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Investigation of rainwater contamination sources in the southern part of Brazil

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Rainwater quality is influenced by air pollutants and can affect sensitive ecosystems. This study was conducted to identify the sources of rainwater contamination in a receptor investigated in the southern part of Brazil. A total of 22 rainwater samples were collected at Florianópolis, Brazil. The sampling station is influenced by continental emissions (soil resuspension, traffic emissions and combustion) and marine aerosols. Over the sampling period, the average pH and electrical conductivity (EC) of the precipitation was found to be 4.97 ± 0.41 and $14.68\,\mu S\,cm^{-1} \pm 13.47$, respectively. In addition to pH and EC, ions and trace metals in the collected rainwater were quantified. The results were investigated by a combination of techniques including principal component analysis (PCA), a back trajectory model and other statistical and graphical interpretation methodologies. A PCA showed that Cl^-, Na^+, Mg^{2+} and part of the K^+ and SO_4^{2-} content were mainly contributed by marine aerosols, whereas the contribution from continental sources (combustion, traffic emissions and other urban activities) was dominant in the content of NO_3^- and part of the SO_4^{2-} and Mn content. Soil resuspension was responsible for the concentrations of most of the trace metals (apart from Mn) and Ca^{2+} in the rainwater. An inverse correlation among the elemental concentrations, amount of rainfall and wind speed was observed. The northern transport pathway was identified as being associated with high concentrations of NO_3^- and slightly decreased pH values. However, the low standard deviation observed for the pH values during the sampling campaign also showed a small variation in the data, suggesting that the acidity is most probably being constantly sourced from a natural origin, such as organic acids.

Keywords: air pollution; rainwater; principal component analysis (PCA); HYSPLIT

1. Introduction

Acid deposition (acid rain) is known to have affected geo-biochemical cycles in many parts of the world.[1] Among the impacts are degradation of air quality and visibility, damage to public health, acidification of lakes and streams, harm to sensitive forests and coastal ecosystems and the acceleration of decay in building materials.[2,3] Over the past several decades, the chemical composition of wet deposition has been measured due to the rapid growth in anthropogenic emissions of SO_x, NO_X, NH_3, dust particles and other materials.[4,5] These air pollutants originate from the burning of fossil fuels, industrial and agricultural processes, soil resuspension, sea spray and other natural processes. Prevailing winds transport the air contaminants over hundreds of kilometres, often far from the source of emission.

The pH (hydrogen ion concentration) of rainwater is determined by the balance between acid (mainly represented by H_2SO_4, HNO_3, HCl and H_2CO_3) and alkaline (mainly represented by NH_3, $Mg(OH)_2$, KOH, NaOH and CaOH) species.[1,6] Dust and gaseous NH_3 can significantly influence precipitation acidity by neutralizing a certain fraction of the acids.[6] When acidity is neutralized, the rainfall becomes loaded with alkaline species. Elevated concentrations of alkaline species in rainfall could neutralize the pH even in areas that have high SO_2 and NO_x emissions.[7] The acidity of rainwater, which is responsible for the lower pH values, is generally related to the acids HNO_3 and H_2SO_4 formed from NO_x and SO_x (mainly emitted by anthropogenic sources).[6] Organic acids such as acetic and formic acids (formed from natural sources) also contribute to the acidity in precipitation, especially in tropical climates.[1,8]

In accordance with Rodhe et al.,[1] the rate of acid deposition during the coming decades will probably continue to decline in developed countries. However, in some other parts of the world, especially in developing countries, deposition of SO_x and NO_x may increase well beyond the present levels.

In addition to acidity, rainwater is always accompanied by some trace elements due to the wet deposition of particulate matters (PMs), which have a severe impact on environmental health.[4] Therefore, a precipitation chemistry study is required to characterize the rainwater in

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developing countries.[9] Determining the chemical and physical characteristics of rainwater helps to evaluate the influence of different sources and enhances the understanding of local and regional dispersion of gases and particles, as well as the potential impacts on ecosystems.[2,3,6,10–14]

The southeast region of the state of Santa Catarina, Brazil, is known for its high pollution levels caused by the intense industrial activity and exploitation of natural resources.[15,16] Moreover, the largest coal burning thermoelectric complex in Latin America, the Thermoelectric Complex of Jorge Lacerda (TCJL), is located in this region. This thermoelectric complex consists of seven power plants with a total capacity of 832 MW and consumes approximately 2.9×10^6 tons of coal per year.[15] The TCJL power plant has electrostatic precipitators that operate at approximately 98% efficiency to remove particulates in the gaseous effluent. To promote dispersion, the emissions are discharged from 100- and 200-m stacks.[15] Despite these measures, local government and community groups remain concerned about the impact of air pollution on the public and environmental health.[17]

In this study, a combination of back trajectory modelling and statistical exploratory tools (principal component analysis, PCA, correlation analysis and graphical interpretation) was applied to gain a better understanding of acid deposition processes in the region of south Santa Catarina. Statistical exploratory analysis utilized a combination of statistical and graphical consolidated methodologies, in order to identify the dominant trends in the meteorological data and rainwater composition. The objective of this study was to investigate the principal sources of rainwater contamination in order to estimate the local and regional atmospheric loadings.

2. Materials and methods

2.1. Sampling and analysis

Rainwater samplings were collected in the city of Florianópolis (27°59′93″S, 48°51′93W) (421,240 inhabitants) [18] in the state of Santa Catarina using rain samplers designed by the *Laboratório de Controle da Qualidade do Ar* (LCQAr) of the *Universidade Federal de Santa Catarina* (UFSC) within a superficial area of 1 m^2 (1m × 1 m). Prior to being used, all the polyethylene sample bottles were soaked in Millipore water for at least 24 h, as described by Martins [16] and Wang et al.[5] The rainwater samplers were placed 1.5 m from the ground, unobstructed by obstacles such as buildings or trees. In-situ measurements of pH and conductivity were taken using a pH meter (Lutron-206, precision ± 0.02 pH) and an electric conductivimeter (Lutron CD 4303, precision ± 1%), respectively. Cations of Na$^+$ and K$^+$ were analysed by an atomic absorption spectrograph (Orion). Anions of Cl$^-$, SO$_4^{2-}$ and NO$_4^{2-}$ were determined by ion chromatography (Dionex model DX-120). Separated aliquots of the samples were acidified to pH < 2 with ultra pure nitric acid (60%) and stored refrigerated after filtration through an 0.45- µm acetate filter in order to remove suspended matter. All samples were preserved at 4°C before laboratory analysis. The trace elements Mn, Fe, Co, Pb, Cd, Cr and Ni were determined by electrothermal atomic absorption spectrometry (Varian Spectra AA 640Z). A total of 22 samples were collected between August 2006 and November 2006. The investigated receptor was situated in the coastal belt of a region of the Atlantic, which has great continental and marine influences (around 2.5 km from the ocean; Figure 1).
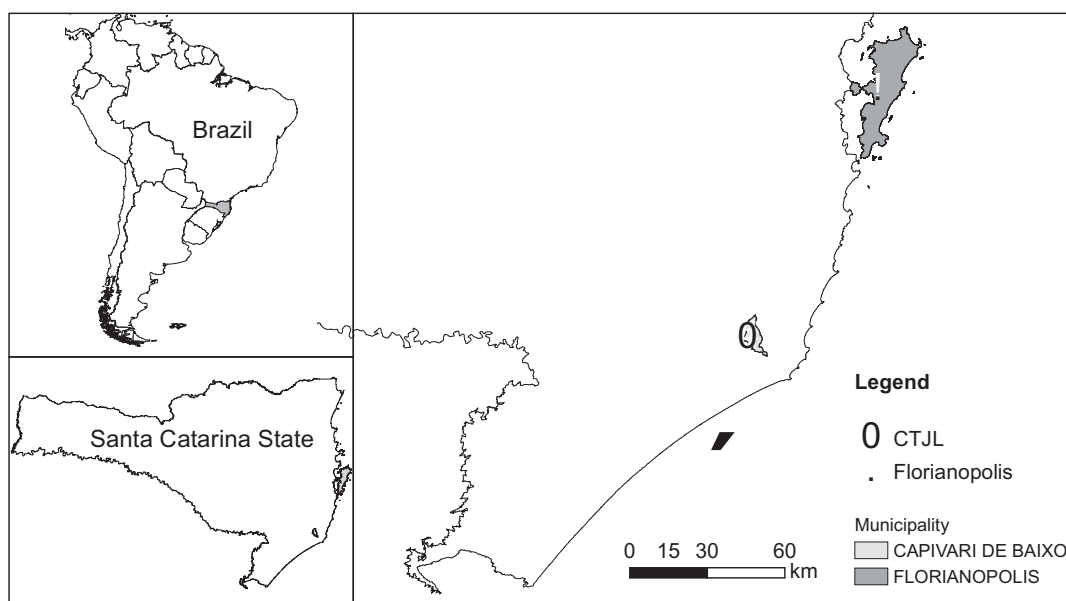

Figure 1.   Variation in ion and trace metal concentrations versus sequential number of rainwater samples.

A meteorological station (Davis Vantage PRO 2, USA) was installed in Florianópolis at the same location at the rainwater sampling station in order to obtain data for rainfall, wind direction, wind intensity, temperature, humidity and atmospheric pressure. The installation was located approximately 5 m above ground level with a 360° unobstructed horizon and unrestricted exposure to the meteorological parameters of interest.

2.2. Statistical exploratory analysis

A statistical exploratory analysis approach was utilized to investigate and characterize the trends for the various rainwater elements. Original data were transformed using an extension of the Box-Cox transformation to approach normality. A Pearson's parametric correlation was employed to define the possible sources of certain elements and to verify the meteorological relationships of the rainwater composition in Florianópolis. A PCA was applied to a set of variables (analysed elements and parameters of rainwater), both to reduce their dimensionality and to investigate the relationship between the elements in the rainwater and characteristics of the sources of pollution.[4,19,20] The principal components with eigenvalues greater than 1 were subjected to a varimax rotation, which maximizes the variance to obtain a pattern of loadings for each factor in order to facilitate the interpretation. After rotation of the factor-loading matrix, the factors were interpreted as either originating or emitted from common sources or regions.[7,21]

Pollution roses were applied to the graphical interpretation in order to identify the provenance of the compounds. This approach allowed the geographical origin and relative importance of the pollution sources affecting the site to be determined.[22–24] This methodology was also applied to compare the real air pollution process with the results obtained by the PCA.

2.3. Back trajectories

Air pollutant back trajectories were used to understand atmospheric transport and identify the origins and pathways of air masses influencing the concentrations of the measured elements in rainwater.[4,19,20]

The HYSPLIT v4.9 model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) (web address: http://www.arl.noaa.gov/ready/hysplit4.html) [25] was employed to compute the back trajectories of the analysed parameters of the rainwater. Meteorological data were provided by the NCEP/NCAR 2.5° (latitude and longitude) global reanalysis archive.[26] For every rainwater sample, 24-hour back trajectories with three starting altitude levels (500, 1500 and 2000 m) were calculated at Florianópolis. Results from HYSPLIT trajectory calculations had an error rate of between 20% and 30% of the travel distance.

However, if a large number of trajectories were analysed, the reliability of the results was improved.[20,27]

Very little is known about the spatial extent of the long-range transport of air pollutants in South America. HYSPLIT has previously been used extensively to compute the back air parcel trajectories for periods ranging from several hours to 14 days. Air mass back trajectory analysis is frequently used to point out the direction and sources of air pollution at a receptor site.[28]

3. Results and discussion

3.1. General results

During the sampling campaign, 22 samples of rainwater were collected. The sampling information is summarized in Table 1. The statistics for the pH values and species concentrations in the rainwater taken during the sampling period at the study site are shown in Table 2. Table 1 gives the predominant wind directions 24 h before collection of the sample. The sequence of the wind direction is arranged according to the order of the observations, using which it is possible to identify wind direction inversions and cold fronts. The superscripts 1 and 2 in Table 1 indicate the first ($-^1$) and second ($-^2$) predominant wind direction. The precipitation accumulated on the sampling date is also included in Table 1. Rain events are distinguished by orographic rainfall (calm winds) and cold fronts.

The volume-average pH value for the entire sampling period was 4.97 ± 0.34 in Florianópolis, with a range from 4.44 to 5.69 (Table 2). The pH values were often below the normal pH (>5.60) of rainfall in an unpolluted atmosphere.[29,30] The slightly low pH value suggested that the site is subject to acidic precipitation.[5] However, according to Cieslik,[31] 'pure' rainwater has a mean pH of 5.6, due to the presence of carbon dioxide (slightly acidic) in air. Moreover, the low standard deviation of the pH values during the sampling campaign also showed a small variation in data, suggesting that the acidity is probably being constantly sourced from a natural origin (from vegetation or soils) or carbon dioxide; organic acids from vegetation or soils may represent a major source of acidity in Brazil [8].

The pH values found were in agreement with the results of Rodhe et al.[1] (pH between 4.8 and 5.2 in the Florianópolis area). This author used the global chemistry transport model, TM3, to predict the global distribution of acidifying wet deposition.

Due to the reduced volume of some rainwater samples, a small number of elements were not analysed. Moreover, in some cases where the sample volume was sufficient, concentrations were still below detection limits. For this reason, some elements (especially trace metals) were quantified with lower frequency.

Unlike pH value and alkalinity, electrical conductivity (EC) showed a large variance among samples (Figure 2).

Table 1. Information for rainwater sampling campaign at Florianópolis in 2006.

Sample number	Sampling day	Sampling time	Wind direction	Accum. precip. (mm)	Event
1	15/Aug	17:30	SSE	10	Cold front
2	01/Sep	18:25	NNW[2]-NNE[1]	12	–
3	16/Sep	16:25	SSW[2]-SSE[1]	3	Cold front
4	20/Sep	10:10	NNE[1]-N[2]	7	–
5	29/Sep	09:15	NNE[1]-SSE[2]	7	Cold front
6	01/Oct	17:35	NNW[1]-N[2]	11	–
7	02/Oct	14:30	N[1]-SE[2]	30	Cold front
8	05/Oct	18:15	NNE	6	–
9	11/Oct	19:50	N[1]-SE[2]	7	Cold front
10	02/Nov	07:10	W[1]-NNE[2]	5	Calm[a]
11	03/Nov	23:00	SSE	0	Cold front
12–14	04/Nov	11:30, 13:25, 16:05	SSE	17	Cold front
15	06/Nov	12:25	NE[2]-NNE[1]	12	–
16	14/Nov	09:50	ENE	9	Calm
17–18	17/Nov	16:50, 21:30	NNE[1]-SSE[2]	14	Cold front
19	18/Nov	19:00	S	14	Cold front
20	26/Nov	16:10	NNE[1]-S[2]	11	Cold front
21	27/Nov	20:15	S	13	Cold front
22	29/Nov	17:25	SSE	22	Cold front

Note: Data are obtained from Martins [16].
[a]Orographic precipitation.

Table 2. Average parameters and species concentrations measured at Florianópolis.

Parameter	Number of samples	Mean ± SD[a]	Min.	Max.	Confidence interval −95%	95%
pH	21	4.97 ± 0.41	4.4	5.69	4.79	5.16
EC ($\mu S\ cm^{-1}$)	21	14.68 ± 13.47	1.70	47.60	8.55	20.81
Hardness ($CaCO_3\ mg\ L^{-1}$)	21	2.26 ± 1.32	0.89	5.69	1.66	2.86
Alkalinity ($CaCO_3\ mg\ L^{-1}$)	21	0.03 ± 0.02	0.02	0.08	0.02	0.04
Na^+ ($\mu mol\ L^{-1}$)	20	59.80 ± 87.26	4.35	295.80	18.60	00.99
K^+ ($\mu mol\ L^{-1}$)	22	3.14 ± 3.26	1.00	10.20	2.17	4.83
Ca^{2+} ($\mu mol\ L^{-1}$)	22	7.98 ± 12.41	ND[b]	58.30	2.99	13.61
Mg^{2+} ($\mu mol\ L^{-1}$)	22	9.00 ± 11.32	0.77	37.60	4.05	13.96
Cl^- ($\mu mol\ L^{-1}$)	21	56.94 ± 101.77	2.54	346.40	10.61	03.26
SO_4^{2-} ($\mu mol\ L^{-1}$)	21	9.94 ± 7.61	1.02	22.80	6.94	13.87
NO_3^- ($\mu mol\ L^{-1}$)	18	15.18 ± 13.63	1.00	49.50	7.01	19.29
Mn ($\mu mol\ L^{-1}$)	20	0.006 ± 0.006	ND	0.024	0.002	0.008
Fe ($\mu mol\ L^{-1}$)	22	0.336 ± 0.327	0.008	1.320	0.191	0.481
Cu ($\mu mol\ L^{-1}$)	9	0.058 ± 0.032	ND	0.122	0.019	0.057
Pb ($\mu mol\ L^{-1}$)	11	0.015 ± 0.009	ND	0.028	0.006	0.014
Cd ($\mu mol\ L^{-1}$)	10	0.017 ± 0.014	ND	0.067	0.000	0.026
Cr ($\mu mol\ L^{-1}$)	12	0.014 ± 0.009	ND	0.024	0.010	0.019
Ni ($\mu mol\ L^{-1}$)	14	0.007 ± 0.005	ND	0.015	0.000	6.489

Note: Standard deviation, confidence interval for mean and minimum and maximum values of the entire sampling campaign. Data are obtained from Martins.[16] Number of samples were analysed for each element.
[a]Standard deviation.
[b]Not detected or below the detection limit.

The EC analysis estimated the quantity of total dissolved salts, so it was reasonable to reach a valid correlation between this parameter and some of the ion concentrations. The average value of EC ($14.7\,\mu S\ cm^{-1}$) found in Florianópolis was much lower than an acid site in China (pH 4.53; *apud* [4] with an EC equal to $42.5\,\mu S\ cm^{-1}$).

In some cases, the slightly high pH and low EC values at Florianópolis might have been due to an increase in the precipitation volume, suggesting that air pollutants are probably being removed and diluted, as shown in Figure 2. Wind directions from the NNE and SSE were the most frequent during the months of the sampling campaign (Figure 3).
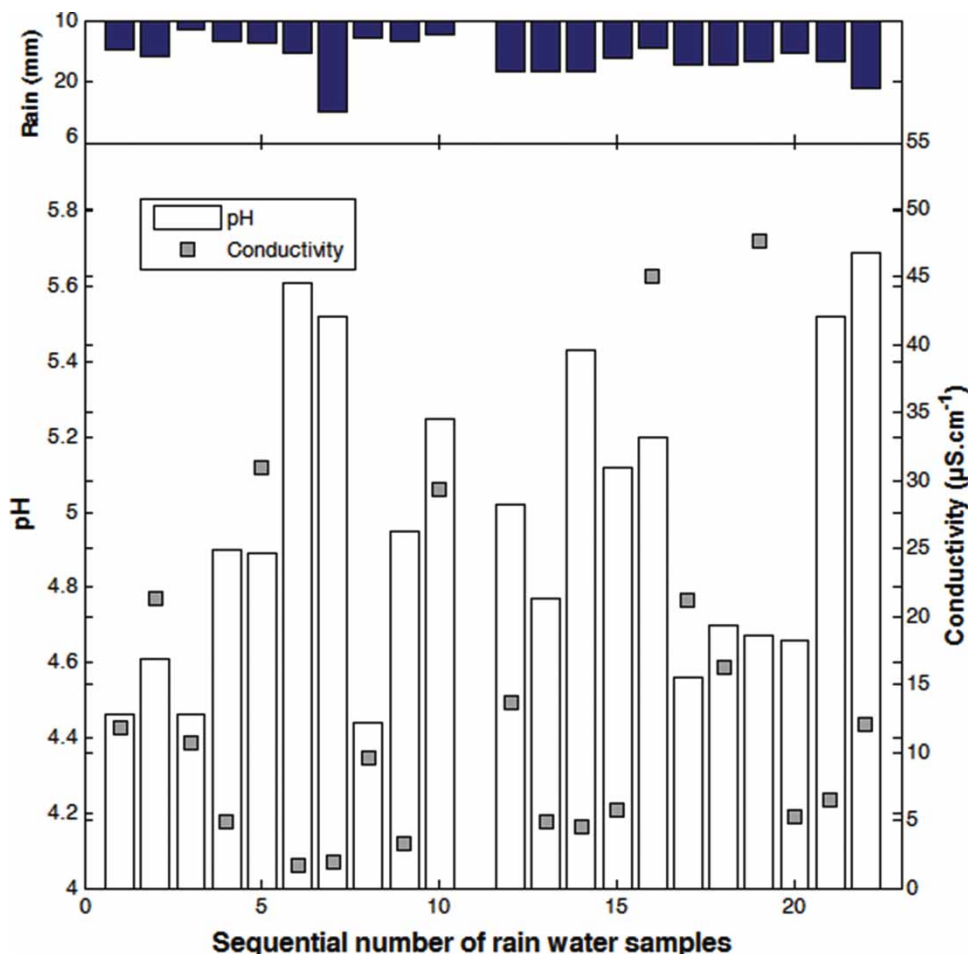
Figure 2. Temporal variation of pH and conductivity versus sequential number of rainwater samples. Precipitation in mm/ day during the sampling date. Sampling campaign frequency was not equispaced.
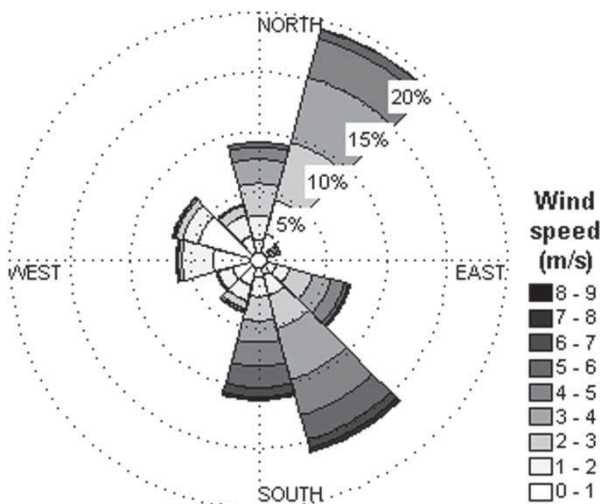

Figure 3. Wind rose of the sampling months. Wind speed in m s[1].

Na^+ and Cl^- were the major ions, with average concentrations of 59.80 and 56.94 μ mol L^{-1}, respectively. The balance between these ions showed that sea salt from the saline spray probably contributed to the elevated levels of these elements at Florianópolis. In addition to Na^+ and Cl^-, the concentrations of NO_3^-, followed by Ca^{2+}, Mg^{2+} and SO_4^{2-}, showed great variability (Table 2). A comparative table (Table 3) shows two examples of the typical ionic composition of precipitation, these being one case from central Europe of acidification by industrial emissions of the oxides of sulphur and nitrogen, and another from northern India showing moderate affects of acidifying species.[1]

Despite the discrepancies in Cl^-, Mg^{+2} and Na^+ concentrations, the ionic concentrations and pH of the studied site were between those of the acidified and dusty regions (Table 3). Table 3 shows that the ion concentrations in the study area (apart from Na^+) were lower than those observed in a megacity (Beijing, China) in a study conducted by Xu and Han (2009) *apud* Olson and Norris (2008). SO_4^{2-}, NO_3^-, Ca^{2+} and Cl^- concentrations were higher in the megacity mainly as a result of industrial activities, vehicle emissions (including road resuspension) and other emissions related to urban activities that contributed to the observed increase in the concentrations of pollutants.[17] Cl^- and Na^+ mean concentrations from the samples collected in this study were

Table 3. Typical composition of precipitation in an acidified region (Europe),[1] a megacity in China (Xu and Han, 2009, *apud* [38]), a rural area in China,[38] a marine area,[32] a dusty region (India),[1] a continental area in Brazil (Ibiúna is a city located in the state of São Paulo, Brazil),[33] an island in Brazil (Ilha Grande) [34] and at Florianópolis (this study) during the sampling campaign.

Parameter	Acidified	Megacity	Rural	Marine	Dusty	Ibiúna	Ilha Grande	This study
Na^+ (μmol L^{-1})	15	25	11	14	13	38	142	60 (19–101)
K^+ (μmol L^{-1})	3	18	9	6	2	8	7	3 (2–5)
Ca^{2+} (μmol L^{-1})	12	304	78	7	20	57	5	16 (6–26)
Mg^{2+} (μmol L^{-1})	5	20	2	2	5	5	20	18 (8–28)
Cl^- (μmol L^{-1})	15	104	14	20	15	21	178	57 (10–103)
SO_4^{2-} (μmol L^{-1})	70	158	76	11	20	31	17	21 (14–28)
NO_3^- (μmol L^{-1})	30	109	17	36	10	22	12	15 (7–19)
pH	4.3	5.1	5.7	5.2	6.2	6.2	5.2	5.0 (4.8–5.2)

Note: Confidence interval is 95% for the measured parameters in this study.[16]

much higher than a marine area in France,[32] and other locations shown in Table 3 had elevated values mainly as a result of three specific events during the sampling campaign (Figure 3). Differences can be observed between ionic concentrations at Florianópolis (coastal city) and at Ibiúna[1] (city located around 70 km from the ocean and 450 km north of Florianópolis).[33] Higher concentrations of Ca^{2+} were found by Conceição et al. [33] in Ibiúna (pH 6.2) compared with Florianópolis (pH 5.0), justifying the higher pH at Ibiúna. Conceição et al. [33] also reported that Ibiúna is little affected by marine aerosols. This last statement could be confirmed by the different concentrations of Na^+ and Cl^- observed at Florianopolis and Ibiúna.

Regarding ionic concentrations at Florianópolis, Souza et al. (2006) observed similar trends at Ilha Grande/Brazil.[34] Despite being separated for 700 km, Florianópolis and Ilha Grande have similar ecologic/ geographical conditions. At both places, scavenging of sea-salt aerosols was the major source of Cl^-, Na^+, Mg^{2+} and Ca^{2+}. Rainwater pH at Ilha Grande varied from 4.3 to 6.3 versus 4.8 to 5.2 at Florianópolis.[34]

Variations in the concentrations of ionic and trace metal species are shown in Figure 4. As discussed earlier, Florianópolis is greatly influenced by sea spray (the source of Cl^-, Mg^{+2} and Na^+), due to the proximity to the ocean. Figure 3 shows similar patterns of Cl^-, Mg^{+2} and Na^+ concentrations. Of the trace metals, similar variations were found for Mn, Fe, Cu and Pb. Fe was the dominant trace metal analysed in the rainwater samples (Table 2 and Figure 3). The concentrations of the other trace elements followed the order: Cu, Cd, Pb, Cr, Ni and Mn. Of these trace elements, Pb, Ni, Cd and Cr are considered to be toxic, even at trace levels.[4]

Apart from Cd and Cr concentrations, rainwater samples collected in Florianópolis contained much lower trace metal concentrations than Mt. Tai in China.[4,5] Compared with a region of the central Mediterranean,[7] of the Pb, Cu and Cd measurements, only the concentration of the latter was higher in the rainwater collected in Florianópolis (1.4 vs. 0.4 μmol L^{-1}).

3.2. Correlation of the measured parameters and elements in precipitation

The relationships between the measured parameters and concentrations of elements (ions and trace metals) were examined through a parametric correlation analysis. Data were previously treated by a Box-Cox transformation. Graphical interpretation was also used to verify the significant relationships.

As suspected, significant negative Pearson's correlation results were found between pH and NO_3^- ($r = -0.63$), SO_4^{2-} ($r = -0.60$) and K^+ ($r = -0.46$) concentrations. The EC showed a significant correlation with K^+ ($r = 0.7$), Mg^{2+} ($r = 0.94$), Cl^- ($r = 0.77$) and SO_4^{2-} ($r = 0.77$), probably sourced from marine aerosols. Na^+ correlated mainly to Cl^- ($r = 0.99$) and also to K^+ ($r = 0.54$), Mg^{+2} ($r = 0.95$) and SO_4^{2-} ($r = -0.60$), suggesting a sea spray origin, since these elements are commonly found in marine aerosols.

Despite a correlation coefficient of -0.6 between sea spray elements and SO_4^2, a valid correlation was also found between sulphates and nitrates ($r = 0.51$), showing that both are probably emitted from a common source, e.g. burning of fossil fuels, industrial processes and combustion of biomass. Therefore, this suggests that there is more than one source of sulphate in Florianópolis.

3.3. Principal component analysis (PCA)

A total of 18 variables were measured in this study. However, the number of species used in the PCA analysis was reduced to 13 parameters (pH, EC, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO^{3-}, Mn, Fe, Pb), because the concentrations of Cu, Cd, Cr and Ni were either below the analytical detection limit or were not detectable. Hardness and alkalinity were not used in this analysis.

PCA was applied to the database and three components were extracted, accounting for 84% of the total variance. A varimax rotation was applied with an initial eigenvalue > 1. The varimax rotated factor loadings are shown in Table 4. The first factor comprised almost 60% of the variance and
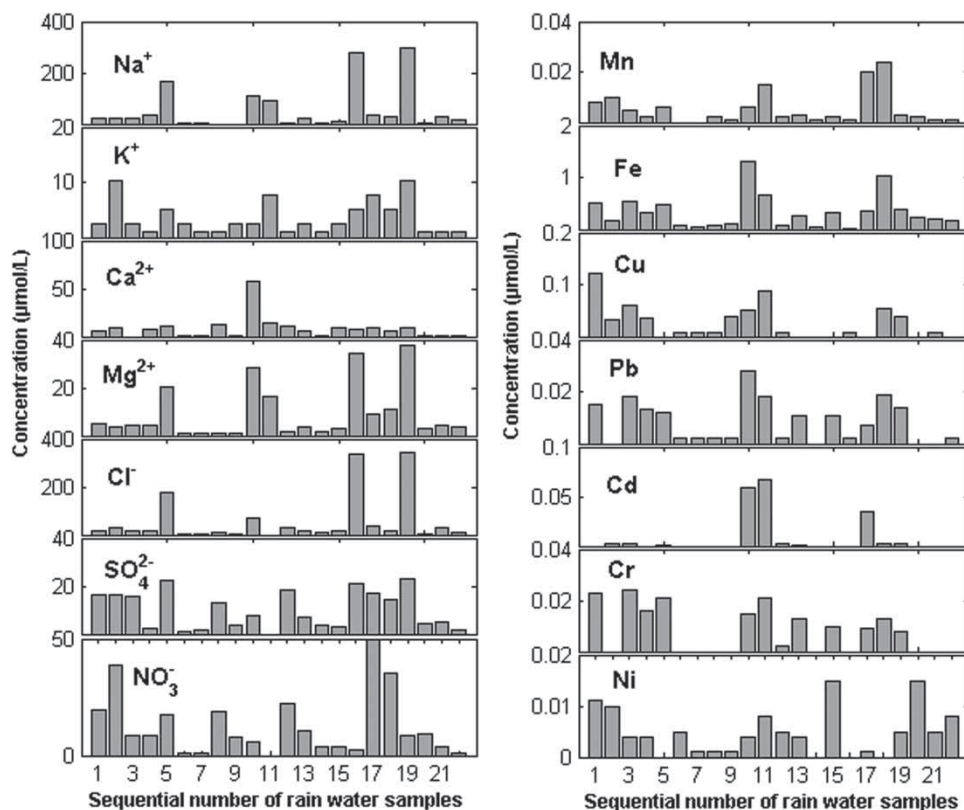
Figure 4. Variation in ion and trace metal concentrations versus sequential number of rainwater samples.

Table 4. Varimax rotated factor loadings of the measured species.

	Factor		
	1	2	3
pH	−0.168	−0.888	−0.185
EC	0.828	0.331	0.108
Na$^+$	0.889	0.133	0.299
K$^+$	0.724	0.489	0.025
Ca^{2+}	0.429	0.468	0.559
Mg^{2+}	0.916	0.156	0.350
Cl$^-$	0.868	0.297	0.152
SO$_4^{2-}$	0.426	0.833	−0.013
NO$_3^-$	0.107	0.974	0.085
Mn	0.404	0.752	0.402
Fe	0.559	0.222	0.745
Pb	0.423	0.253	0.787
Ni	−0.093	−0.111	0.700

had high loadings for EC, hardness, Cl$^-$, Mg^{2+}, K$^+$ and Na$^+$, suggesting a marine component. In this study, the ratio of Cl$^-$/Na$^+$ was shown to be about 1 and was also the most frequent, which can be a strong indicator of marine aerosols.[5,7,35] Despite the high correlation coefficient with factor 2, sulphate also showed a moderate correlation with factor 1. As noted earlier, SO$_4^{2-}$ could be originating from marine sea spray.

Component 2, which explained 14% of the total variance in the investigated data set, had high loading values for NO$_3^-$. SO$_4^{2-}$ and Mn were characteristic. Secondary aerosols correlated well with factor 2, similar to a study conducted by Mihajlidi-Zeliæ et al.[7] It is well known that combustion presents one of the main anthropogenic sources of SO$_2$ and NO$_x$, which are converted to particles in atmospheric reactions. The relationship between pH, NO$_3^-$ and SO$_4^{2-}$ is also well known, because nitrate and sulphate could be derived from acidity precursors (NO$_x$ and SO$_2$). Manoli et al.[36] note that Mn is one of the combustion tracers. Thermoelectric Complex Jorge Lacerda emissions, and others emissions related to urban activities, could be contributing to the observed increase in Mn, NO$_3^-$ and SO$_4^{2-}$ concentrations and, consequently, in the pH decay of rainwater reaching Florianópolis. However, according to Andreae et al.,[37] most of the precipitation acidity in the central Amazon region can be attributed to organic acids, with sulphuric and nitric acids contributing only about 10–20% of the hydrogen ion concentration. Vertical profiles of carboxylic acids through the canopy of tropical and subtropical regions suggest that, in remote continental areas, direct emissions of organic acids from vegetation or soils may represent major atmospheric sources.[8,38] Keene and Galloway [8] also highlight secondary production from the photooxidation of isoprene as an important source of organic acids in Brazil. The slightly low pH (around 5) in Florianópolis suggests

the presence of organic acids and carbon dioxide sourced from a natural origin. This could explain the mean pH values. Small variations could be sourced from mobile and industrial origins.

Factor 3 (9.8% of the total variance) accounts for the variability in most of the trace metals, including Fe, Pb and Ni. These heavy metals also correlate to Cr and Cu, with all of them being found on the PM of soil resuspension. Ca^{2+} in rainwater originates from dust, marine aerosols and other sources. It might therefore explain why this element was well correlated to all the factors.

As Mihajlidi-Zeliæ et al.[7] note, the acidity of the precipitation depends on the availability of acid precursors and alkaline species, such as NO_3^-, SO_4^{2-} and K^+. Although the correlation to these elements possibly originates in anthropogenic emissions, pH values had low variability among the samples collected at Florianópolis. Organic acids could be the major contributor to the low mean pH values for south Santa Catarina. The quantification of organic acids could help to understand the variation in the pH.

Sulphate ions are formed in the atmosphere by gas particle conversion processes arising from the reaction of sulphuric acid with alkaline species, e.g. ammonia, sea salt or dust. In other words, in addition to combustion processes, sulphates can also originate from natural sources, such as marine sea spray, aerosols and resuspended PM, as can be seen from the PCA and also through the correlation between elements.[7]

In accordance with the PCA and correlation analysis, with the exception of Cd, strong correlations were found among the trace metal elements, indicating the existence of a continental source. Soil resuspension, burning of fossil fuels by vehicles and biomass combustion are the most probable sources.

3.4. Identification of source regions through back trajectories and pollution roses

The wind rose[2] presented in Figure 5 clearly shows two prevailing wind directions (from SSE and NNE), from where the strongest winds originate. Continental winds over Santa Catarina are predominantly weak; the dominant winds are from North. However, southern winds are commonly accompanied by cold fronts and rain. These patterns occur throughout the year. The pH values presented in Figure 5 show that the lowest values are characteristic of the precipitation, which is under the influence of the northeast and southeast wind directions. However, the rose representing pH indicates that the lowest pH values occur most often under northeast wind conditions.

The concentration (pollution) roses of measured ionic species are shown in Figure 5. The largest contribution of marine salt ions (Cl^-, Na^+ and Mg^{2+}) is derived from the NNE–NE segment. However, they are also sourced from the South. Florianópolis is on an island and, for this reason, marine aerosols can be loaded from more than one wind direction (Figure 1). The increased concentration of marine spray ions is probably one of the causes of the increase in the EC.

As already noted, the contributions of SO_4^{2-} content from the southeast and northeast segments may be derived from both sea aerosols and local emissions.

The NO_3^- and K^+ concentration rose (Figure 6) indicated that winds from the east–northeast (ENE) direction resulted in the highest concentration of ions at Florianópolis. Northeast winds are rarely associated with precipitation events. High concentrations of NO_3^-, K^+ and also SO_4^{2-} at Florianópolis probably result from the lower rainfall under these wind directions. In a prevailing ENE wind, emissions related to urban activities could be contributing to the observed increase in concentrations of NO_3^-, and also a part of the amounts of SO_4^{2-} and K^+. Concentration roses show a similar provenance for EC and marine aerosol species (Cl^-, Na^+, SO_4^{2-} and Mg^{2+}), confirming the antecedent correlations. The origin of the pollution sources remains unclear: a longer sampling campaign could help to explain the uncertainties. On the other hand, the largest amount of rainfall under prevailing SSE winds increases the pH values. A valid correlation between the accumulated rain and pH value was found with a coefficient of 0.51.
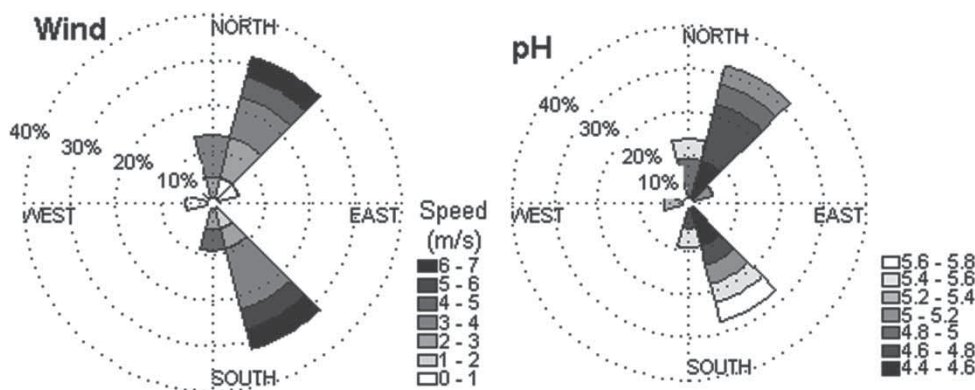

Figure 5. Roses of winds, temperature, pH and rainfall on the sampling days. Temperature in °C, wind speed in m/s and rain in mm (daily accumulated precipitation).
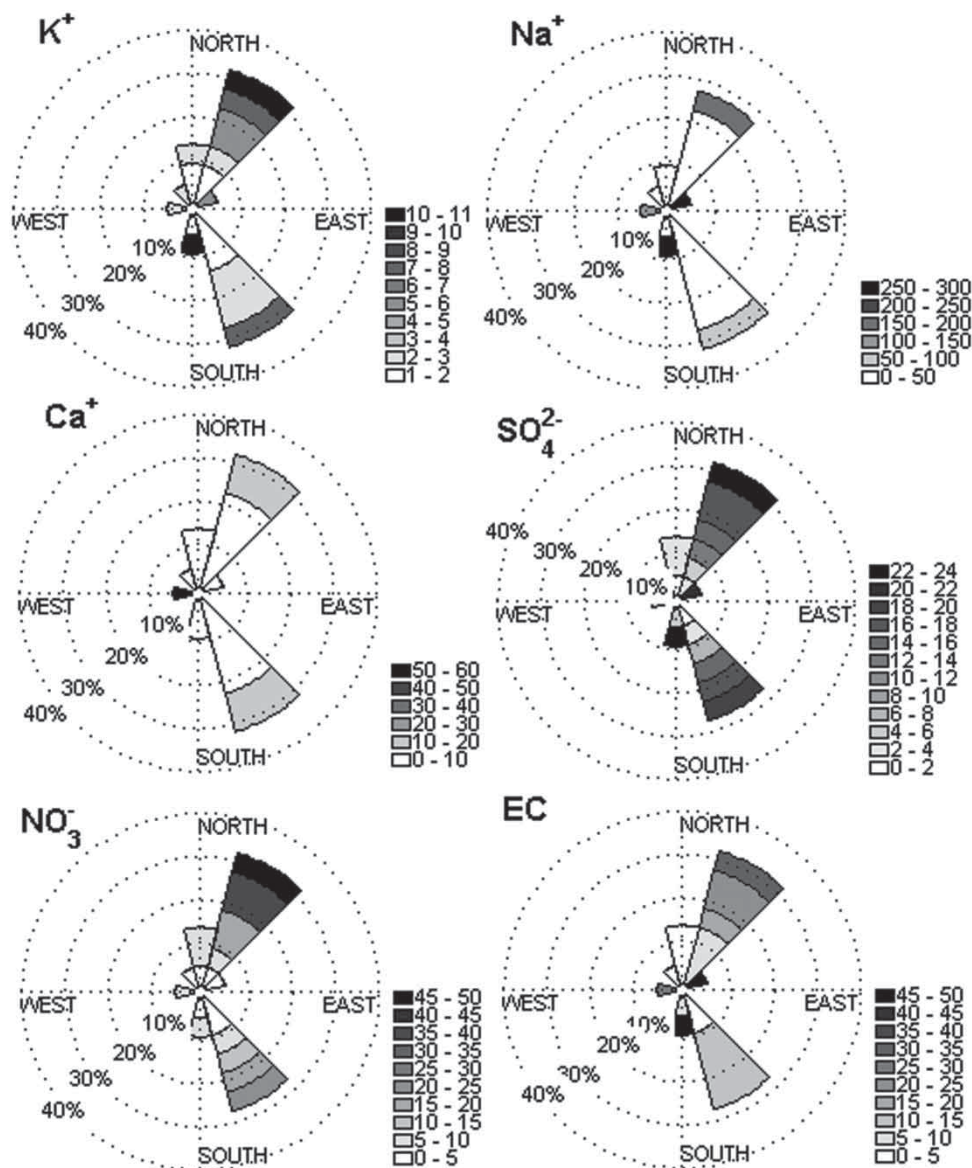
Figure 6. Roses of ionic species concentrations. Scales are not the same. Figure is employed to verify the most polluted events. Concentration scales in μmol L^1.

The concentration roses of trace metals are shown in Figure 7. Soil resuspension, traffic emissions, industrial emissions and other urban activities probably contributed to the elevated trace metal levels at this location. It seems that short-range transport causes the increase in the concentration of trace metals where local sources (road dust resuspension, vehicle emissions, sea spray and soil resuspension) close to sampling point are located. With the exception of Cd, a strong inverse correlation was found between wind speed and concentrations of Mn ($r = -0.84$), Fe ($r = -0.62$), Pb ($r = -0.6$), Cr ($r = -0.64$) and Ni ($r = -0.76$). It is known that strong wind conditions are favourable for pollutant dispersion.[39] A short- and long-range transport could explain the weak correlation between cadmium and wind speed. Emissions from TCJL, located

at around 100 km from Florianópolis, have high loadings of Cd and could be transported to the investigated site under a south segment wind (indicated by the shaded part of the Cd concentration rose). However, a large amount of data must be included in order to evaluate the long-range emission sources. Local emissions, soil resuspension and other short-range emissions are the most probable sources.

Back trajectories can provide more detailed information about source regions, including local, regional and even remote regions downwind of receptor sites.[40] Cluster analysis techniques can be applied to classify back trajectories with similar transportation characteristics. This last methodology was used in this study to identify the relationship between atmospheric transport patterns, the measured
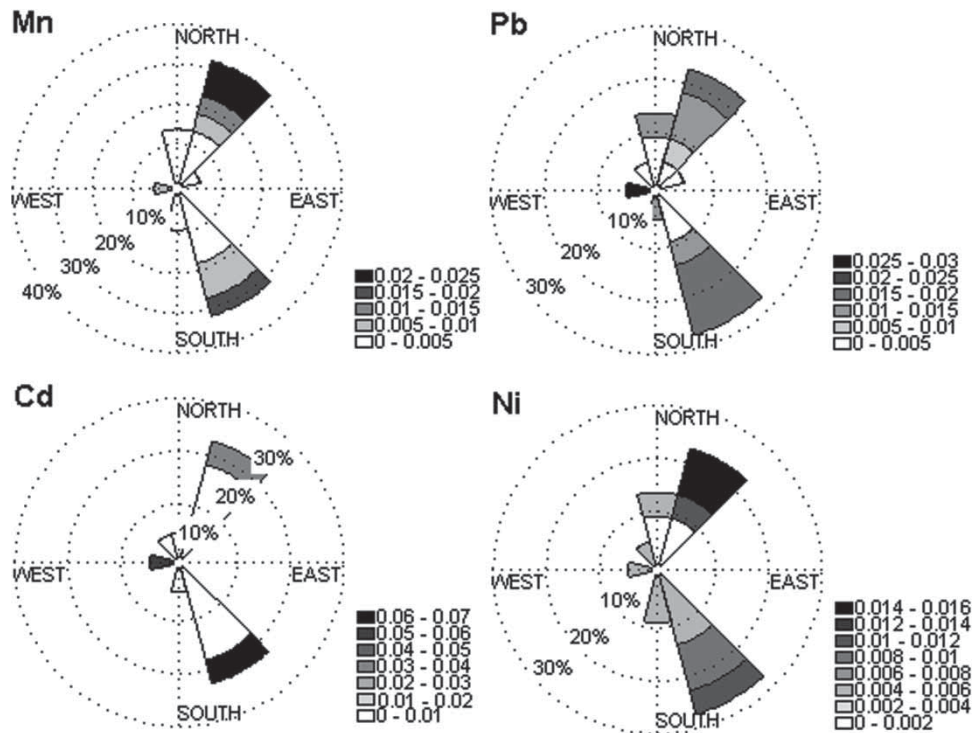
Figure 7.   Roses of trace metal concentrations. Scales are not the same. Figure is used to verify the most polluted events. Concentration scales in μmol L^1.

concentrations [41] and factors extracted from the PCA analysis.

To identify the dominant pathways of the pollutants in rainwater, trajectories were calculated four times a day in the sampling period (from August to November), using a HYSPLIT daily trajectory menu option to create an endpoints file for each start time (0, 6, 12 and 18 hours) from which the model starts to run. All days (including sampling date and days with no rain) were considered in computing these trajectories. This procedure was employed to aggregate multiple trajectories into groups through the clustering method in HYSPLIT. Back trajectories with four start altitude levels (10, 500, 1500 and 2000 m) were calculated for Florianópolis. A detailed review of this method can be found in the HYSPLIT user's guide [25] and in Karaca and Canci.[40]

As discussed earlier, there are two main types of rainwater pollution at Florianópolis: marine and continental (close to the sampling location). Figure 8(a) shows five main pathways (Clusters) of rainwater contaminants computed from August to November 2006 at an altitude of 10 m. A total of 56% of all the trajectories were derived from the northern region (Clusters 2 and 3), whereas 54% (Clusters 1, 4 and 5) originated in the south. The largest part of the trajectories (87%) passed through the ocean and is probably associated with marine aerosols. TCJL emissions, and other emissions related to urban activities of south Santa Catarina, can occur under the meteorological conditions of Cluster 4. Dust and other gases sourced from the northern region probably reach

Florianópolis under Cluster 2 atmospheric conditions. The calculated air mass pathways indicated the general airflow rather than the exact pathway of an air mass.

Figure 8(b) represents the clustered trajectories at an altitude level of 500 m. Five main pathways were found (two continental and three marine). Continental pathways accounted for 55% of the trajectories reaching Florianópolis.

Typical distribution characteristics and patterns of the trajectories, grouped into clusters for altitude levels of 1000 and 1500 m, are summarized in Figure 8(c) and (d), respectively. Trajectories in Cluster 4 at 500 m, Cluster 6 at 1000 m and Cluster 5 at 1500 m are typically long continental trajectories arriving from the north. All of the contaminated rainwater episodes within these groups were probably enriched from upwind regional and local emission sources. Cluster 1 trajectories at 1000 m and 1500 m have short transport patterns, indicative of slow-moving air masses. Clusters 2, 3, 4 and 7 at 1000 and 1500 m cover the Atlantic Ocean, and trajectories in this cluster have long transport patterns. Members of Cluster 5 at 1000 m are very similar to Cluster 6 at 1500 m, whereas members of Cluster 6 at 1000 m are similar to Cluster 5 at 1500 m, but their geographical patterns are completely different. Trajectories in Cluster 5 at 1000 m and 6 at 1500 m are typically long-range, arriving from a S–SW direction, whereas Clusters 6 at 1000 m and 5 at 1500 m are sourced from the north.

Average values of the clusters with respect to some rainwater elemental concentrations are given in Table 5.
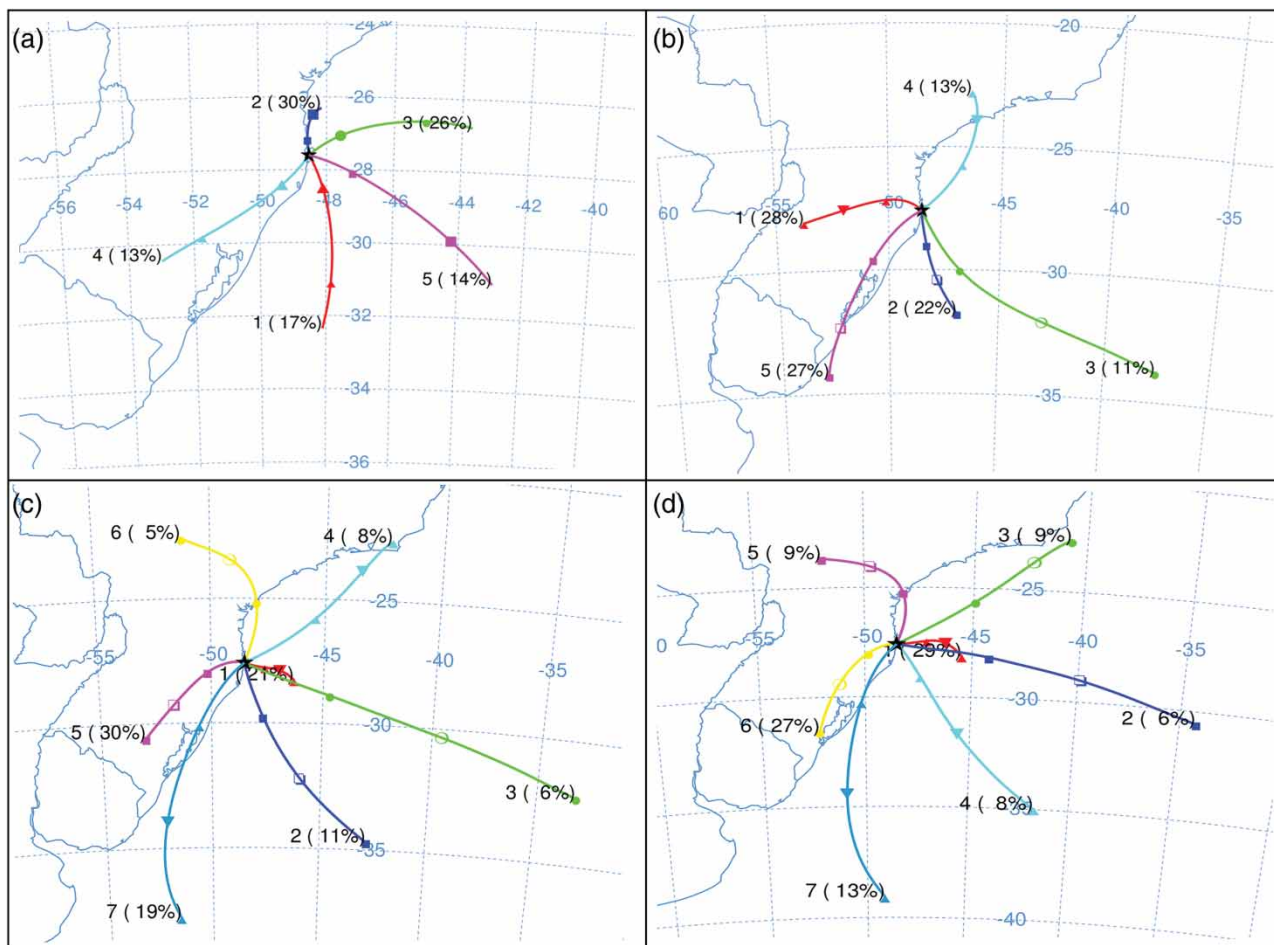
Figure 8.   Clusters and trajectories with an arriving altitude of (a) 10 m, (b) 500 m, (c) 1000 m and (d) 1500 m.

Clusters 1 (at 500 m), 5 (at 1000 m) and 6 (at 1500 m) are the most populated clusters with respect to elements grouped in Factors 2 and 3 on the PCA (Table 4), since they are influenced by continental air masses. However, due to the reduced number of collected samples, no representative pollution patterns were found (Table 5).

The episodic events seem to have a marine source spread across the city. As noted earlier, the composition associated with high loadings is probably the result of a small amount of precipitation, which most often originates from the north segment. Southern winds are commonly accompanied by cold fronts and heavy rainfall events.

The location of the sources of the rainwater pollutants could be determined through the Potential Source Contribution Function (PSCF). This last technique combines meteorology in the form of air parcel back trajectories and the apportioned source contributions to provide a conditional probability field showing the likely source areas for materials transported to the site from distant areas.[42] However, PSCF requires a large number of samples and considerable analysis, and was therefore not applied in the present study.

The GeoLocation option in HYSPLIT was used to indicate the most probable source regions between the sampling dates. Source regions that may have contributed to the air pollution at the measurement location are presented in Figure 9, on which the most probable sources of rainwater pollution are coloured blue. Variation in rainwater composition was dependent on the air mass pathway.[43] However, due to the reduced number of samples collected, no representative patterns were found (Table 5). The episodic events seem to have been affected by local (continental and marine) sources spread across the city. As noted earlier, the composition associated with high loadings is probably the result of the low levels of precipitation, most often sourced from the northern segment. Southern winds are commonly accompanied by cold fronts and heavy rainfall events.

4.   Conclusions

A combination of modelling (back trajectories), pollution (concentration) roses and statistical methods (PCA and Pearson's correlation) were applied to identify dominant

Table 5. Average elemental concentration values by cluster.

	Cluster 500 m				Cluster 1000 m					Cluster 1500 m				
	1	3	4	5	1	2	3	5	6	1	2	3	5	6
%	28%	11%	13%	27%	21%	11%	6%	30%	5%	29%	6%	9%	9%	27%
N	7	4	10	1	2	1	7	11	1	2	7	3	9	1
pH	4.55	5.38	5.07	4.89	5.37	5.52	5.22	4.68	4.89	5.41	5.21	4.88	4.71	4.89
EC	19.53	17.35	9.07	31.00	3.75	6.50	12.41	17.64	31	23.40	6.80	14.07	17.59	31.00
Na^+	81.90	82.65	23.18	165.3	6.52	30.40	51.58	69.57	165.3	141.38	13.05	108.70	60.87	165.30
K^+	5.25	2.42	2.54	5.11	2.56	1.00	1.81	4.83	5.11	3.84	1.45	2.04	5.33	5.11
Ca^{2+}	8.27	4.64	9.60	10.10	4.88	1.00	4.98	11.53	10.1	4.39	5.12	23.70	6.30	10.10
Mg^{2+}	12.01	11.33	4.86	20.10	2.04	4.31	7.09	10.91	20.1	17.72	2.61	9.99	10.48	20.10
Cl^-	73.65	100.30	17.49	177.70	11.61	32.80	59.82	54.33	177.7	169.96	14.57	26.84	61.94	177.70
SO_4^{2-}	16.52	7.75	6.61	22.40	2.17	5.04	7.98	13.10	22.4	10.91	5.48	8.18	13.93	22.40
NO_3^-	23.25	2.72	10.82	17.60	2.28	3.72	7.13	20.04	17.6	1.80	7.26	10.61	21.54	17.60
Mn	0.011	0.001	0.003	0.006	0.002	0.001	0.001	0.009	0.006	0.001	0.002	0.003	0.010	0.006
Fe	0.506	0.167	0.271	0.467	0.199	0.195	0.136	0.489	0.467	0.049	0.178	0.503	0.452	0.467
Cu	0.062	0.009	0.026	ND	0.009	0.009	0.015	0.055	ND	0.009	0.017	0.033	0.058	ND
Pb	0.013	0.005	0.009	0.012	0.007	ND	0.005	0.014	0.012	0.002	0.007	0.011	0.015	0.012
Cd	0.018	0.000	0.011	0.001	ND	ND	0.001	0.021	0.001	0.000	0.001	0.030	0.019	0.001
Cr	0.016	0.010	0.012	0.021	0.010	ND	0.010	0.016	0.021	ND	0.010	0.015	0.016	0.021
Ni	0.005	0.009	0.005	ND	0.010	0.005	0.004	0.006	ND	0.005	0.006	0.002	0.007	ND

Note: Percentage of trajectories are grouped in each cluster during sampling period (August to November 2006). Number of trajectories (n) with respect to sampling dates.
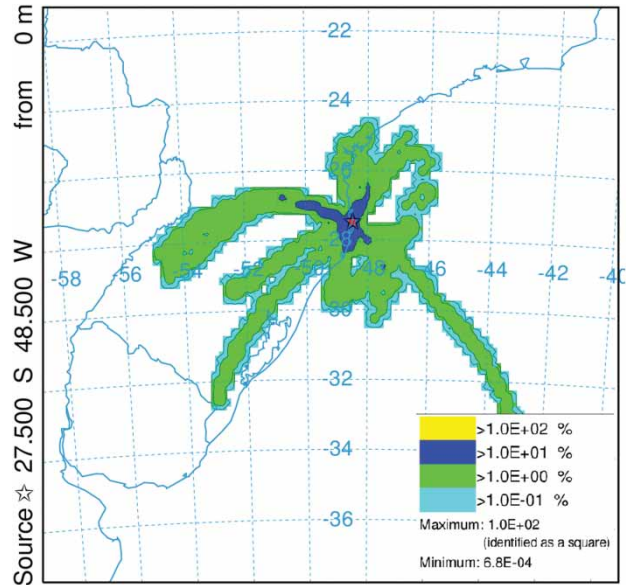

Figure 9. Source regions that may have contributed to rainwater contamination at Florianópolis during the sampling dates.

sources of rainwater acidity and contaminants at a site located in Florianópolis, Brazil. It should be noted that the total number of samples was relatively small (22 samples), although the results of the modelling, PCA and other analyses were nonetheless in agreement. Compared with other overseas studies, lower concentrations of trace elements were found in the rainwater. Apart from Na^+ and Cl^- levels, the ionic concentrations and pH levels at the studied site were intermediate between the acidified and dusty regions.

The PCA suggested that rainwater contamination is mainly derived from marine, crustal, urban activity and traffic origins. Marine aerosols (Factor 1) were responsible for major amounts of Na^+, Cl^-, Mg^{+2}, the EC and part of the SO_4^{2-} and K^+ concentrations. Combustion processes (Factor 2) and traffic emissions were identified as the main source of NO_3^- and a fraction of the SO_4^{2-} and Mn. This last factor is also the major one responsible for pH decreases, even if only in a small proportion. However, organic acids (not analysed in this study) should make the greatest proportionate contributions to free acidity in precipitation in Santa Catarina. Soil resuspension (Factor 3) appeared to be the main source of trace metals at Florianópolis. Additional analysis with a larger data set and the use of an expanded speciation of the organic and inorganic components would improve the identification and quantification of the sources of rainwater pollution. Despite the continuing concern about the impact of TCJL on air pollution, its environmental influence was not clearly observed.

The northern segment of air masses presented the highest concentration of trace elements, whereas western winds contained the highest concentrations of marine aerosols. The high element content of some wind events probably arise because there is a smaller probability of rain being

caused by winds from W, NW, N, NE and ENE directions. Rainfall amount and wind speed played an important role in diluting rainwater pollutants.

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Funding

Notes

1. Small city located in the state of São Paulo with 71,217 inhabitants.
2. Analysis conducted using data from the meteorological station and measured concentrations.

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