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Fog and rain water chemistry in the western Mediterranean basin (Valencia region, Spain)

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Abstract

The present study attempts to characterize the chemistry composition of fog and rain water in the eastern region of the Iberian Peninsula (Valencia, Spain). This research is based upon a network of seven cylindrical fog water collectors distributed over 4 coastal- and 3 inland-mountain ranges. The fog and rain water samples were collected during the 9-month study-period April-December 2008. The fog and rain water samples were analysed for pH, Cond. and Alk., and the following ion concentrations: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-} and SO_4^{2-}. The stations also collected other atmospheric measurements such as 10-min temperature, humidity, wind speed and direction, fog and precipitation. In addition, the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model was used for each fog event in order to know the origin and the pathway of air masses during the previous five days. Preliminary results show two main origins of the air masses, one of them associated with recirculation processes over the Mediterranean Sea, whose fog water samples were more contaminated, and other associated with advection from the Atlantic Ocean, whose fog water samples were cleaner. The chemical composition of the fog and rain is of crucial importance for future applications of water.

1. Introduction

Since 2003, the CEAM Foundation maintains a fog collection network in the Valencia Region (Spain), in the eastern fringe of the Iberian Peninsula. Ten passive fog collectors have been installed since then, covering the region from North to South, as well as from the coast to the inland areas [8]. High fog collection rates have been measured in some of the experimental sites, which have allowed to develop a reforestation project [4]. The overall aim of this work is to describe the chemical composition of fog and rain water collected in the Valencia Region (Spain). To our knowledge, no research has yet attempted to study the chemical features of fog and its meteorological origin in Spain. Only in the Canary Islands have been carried out chemical studies about composition of fog [6], so this work is designed to gain a better understanding of fog, which is of crucial importance for future applications of collected fog water.

2. Methodology

2.1 Sites description

Seven of the ten stations of the fog passive collector network were selected for this study. Their locations covered an area bounded between 40.01º and 38.56º latitude and 0.13º and -0.89º longitude, and their altitudes ranged between 1,256 and 428 m a.s.l.. Four of the stations were located less than 7 km inland and 3 of them were placed in a distance of more than 40 km from the nearest coastline (figure 1).

2.2 Fog and rain water collection

Fog and rain water samples were collected from April to December 2008 on a fortnightly basis. The fog water was collected by using a handmade passive string fog collector (i.e., omnidirectional collection efficiency) based on the ASRC (Atmospheric Science Research Center, State University of New York) device [5]. It basically consisted of a cylinder, 26 cm in diameter and 46 cm in height (fog

collection surface: 1196 cm^2), strung with five concentric rows of 0.8 mm thick nylon line. A rain shield was attached to the top of the string collector to prevent contamination by rain as far as possible. The rain water was sampled by using a tipping bucket raingauge located at the top of the weather station (rain collection surface: 212 cm^2). Both fog and rain water, once collected by the meteorological devices, dripped into a 2 L polyethylene bottle, where remained until the next sampling date. At every sampling site, the experiment was complemented with 10-minute measurements of temperature, relative humidity, fog, rain and wind speed and direction (figure 1), which provided information about the exact time of the collected samples.

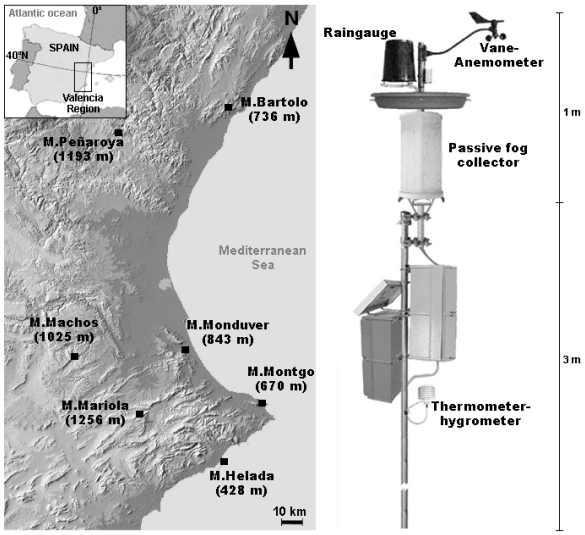

Figure 1: Terrain map of the Valencia Region showing locations of fog water collectors (left) and example of passive fog collector and meteorological measuring equipment (right)

2.3 Trajectories

Backward trajectories are a widely used method for the identification of the origin and the pathway of air masses and are often used to study the advection of air pollutants ([1], [2]). In this work, for every fog sample, we calculated the backward trajectory of every fog event which occurred during the 15-day sampling period using the HYSPLIT model ([3], [7]), (http://www.arl.noaa.gov/ready.php). Each trajectory indicated the path followed by the respective air masses during the last 5 days (120 h) at 1 m above surface level.

2.4 Chemical analysis and quality control

The rain and fog samples were stored in 250 ml polyethylene bottles at 4º C in the refrigerator prior the analysis. The electrical conductivity was measured using a conductivity meter Jenway 4520 and the pH with a pH meter Crison GLP21. Then the samples were filtered through 0.45 µm pore size Sartorius cellulose acetate filters and measured the anions (Cl^-, NO_3^-, SO_4^{2-}) by anion chromatography (Dionex DX120; AS4A column; electrical autosupression ASRS 300; and Na_2CO_3/$NaHNO_3$ eluent), the cations (Ca^{2+}, Na^+, K^+, Mg^{2+}) by optical ICP (Perkin Elmer 4300 DV) and alkalinity by Gran Titration (Crison Compact Titrator). All analyses included synthetic samples of known concentrations to check precision and accuracy of the results.

2.5 Statistical methods

As the bottles stayed in field for 15-day periods, samples could contain water from different fog and rain episodes and therefore, from different origin. To avoid this and to study the chemical composition of fog water in relation to its origin, firstly we computed, for every fog sample, the backward trajectory of every fog event, and secondly, only samples whose trajectories had similar pathways were used in the analysis. With these pure samples, two multivariate statistical analyses were performed: (a) Clustering Analysis to divide the samples into groups, and (b) Principal Component Analysis to interpret the results.

3. Results

3.1 Ion concentrations in fog and rain

119 bottle samples were collected (71 of fog and 48 of rain) during the campaign. Table 1 reports the descriptive statistics of fog and water concentration samples. Overall, conductivity, alkalinity and ion concentrations varied widely, with maximum and minimum values which showed large differences. The average pH of fog varied from 6.39 to 6.97, whereas rain presented slightly higher pH values (~7), except for two inland stations which showed a moderately acid pH (M.Machos and M.Peñaroya). In general, conductivity and ion concentrations presented the same pattern, with higher values in fog samples. At inland stations Ca^{2+} and NO_3^- were the prevailing ions, whereas at coastal stations Na^+ and NO_3^- were the dominant ions.

3.2 Origin of the collected fog water

Only 24 fog samples were used to perform this analysis. All of them could contain water collected from different fog episodes, but always with a similar backward trajectory. This ensured there was no sample with a mix of origins. The Cluster Analysis produced 2 different groups of greatest possible distinction. The cluster 1 contained 9 samples, while the cluster 2 grouped 15. The Principal Component Analysis was used to explore the data relationship. 3 components were extracted, which explained 93 % of the total variance. The component 1 explained 78 % of the total variance and was positively correlated with the ion concentration and conductivity, as well as weakly with alkalinity and pH, so it was interpreted as a size factor. The combination of both statistical analyses showed that the cluster 1 members presented higher values for the component 1, while the cluster 2 members showed lower values. To conclude, the cluster 1 contained samples with larger ion concentrations and the cluster 2 included less contaminated fog water samples (table 2).

Table 2: Chemical composition of fog water from the two clusters. Conductivity in µS cm^{-1}, Alkalinity in µeq l^{-1}, Ion Concentrations in mg l^{-1}

	Cluster 1 (n=9)			Cluster 2 (n=15)		
	avg	max	min	avg	max	min
pH	6.93	7.43	6.16	6.09	6.81	5.31
Cond	477.7	807.0	258.0	77.4	288.0	11.1
Alk	458.2	725.9	179.3	59.7	311.4	5.0
Ca^{2+}	56.8	156.9	18.6	5.1	16.3	0.6
K^{+}	2.2	4.2	0.6	0.5	1.3	0.1
Mg^{2+}	8.6	28.0	1.6	1.0	2.6	0.1
Na^{+}	48.7	179.5	5.2	5.3	16.5	0.5
Cl^{-}	48.6	102.9	10.8	10.9	40.2	0.7
NO_3^{-}	111.2	318.8	62.7	16.0	57.7	1.9
SO_4^{2-}	49.0	184.7	16.0	7.9	28.2	1.4

Backward trajectories of the cluster 1 samples were mainly associated with the Azores High, with large runs over the Mediterranean Sea (E and NE winds) and also presented recirculation processes (sea breezes). Most of them were collected in summer (figure 2, top). Backward trajectories of the cluster 2

Table 1: Chemical composition of fog and rain water from the seven mountainous sites of the Valencia Region (April-December 2008). Conductivity in µS cm^{-1}, Alkalinity in µeq l^{-1}, Ion Concentrations in mg l^{-1}

Station	M.Bartolo		M.Helada		M.Monduver		M.Montgo		M.Machos		M.Mariola		M.Peñaroya	
Type	Rain	Fog	Rain	Fog	Rain	Fog	Rain	Fog	Rain	Fog	Rain	Fog	Rain	Fog
N samples	3	8	7	6	11	18	0	2	10	12	9	12	8	13
pH avg	6.79	6.53	6.94	6.97	6.93	6.39	-	6.46	4.94	6.50	7.08	6.80	4.32	6.69
max	6.93	7.19	7.89	7.47	7.48	6.81	-	6.46	5.93	7.44	8.02	7.50	6.92	7.43
min	6.59	5.87	5.96	6.63	6.25	5.31	-	6.46	3.32	5.60	6.61	5.30	3.50	5.72
Cond avg	154.7	483.8	308.3	747.0	88.1	286.9	-	466.0	131.3	164.9	182.0	169.8	90.8	255.8
max	397.0	1024.0	535.0	1170.0	335.0	840.0	-	564.0	344.0	539.0	580.0	525.0	244.0	772.0
min	28.2	50.5	141.7	253.0	22.2	11.1	-	368.0	23.8	39.8	20.2	2.2	45.8	24.1
Alk avg	175.0	310.3	321.5	833.4	290.4	264.4	-	301.8	21.7	261.7	264.0	358.9	26.4	313.7
max	420.9	725.9	519.0	1862.2	619.1	710.3	-	349.0	71.3	1200.4	911.2	1025.4	158.3	1207.8
min	31.0	5.0	128.6	298.8	67.4	26.8	-	254.6	0.0	0.0	75.3	0.0	0.0	16.7
Ca^{2+} avg	6.6	82.6	30.3	85.6	19.8	37.6	-	55.3	13.9	15.2	32.8	68.4	8.0	41.0
max	11.5	180.8	89.5	229.9	82.4	179.2	-	57.4	74.2	57.8	183.1	491.1	41.0	190.0
min	3.5	2.4	7.5	23.3	1.9	0.6	-	53.2	1.9	2.2	2.6	1.3	1.1	2.3
K^{+} avg	0.4	4.8	1.6	8.1	1.4	1.4	-	3.4	0.9	0.8	2.2	2.0	1.3	2.0
max	0.7	10.1	4.2	16.9	7.4	4.4	-	4.0	4.8	2.2	13.7	12.3	8.0	7.3
min	0.2	0.1	0.7	3.1	0.1	0.1	-	2.7	0.1	0.2	0.1	0.2	0.1	0.2
Mg^{2+} avg	1.2	14.8	5.5	100.2	4.3	6.1	-	14.5	2.6	2.1	3.5	6.2	0.9	3.7
max	2.3	35.1	15.8	481.9	19.7	28.0	-	18.0	14.0	5.6	16.2	41.7	4.8	14.0
min	0.6	0.4	2.1	10.9	0.4	0.1	-	11.0	0.3	0.6	0.3	0.4	0.1	0.2
Na^{+} avg	6.9	92.1	31.0	151.8	21.6	30.8	-	88.9	8.6	11.0	16.2	33.4	2.4	17.7
max	13.8	240.5	83.6	446.0	129.8	179.5	-	103.8	57.4	31.8	64.3	232.0	11.1	66.2
min	3.0	1.6	7.8	66.1	0.7	0.5	-	74.1	0.6	0.8	0.8	1.3	0.2	0.5
Cl^{-} avg	18.2	56.9	39.3	98.0	16.7	28.1	-	54.9	16.2	14.4	13.8	23.9	23.5	14.7
max	45.0	102.9	67.1	231.9	102.1	84.0	-	64.3	53.6	43.5	46.4	81.7	144.3	32.6
min	4.5	6.3	14.0	11.0	1.7	1.2	-	45.4	1.8	3.8	0.6	2.0	2.6	0.7
NO_3^{-} avg	15.1	105.3	28.8	98.7	14.8	47.7	-	63.5	9.7	26.2	10.8	52.3	9.7	50.1
max	29.1	318.8	57.3	273.1	127.2	165.9	-	63.7	38.9	82.9	71.0	243.8	53.5	155.4
min	5.6	7.3	8.2	5.5	0.2	0.1	-	63.3	0.6	1.1	0.1	1.9	0.8	7.3
SO_4^{2-} avg	13.6	55.8	16.2	52.7	8.1	21.4	-	33.9	5.3	13.6	18.5	20.9	8.0	18.2
max	30.5	184.7	26.3	164.4	50.8	83.0	-	38.0	16.0	40.2	94.5	94.0	49.1	64.3
min	3.4	6.3	6.6	5.9	1.5	1.7	-	29.8	1.2	1.2	0.8	1.9	1.0	1.4

samples were associated with long-distance air masses coming from the Atlantic Ocean, which barely traveled over the Mediterranean Sea, and they were collected in spring or autumn (figure 2, bottom).

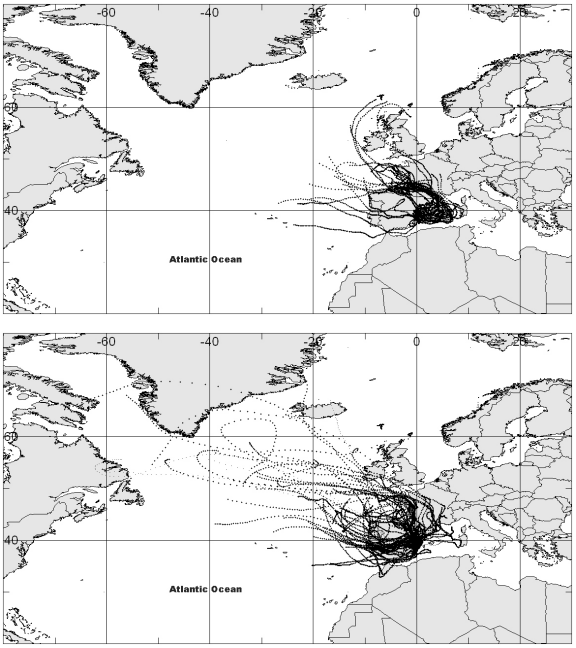

Figure 2: 120 h backward trajectories for every fog event collected for the cluster 1 (top) and the cluster 2 samples (bottom)

4. Conclusions

This study has characterized the chemical composition of the fog and rain at 7 different sites of the Valencia Region. Besides, the backward trajectories analysis has showed different ion concentrations depending on the origin of the air masses. Air masses associated with recirculation processes over the Mediterranean Sea brought water samples with larger ion concentrations than those which came directly from the Atlantic Ocean. Future studies will analyze the synoptic patterns associated with the two clusters found here, as well as the role played by dry deposition.

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