile species among atmospheric phases. In turn, for coarse particles, the predominant sources were: (i) gas-phase species and ab/adsorbed onto pre-existing particles afterwards; (ii) primary emission of coarse particles from anthropogenic sources; and (iii) sea salt spray and/or soil resuspension. Finally, particle dry deposition was a very important mechanism representing air-to-sea fluxes of major species.

Key words: particle dry deposition, PM, major ions, tropical atmosphere, Baía de Todos os Santos bay, Brazil.

INTRODUCTION

The coastal atmosphere adjacent to large urban areas can be strongly affected by the emission of air pollutants (Gao et al. 1996, He and Balasubramanian 2008, Fang et al. 2006). The major airborne pollutants include the ionic species such as SO₄²⁻, NO₃⁻, Na⁺, and NH₄⁺, among others,

associated with suspended aerosol particles (He and Balasubramanian 2008). Moreover, aerosols greatly vary in their size, chemical composition, and temporal variations (IPCC 2007, He and Balasubramanian 2008, Lee and Hieu 2013). The input of nutrient ions from atmosphere to the oceans has an important influence on their productivity and other associated processes (Koçak et al. 2004, Witt et al. 2010). Indeed, high concentration of

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such ionic species in particulate matter in the coastal atmosphere could not only enhance the air-to-sea deposition fluxes to coastal waters and affect the quality of the coastal ecosystem, but also deteriorate air quality and influence human health (He and Balasubramanian 2008).

Particulate matter (PM) with aerodynamic diameter less than $2.5\ \mu\text{m}$ (PM_{2.5}) exhibits stronger relation with health than those with aerodynamic diameters less than $10\ \mu\text{m}$ (PM₁₀), although some other studies have reported a strong potential of PM₁₀ to human health (Salma et al. 2002, Kappos et al. 2004, Verma et al. 2010, Kumar et al. 2010). Organic acids and water-soluble inorganic ions are important groups of compounds identified in the atmospheric aerosol (Jacobson et al. 2000, Bourotte et al. 2007). More attention has been paid to carboxylates due to their potential to modify the hygroscopic properties of atmospheric particles, including cloud condensation nuclei activity (CCN) and hence to change global radiation balance (Kerminen 2001, Peng et al. 2001). Major water-soluble inorganic ions are associated with atmospheric visibility degradation, adverse human health effects, and acidity of precipitation (Dockery and Pope 1996, IPCC 2007, Lee and Hieu 2013, Zhang et al. 2011). Carboxylates and water-soluble ions in variable concentrations have been reported in urban, rural and marine atmosphere (Kawamura and Sakaguchi 1999, Kerminen et al. 2000, Nicolas et al. 2009). Some sources origins are fossil fuel combustion (Narukawa et al. 1999), sea spray, traffic and industrial emissions and photochemical oxidation of precursors from anthropogenic and biogenic origins (Kawamura and Sakaguchi 1999, Limbeck and Puxbaum 1999, Chakraborty and Gupta 2010). Other sources for the carboxylic acids in marine atmosphere include in-cloud and heterogeneous formations (Warneck 2003).

The chemical composition of fine (PM_{2.5}) and even that of coarse (PM₁₀) aerosols are important to gain insight into sources, about their toxicity, and to evaluate the effectiveness of abatement strategies

for relevant emission sectors. In different parts of the world carboxylic acids and ionic concentrations in the PM_{2.5} and PM₁₀ aerosols have been studied (Limbeck et al. 2001, Limon-Sanchez et al. 2002, Kawamura and Yasui 2005, Karthikeyan and Balasubramanian 2006, Mkoma et al. 2009). However, studies on the South Atlantic region or in Brazil are scarce (Kubátová et al. 2000, Allen et al. 2004, da Rocha et al. 2005, Bourotte et al. 2007, Mariani and de Mello 2007, Kundu et al. 2010). Nevertheless, studies about major ions in tropical atmosphere are few and some lack of knowledge still remains. In this study, the main objective was to provide an insight into the levels and source profiles of carboxylate and water-soluble inorganic ions in PM_{2.5} and PM₁₀ size fractions in South Atlantic by observing them in the Baía dos Todos Santos bay, Brazil.

EXPERIMENTAL

SAMPLING SITE AND AEROSOL COLLECTION

Baía de Todos os Santos Bay (BTS), Northeastern Brazil, is the second largest Brazilian bay ($1233\ \text{km}^2$). A large urban area (about 3 million inhabitants), and an important industrial complex (petrochemical, chemical, textile, fertilizers, paper mill, etc.) are located in the BTS basin. The sampling site considered in this study is located in the Baía de Todos os Santos bay (Fig. 1). An intensive sampling campaign was carried out at a coastal site in Base Naval de Aratu (BNA) ($12^\circ 48' 19.0''\text{S}$; $38^\circ 29' 54.2''\text{W}$, at sea level) from the 13th to 27th of September 2010. Possible aerosol sources include harbour activities, industries and marine and urban pollution. Aerosol samples were collected using two high volume samplers (Energética, Brazil, flow rate $1.13\ \text{m}^3\ \text{min}^{-1}$) equipped with PM_{2.5} and PM₁₀ inlets (Thermo Andersen, USA) in order to sample particles smaller than $2.5\ \mu\text{m}$ (fine particles) and smaller than $10\ \mu\text{m}$ (coarse particles), respectively. Sample collection was done under flow rate $1.13\ \text{m}^3\ \text{min}^{-1}$,

with Whatman quartz fiber filters (20.3 cm x 25.4 cm; Whatman Inc., Maidstone, UK) which were pre-baked at 550 °C in a furnace to eliminate any adsorbed organics before use. The sampling was carried out approximately in 24 h intervals and exchange of filters during the sampling periods was done at 7:00 AM. A total of 15 sets of samples were

collected for each sampler and used in this study. After sampling, the actual samples were folded face to face, placed in polyethylene plastic bags, and kept frozen at -4 °C during storage then transported cool to the laboratory for analysis. All the procedures were strictly quality-controlled in order to avoid any possible contamination of the samples.



Fig. 1 - Map of Baía de Todos os Santos bay, showing the sampling site (BNA) of this study.

The meteorological data, including ambient temperature (22.5-24.9°C), relative humidity (72-84%), solar radiation (145-340 W m⁻²), and wind speed (3.9-8.0 m s⁻¹) for the sampling days are shown in Fig. 2a. Backward air mass trajectories were calculated during the whole sampling events by using the NOAA HYSPLIT database (2011 <http://ready.arl.noaa.gov/HYSPLIT.php>). A one-dimensional trajectory was calculated starting 96 h before the arrival time (00:00 UTC) and 500 m a.g.l. (Fig. 2b). During all sampling times, air trajectories were of typically oceanic contribution.

CHEMICAL ANALYSIS

For particulate mass measurements, the filter samples were weighed before and after sampling

with an analytical microbalance Mettler Toledo MX5 (reading precision at 1 µg). Before weighing, the filters were conditioned in a chamber equipped with hydro-thermometer clock at a temperature of 20 °C and the relative humidity of 40% for 48 h and the weightings were done under these conditions.

For determination of the carboxylate and inorganic ions one-half of 28.29 cm² portions punched from each quartz fiber filter was extracted using 5 mL Milli-Q ultrapure water (resistivity of 18.2 MΩ cm, Barnstead International, USA) in a shaker tube Model AT56 (Fanem Ltd, São Paulo, Brazil) for 5 minutes, followed by filtering through syringe type PTFE filters (0.45 µm pore size, 15 mm diameter, Sartorius, Germany). Filter extract samples were analysed for carboxylate and water-soluble ions using a Dionex Ion

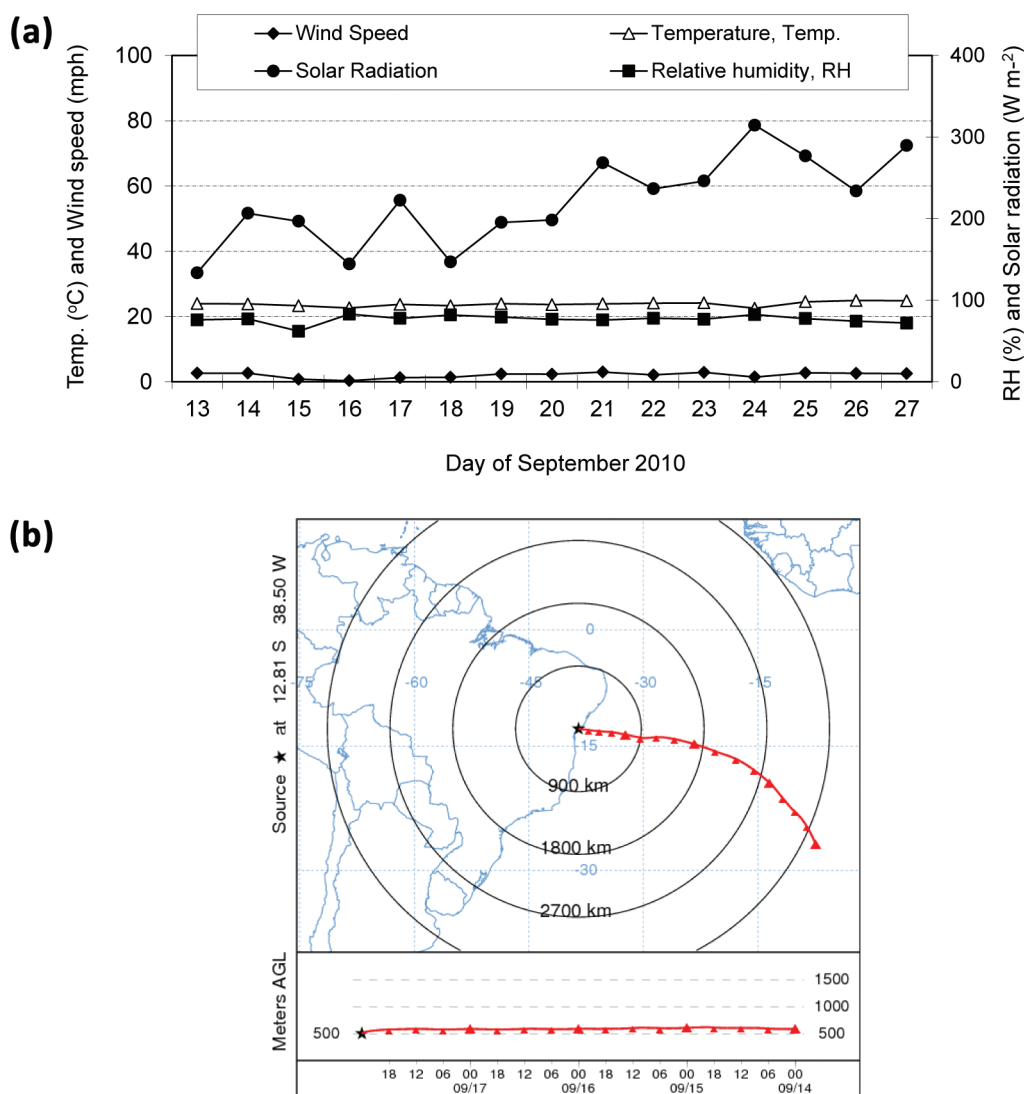


Fig. 2 - Time trends of meteorological parameters **(a)** and backward trajectory **(b)** during sampling period at BNA.

Chromatograph (modules model ICS 1100 for cations and ICS 2100 for anions) with conductivity detector and 100 μL sampling loop. Chromatographic methods for determination of both cationic and anionic species followed a modified procedure reported by Mkoma et al. (2014). Briefly, carboxylate and water-soluble anions were determined by using AS11-HC analytical column (2 x 250 mm, Dionex, USA), an AS11-HC guard column (2 x 50 mm, Dionex, USA) and anion self-regenerating suppressor (ASRS-300, 2 mm membrane thickness, Dionex, USA) in electrolytic mode. The eluent gradient program was gradually

increasing from 0.6 to 8.0 mmol L^{-1} KOH over 35 minutes. The anionic analysis was operated under a flow rate of 0.38 mL min^{-1} and with a suppressor current of 36 mA. In turn, the determination of water-soluble cations was performed utilizing a CS16 analytical column (3 x 250 mm, Dionex, USA) with a CG16 Guard column (3 x 50 mm, Dionex, USA) and a cation self-regenerating suppressor (CSRS-300, 2 mm membrane thickness, Dionex, USA) in electrolytic mode. An eluent of 17.5 mmol L^{-1} H_2SO_4 in isocratic mode at a flow rate of 0.35 mL min^{-1} and with a suppressor current of 43 mA were used.

The injection volume during all analyses was 25 μL . Peak identification was confirmed based on a match of IC retention times and standard samples. The limit of detection (LOD) corresponded to a range of 0.38 to 0.81 pg m^{-3} for carboxylates, 0.38 to 1.1 pg m^{-3} for water-soluble anions and 1.0 to 4.0 pg m^{-3} for cations. Precision was better than 5% for all species in this study.

STATISTICAL ANALYSES

Experimental data were analyzed by calculating the Spearman's correlation coefficients using STATISTICA 6.0 (Statsoft, USA) program. In addition, Principal Component Analysis (PCA) and Cluster Analysis (CA), using Ward's Method and Euclidian distances, were performed. The calculations were performed using the individual experimental values for each sample.

RESULTS AND DISCUSSION

PM MASS CONCENTRATIONS

Table I shows the mean PM mass concentrations, associated standard deviations and ranges as derived from the high volume samplers. The mean concentrations of PM_{2.5} and PM₁₀ masses were 13.9 $\mu\text{g m}^{-3}$ and 24.8 $\mu\text{g m}^{-3}$, respectively, with a PM_{2.5}/PM₁₀ mean mass ratio and standard deviation of 0.6 ± 0.2 . Currently in Brazil, the daily and annual average standard limit values for inhalable particulate matter are 150 and 50 $\mu\text{g m}^{-3}$ respectively (CONAMA 1990). The mean for the PM_{2.5} and PM₁₀ mass concentrations at Base Naval de Aratu in Salvador were below these average limit values. However our data were in line with the levels reported in other cities in Brazil (Bourotte et al. 2007, Mariani and Mello, 2007). Compared with the United States Environmental Protection Agency (US EPA) the average daily limit value in ambient air of 65 $\mu\text{g m}^{-3}$ for PM_{2.5} and 150 $\mu\text{g m}^{-3}$ for PM₁₀ (US EPA 1997), almost 21% of the PM_{2.5} and 17% of the PM₁₀ mass concentrations from this study

were lower than the standards, showing that particulate pollution, was not a problem during our sampling campaign in the study area.

CONCENTRATIONS OF CARBOXYLATE AND INORGANIC IONS

The mean and associated standard deviations, minimum and maximum concentrations of the carboxylate and inorganic ions are presented in Table I.

The total concentrations of the carboxylates ranged from 57 to 121 ng m^{-3} with a mean of 78 ng m^{-3} in PM_{2.5} size fraction, and from 60 to 122 ng m^{-3} with a mean of 81 ng m^{-3} in PM₁₀ fraction. Acetate was the most abundant species with mean concentrations of 31 ng m^{-3} in the PM_{2.5} and 34 ng m^{-3} in the PM₁₀ aerosols ranging from 26 to 46 ng m^{-3} . Its relative abundance in the total measured carboxylate ions in PM_{2.5} and PM₁₀ fractions was 40% and 17% respectively. The second most abundant carboxylate ion, on a mean, was oxalate which accounts for nearly 28% and 13% of the total carboxylates concentrations in the PM_{2.5} and PM₁₀ aerosols. The malonate, formate, and pyruvate were also found in substantial amount but succinate was the least abundant accounting for about 1-2% of the total carboxylates in the two size fractions. It should be noted that among the analysed dicarboxylates, oxalate was the most abundant as reported in other studies (Mochida et al. 2003, Warneck 2003). However, acetate, oxalate and malonate together contributed 80% to the total carboxylates PM_{2.5} and PM₁₀ masses while the total carboxylates accounted for 0.56% and 0.33% to the total PM_{2.5} and PM₁₀ mass, respectively. In comparison to some other studies, the mean concentrations of the measured carboxylate ions were lower to those reported in costal urban atmosphere and marine sites. For instance, Kawamura and Yassui (2005) have studied atmosphere of Tokyo and have found the following levels at 233, 52 and 53.9 ng m^{-3} , for oxalate, malonate and succinate, respectively. Khare et al. (1995) have studied atmosphere of India and found 240 and 440 ng m^{-3} for formate

TABLE I
Mean concentrations and associated standard deviation, ranges
(ng m⁻³) and relative abundances (%) of carboxylate and inorganic
ions in PM2.5 and PM10 aerosols from BNA in Salvador.

Species	PM2.5					PM10				
	Mean	SD	Min.	Max.	Rel. Ab.	Mean	SD	Min.	Max.	Rel. Ab.
PM mass (μg m ⁻³)	13.9	2.7	8.5	17.2	-	24.8	5.9	17.8	39.7	-
<i>Carboxylate ions</i>										
Formate	7.9	2.3	5.4	14	9.9	9.1	2.8	6.1	15	4.3
Acetate	31	2.8	26	35	40	34	5.0	27	46	17
Oxalate	23	8.6	12	42	28	28	8.7	17	45	13
Malonate	12	4.0	8.6	20	15	11	1.6	9.2	12	4.8
Succinate	1.9	2.1	0.3	5.9	2.0	1.9	1.5	0.2	3.5	0.90
Pyruvate	6.7	1.3	4.4	9.5	8.5	7.0	1.9	3.4	12	3.4
<i>Σcarboxylates</i>	<i>78</i>	<i>18</i>	<i>57</i>	<i>121</i>		<i>81</i>	<i>18</i>	<i>60</i>	<i>122</i>	
<i>inorganic ions</i>										
NH ₄ ⁺	30	8.5	18	54	1.4	51	10	35	72	1.1
NO ₃ ⁻	112	37	62	184	5.2	175	64	102	303	3.7
SO ₄ ²⁻	350	148	206	730	16	561	137	368	882	12
Cl ⁻	143	42	82	225	6.9	511	146	341	842	10
Na ⁺	899	179	683	1192	42	2431	551	1649	3603	49
K ⁺	180	43	126	264	8.4	571	122	387	763	12
Mg ²⁺	315	69	253	472	15	274	67	202	413	5.6
Ca ²⁺	113	18	82	150	5.3	311	69	214	454	6.6
<i>Σinorganic ions</i>	<i>2143</i>	<i>295</i>	<i>1604</i>	<i>2535</i>		<i>4880</i>	<i>841</i>	<i>3621</i>	<i>6699</i>	

and acetate, respectively. Da Rocha et al. (2012) in a study of atmosphere of the São Paulo city found 70.4; 10.3; 150, and 33.6 ng m⁻³ for formate, acetate, oxalate and succinate, respectively.

At BNA in Salvador, among possible sources, photochemical reactions during the daytime appeared to be an important source of formate, as found in literature (Allen et al. 2004, da Rocha et al. 2003, 2005), whereas acetate appeared to be mainly from primary sources such as industrial and vehicular emissions. It is noteworthy to mention that Brazilian gasoline possesses around 22-26% of hydrated ethanol and it is often called “gasohol”. Moreover, one such particularity of light-duty vehicles in Brazil (56 % of vehicular fleet) is “flexfuel” which run regularly with any proportion of hydrated ethanol-to-gasohol (DENATRAN 2013). Those specific details would explain the higher levels of acetate found in this study.

The concentrations of the individual inorganic ions in both size fractions were in the order of SO₄²⁻ > Cl⁻ > NO₃⁻ for the anions while for the cations Na⁺ was the most abundant and NH₄⁺ the least abundant cationic species. On an average SO₄²⁻ and Cl⁻ accounted for 16% and 6.7%, respectively, of the total water-soluble ions in PM2.5 mass and 11% and 10%, respectively, of the PM10 mass. Other ions were in the order of Na⁺ > Mg²⁺ > K⁺ > Ca²⁺ in the PM2.5 fraction and Na⁺ > K⁺ > Ca²⁺ > Mg²⁺ in the PM10 fraction. The NH₄⁺ was the minor contributor (1.0 – 1.4%) to the total ions in both size fractions. As for the higher concentrations of Na⁺ and Cl⁻ at BNA, it is presumably mainly derived from sea salt, as the sampling site was about less than 1 km from the southern Atlantic Ocean and all backward air mass trajectories during this sampling campaign were essentially oceanic. For SO₄²⁻ the higher levels could be attributed to secondary formation

processes (such as gas-to-particle conversion) (Allen et al. 2004, Campos et al. 2007). The sea salt ratios were calculated for each inorganic ion using Na^+ as a reference species, assuming all Na^+ to be of marine origin. The ratios for $\text{SO}_4^{2-}/\text{Na}^+$, Cl^-/Na^+ , K^+/Na^+ , $\text{Mg}^{2+}/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$ in $\text{PM}_{2.5}$ were 0.42 (0.25), 0.17 (1.81), 0.20 (0.04), 0.35 (0.04), 0.13 (0.12) respectively. The corresponding values in PM_{10} aerosols were 0.24 (0.25), 0.22 (1.81), 0.24 (0.04), 0.11 (0.04), 0.13 (0.12) respectively. The values in the parentheses represent the average ratios for each ion in seawater (Brewer 1975). Larger ratios of ions indicate the incorporation of non-marine constituents in aerosols. The small ratio of Cl^-/Na^+ could be due to modifications caused by non-marine constituents. In fact, the small ratio of Cl^-/Na^+ could be caused by the modifications suffered by sea salt aerosol by incorporation non-marine sources. The chloride loss may be explained by the heterogeneous reaction of airborne sea salt with acidic gases and aerosol species (Millero 2006, Allen et al. 2004). High K^+/Na^+ and $\text{Mg}^{2+}/\text{Na}^+$ ratios also show a non-marine source. This source could be either anthropic such as industrial (maybe a fertilizer plant present in BTS basin) or dust resuspension. But if dust resuspension were this source, the $\text{Ca}^{2+}/\text{Na}^+$ ratio would also be

higher than seawater ratio and it is not. Therefore, it seems dust resuspension is a negligible source and the additional non-marine source for K^+ and Mg^{2+} seems to be industrial and Na^+ and Ca^{2+} are originated from sea salt spray.

Considering that besides sea salt spray, there are no other important sources for Na^+ in the site under study, we tentatively suggest that the lower Cl^-/Na^+ mean ratios than the sea-water ratio indicate that a minor fraction of Na^+ may be contributed from mineral dust resuspension.

FINE TO PM_{10} RATIOS AND TIME SERIES FOR SELECTED SPECIES

The average fine ($\text{PM}_{2.5}$) to PM_{10} percentage ratios and associated standard deviations for the PM mass, carboxylate and water-soluble ions are shown in Fig. 3. The ratios were calculated on the basis of the data for the $\text{PM}_{2.5}$ and PM_{10} samples taken in parallel and then averaged over all samples from the campaign. The mean fine to PM_{10} ratios for all species with the exception of those for succinate, Na^+ , K^+ , Ca^{2+} and Cl^- were predominantly associated with the fine size fraction (for more than 50%). For most carboxylate ions, the higher ratios (even larger than 80%) are considered to be attributed from secondary organic aerosols (SOA), vehicular and

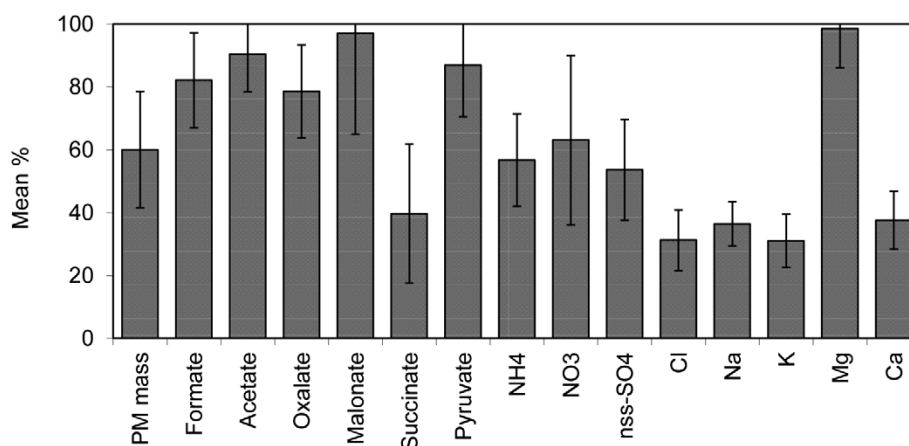


Fig. 3 - Mean fine ($\text{PM}_{2.5}$) to PM_{10} percentage ratio and associated standard deviation for the PM mass, carboxylate and water-soluble ions from BNA.

industrial emissions. The different size distributions between formate and/or acetate and oxalate could be related to their different physical characteristics. Formate and acetate in the PM_{2.5} fraction could easily volatilize (more volatile than oxalate) to the gas phase, part of which could be absorbed on the PM₁₀ particles. The higher mean temperature (24 °C) during sampling period at BNA might be the main reason for the found PM_{2.5} to PM₁₀ ratios for the carboxylate ions.

For the water-soluble inorganic ions, as expected, the sea salt species (Na^+ , Cl^-) and the indicator species for crustal matter (Ca^{2+}) were predominantly (for more than 62%) associated with the PM₁₀ size fraction. Ammonium, NO_3^- , and SO_4^{2-} were mainly present in the fine size fraction suggesting that these species originated from anthropogenic high temperature sources and/or gas-to-particle conversion. About half of the PM₁₀ SO_4^{2-} and most of the fine SO_4^{2-} were non-sea salt (nss) SO_4^{2-} . The nss- SO_4^{2-} is probably due to oxidation of SO_2 , which is predominantly from anthropogenic origin (e.g. burning of S-containing fossil fuels and non-ferrous smelters). Potassium was associated with the PM₁₀ particles (about 70%) suggesting vegetative emissions and crustal source.

TIME SERIES OF THE PM MASS AND SELECTED AEROSOL SPECIES

The time series of the PM mass, selected carboxylate and inorganic ions in PM_{2.5} and PM₁₀ size fractions as a function of sampling time is shown in Figs. 4a and 4b. In these figures the oxalate in both size fractions, nss- SO_4^{2-} in the PM_{2.5} and Na^+ in the PM₁₀ aerosols showed a pronounced variation during the campaign. Other species showed slight variations during sampling period while that of formate and pyruvate in both size fractions and Cl^- in the PM₁₀ aerosols, there was no clear variation that could be noted. The observed behaviour of the species during sampling period could be a result from the variations in sources strengths and in

meteorological conditions, such as mixing height and relative humidity (RH). Additionally, the high RH (mean: 76%) during the campaign could serve as a removal mechanism hence lead to a daily variation in carboxylate (and also inorganic) ion levels.

In this study, the concentrations of oxalate were higher to a factor of 3 than that of formate during the sampling period. On the other hand, the concentrations of acetate were higher than those of formate and oxalate. The ratio of oxalate to total dicarboxylates can be used to evaluate the aging process of organic aerosols (Kawamura and Sakaguchi 1999). In this study, the oxalate/total dicarboxylates ratio did not vary significantly during the sampling period (range 0.48–0.98), indicating that the aerosols emitted from various sources and transported to this site were equally aged. Since there was RH quite high during the whole period of the campaign, it is assumed that oxalate was also produced in aqueous phase during the aging process. Aqueous phase chemistry in aerosol and/or cloud droplets is important in the production of oxalate (Warneck 2003).

ION BALANCE

Ion balance for both size fractions of PM from BNA was done (Table II). Results of Σ anions/cations for PM_{2.5} and PM₁₀ were well below one unity. This indicates that there is a quite reasonable anion deficiency in PM, thus suggesting that positive charges from cations are not totally neutralized by negative charges from anions. This can happen for some reasons: it may represent the contributions from other weak acidic species such as CO_3^{2-} and/or HCO_3^- (not measured in this study) and/or this apparent anion deficiency. The anion deficiency can indicate that the PM from BNA is, in fact, basic. Since we did not find high enough NH_4^+ atmospheric levels in order to play an important role of the neutralizing the atmospheric gas phase, it seems quite reasonable to suggest that sea spray and,

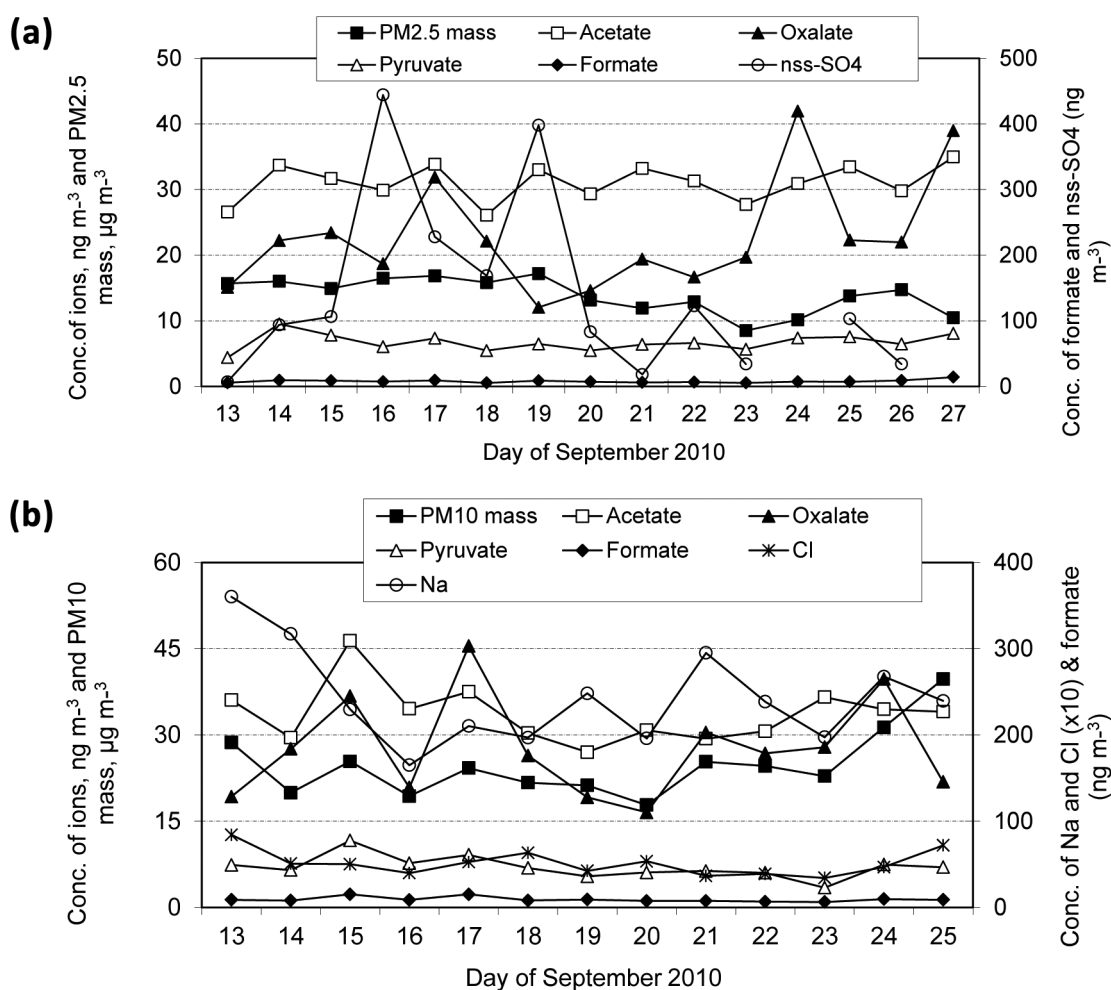


Fig. 4 - Time series of the PM mass, acids and nss-SO_4^{2-} in the PM2.5 size fractions (a) and in the PM10 size fractions (b) at BNA.

in a lesser extension, soil dust resuspension, can probably act as neutralization agents of acidic gas phase of the atmosphere. In fact, evidences of it are found in previous studies in a nearby area of BTS by Campos et al. (2007). In these studies it was shown that sea spray salts present in the basic aerosol were responsible for up to 81 % of rainwater samples neutralization and that acid gaseous species emitted from anthropic sources were condensed onto sea spray aerosol. These explanations are in good agreement with our findings in the present study. This may be a good explanation for the excess of positive charges (and consequently the amount of anion

deficiency) found by $\Sigma \text{anions} / \Sigma \text{cations} < 1$ from the present study.

DIAGNOSTIC RATIOS AND PEARSON'S CORRELATION

The correlation coefficients of PM mass, carboxylates and source indicators shown in Table III were performed in order to understand their possible sources and formation mechanisms. The selected source indicators include K^+ for vegetation emissions, Na^+ and Cl^- for sea spray, and SO_4^{2-} for anthropic emission and/or secondary formation (gas-to-particle conversion from gaseous SO_2). Solar radiation and wind speed have been used as additional parameters to illustrate the atmospheric behaviours of carboxylate ions.

TABLE II
Ion balance (units in neq m^{-3}) of samples from BNA.

Species	PM2.5		PM10	
	mean	SD	mean	SD
acetate	0.5	0.05	0.6	0.08
formate	0.2	0.05	0.2	0.06
oxalate	0.5	0.2	0.6	0.20
malonate	0.2	0.1	0.05	0.09
succinate	0.02	0.03	0.02	0.02
pyruvate	0.08	0.01	0.08	0.02
NO_3^-	1.8	0.6	2.8	1.0
SO_4^{2-}	7.3	3.1	12	2.9
Cl^-	4.0	1.2	14	4.1
NH_4^+	1.7	0.5	2.6	1.0
Na^+	39	7.8	106	24
K^+	4.6	1.1	15	3.1
Mg^{2+}	26	5.8	23	5.6
Ca^{2+}	5.7	0.9	16	3.4
Σanions	15	5.3	30	8.5
$\Sigma \text{cations}$	77	16	161	37
$\Sigma \text{anions} / \Sigma \text{cations}$	0.19	0.33	0.19	0.23
Anions deficiency	63	11	131	29

It can be observed from Table III that there were possible similar sources for formate and other carboxylate ions as verified by a good correlation between them in the PM2.5 ($0.51 < r < 0.80$) and PM10 ($0.50 < r < 0.87$) aerosols. Succinate is poorly correlated with oxalate ($r = 0.08$) but most closely correlated with malonate ($r = 0.85$) in the PM2.5 aerosols. The former correlation indicates that the oxidation of unsaturated fatty acids, which usually occurs in marine atmospheres (Kawamura and Sakaguchi 1999) is not a likely source for succinate, but it seems to be an important source for both formate and oxalate at this site, while the latter is a feature of the photochemically induced decomposition of succinate into malonate (Yao et al. 2002). Nitrate is well correlated to succinate ($r = 0.70$) in PM2.5 but not correlated ($r = -0.70$) in PM10. This probably evidences photochemical reactions being also important for NO_3^- in PM2.5 but the opposite happens for this species in PM10. Good correlation was also observed between NO_3^- and SO_4^{2-} ($r = 0.68$) for PM10 and ($r = 0.84$) for

PM2.5 that probably shows that vehicular and/or industrial emissions were important sources for those species.

In the PM2.5 aerosols, Na^+ is correlated with malonate and pyruvate and in both size fractions with K^+ . Sea salt is a known source of Na^+ and even Cl^- in urban atmosphere (Hsieh et al. 2007). Kerminen et al. (2000) showed that most of the sea salt derived aerosols have particle diameter between 1 and 5 μm . In this study, Na^+ was found in a pronounced amount in the PM2.5 and PM10 size fractions and to a slightly extent for Cl^- , suggesting sea spray could be one of the contributing sources of the aerosol components at the site.

Sulfate has been used as reference to investigate the major formation routes of carboxylate ions (Yu et al. 2005). As shown in Table III, acetate and pyruvate showed slight good correlation with SO_4^{2-} in PM10 aerosols, suggesting that vehicular emission can probably play an important role in the formation of acids at BNA in Salvador. On the other hand, the poor correlation of malonate with SO_4^{2-} ($r = 0.28$) suggests that malonate was possibly emitted by another source (Peng et al. 2001). Formate and oxalate showed poor correlations with SO_4^{2-} in both size fractions, indicating that they were mainly originated from primary emissions sources and/or atmospheric processes different from those of SO_4^{2-} . Poor correlation between NH_4^+ and SO_4^{2-} indicates they were emitted from different sources and also, due to the found low levels of NH_4^+ , the reaction between their vapour precursors leading to nucleation of new particles was not a relevant process. Moderate to high correlations among Ca^{2+} and formate, acetate, and oxalate ($0.53 < r < 0.70$) for both particle fractions and for malonate ($r = 0.98$) in PM10 as well as Mg^{2+} and oxalate ($r=0.73$) indicates either they have similar sources (being emitted as magnesium and/or calcium salts) or those carboxylic acids were emitted in vapour phase and then condensed onto Ca^{2+} and Mg^{2+} rich particles, such as sea salt particles. Nitrate is well

TABLE III
Correlation coefficients for PM mass, acids, selected ions and meteorological parameters in the PM_{2.5} (upper diagonal triangle) and in the PM₁₀ size fractions (lower diagonal triangle) at BNA, Salvador. Correlation coefficients larger than 0.50 are indicated in bold.

	PM mass	formate	acetate	oxalate	malonate	succinate	pyruvate	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Solar Rad	WS
PM mass																	
formate			0.01	-0.40	-0.09	-0.07	-0.01	-0.43	0.57	0.65	0.37	-0.21	-0.17	-0.47	0.02	-0.71	-0.37
acetate	0.12		0.69	0.53	0.67	0.64	0.65	0.41	0.34	0.08	-0.23	0.43	0.59	0.46	0.53	0.33	-0.02
oxalate	0.25	0.70		0.37	0.68	0.53	0.80	0.07	0.28	0.16	-0.17	0.41	0.42	0.34	0.53	0.57	0.11
malonate	0.17	0.66	0.48		0.20	0.08	0.51	0.52	-0.24	-0.30	0.05	0.45	0.71	0.73	0.57	0.62	-0.23
succinate	0.53	0.76	0.74	0.83		0.85	0.68	0.60	0.38	0.20	-0.36	0.40	0.43	0.04	0.43	0.24	0.32
pyruvate	-0.36	-0.22	-0.57	-0.05	-1.00		0.68	0.42	0.70	-0.15	-0.41	0.35	0.20	0.07	0.01	0.08	0.47
NH ₄ ⁺	0.18	0.87	0.69	0.50	0.72	-0.44		0.17	0.28	0.04	-0.16	0.53	0.53	0.37	0.44	0.49	-0.04
NO ₃ ⁻	0.06	-0.14	-0.30	0.26	0.31	0.36	-0.08		-0.21	-0.39	-0.04	0.34	0.43	0.42	0.20	0.25	0.00
SO ₄ ²⁻	0.23	0.21	0.35	0.46	0.43	-0.71	0.42	0.18		0.84	-0.13	0.14	0.09	-0.08	0.01	-0.27	-0.26
Cl ⁻	0.29	0.41	0.52	0.24	0.28	-0.41	0.73	0.12	0.68		0.15	-0.17	-0.07	-0.35	0.14	-0.42	-0.48
	0.47	0.15	0.15	-0.24	-0.95	-0.06	0.28	-0.21	-0.19	0.31		-0.60	-0.38	-0.42	0.20	-0.39	-0.53
Na ⁺	0.31	-0.10	-0.14	-0.03	0.42	0.00	0.01	0.90	-0.05	0.11	0.40		0.86	0.78	-0.01	0.60	0.37
K ⁺	0.35	-0.01	-0.09	0.19	0.51	0.02	0.06	0.90	0.08	0.12	0.23	0.96		0.76	0.40	0.55	0.07
Mg ²⁺	0.59	-0.10	0.12	0.10	-0.73	-0.37	0.04	0.15	0.19	0.20	0.49	0.53	0.46		0.16	0.77	0.15
Ca ²⁺	-0.12	0.70	0.58	0.65	0.98	-0.03	0.67	0.40	0.35	0.46	-0.07	0.28	0.40	-0.08		0.24	-0.42
Solar Rad	0.53	-0.05	-0.04	0.45	0.87	-0.17	-0.17	0.43	0.29	-0.13	-0.34	0.07	0.26	0.26	-0.09		0.36
WS	0.21	-0.58	-0.48	-0.36	-0.15	0.52	-0.67	0.54	-0.38	-0.38	0.11	0.53	0.49	0.18	-0.27	0.32	

*Solar rad. = Solar radiation

#WS = wind speed

correlated to succinate ($r = 0.70$) in PM_{2.5} but not correlated ($r = -0.70$) in PM₁₀. Wind speed was poorly correlated with most carboxylates except with succinate in the PM₁₀ aerosols. This indicates that in addition to secondary formation, the carboxylates were mainly generated from local sources, while succinate might be related to long range aerosols transport to the sampling site. Concentrations of acetate, oxalate and malonate generally showed a good correlation with solar radiation suggesting that the acids were largely produced by secondary photochemical processes in the atmosphere (Kawamura and Yasui 2005). The ratio of malonate to succinate is used as an indicator of enhanced photochemical production of dicarboxylates in the atmosphere (Kawamura and Sakaguchi 1999). Malonate is derived from the incomplete combustion of fossil fuels or from the secondary atmospheric production. The mean malonate/succinate ratio of 1.6 (range: 0.56–2.9) in atmospheric aerosol and the lower average ratio of 0.35 (range: 0.25–0.44) were observed in vehicular exhaust because malonate is thermally less stable than succinate (Kawamura and Ikushima 1993). In this study substantially higher mean malonate/succinate ratio (5.3) in the PM_{2.5} aerosols were observed suggesting larger contribution from secondary sources to the atmospheric particulate acids (Kawamura and Sakaguchi 1999).

The ratio of formate-to-acetate has been used as a good indicator of the relative contributions of *in-situ* formation (high ratio) and secondary sources (low ratio) to carboxylate ions (Talbot et al. 1990, Grosjean 1992, da Rocha et al. 2012). As can be seen in Table III, the lower formate/acetate ratios (mean of about 0.26) for both size fractions particles can also indicate that the secondary formation was an important contributing source of those ions. This suggestion is supported by the fact that higher mean average temperature during sampling period (mean, 24 °C) might be the controlling factor in determining the relative contribution of the primary and secondary sources to these species.

PRINCIPAL COMPONENT ANALYSIS (PCA) AND CLUSTER ANALYSIS (CA)

PCA from PM_{2.5} is shown in Table V and Fig. 5. Firstly, for PM_{2.5} (Fig. 5a and Table Va), the adjusted model is composed by three components (PC) that explains 68 % of total variance. PC1 explains 36 % and shows high scores for formate, acetate, oxalate, pyruvate, Na⁺, K⁺, Mg²⁺, total diacids and solar radiation. This PC provokes a separation in the dataset, demonstrated by those high scores for the indicated variables. PC1 represents a probable photochemical formation of (di)carboxylic acids in vapor phase and a posterior gas-to-particle conversion onto sea salt particles. In turn, sea salt particles are formed by the drying action caused by solar radiation on seawater droplets allowed to be in suspension in the atmosphere. PC2 explains 18 % of variance and brings high scores for SO₄²⁻, Ca²⁺, Cl⁻ and wind speed. This component also provokes differentiation among data, separating these variables from those explained by PC3. Species presented by PC2, due to high scores for wind speed, had been involved in long range transportation processes. Since SO₄²⁻ is a good tracer for anthropogenic sources, this could be emitted by industries (from petrochemical complex) and/or by vehicles (from Salvador Metropolitan Area) as SO₄²⁻ or SO₂ and be transported to BNA and causing modification of Cl⁻ and Ca²⁺ rich particles (probably from sea salt spray and/or soil suspension). Finally, PC3 explains 14 % of variance and is presented by NO₃⁻, temperature and relative humidity. In this case, nitrate which is a volatile species, represents the change among atmospheric phases (from gas-to-particle and vice-versa) and the contribution of removal processes due to high RH. These explanations could also be verified by the groupings from Cluster analysis (Fig. 6a), Pearson correlations (Table III) and diagnostic ratios (Table IV).

In relation to PM₁₀, PCA (Fig. 5b and Table Vb) could explain 67 % of the total variance. PC1 explains 34.8 % with positive scores for formate,

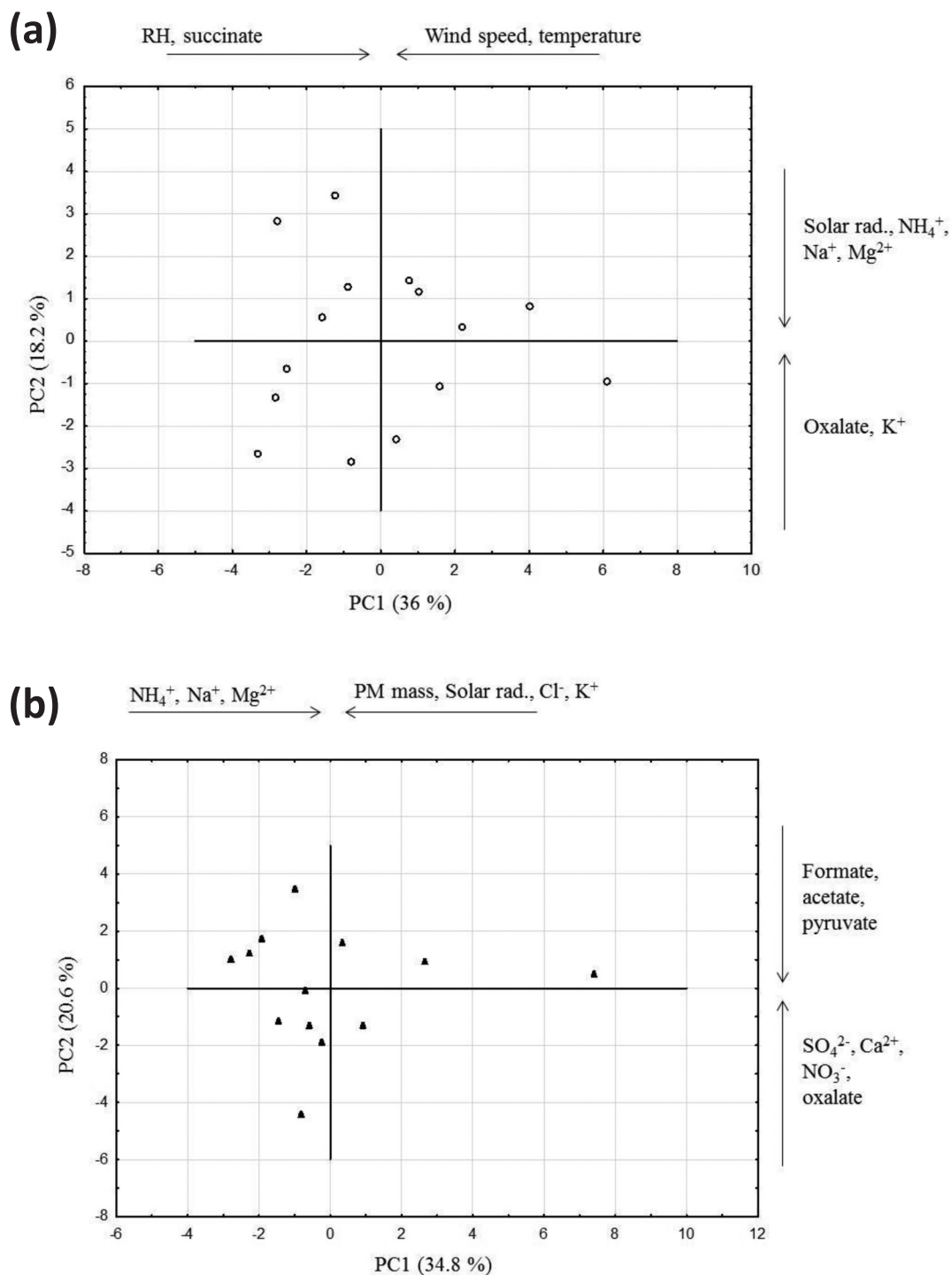


Fig. 5 - Principal component analysis at 95 % confidence level for **(a)** $\text{PM}_{2.5}$ and **(b)** PM_{10} according to ions species, from BNA.

major part of PM_{10} samples. These explanations are in good agreement with information from cluster analysis (Fig. 6b), Pearson correlations

(Table III), and diagnostic ratios (Table IV). The dendrogram shows the formation of three groups of samples. Two of them have more similarity and

TABLE IV
Mean ratios and associated standard deviations and range for carboxylate ions and K^+ in PM2.5 and PM10 aerosols at BNA in Salvador.

Ratio	PM2.5		PM10	
	mean	range	mean	range
Malonate/Succinate	5.3	3.0–7.8	5.8	3.4–40
Formate/Acetate	0.25	0.18–0.41	0.27	0.17–0.40
Oxalate/dicarboxylates	0.72	0.48–0.98	0.83	0.69–0.97
Oxalate/ K^+	0.13	0.08–0.18	0.05	0.04–0.06

TABLE V
Principal Component Analysis (PCA) for both particle size fractions. High loadings are indicated in bold.

(a) PM2.5				(b) PM10			
Species	PC 1 (36 %)	PC 2 (18 %)	PC 3 (14 %)	Species	PC 1 (34.8 %)	PC 2 (20.6 %)	PC 3 (11.5 %)
mass	-0.52	-0.58	0.29	mass	0.11	-0.62	0.41
Formate	0.64	-0.51	0.17	Formate	0.80	0.11	0.01
Acetate	0.61	-0.46	0.23	Acetate	0.81	0.01	-0.01
Oxalate	0.82	-0.21	-0.26	Oxalate	0.72	-0.01	0.63
Malonate	-0.57	-0.56	-0.11	Malonate	-0.49	-0.12	0.42
Succinate	-0.52	0.34	0.45	Succinate	-0.60	-0.11	-0.30
Pyruvate	0.67	-0.50	0.12	Pyruvate	0.89	-0.01	-0.23
NH_4^+	0.53	-0.01	-0.36	NH_4^+	-0.01	-0.91	-0.31
NO_3^-	-0.18	-0.58	0.70	NO_3^-	0.60	-0.01	0.33
SO_4^{2-}	-0.42	-0.63	0.57	SO_4^{2-}	0.72	-0.23	-0.23
Cl ⁻	-0.39	-0.38	-0.53	Cl ⁻	0.01	-0.54	-0.41
Na ⁺	0.76	0.09	0.43	Na ⁺	-0.01	-0.89	-0.20
K^+	0.82	-0.18	0.26	K^+	0.13	-0.88	0.01
Mg^{2+}	0.83	0.12	0.12	Mg^{2+}	-0.01	-0.72	0.30
Ca^{2+}	0.42	-0.64	-0.22	Ca^{2+}	0.81	-0.18	-0.11
Dicarboxylates	0.93	-0.01	-0.08	Dicarboxylates	0.82	-0.01	0.28
Solar Radiation	0.84	0.23	0.02	Solar Radiation	-0.01	-0.19	0.89
Wind Speed	0.25	0.70	0.29	Wind Speed	-0.59	-0.60	0.11
Temperature	0.13	0.45	0.63	Temperature	-0.90	-0.11	0.22
RH(%)	-0.18	0.15	0.50	RH(%)	-0.74	0.17	0.29

acetate, oxalate, pyruvate, NO_3^- , SO_4^{2-} , Ca^+ , and total diacids and high negative values for succinate, wind speed and temperature. This PC causes little separation in the dataset, indicating similar concentration levels for the species in question. First of all, since meteorological variables such as wind speed and temperature correlate well with succinate this means that it may be emitted or formed in atmosphere as acid succinic in gas phase and be ab/adsorbed onto pre-existing particles. On the other hand, this happens the other way

around for formate, acetate, oxalate, pyruvate, NO_3^- , SO_4^{2-} , Ca^+ and total diacids. This means that they are either primarily emitted as coarse particles from anthropogenic sources or are result of ageing and growing of fine particles. PC2 explains 20.6 % PM10 mass, NH_4^+ , Na^+ , and Mg^{2+} and makes the separation of dataset into two groups. This PC can be related to sea salt spray and/or soil resuspension. PC3 explains 11.5 % of variance and is represented by solar radiation. This can explain that photochemical reactions were not important for a

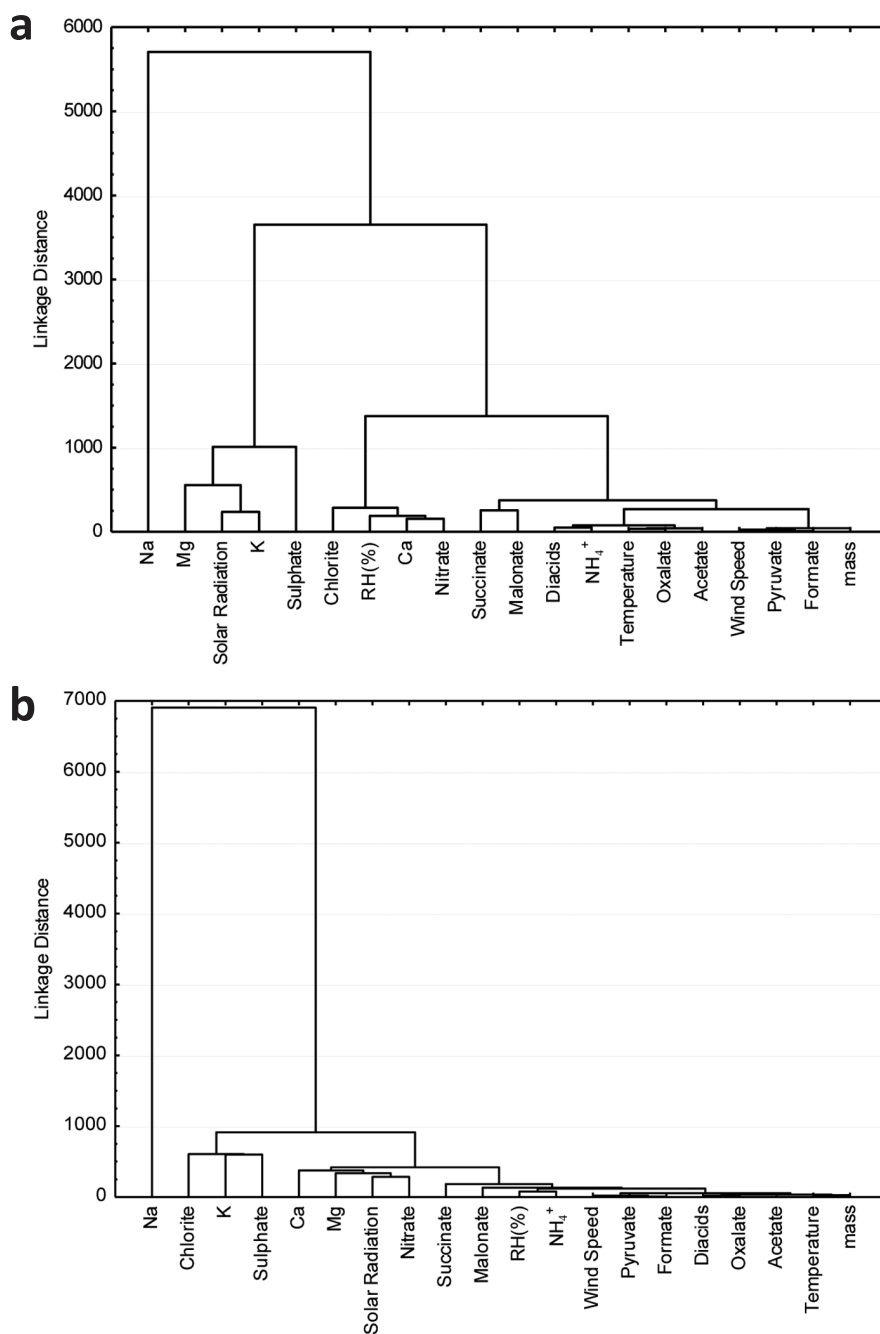


Fig. 6 - Cluster analysis at 95 % confidence level for (a) PM2.5 and (b) PM10, from BNA.

the third group is presented by few samples with different characteristics of the others.

ESTIMATES OF DRY DEPOSITION FLUXES

The dry atmospheric deposition fluxes (F_d) were calculated by multiplying the geometric mean

particulate concentration in air of the element of interest (i) by the elemental dry settling velocity (V_d):

$$F_d = C_i \times V_d$$

The term V_d varies with particle size and is dependent on climatological and physical

conditions in the troposphere, especially in coastal environments (Herut et al. 2001). The V_d values considered in this study were reported elsewhere (Cadle et al. 1985, Chu et al. 2008, Khare et al. 1998). Even though keeping in mind the uncertainties of the term V_d , the dry deposition fluxes of selected major ions were calculated since this is the first approach to have an insight about this parameter and, therefore, about major ions air-to-sea fluxes for BTS. Anyway, similar estimates were done in recent studies for major

ions and also other compounds (da Rocha et al. 2009, 2012, Pereira et al. 2007, Vasconcellos et al. 2011, Machado et al. 2009).

Table VI presents estimates of dry deposition fluxes (F_d) for selected ions in both fine (PM_{2.5}) and coarse (PM₁₀) particulate matter. Since during sampling campaign there were no rain events and there were high F_d values found (mainly for inorganic species), we could say particle dry deposition is a very important removal mechanism of these species during dry periods.

TABLE VI
Estimates of particle dry deposition fluxes (F_d) for major ions in BNA.

	Dry Settling Velocity (V_d) (cm s ⁻¹)	PM _{2.5}		PM ₁₀	
		Geometric Mean (ng m ⁻³)	Dry Deposition Flux (F_d) (mg m ⁻² day ⁻¹)	Geometric Mean (ng m ⁻³)	Dry Deposition Flux (F_d) (mg m ⁻² day ⁻¹)
formate	0.5 ^a	7.59	3.28	8.72	3.77
acetate	1.0 ^a	30.9	26.7	33.3	28.8
Cl ⁻	4.1 ^b	138	489	493	1747
NO ₃ ⁻	0.27 ^b	107	24.9	165	38.6
SO ₄ ²⁻	0.52 ^b	327	147	546	246
Na ⁺	3.49 ^b	883	2663	2377	7168
NH ₄ ⁺	0.13 ^b	29.1	3.26	49.9	5.61
K ⁺	3.9 ^b	176	592	559	1883
Mg ²⁺	1.5 ^c	309	399	267	346
Ca ²⁺	2.1 ^c	112	203	304	552

^aKhare et al. 1998; ^bChu et al. 2008; and ^cCadle et al. 1985.

CONCLUSIONS

The PM_{2.5} and PM₁₀ aerosols samples were collected from a site at Baia de Todos os Santos bay in Salvador, Brazil. Among the analysed carboxylate ions, formate was found to be the dominant species in almost all samples followed by acetate and oxalate. Of the other ionic components, SO₄²⁻, Cl⁻, and Na⁺ made a larger contribution to the total water-soluble inorganic aerosol mass. Main sources for fine particles were: (i) photochemical formation of carboxylic and dicarboxylic acids in vapor phase and a posterior gas-to-particle conversion onto sea salt particles; (ii) emissions from anthropic sources (vehicles and/or industries) within participation in

long range transportation processes; and (iii) the interchanging of volatile species among atmospheric phases (from gas to particle and vice-versa). In turn, for coarse particles, the predominant sources were: (i) gas-phase species and ab/adsorbed onto pre-existing particles afterwards; (ii) either primary emission of coarse particles from anthropogenic sources or the ageing and growing of fine particles; and (iii) sea salt spray and/or soil resuspension. Finally, particle dry deposition was a very important mechanism representing air-to-sea fluxes of major species. This is one of very few studies that report comprehensive data about major ions from a tropical coastal atmosphere which is also affected by an urban environment in South Atlantic.

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RESUMO

A atmosfera de regiões costeiras adjacentes a regiões urbanas podem ser afetadas pela emissão de diferentes poluentes atmosféricos, dentre eles, os íons majoritários. Nesse estudo foram estudadas a composição química e as fontes de carboxilatos e íons solúveis em água em partículas finas e grossas bem como as estimativas de fluxo de deposição seca em um sítio em uma região costeira tropical afetada por uma Região Metropolitana. As concentrações médias de carboxilatos totais foram 78 ng m^{-3} na fração fina e 81 ng m^{-3} na fração grossa do material particulado (MP). Os valores correspondentes de concentração para os íons inorgânicos foram 2143 ng m^{-3} e 4880 ng m^{-3} , respectivamente, para as frações fina e grossa. As principais fontes para as partículas finas foram: (i) formação fotoquímica de ácidos carboxílicos na fase vapor e posterior conversão gás-partícula sobre partículas de sal marinho, (ii) emissões de fontes antrópicas envolvendo processos de transporte de longas distâncias; e (iii) a interconversão de espécies voláteis entre fases atmosféricas. Por sua vez, as fontes predominantes para as partículas grossas foram: (i) espécies gasosas ab/adsorvidas em partículas pré-existent, (ii) emissão primária de partículas grossas de fontes antrópicas, e (iii) spray marinho e/ou ressuspensão do solo. Finalmente, a deposição seca de partículas representa o fluxo de íons majoritários na interface ar-oceano.

Palavras-chave: deposição seca de partículas, MP, íons majoritários, atmosfera tropical, Baía de Todos os Santos, Brasil.

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